FUNDAMENTALS OF NATURAL GAS PROCESSING

THIRD EDITION

Arthur J. Kidnay
William R. Parrish
Daniel G. McCartney

CRC Press
Taylor & Francis Group

Fundamentals of Natural Gas Processing

Taylor & Francis
Taylor & Francis Group
http://taylorandfrancis.com

Fundamentals of Natural Gas Processing

Third Edition

Arthur J. Kidnay, William R. Parrish,
and Daniel G. McCartney

CRC Press
Taylor & Francis Group
Boca Raton London New York

CRC Press is an imprint of the
Taylor & Francis Group, an **informa** business

CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

© 2020 by Taylor & Francis Group, LLC
CRC Press is an imprint of Taylor & Francis Group, an Informa business

No claim to original U.S. Government works

Printed on acid-free paper

International Standard Book Number-13: 978-1-138-61279-2 (Hardback)

This book contains information obtained from authentic and highly regarded sources. Reasonable efforts have been made to publish reliable data and information, but the authors and publisher cannot assume responsibility for the validity of all materials or the consequences of their use. The authors and publishers have attempted to trace the copyright holders of all material reproduced in this publication and apologize to copyright holders if permission to publish in this form has not been obtained. If any copyright material has not been acknowledged, please write and let us know so we may rectify in any future reprint.

Except as permitted under U.S. Copyright Law, no part of this book may be reprinted, reproduced, transmitted, or utilized in any form by any electronic, mechanical, or other means, now known or hereafter invented, including photocopying, microfilming, and recording, or in any information storage or retrieval system, without written permission from the publishers.

For permission to photocopy or use material electronically from this work, please access www.copyright.com (http://www.copyright.com/) or contact the Copyright Clearance Center, Inc. (CCC), 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400. CCC is a not-for-profit organization that provides licenses and registration for a variety of users. For organizations that have been granted a photocopy license by the CCC, a separate system of payment has been arranged.

Trademark Notice: Product or corporate names may be trademarks or registered trademarks, and are used only for identification and explanation without intent to infringe.

Visit the Taylor & Francis Web site at
http://www.taylorandfrancis.com

and the CRC Press Web site at
http://www.crcpress.com

This book is dedicated to our wives, Joan and Carol, for their enduring support and endless patience throughout the preparation of this book.

We recognize our late coauthor, Dr. Arthur J. Kidnay who saw the need for this book and contributed to the first and second editions. His guidance is missed by all who knew him.

Taylor & Francis
Taylor & Francis Group
http://taylorandfrancis.com

Contents

Preface xvii
Acknowledgments xix
Authors xxi
Notation xxiii

PART 1

Chapter 1 Processing Principles 3

1.1 Introduction 3
1.2 Units and Conversions 3
1.2.1 Basic Units 4
1.2.2 Derived Units 4
1.2.3 Other Important Units in Gas Processing 6
1.2.4 Mathematical Symbols 6
1.3 Basic Chemistry Concepts 6
1.3.1 Structure and Nomenclature 7
1.3.2 Important Chemical Properties 8
1.3.3 Important Physical Properties 10
1.3.4 Mixtures 17
1.4 Specification Test Methods 21
1.4.1 Copper Strip Test 21
1.4.2 Reid Vapor Pressure 21
1.5 Thermodynamics 21
1.5.1 Introduction 21
1.5.2 First Law of Thermodynamics 22
1.5.3 Forms of Energy 22
1.5.4 State and Path Functions 26
1.5.5 Important Thermodynamic Paths 27
1.5.6 Pressure-Enthalpy (PH) Diagrams 28
Discussion Questions 29
Exercises 30
References 30

Chapter 2 Pumps 33

2.1 Introduction 33
2.2 Pump Fundamentals 34
2.2.1 Energy Balance 34
2.2.2 Head 34
2.3 Centrifugal Pumps 36
2.3.1 Power, Pump Efficiency, and Temperature Rise 38
2.3.2 Suction Head, Suction Lift, Total Head 40
2.3.3 Net Positive Suction Head and Cavitation 40
2.3.4 Characteristic Curves 41
2.3.5 System Curves 45

2.3.6 Affinity Laws 46
2.3.7 Coordinating Pump and System 46
2.4 Reciprocating Pumps 47
2.4.1 Pump Fundamentals 48
2.5 Rotary Pumps 49
2.6 Pump Comparisons 50
2.6.1 Centrifugal 50
2.6.2 Positive Displacement 50
Discussion Questions 51
Exercises 51
References 52

Chapter 3 Heat Transfer 53

3.1 Introduction 53
3.2 Modes of Heat Transfer 53
3.2.1 Conduction 53
3.2.2 Convection 56
3.2.3 Radiation 56
3.2.4 Heat Transfer Coefficients 57
3.3 Cooling and Heating Sources 61
3.3.1 Cooling Sources 61
3.3.2 Hot Fluids 61
3.4 Heat Exchanger Types 62
3.4.1 Shell and Tube 62
3.4.2 Kettle Exchangers 62
3.4.3 Air-Cooled Exchangers 64
3.4.4 Wet Surface Air Coolers 65
3.4.5 Plate Frame Exchangers 65
3.4.6 Plate-Fin Exchangers 67
3.4.7 Printed Circuit Heat Exchangers 69
3.5 Condensers 69
3.6 Reboilers 70
3.6.1 Kettle Reboiler 70
3.6.2 Recirculating Thermosyphon 70
3.6.3 Pump-through Reboiler 71
3.6.4 Once-through Reboiler 71
3.6.5 Internal Reboilers 72
Discussion Questions 73
Exercises 73
References 74

Chapter 4 Separation Processes 75

4.1 Introduction 75
4.2 Distillation 75
4.2.1 Basic Concepts 75
4.2.2 Types of Columns 83
4.3 Absorption 85
4.3.1 Basic Concepts 85
4.3.2 Physical Absorption 85
4.3.3 Chemical Absorption 85

4.3.4 Solvent Selection 86
4.3.5 Regenerative Absorption Processes 86
4.4 Column Internals 88
4.5 Adsorption 91
4.5.1 Basic Concepts 91
4.5.2 Adsorption Process 93
4.6 Membranes 96
4.6.1 Basic Concepts 96
4.6.2 Membrane Process 98
4.7 Summary 102
Discussion Questions 103
Exercises 103
References 104

Chapter 5 Phase Separation Equipment 105

5.1 Gas–Liquid Separators 105
5.1.1 Primary Separation 106
5.1.2 Gas Gravity Separation 106
5.1.3 Gas Polishing 107
5.1.4 Liquid Accumulation Section 110
5.2 Filter Separators and Coalescing Filters 110
5.3 Cyclone Separators 112
5.4 Liquid–Liquid Separators 113
5.5 Residence Time for Various Separator Applications 114
5.6 Filters 115
Discussion Questions 117
References 117

PART 2

Chapter 6 Overview of the Natural Gas Industry 121

6.1 Introduction 121
6.1.1 World Natural Gas 122
6.1.2 U.S. Natural Gas 123
6.2 Sources of Natural Gas 125
6.2.1 Geological Background 125
6.2.2 Resource 129
6.2.3 Gas Compositions 132
6.2.4 Impurities 134
6.3 Classification 135
6.3.1 Liquids Content 135
6.3.2 Sulfur Content 136
6.4 Principal Products and Markets 136
6.4.1 Methane 137
6.4.2 Ethane 137
6.4.3 Propane 137
6.4.4 Ethane–Propane Mix 138
6.4.5 Isobutane 138

6.4.6 *n*-Butane 138
6.4.7 Natural Gas Liquids 138
6.4.8 Natural Gasoline 138
6.4.9 Sulfur 138
6.5 Product Specifications 139
6.5.1 Natural Gas 139
6.5.2 Liquid Products 139
6.6 Combustion Characteristics 141
6.6.1 Heating Value 141
6.6.2 Wobbe Number 143
Discussion Questions 144
Exercises 144
References 145
Web Sites 147

Chapter 7 Overview of Gas Plant Processing 149

7.1 Roles of Gas Plants 149
7.2 Plant Processes 150
7.2.1 Field Operations and Inlet Receiving 151
7.2.2 Inlet Compression 151
7.2.3 Gas Treating 151
7.2.4 Dehydration 151
7.2.5 Hydrocarbon Recovery 151
7.2.6 Nitrogen Rejection 151
7.2.7 Trace Components 152
7.2.8 Outlet Compression 152
7.2.9 Liquids Processing 152
7.2.10 Sulfur Recovery 152
7.2.11 Storage and Transportation 152
7.2.12 Liquefaction 152
7.3 Important Support Components 153
7.3.1 Utilities 153
7.3.2 Process Control 155
7.3.3 Safety Systems 155
7.4 Contractual Agreements and Economics 156
7.4.1 Fee-Based Contracts 156
7.4.2 Percentage of Proceeds Contracts 156
7.4.3 Keep Whole or Wellhead Purchase Contracts 157
7.4.4 Alternate Contract Provisions 157
7.4.5 Capital Expenditures 157
7.5 Operational Measures 158
7.5.1 Shrinkage 158
7.5.2 Energy Efficiency 158
7.5.3 Processing Margin (Frac Spread) 159
Discussion Questions 160
References 160

Chapter 8 Field Operations and Inlet Receiving 163

8.1 Introduction 163
8.2 Field Operations 164

8.2.1 Wellhead Operations ... 164
8.2.2 Gathering Systems ... 165
8.2.3 Compressor Stations ... 166
8.2.4 Pipeline Fieldwork ... 168
8.2.5 Pigging ... 168
8.2.6 Gas Metering ... 171
8.3 Gas Hydrates ... 172
8.3.1 Properties ... 173
8.3.2 Hydrate Formation Prediction ... 175
8.3.3 Hydrate Inhibition ... 177
8.4 Inlet Receiving ... 182
8.4.1 Manifolded Piping ... 182
8.4.2 Inlet Vessels ... 184
8.4.3 Comparison of Slug Catcher Configurations ... 184
8.5 Safety and Environmental Considerations ... 185
Discussion Questions ... 185
Exercises ... 186
References ... 186
Web Sites ... 187

Chapter 9 Compression ... 189

9.1 Introduction ... 189
9.2 Fundamentals ... 190
9.2.1 Thermodynamics of Compression ... 190
9.2.2 Multistaging ... 194
9.2.3 Compressor Efficiencies ... 195
9.3 Drivers ... 197
9.4 Compressor Types ... 198
9.4.1 Positive Displacement Compressors ... 199
9.4.2 Dynamic Compressors ... 202
9.5 Capacity and Power Calculations ... 206
9.5.1 Capacity ... 207
9.5.2 Power Requirements ... 210
9.6 Comparison of Reciprocating and Centrifugal Compressors ... 213
9.7 Safety and Environmental Considerations ... 213
Discussion Questions ... 214
Exercises ... 214
References ... 215

Chapter 10 Gas Treating ... 217

10.1 Introduction ... 218
10.1.1 The Problem ... 218
10.1.2 Acid Gas Concentrations in Natural Gas ... 218
10.1.3 Purification Levels ... 219
10.1.4 Acid Gas Disposal ... 219
10.1.5 Purification Processes ... 219
10.2 Chemical Absorption Processes ... 222
10.2.1 Amines ... 222
10.2.2 Alkali Salts ... 232

10.3 Physical Absorption 233
10.3.1 Solvent Properties 233
10.3.2 Representative Process Conditions 235
10.3.3 Hybrid Processes 237
10.4 Adsorption 237
10.5 Cryogenic Fractionation 239
10.6 Membranes 240
10.6.1 Carbon Dioxide Removal from Natural Gas 241
10.6.2 Operating Considerations 241
10.6.3 Advantages and Disadvantages of Membrane Systems 243
10.7 Nonregenerable Hydrogen Sulfide Scavengers 243
10.8 Biological Processes 244
10.9 Safety and Environmental Considerations 245
10.9.1 Amines. 245
10.9.2 Adsorbents and Scavengers 245
10.9.3 Membranes 245
Discussion Questions 245
Exercises 246
References 246

Chapter 11 Gas Dehydration 249

11.1 Introduction 250
11.2 Water Content of Hydrocarbons 251
11.3 Gas Dehydration Processes 254
11.3.1 Absorption Processes 255
11.3.2 Adsorption Processes 261
11.3.3 Nonregenerable Desiccant Processes 273
11.3.4 Membrane Processes 273
11.3.5 Other Processes 274
11.3.6 Comparison of Dehydration Processes 274
11.4 Safety and Environmental Considerations 275
Discussion Questions 275
Exercises 275
References 276

Chapter 12 Hydrocarbon Recovery 279

12.1 Introduction 279
12.1.1 Retrograde Condensation 280
12.2 Process Components 281
12.2.1 Refrigeration System 281
12.2.2 Turboexpansion 286
12.2.3 Heat Exchange 290
12.2.4 Gas–Liquid Separators 290
12.2.5 Fractionation 291
12.3 Liquids Removal Processes 292
12.3.1 Dew Point Control and Fuel Conditioning 293
12.3.2 Low Ethane Recovery 296
12.3.3 High Ethane Recovery 299

12.4 Safety and Environmental Considerations 303
Discussion Questions 303
Exercises 304
References 305

Chapter 13 Nitrogen Rejection 307

13.1 Introduction 307
13.2 Nitrogen Rejection for Gas Upgrading 308
13.2.1 Cryogenic Distillation 309
13.2.2 Pressure Swing Adsorption 310
13.2.3 Membranes 310
13.3 Nitrogen Rejection for Enhanced Oil Recovery Using Cryogenic Distillation 311
13.4 Safety and Environmental Considerations 313
Discussion Questions 313
Exercises 313
References 314

Chapter 14 Trace Component Recovery or Removal 315

14.1 Introduction 315
14.2 Helium 316
14.2.1 Introduction 316
14.2.2 Recovery Methods 316
14.3 Hydrogen 319
14.4 Oxygen 319
14.5 NORM 320
14.6 Arsenic 323
14.7 Mercury 323
14.7.1 Environmental Considerations 323
14.7.2 Mercury Corrosion 324
14.7.3 Removal Processes 324
14.8 Benzene, Toluene, Ethylbenzene, and Xylenes 325
14.9 Methanol 327
14.9.1 Methanol Removal 327
Discussion Questions 328
Exercises 328
References 329
Web Sites 330

Chapter 15 Liquids Processing 331

15.1 Introduction 331
15.2 Condensate Processing 332
15.2.1 Sweetening 333
15.2.2 Dehydration 333
15.3 NGL Processing 333
15.3.1 Sweetening 334
15.3.2 Dehydration 338
15.3.3 Fractionation 340

15.4 Safety and Environmental Considerations 341
Discussion Questions 341
Exercises 342
References 342

Chapter 16 Acid Gas Processing and Disposal 345

16.1 Introduction 345
16.1.1 Carbon Dioxide 346
16.1.2 Hydrogen Sulfide 346
16.2 Properties of Sulfur 346
16.2.1 Solid State 347
16.2.2 Liquid State 348
16.2.3 Vapor State 348
16.3 Sulfur Recovery Processes 348
16.3.1 Claus Process 349
16.3.2 Small- to Medium-Scale Recovery Processes 357
16.4 Sulfur Storage 361
16.5 Acid Gas Injection 361
16.5.1 Enhanced Oil Recovery 361
16.5.2 Injection Wells 362
16.6 Safety and Environmental Considerations 364
Discussion Questions 365
Exercises 365
References 366

Chapter 17 Transportation and Storage 369

17.1 Introduction 369
17.2 Gas 370
17.2.1 Transportation 370
17.2.2 Market Centers 375
17.2.3 Gas Storage Facilities 375
17.3 Liquids 380
17.3.1 Transportation 380
17.3.2 Storage 382
Discussion Questions 383
Exercises 384
References 384

Chapter 18 Liquefied Natural Gas 387

18.1 Introduction 387
18.1.1 Peakshaving Plants and Satellite Facilities 388
18.1.2 Baseload Plants and Stranded Reserves 389
18.2 Gas Treating before Liquefaction 394
18.3 Liquefaction Cycles 395
18.3.1 J–T Cycles 395
18.3.2 Expander Cycles 399
18.3.3 Cascade Cycles 402
18.4 Storage of LNG 410

18.4.1 Cryogenic Aboveground Storage 410
18.4.2 Cryogenic In-Ground Storage 413
18.4.3 Rollover 414
18.5 Transportation 415
18.5.1 Truck Transport 415
18.5.2 Pipelines 415
18.5.3 Marine Transport 416
18.6 Regasification and Cold Utilization of LNG 419
18.6.1 Regasification 419
18.6.2 Cold Utilization 420
18.7 Economics 420
18.7.1 Liquefaction Costs 421
18.7.2 Shipping Costs 423
18.7.3 Regasification Terminal Costs 423
18.8 Safety and Environmental Considerations 423
Discussion Questions 424
Exercises 424
References 425
Web Sites 428

Chapter 19 Capital Costs of Gas Processing Facilities 429

19.1 Introduction 429
19.2 Basic Premises for All Plant Component Cost Data 429
19.3 Amine Treating 430
19.4 Glycol Dehydration 430
19.5 NGL Recovery with Straight Refrigeration (Low Ethane Recovery) 430
19.6 NGL Recovery with Cryogenic Processing (High Ethane Recovery) 431
19.7 Sulfur Recovery and Tail Gas Cleanup 432
19.7.1 Sulfur Recovery at High Capacities 432
19.7.2 Sulfur Recovery at Low Capacities 433
19.8 Corrections to Cost Data 435
Discussion Questions 435
References 435

Chapter 20 Natural Gas Processing Plants 437

20.1 Introduction 437
20.2 Plant with Sweet Gas Feed and 98% Ethane Recovery 437
20.2.1 Overview of Plant Feed and Product Slate 437
20.2.2 Inlet Compression 439
20.2.3 Heat Exchange 439
20.2.4 Dehydration 439
20.2.5 Propane Refrigeration 439
20.2.6 Hydrocarbon Recovery 439
20.2.7 Amine Treating 439
20.2.8 Deethanizer 440
20.2.9 Outlet Residue Sales Gas Compression 440
20.3 Plant with Sour Gas Feed, NGL, and Sulfur Recovery 440
20.3.1 Overview of Plant Feed and Product Slate 441
20.3.2 Inlet Receiving 441

20.3.3 Inlet Compression 441
20.3.4 Gas Treating 441
20.3.5 Sulfur Recovery 442
20.3.6 Dehydration 442
20.3.7 Hydrocarbon Recovery 442
20.3.8 Liquids Processing 442
20.4 Plant with Sour Gas Feed, NGL Recovery, and Nitrogen Rejection 442
20.4.1 Overview of Plant Feed and Product Slate 443
20.4.2 Inlet Receiving 444
20.4.3 Gas Treating 444
20.4.4 Sulfur Recovery 444
20.4.5 Dehydration 444
20.4.6 NRU and Cold Box 444
20.4.7 Liquids Processing 444
Discussion Questions 445
Exercises 445
References 446

Appendix A: Glossary of Gas Process Terminology 447

Author Index 457

Subject Index 461

Preface

The natural gas industry began in the early 1900s in the United States and is still evolving. Natural gas is a high-quality fuel and chemical feedstock; it plays a vital role in the industrial world and is an important export for many countries. Several high-quality books[1] provide guidance to engineers in the field of natural gas processing. This book provides an introduction to the natural gas industry to a reader entering the field. It also helps those providing a service to the industry in a narrow application to better understand how their products and services fit into the overall process.

Most of the book can be understood even by those who do not have a background in chemical engineering. To help these readers understand the more technical issues, this edition is divided into two parts. The first part, consisting of the first five chapters, provides an overview of the basic concepts to help the non-engineer better appreciate some of the technical discussions. It also provides a concise review for engineers but can either be browsed or skipped by knowledgeable readers. The topics covered in this part are applicable throughout the chemical processing industry.

The second part contains 15 chapters and addresses natural gas processing. To help the reader understand the need of each processing step, these chapters follow the gas stream, starting from the gas at the wellhead to the gas entering the marketplace. These chapters focus primarily on gas plant processes. Wherever possible, the advantages, limitations, and ranges of applicability of the processes are discussed so that their selection and integration into the overall gas plant can be fully understood and appreciated.

The book compiles information from personal experience, books, the open literature, and meeting proceedings[2] to provide an accurate picture of where the gas processing technology stands today, as well as to indicate some relatively new technologies that could become important in the future. An invaluable aspect of this book is the insight contributed by experts in certain applications.

The second edition was published when shale gas just began as an important resource. The third edition addresses recent changes in processing technology and updates references.

This edition includes both discussion questions and exercises, which makes this book more suitable as a textbook in upper-level or graduate engineering courses. The book has two appendices. The first contains an updated glossary of gas processing terminology. The second has useful conversion factors and physical properties data; it also contains a chart included in the text. The second appendix is provided only in electronic format so that charts can be enlarged for better readability. Appendix B can be accessed at https://www.crcpress.com/Fundamentals-of-Natural-Gas-Processing-Third-Edition/Kidnay-Parrish-McCartney/p/book/9781138612792.

[1] For example, *GPSA Engineering Data Book* (GPSA Midstream Suppliers, Tulsa, OK, 14th edition, 2016) and the fifth edition of Kohl and Nielsen, *Gas Purification* (Gulf Publishing, Houston, TX, 1997).

[2] The two most important meetings involving natural gas processing in the United States are the annual meetings of the GPA MIdstream Association and the Laurance Reid Gas Conditioning Conference.

Taylor & Francis
Taylor & Francis Group
http://taylorandfrancis.com

Acknowledgments

We would like to acknowledge the assistance of numerous people in preparing the third edition of this book. This book could not have been written without the aid of the GPA Midstream Association. Johnny Dreyer and Marty Erne graciously supplied material from both GPA Midstream and affiliated organization, GPSA Midstream Suppliers Association. Carter Tannehill and Ajey Chandra kindly provided us with the updated data on capital costs of gas processing facilities for Chapter 19 and offered editorial comment. Almost all of the private communications referenced in this book involved numerous communications. Many others provided valuable input to this third edition, including Bill Echt, Ed Wichert, Dendy Sloan, Caroline Koh, Dale Embry, and Petra Drinkwine. Barbara Belt reviewed most of the exercises. A number of companies generously provided us with drawings and photographs. Virtual Materials Group provided the pressure–enthalpy diagrams in the appendix. Another company supplied a modified drawing with their product names replaced with generic names so that the figure could be used. Finally, we would like to acknowledge the patience and support of the editorial staff at Taylor & Francis.

Taylor & Francis
Taylor & Francis Group
http://taylorandfrancis.com

Authors

The late Arthur J. Kidnay, PhD, PE, provided the inspiration for this book and co-wrote the first and second editions.

William R. Parrish, PhD, PE, is a retired senior research associate. He spent 25 years in research and development at ConocoPhillips (formerly Phillips Petroleum Company) where he obtained physical properties data needed for new processes and for resolving operation problems. He provided company-wide technical expertise on matters involving physical properties and gas hydrates. He also participated on six gas plant optimization teams. He has 49 technical publications and holds two patents. He teaches a continuing education course in gas processing to engineers and scientists from the natural gas industry.

Dr. Parrish represented his company on numerous technical advisory and research committees, including the Gas Processors Association's Enthalpy Committee of Section F. Dr. Parrish received the Donald L. Katz award by the GPA Midstream Association in recognition of his outstanding research and teaching service to the industry. He also participated in Department of Energy peer review committees. He is a Fellow of the American Institute of Chemical Engineers and is actively involved in development of the Professional Engineer (P.E.) chemical engineering exam.

Daniel G. McCartney, PE, has been involved with gas processing for over 50 years. He began his career with Warren Petroleum, which later was part of Chevron. He managed process engineering for Warren and provided gas processing engineering support throughout Chevron. Following retirement from Chevron, he joined Black & Veatch, where he provided technical expertise on gas processing, LNG, and sulfur projects. Subsequent to his retirement from Black & Veatch, he provides consulting and teaches a continuing education course in gas processing.

Mr. McCartney has contributed to the GPA Midstream Association for over 30 years and serves as chair of a research subgroup. He was awarded the GPA Citation for Service in recognition of his service to the gas processing industry. Mr. McCartney is a senior advisory board member at the Laurance Reid Gas Conditioning Conference. He has authored or coauthored a number of technical papers in the areas of gas processing and LNG and holds one patent.

Taylor & Francis
Taylor & Francis Group
http://taylorandfrancis.com

Notation

A	Area, ft^2 (m^2)
B	Constant in equation, units depend on equation
bhp	Brake horsepower
bkW	Brake kilowatt
C	Constant in equation, units depend upon equation
	Concentration
	Percent clearance
C_P	Heat capacity at constant pressure, Btu/lb-mol-°F (kJ/kg-mol-°C) or Btu/lb_m-°F (kJ/kg-°C)
C_{SS}	Correction factor for adsorption of unsaturated gas
C_T	Correction factor adsorption bed temperature
C_V	Heat capacity at constant volume, Btu/lb-mol-°F (kJ/kg-mol-°C) or Btu/lb_m-°F (kJ/kg-°C)
$\boldsymbol{D}$	Diffusivity, ft^2/h (m^2/s)
D	Diameter, ft (m)
F	Factor in equations, units depend upon equation
	Degrees of freedom
f	Fraction
g	Acceleration due to gravity, 32.2 ft/s^2 (9.81 m/s^2)
g_c	32.2 $ft\text{-}lb_m/s^2\text{-}lb_f$ USES (United States Engineering System) only
h	Total pump head, ft (m)
	Enthalpy Btu/lb_m (kJ/kg)
	Heat transfer coefficient $Btu/ft^2\text{-}h\text{-}°F$ ($W/m^2\text{-}°C$)
H	Enthalpy, Btu/lb-mol (J/kg-mol)
h_d	Total discharge head, ft (m)
h_f	Head loss due to friction, ft (m)
h_{ke}	Kinetic energy expressed as head, ft (m)
h_l	Suction lift, ft (m)
h_P	Pressure expressed as head, ft (m)
h_{PE}	Potential energy expressed as head, ft (m)
h_R	Absolute head in liquid receiver, ft (m)
h_S	Static suction head, ft (m)
h_T	Head in liquid supply tank, ft (m)
h_{VP}	Vapor pressure of liquid being pumped, ft (m)
h_w	Work expressed as head, ft (m)
hhp	Hydraulic horsepower
hkW	Hydraulic kilowatts
$\boldsymbol{J}$	Molar flux, $lb\text{-}mol/ft^2\text{-}h$ ($kg\text{-}mol/m^2\text{-}s$)
$K = y/x$	Equilibrium constant, dimensionless
k	Thermal conductivity, Btu/h-ft-°F (W/m-°C)
	Decay rate constant, s^{-1}
L	Length, ft (m)

m	Mass, lb_m (kg)
	Number of compressor stages, dimensionless
$\dot{m}$	Mass flow rate, lb_m/h (kg/s)
MW	Molecular weight (molar mass), lb_m/lb-mol (g/g-mol)
n	Number of moles, lb-mol (g-mol)
	Shaft speed, rpm
$\dot{n}$	Molar flow rate, lb-mol/h (kg-mol/h)
NPSH	Net positive suction head, ft (m)
P	Pressure, psi (bar)
$\boldsymbol{P}$	Permeability, lb-mol/ft-psia-hr (kg-mol/m-bar-s)
PD	Piston displacement, ft^3/min (m^3/h)
p_i	Partial pressure of component i, psia (bara)
PR	Pressure ratio, also called compression ratio, dimensionless
q_L	Heat leak, Btu/lb_m (kJ/kg)
Q	Volumetric flow rate, ft^3/min (m^3/h)
	Heat, Btu (kJ)
R	Universal gas constant (see Appendix B for values in various units)
R_K	Relative ratio of K values, dimensionless
s	Entropy Btu/lb_m-°F (J/kg-K)
S	Solubility, lb-mol/psia-ft^3 (kg-mol/bara-m^3)
SpGr	Specific gravity (relative density), dimensionless
T	Absolute temperature, °R (K)
t	Temperature, °F (°C)
u	Velocity, ft/min (m/min)
	Internal energy Btu/lb_m (kJ/kg)
U	Overall heat transfer coefficient Btu/ft^2-h-°F (W/m^2-°C)
V	Volume ft^3 (m^3)
	Displacement volume (reciprocating pump) ft^3 (m^3)
v	Volume, ft^3/lb-mol (m^3/g-mol)
V_{EFF}	Volumetric efficiency (dimensionless)
V_S	Superficial velocity, ft/min (m/s)
V_T	Terminal velocity for droplet descending through continuous phase, ft/s (m/s)
W	Water content of gas lb_m/MMscf (mg/Nm^3)
w_S	Shaft work (positive if work done by system), Btu/lb_m (kJ/kg)
X	Weight fraction, dimensionless
x	Mole fraction in liquid phase, dimensionless
y	Mole fraction in vapor phase, dimensionless
Z	Elevation difference, ft (m)
z	Compressibility factor (Pv/RT) dimensionless

Greek Symbols

α_{1-2}	Selectivity, the ratio of permeabilities, $\boldsymbol{P}_1/\boldsymbol{P}_2$ in membranes
	Relative volatility, ratio of K_1/K_2, dimensionless
γ	Ratio of heat capacities, C_P/C_V, dimensionless

	Liquid phase activity coefficient, dimensionless
η	Efficiency, dimensionless
κ	Polytropic constant, dimensionless
μ	Viscosity, cP (m-Pa-s)
	Joule–Thomson coefficient, °F/psi (°C/bar)
λ	Heat of vaporization, Btu/lb_m (kJ/kg)
ρ	Density, lb_m/ft^3 (kg/m^3)
Θ	Time, min (s)
φ	Fugacity coefficient
	Number of phases, dimensionless

Subscripts

1	Entering
2	Exiting
A	Actual
avg	Average value
b	Base value
c	Critical property
F	Feed
g	Gas phase
i	Component *i*
	Initial value
	Inhibitor
	Inside
in	Inlet
o	Outside
out	Outlet
IS	Isentropic
lm	Log mean average
m	Mixture
MTZ	Mass transfer zone
L	Liquid
P	Polytropic
R	Relative
	Reference
	Reduced condition
rg	Regeneration
Sat	Saturation condition
si	Sieve
st	Steel
V	Vapor
	Volumetric
w	Water

Superscripts

L	Liquid
Sat	Saturation condition
V	Vapor

Part 1

Taylor & Francis
Taylor & Francis Group
http://taylorandfrancis.com

1 Processing Principles

1.1 INTRODUCTION

This chapter introduces the reader to the fundamentals needed to better understand the following chapters. It is intended for those new to gas processing and those having limited chemistry background. It contains three major sections:

1. Process terminology and units
2. Basic concepts of chemistry
3. Thermodynamics

The last two topics are major fields of science. This chapter provides only a brief introduction to the subjects to give readers without a chemical engineering education sufficient background to comprehend more technical sections in later chapters.

1.2 UNITS AND CONVERSIONS

There are two general systems of units in use today, the International System of Units (SI) and the U.S. Engineering System (USES) and their variants. The USES is in general use in the United States, but all other industrialized countries use a system based on SI.[1] This section discusses the commonly used units and gives some conversions between USES and SI.

The book uses dual units in the text, examples, and graphs whenever possible (USES first followed by SI in parentheses) but there are cases where it will be necessary to make individual conversions. Appendix B.1[2] provides a set of unit conversions that should be adequate for most situations. For example, the SI unit of pressure is the pascal (commonly kPa or MPa), but both bar and kg/cm^2 are frequently used.

The section below gives basic units. This is followed by commonly used combinations of units. Before discussing units, the definition of commonly used prefixes is needed. Frequently, quantities in gas processing involve large values. To make large numbers more manageable in the USES, the following prefixes are used:

M = thousand	= 1,000	= 10^3
MM = million	= 1,000,000	= 10^6
B = billion	= 1,000,000,000	= 10^9
T = trillion	= 1,000,000,000,000	= 10^{12}
Quad	= 1,000,000,000,000,000	= 10^{15}

Note that these prefixes do not follow SI conventions. The letter M usually represents 10^6 (which follows SI convention) outside the United States. To avoid confusion, 10^3 and 10^6 are sometimes used.

In this book, M represents 10^3 when using USES-based units. The book also follows the U.S. convention for the comma as shown in the numbers above, not a fractional number or space as is often used elsewhere. The Quad represents an extremely large number and is used only when discussing energy terms on a national or world scale.

[1] NIST (2017) provides a complete discussion on SI and Klinkenberg (1969) gives an excellent summary of the Engineering System.

[2] See Appendix B on publisher website: www.crcpress.com/Fundamentals-of-Natural-Gas-Processing-Third-Edition/Kidnay-Parrish-McCartney/p/book/9781138612792

The prefixes for SI are not followed throughout all countries using SI when applied to volumes. To avoid potential confusion, large values for volumes will use the exponential format. For example, 3,000,000 m^3 will be presented as $3 \times 10^6 m^3$. Prefixes for all other units in SI will follow the SI convention.

Conversion between USES and SI units rarely provides exact results, e.g., 80.00°F = 26.67°C. The precision of a given value dictates the number of significant figures given in the conversion. If converting 80°F and 80.0°F, the conversions will be 27°C and 26.7°C, respectively.

1.2.1 Basic Units

Table 1.1 lists five important basic units used in gas processing. The conversion from one unit system to the other is included. Of the five basic units only time is common to both sets of units.

The USES uses the pound-force (lb_f) as a base unit and it is defined as the force a standard gravitational field exerts on a mass of one pound (lb_m). However, using Newton's second law (force = mass × acceleration) a lb-force should be equal to (1 lb_m) × (32.174 ft/s^2) where 32.174 ft/s^2 is the standard acceleration of gravity (denoted as g). To maintain numerical and dimensional consistency it is necessary to define the term $g_c = 32.174$ ft-lb_m/s^2-lb_f. Thus, when using USES, Newton's second law becomes force = mass × g/g_c. As a result, whenever there is a mass–force conversion in USES units g_c must be used to obtain numerically and dimensionally correct values.

The two temperature scales, kelvin (K) and Rankine (°R) are absolute, that is, the zero point is absolute zero. These are awkward to use at ambient temperatures and above so the two relative scales, Fahrenheit (°F) and Celsius (°C) are used. The relationship between the four temperature scales is given below:

$$t(°\mathrm{F}) = T(°\mathrm{R}) - 459.67$$
$$t(°\mathrm{C}) = T(\mathrm{K}) - 273.15$$
$$T(\mathrm{K}) = T(°\mathrm{R})/1.80$$
$$t(°\mathrm{F}) = 1.80t(°\mathrm{C}) + 32$$

Note that by convention the degree symbol is not used with the unit symbol K, and kelvin is not capitalized. It is also common convention to use T to refer to a temperature on an absolute scale and t to refer to a temperature on a relative scale.

1.2.2 Derived Units

Table 1.2 lists other important derived units commonly used in gas processing. These are convenient combinations of the basic units. The table gives the accepted derived name. Other important combinations of units are mentioned in Section 1.2.3.

TABLE 1.1
Five Basic Units Important in Gas Processing

	Engineering System (USES)		International System of Units (SI)	
	Base Unit		Base Unit	
Basic Quantity	Name	Symbol	Name	Symbol
Length	foot	ft (= 0.3048 m)	meter	m (= 3.2808 ft)
Mass	lb mass	lb_m (= 0.4536 kg)	kilogram	kg (= 2.205 lb_m)
Force	lb force	lb_f (=4.448 N)		
Time	second	s	second	s
Temperature	Rankine	°R (= 0.5556 K)	Kelvin	K (= 1.80°R)

TABLE 1.2
Important Derived Units in Gas Processing

	Engineering System (USES)		International System of Units (SI)	
	Unit		Unit	
Basic Quantity	Name	Symbol	Name	Symbol
Area	Square foot	ft^2 (= 0.0929 m^2)	Square meter	m^2 (= 10.76 ft^2)
Volume	Cubic foot	ft^3 (= 0.02832 m^3)	Cubic meter	m^3 (= 35.31 ft^3)
Force			Newton	N (= 0.2248 lb_f)
Pressure	lb_f per square inch	psi (= 6,895 Pa)	Pascal	Pa (= 0.0001450 psi)
Energy	British thermal unit	Btu (= 1,055 J)	Joule	J (= 0.0009478 Btu)
Power	Horsepower	hp (= 746.0 W)	Watt	W (= 0.001341 hp)

Both area and volume are simple multiples of length. The others are derived from physical laws and definitions as discussed below.

1.2.2.1 Force

Force is defined as mass times acceleration. This is correctly done in the SI system (1 N = 1 kg m/s^2).

1.2.2.2 Pressure

This is one of the most common and important of the numerous derived units; it is defined as force per unit area. In USES, the accepted unit is pound-force per square inch (lb_f/in^2) or psi. In SI the defined unit is the pascal (Pa), defined as one Newton per square meter (1 Pa = 1 N/m^2). In both systems, it is a common practice to convert pressures into other convenient units, such as bar, inches of Hg, mm Hg and ft H_2O as shown below:

$$1\,\text{psi} = 6{,}890\,\text{Pa} = 2.04\,\text{in Hg}(32°\text{F}) = 51.7\,\text{mm Hg}(32°\text{F}) = 2.31\,\text{ft H}_2\text{O}(32°\text{F})$$

$$1\,\text{bar} = 10^5\,\text{Pa} = 14.50\,\text{psi} = 29.53\,\text{in Hg}(32°\text{F}) = 750.1\,\text{mm Hg}(32°\text{F}) = 10.20\,\text{ft H}_2\text{O}(32°\text{F})$$

When using the height of a liquid column as the pressure measurement (mercury or water), the temperature must be specified because it affects liquid density and thus pressure value. In the above examples, pressures are based upon the density of mercury (Hg) and water at 32°F (0°C).

There are three different types of pressure measurements: absolute, gauge, and differential. Absolute pressure is the pressure relative to an absolute vacuum, zero pressure, and has the suffix "a" added to psi and often to bar which is the convention this book follows. While seldomly measured, absolute pressure is important in many calculations.

Gauge pressure is the most common because most gauges measure the difference between system pressure and atmospheric pressure. Gauge pressure is denoted by adding the suffix "g", e.g., psig and barg. Gauge pressure is converted to absolute pressure by adding atmospheric pressure to gauge pressure. This correction is 14.696 psi (1.000 atmosphere) or 1.01325 bara at sea level. At an elevation of 1 mi (1.6 km) the correction drops to 12.5 psi (0.86 bar).

Differential pressure is like gauge pressure except that pressure reading is made relative to another system pressure. If one side of a gauge is open to the atmosphere the differential pressure is identical to gauge pressure. Differential pressure sometimes is denoted by the suffix "d" unless it is clear from context.

To avoid ambiguity, the suffix should always be added to a reported pressure value. In USES if no suffix is included the pressure is most likely gauge pressure. This book uses psi and bar as pressure units. Suffixes are added to both pressure units to denote gauge or absolute pressure.

1.2.2.3 Energy

From a physics perspective, energy is defined as the work required to move a force a given distance. The unit ft-lb_f is used in USES in mechanical calculations; the Btu[3] is used for heat or chemical energy. The Joule (J) which is a Newton-meter, is the only energy unit in the SI system.

1.2.2.4 Power

Power is the rate of energy used or produced. The common power unit in USES is horsepower (hp) although ft-lb_f/h is sometimes used. The SI uses only the Watt (W) which is a N/s.

1.2.3 Other Important Units in Gas Processing

There are a number of combinations of units commonly used in the gas industry. Some are listed here and described in more detail in other sections.

1.2.3.1 Standard Volume

Gas quantities are typically defined in terms of volumes of gas. To convert volumes into mass the temperature and pressure of the gas volume must be known. In USES, the common unit is standard cubic feet (scf). Standard conditions are 14.696 psia (1.01325 bara) and 60.0°F (15.6°C). One lb-mol of an ideal gas has a volume of 379.49 scf (see Section 1.3 for definition of a mole).

There are two standards used with the SI system. The Normal cubic meter (Nm^3) has standard conditions of 0.0°C (32.0°F) and 1.01325 bara (14.696 psia). The other is the Standard cubic meter (Sm^3) which has standard conditions of 15.0°C and 1.01325 bara. One kg-mol of an ideal gas has a volume of 22.414 Nm^3 and 23.645 Sm^3.

Appendix B.2 lists conversions among various standard volumes.

1.2.4 Mathematical Symbols

The book uses two common mathematical Greek symbols in many equations. The first is delta, Δ, which denotes change, e.g., Δt indicates the difference between two temperatures. The second is sigma, Σ, which is the symbol for summation. Other Greek symbols are used and are defined when introduced and in the "Notation" section at the end of the book.

1.3 BASIC CHEMISTRY CONCEPTS

This section discusses only those concepts considered essential for a fundamental understanding of gas processing; it should not be viewed as a chemistry primer.

Before discussing the various concepts of chemistry, the definitions of atoms, molecules, and moles are needed. Atoms are the building blocks of all matter. Molecules consist of two or more atoms in a definite structure held together by chemical bonds. For example, a water molecule, H_2O, contains two hydrogen atoms and one oxygen atom. A molecule that contains two or more different kinds of atoms is a chemical compound.

Individual molecules are extremely small making routine calculations based upon molecules cumbersome. To simplify calculations the mole is used. A mole is the amount of substance of a system which contains as many molecules as there are atoms in 0.012 kg of carbon 12 (NIST, 2017). The molar mass or molecular weight of a pure substance is the mass of 1 mol of the substance. For example, the molar mass of hydrogen is 1 and the molar mass of oxygen is 16. Therefore, the mass of 1 mol of water is 18 g (18 g/mol). In engineering units lb-mol are used. One lb-mol of water would

[3] There are several Btu units. The Btu (IT) which is most commonly used, and the one used in this book, is 0.04% higher than the Btu (Thermochemical). See the *Engineering Data Book* (2016) for more detail.

have a mass of 18 lb_m (18 lb_m/lb-mol). While "molar mass" is now considered the proper term, "molecular weight" is still commonly used in the gas industry.

1.3.1 Structure and Nomenclature

This section illustrates only the structures of the most important compounds encountered in gas processing. Most of these compounds contain only hydrogen and carbon and are therefore called hydrocarbons. Descriptions of the chemicals used in major processes (e.g., amines, glycols) are given in later chapters.

1.3.1.1 Alkane Hydrocarbons

Alkane (also called paraffin or saturated) hydrocarbons contain carbon atoms fully bonded to other carbon or hydrogen atoms. The general formula for an alkane is $C_nH_{2n+2,}$ where n = number of carbon atoms. Figure 1.1 shows the structure of some major components of natural gas.

1.3.1.2 Aromatic Hydrocarbons

So-called because many of the early compounds identified in this category have a spicy odor. Figure 1.2 shows those of interest in gas processing. Note that the shorthand symbol for benzene is the six-member ring structure shown in all of the other compounds. The aromatics shown are referred to as BTEX (benzene, toluene, ethyl benzene, and xylene). Chapter 14 discusses why and where these compounds are important in gas processing.

The BTEX compounds differ in the type and number of alkyl groups replacing hydrogen atoms on the benzene ring. An alkyl group, given the symbol "R," is a hydrocarbon with one hydrogen

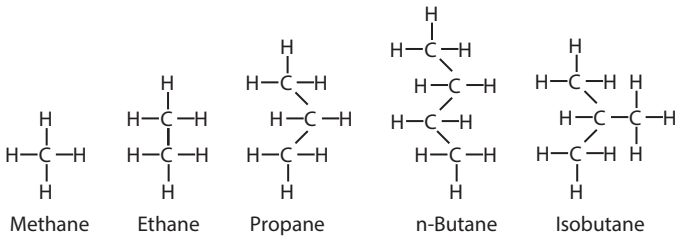


FIGURE 1.1 Structure of major alkane hydrocarbons in natural gas.

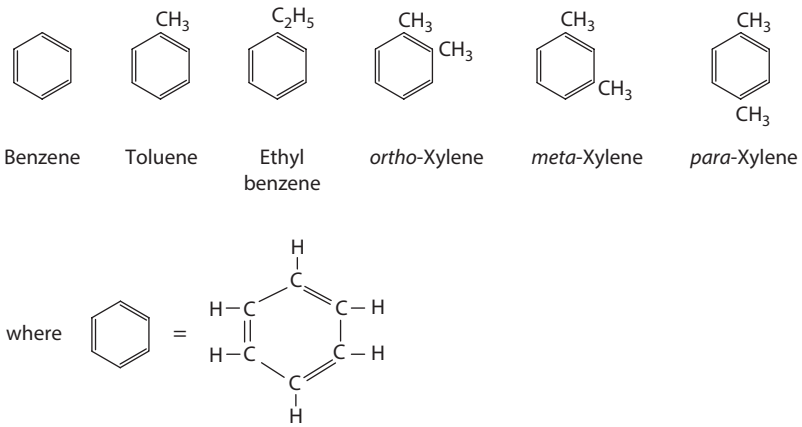


FIGURE 1.2 Aromatic hydrocarbons found in natural gas.

atom removed. Thus, toluene is benzene with one alkyl group, a methyl group; ethylbenzene contains benzene plus one ethyl group.

1.3.1.3 Sulfur Compounds

In addition to elemental sulfur, there are a number of sulfur compounds found in natural gases. The simplest is hydrogen sulfide, H_2S. Replacing one hydrogen atom with a hydrocarbon group creates a mercaptan with the structure RSH where R represents an alkyl group. Mercaptans are extremely odiferous and as a result are used to odorize natural gas and liquid propane (see Chapter 17 for more details).

Replacing both hydrogen atoms on H_2S with alkyl groups generates a sulfide, $R_1–S–R_2$. The R groups need not be the same. While still odiferous, they are less so than mercaptans.

Finally, disulfides are formed when two mercaptans combine. They are oily odiferous compounds with the structure $R_1–S–S–R_2$.

Sulfur compounds are discussed in Chapters 10 and 15.

1.3.1.4 Oxygen Compounds

The common oxygen compounds naturally occurring in natural gas are carbon dioxide and water. Replacing a hydrogen atom on the water molecule with an alkyl group generates an alcohol, giving the structure R–OH. The OH group is called a hydroxyl group. An important alcohol is methanol, CH_3OH. While not found naturally in natural gas, alcohols are important in the natural gas industry. Chapters 8 and 11 cover applications using alcohols.

Glycols contain two hydroxyl groups with the structure HO–R–OH. Chapters 8, 11, and 15 discuss applications of glycols.

Some gas processing solvents contain oxygen between alkyl groups with the structure of $R_1–O–R_2$. These compounds are called ethers. Chapter 8 has examples of ether compounds which also include hydroxyl groups.

1.3.1.5 Nitrogen Compounds

Although elemental nitrogen is common, nitrogen compounds do not exist naturally in natural gas. However, they are important in gas treating. The simplest nitrogen compound in gas processing would be ammonia, NH_3. Replacing the hydrogen atoms in the ammonia molecule with alkyl groups creates amines. Amines with one hydrogen atom replaced by an alkyl group are called primary amines. A secondary amine has two alkyl groups and an amine with three alkyl groups is a tertiary amine. Chapter 10 discusses some of the important amine compounds used in gas processing.

1.3.2 Important Chemical Properties

This section briefly discusses three important chemical properties of compounds found in natural gas: reactivity, solubility, and hydrogen bonding.

1.3.2.1 Reactivity

With the exception of water, nitrogen, helium, and carbon dioxide all common components in natural gas are combustible, i.e., react with oxygen to generate heat. The heat of combustion is discussed in Section 1.3.3. Otherwise the hydrocarbons are nonreactive and stable at ambient temperature. Ethane and heavier hydrocarbons will thermally crack, or decompose, at high temperatures. The heavier the compound the easier it is to crack. Chapter 11 discusses some problems caused by thermal decomposition of heavier compounds.

Adding oxygen, sulfur, or nitrogen atoms to a hydrocarbon tends to make the compound less thermally stable and more reactive with other compounds. Unfortunately, a number of sulfur compounds are reactive at ambient conditions. These include hydrogen sulfide and mercaptans. Sulfides and disulfides are much less reactive but are subject to thermal decomposition. While alcohols are relatively thermally stable, glycols are subject to thermal decomposition. Amines used in natural

gas processing generate small quantities of heat stable salts (see Chapter 10 for details). Both glycols and amines react with trace amounts of oxygen to generate undesirable compounds.

1.3.2.2 Solubility

Solubility of a gas into a liquid is a function of temperature, pressure, and chemical nature. Mutual solubility of two liquids depends primarily on temperature and the chemical nature of components. This discussion focuses only on mutual solubility.

Solubility follows the adage of "like attracts like." Consider the following:

- Liquid hydrocarbons are completely soluble, or miscible, in other liquid hydrocarbons at typical gas processing conditions.
- Liquid hydrocarbons and water are essentially insoluble in one another.
- Methanol and ethanol are completely miscible in water and in liquid hydrocarbons because these compounds contain both hydrocarbon and water-like groups.
- Methanol and ethanol prefer the water phase if both water and a liquid hydrocarbon are present.

1.3.2.3 Hydrogen Bonding

The observations above are explainable in terms of an important chemical property called hydrogen bonding. Hydrogen bonding occurs in compounds containing hydroxyl (OH) groups or nitrogen. Hydrocarbons contain only carbon and hydrogen and cannot hydrogen bond. Because of this they are "nonpolar." Water is a polar compound. This is because the oxygen atom strongly attracts the one electron on each of the hydrogen atoms. Thus the oxygen atom becomes more negative while the hydrogen atoms become more positive. The positive nature of the hydrogen atom attracts the oxygen atom of a nearby water molecule; a weak bond forms between the oxygen of one molecule and the hydrogen of another molecule as shown in Figure 1.3a. This weak bond is called "hydrogen bonding" (see, e.g., Prausnitz et al., 1999). Hydrogen bonding can occur whenever hydroxyl groups are present such as shown in Figure 1.3b for an alcohol. It also may be present with amines, such as the primary amine shown in Figure 1.3c. (Chapter 10 discusses amine chemistry.) Hydrogen bonding plays an important role in several separation processes used in gas processing.

To see how important hydrogen bonding is, consider the normal boiling point (NBP) temperatures (the boiling temperature at 14.7 psia (1.01 bara)) of four compounds (see Table B.1):

- Ethane (C_2H_6) with a molar mass of 30, boils at –127°F (–88°C)
- *n*-Heptane (C_7H_{16}) with a molar mass of 100, boils at 209°F (98°C)
- Hydrogen sulfide (H_2S) with a molar mass of 34, boils at –76°F (–61°C)
- Water with a molar mass of 18, boils at 212°F (100°C)

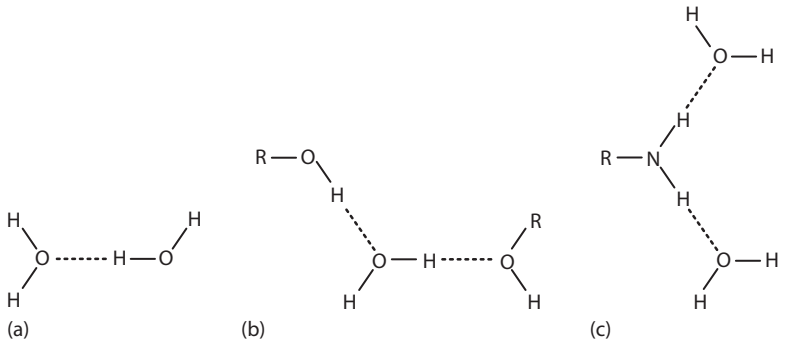


FIGURE 1.3 Hydrogen bonding (a) between two water molecules, (b) between water and an alcohol, and (c) between water and a primary amine.

Comparing ethane with *n*-heptane, as a first approximation the NBP increases with increasing molar mass. However, H_2S has a similar structure to H_2O. It has a higher molar mass but an NBP that is 288°F (160°C) below that of H_2O. The alkane having an NBP comparable to water is *n*-heptane which has a molar mass of 100. Water has the lowest molar mass of the four but has the highest NBP because of hydrogen bonding.

Considering solubility, nonpolar liquids will be soluble in hydrocarbons but only slightly soluble in water; liquids capable of hydrogen bonding, e.g., the hydroxyl group of alcohols and glycols and the nitrogen atom in amines, will be soluble in water and possibly in hydrocarbons. Note that the strength of the hydrogen bonding, and water solubility, varies depending upon structure. For example, methanol and ethanol are completely miscible with water. Increasing the number of carbons on an alcohol decreases its ability to hydrogen bond and its solubility in water.

1.3.3 Important Physical Properties

1.3.3.1 Density and Relative Density

1.3.3.1.1 Density

Density is defined as the mass of a substance divided by the volume it occupies at a specified pressure and temperature. The normal symbol for density is ρ, and typical units are lb_m/gal, lb_m/ft^3, or kg/m^3. It is the reciprocal of specific volume.

Table 1.3 lists density values for pure methane at two temperatures and pressures. At –200°F (–129°C) methane is a liquid at the given pressures. Note that doubling the pressure changes the liquid density by only 1%. In general, unless the pressure difference is large or the temperature is near the critical temperature (defined in Section 1.3.3.2), liquid density is usually considered independent of pressure, i.e., liquid is incompressible.

For methane gas at 70°F (21°C) the situation is different. There is a 107% change by doubling the pressure. Gas densities are strongly affected by pressure changes under all situations.

Because as a general rule temperature affects all properties to some extent, it is not surprising that the density of both liquids and gases is affected by temperature changes. For gases at low to moderate pressures, volumes can often be estimated using the ideal gas law

$$PV = nRT \tag{1.1}$$

where

P is the absolute pressure
V is the total volume
n is the number of moles
R is the gas constant
T is the absolute temperature

TABLE 1.3
Effect of Temperature and Pressure on Methane Density

	Methane Density (lb_m/ft^3)				Methane Density (kg/Nm^3)		
t/°F	Phase	300 psia	600 psia	*t*/°C	Phase	20.7 bara	41.4 bara
–200	Liquid	23.20	23.44	–129	Liquid	371.6	375.5
70	Vapor	0.879	1.86	21	Vapor	14.08	29.25

Source: Lemmon et al. (2017).

The value of the gas constant is independent of molar mass of the gas but does depend upon the temperature, pressure, and volume units used. Appendix B.2.1 gives values for the gas constant in various units. The ideal gas law assumes that the gas molecules have neither volume nor attraction to each other, i.e., infinitely small spheres with finite mass. The equation is extremely useful for simple calculations but should not be used for exacting calculations without being checked against more accurate methods.

Example 1.1

Estimate the density of methane (molar mass = 16.042) at 100°F (37.8°C) and 100 psig (6.9 barg) using the ideal gas law.

Solution

P = 100 psig + 14.7 = 114.7 psia (7.91 bara) (note conversion to absolute pressure)
T = 100°F + 459.67 = 559.67°R (310.93 K) (note conversion to absolute temperature scale)
R = 10.7315 psia-ft^3/lb-mol-°R (8.314 × 10^{-5} bar-m^3/mol-K) (Appendix B.2.1)

Rearranging the ideal gas law to solve for density (n/V) gives:

$$n/V = P/RT = 114.7/(10.7315 \times 559.67) = 0.0191\,\text{lb-mol/ft}^3\left(306.0\,\text{mol/m}^3\right)$$

Convert from moles to mass:

$$0.0191\,\text{lb-mol/ft}^3 \times 16.042\,\text{lb}_\text{m}/\text{lb-mol} = 0.306\,\text{lb}_\text{m}/\text{ft}^3\left(4.91\,\text{kg/m}^3\right)$$

This is 1.3% less than the more accurate value of 0.310 lb$_m$/ft^3 (4.97 kg/m^3) (Lemmon et al., 2017).

The ideal gas law is also useful for estimating volumes based upon temperature and pressure differences. For a constant number of moles Equation 1.1 can be rearranged to give:

$$\frac{V_2}{V_1} = \frac{P_1}{P_2} \times \frac{T_2}{T_1} \tag{1.2}$$

where the subscripts denote two different sets of conditions. The calculations can be made more accurate by including a ratio of the compressibility factors (z_2/z_1) where $z = PV/nRT$. Appendix B.4 discusses how to estimate the compressibility factor.

Example 1.2

There are 140 MMscfd (3.75 × 10^6 Nm^3/d) of feed gas entering a gas plant at 77°F (25°C) and 900 psig (62 barg). Using Equation 1.2 estimate the actual volumetric flow rate of gas entering the plant assuming ideal gas behavior.

Solution

From Section 1.2.3 the standard conditions for the gas are 60°F (15.6°C) and 14.7 psia (1.01 bara). Then

$$\frac{V_2}{V_1} = \frac{P_1}{P_2} \times \frac{T_2}{T_1} = \frac{14.7}{914.7} \times \frac{(77 + 459.67)}{(60 + 459.67)} = 0.0166$$

Then the actual volumetric flow rate is 140 MMscfd × 0.0166 = 2.3 MMcfd (0.76 m^3/s).

Example 1.3

Obtain a better estimate of the actual inlet gas flow rate in Example 1.2 using the compressibility factor, *z*. The molar mass of the gas is 19.

Solution

The graphs in Appendix B.4 require specific gravity to compute pseudo critical temperature and pressure. From Equation 1.3 the specific gravity of this gas is 19/28.9625 = 0.66.

From Figure B.28 the pseudo critical temperature is 375°R and critical pressure is 670 psia. The reduced temperature is (77 + 459.67)/375 = 1.43 and reduced pressure is 914.7/670 = 1.36. From Figure B.29 the compressibility factor is 0.84. The volume ratio to convert to actual flow rates is then

$$\frac{V_2}{V_1} = \frac{P_1}{P_2} \times \frac{T_2}{T_1} \times \frac{z_2}{z_1} = \frac{14.7}{914.7} \times \frac{(77+459.67)}{(60+459.67)} \times \frac{0.84}{1} = 0.014$$

With the correction for compressibility the actual volumetric flow rate is 140 MMscfd × 0.014 = 2.0 MMcfd (0.64 m^3/s).

1.3.3.1.2 Relative Density (Specific Gravity)

The relative density (specific gravity) is the ratio of the mass of a given volume of a substance to that of an equal volume of another substance used as a standard. Unless stated otherwise, air is used as the standard for gases and water for liquids.

For gases at the same temperature and pressure

$$\text{Relative density} = \text{gas density/air density} \tag{1.3}$$

and for ideal gases

$$\begin{aligned}\text{Relative density} &= \text{molar mass of gas/molar mass of dry air} \\ &= \text{molar mass of gas}/28.9625\left(\text{GPA Midstream Standard 2145-16, 2016}\right)\end{aligned} \tag{1.4}$$

The composition of dry air is slowly changing, and natural gas contracts have been written based upon the molar mass value of 28.9625 g/mol. To maintain consistency the definition of relative density for natural gas was modified to be based solely on a fixed reference value (28.9625 g/mol), not on the molar mass of air. The differences between fixed value and 2019 value is on the order of 0.04% and important only for accounting purposes.

For liquids

$$\text{Relative density} = \frac{\text{Liquid density}}{\text{Water density}} \tag{1.5}$$

Normally the densities are at the same temperature, commonly 60°F (15.6°C).[4] If temperatures are different, both temperatures should be given. Pressure has essentially no effect on densities of liquids unless temperature is near the liquid's critical point (see following section).

Example 1.4

A condensate has a relative density of 0.65 at 60°F (15.6°C). What is the absolute liquid density?

Solution

At 60°F (15.6°C) the density of water is 62.367 lb_m/ft^3 (999.02 kg/m^3).

Therefore, the absolute density of the condensate is 0.65 × 62.367 = 40.54 lb_m/ft^3 (649.4 kg/m^3).

[4] Relative densities of liquids are sometimes referenced to water at 39.2°F (4°C) because water density is maximum at that temperature.

The American Petroleum Institute (API) uses a scale of measurement for the relative density of liquid petroleum products which is expressed in degrees API: the API gravity is sometimes measured directly by using a hydrometer. However, vibrating tube densimeters are now commonly used. The relationship between API gravity and relative density is

$$\text{API} = \frac{141.5}{\text{Relative density}} - 131.5 \tag{1.6}$$

with the relative density measured at 60°F (15.6°C). The API gravity is commonly used when working with stabilized condensate and natural gasoline.

Example 1.5

What is the API gravity of the condensate in Example 1.4?

Solution

The relative density was measured at 60°F (15.6°C) so the value can be directly inserted into Equation 1.6

$$\text{API} = \frac{141.5}{\text{Relative density}} - 131.5 = \frac{141.5}{0.6500} - 131.5 = 86°\text{API}$$

1.3.3.2 Vapor Pressure

There are two "vapor pressures" used in the gas industry, true vapor pressure and Reid vapor pressure (RVP), and they are not equal. RVP is used only for mixtures and is discussed in Section 1.4.2.

The concept of vapor pressure for a pure fluid can be illustrated by the following example. A container, equipped with a pressure gauge, an inlet liquid line, and an outlet line leading to a vacuum pump, is inserted into a constant temperature bath. The container is completely evacuated, and then a pure liquid is introduced. Some of the liquid vaporizes but once vaporization stops and the pressure and temperature are constant, the liquid and a vapor phase are in equilibrium. The measured pressure and temperature constitute one point on the vapor pressure curve (also referred to as the saturation curve).

If the bath temperature is changed the equilibrium between liquid and vapor is reestablished at a new pressure. Repeating this procedure for a series of temperatures will generate the vapor pressure curve for the pure fluid. The same experiments can be carried out for a pure liquid in equilibrium with its solid phase to generate a fusion curve and a pure solid in equilibrium with its vapor phase to generate a sublimation curve. Figure 1.4 shows a typical set of pressure–temperature relationships that would result from these measurements.

At the triple point the solid, liquid, and vapor phases are at equilibrium. Starting at the triple point and moving up the vapor pressure curve both pressure and temperature rise until the critical point is reached; at this point, the density of the liquid and vapor are equal and the fluid is a single phase. Above the critical temperature (usually given the symbol T_c) there can be only one fluid phase present.

Below the triple point the solid and vapor phases are in equilibrium. Vapor pressures at and below the triple point are usually very low. The one notable exception is carbon dioxide which has a triple point temperature of −69.81°F (−56.56°C) and pressure of 75.1 psia (5.18 bara) (Lemmon et al., 2017).

Note that to specify a point where there is only one phase present, e.g., the vapor phase, in Figure 1.4 both temperature and pressure must be stated. If two phases are present, e.g., along the vapor pressure curve, selecting either the temperature or pressure defines the location on the figure. Finally there is only one point, the triple point, where three phases are present. This pattern follows the Gibbs Phase Rule (Smith et al. 2018).

$$F = N - \varphi + 2 \tag{1.7}$$

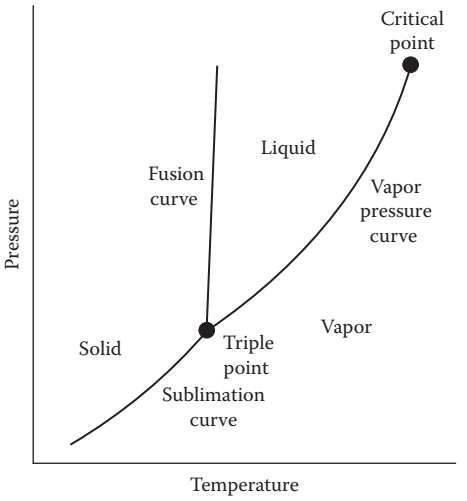


FIGURE 1.4 Pressure-temperature diagram for a pure fluid.

where

F is the number of degrees of freedom
N is the number of components
φ is the number of phases present

The degrees of freedom are the number of conditions that must be specified to define a point on curves such as in Figure 1.4. For example, using Equation 1.7 for a pure component ($N = 1$) along the vapor pressure curve ($\varphi = 2$) yields $F = 1$. As noted above, once either temperature or pressure is specified, the other is known.

If there are two phases present for a binary mixture ($N = 2$), the degrees of freedom increases by one. Therefore, specifying two of the three variables among temperature, pressure, and composition defines the other variable. Chapter 4 discusses mixtures in more detail. The concept of degrees of freedom is encountered frequently in gas processing.

1.3.3.3 Heats of Phase Change

There is always a heat effect associated with any phase change, be it solid–vapor, liquid–vapor, or solid–liquid. In gas processing, the most important phase changes are liquid–vapor and solid–liquid. This discussion is limited to these two topics.

The amount of heat that must be added to a given quantity of liquid to convert a pure component into a vapor at the same temperature and pressure is the heat of vaporization. The units are Btu/lb_m or Btu/lb-mol (kJ/kg, kJ/kg-mol). The heat of vaporization is a strong function of temperature and decreases to zero at the critical point. Table 1.4 shows a few representative values.

The heat of vaporization for fluids decreases with increasing temperature, and for propane is zero at 206°F (97°C) because this is the critical temperature (at the critical point liquid and vapor properties are the same). Note that water's heat of vaporization is much greater than those for propane and *n*-butane. The high heat of vaporization is a direct result of the polar nature of water discussed in Section 1.3.2 because additional energy is required to break the hydrogen bonds.

Heats of fusion are always smaller than heats of vaporization near the triple point. It simply takes less energy to change a solid into a liquid than to vaporize a liquid. Table 1.5 shows a few values of heats of fusion.

Note again the high value for water which is caused by the energy required to break the hydrogen bonding.

TABLE 1.4
Heats of Vaporization, Btu/lb$_m$ (kJ/kg)

	80°F (27°C)		206°F (97°C)	
	Btu/lb$_m$ (kJ/kg)	Btu/lb-mol (kJ/kg-mol)	Btu/lb$_m$ (kJ/kg)	Btu/lb-mol (kJ/kg-mol)
Water	1,048 (2,440)	18,864 (43,870)	974 (2,264)	17,530 (40,750)
Propane	142 (331)	6,260 (14,600)	0	0
n-Butane	163 (380)	9,470 (22,090)	120 (278)	6,970 (16,160)

Source: Lemmon et al. (2017).

TABLE 1.5
Heats of Fusion for Several Compounds

	Btu/lb$_m$ (kJ/kg)	Btu/lb-mol (kJ/kg-mol)
Water at 32°F (0°C)	143.3 (333.5)	2,582 (6,008)
Hydrogen sulfide −96.8°F (−85.5°C)	30.1 (70.0)	1,020 (2,380)
Ethane at −297.8°F (−183.2°C)	40.8 (95.0)	1,230 (2,860)
Propane at −305.8°F (−187.6°C)	34.3 (79.9)	1,510 (3,520)
n-Butane at −281.0°F (−138.3°C)	34.5 (80.2)	2,000 (4,660)

Source: Speight (2017).

1.3.3.4 Heat Capacity

Heat capacity is a measure of the amount of heat required to change the temperature of a unit mass or mole by one degree. It has units of Btu/lb$_m$-°R (J/kg-K) or Btu/lb-mol-°R (kJ/kg-mol-K). When adding heat at constant pressure the amount of energy required depends upon the heat capacity at constant pressure, C_P. If heat is added at constant volume the heat capacity at constant volume, C_V, must be used.[5] Heat capacities at constant pressure are used for nearly all calculations because most processes occur at nearly constant pressure.

Unless close to the critical point, the liquid C_P and C_V are essentially equal. For an ideal gas the molar heat capacities are related by

$$C_P = C_V + R \tag{1.8}$$

While the pressure effect on heat capacity is often small and ignored, heat capacity is a strong function of temperature. Tables B.2 and B.3 give numerical values for molar ideal gas heat capacities at different temperatures. Note that heat capacity is on a per unit change in temperature. Therefore, heat capacities reported in absolute temperatures are identical to those at corresponding relative temperatures.

1.3.3.5 Heat of Combustion

Natural gas is traded on the basis of heating value. The heating value is either measured directly using a combustion calorimeter or calculated from gas composition (Gas Processors Association, 2014). Below is a simple reaction for the combustion of methane:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

[5] Heat can be added to liquid and vapor along the saturation line. In this case, C_{Sat}, is used. This term is not commonly used in the gas industry.

The heat produced is the heat of combustion or heating value. All of the above components except water will be a gas at standard conditions. Water can be either a gas or liquid. If all water is condensed, the heat generated is called the Gross or Higher Heating Value (HHV). From Table B.1 the HHV for methane is 1,010 Btu/scf (37.71 MJ/Sm^3). If the water product is all vapor, the heating value, called Lower or Net Heating Value (LHV) is the HHV less the heat of vaporization for water. The LHV from Table B.1 is 909.4 Btu/scf (33.95 MJ/Sm^3). While HHV values are used in trading of energy fuels, the LHV is commonly used in fired unit calculations where the water product of combustion is not condensed.

1.3.3.6 Viscosity

Viscosity is the resistance a fluid has to motion; it is often referred to as internal friction. It is important in gas processing because viscosity is responsible for pressure drop through process equipment and lines. Typical units for viscosity are lb_f-s/ft^2, lb_m/ft-s (Pa-s, poise (0.1 Pa-s), and centipoises, cP (mPa-s)[6]). The centipoise and mPa-s, which are equivalent, are the commonly used viscosity units in the gas industry.

Table 1.6 lists the viscosities of some commonly used liquids in gas processing. Note that the viscosity decreases with increasing temperature. For typical operating pressures in gas processing, pressure has a negligible effect on viscosity of liquids and gases unless near the critical point.

Table 1.7 presents the viscosity of several gases at a function of temperature and low pressure. For methane pressures below about 750 psia (50 bara) the viscosity is constant. Even at 3,000 psia (200 bara) the viscosity has increased by about 1%.

TABLE 1.6
Viscosity of Some Liquids in Gas Processing, cP (mPa-s)

	Temperature, °F (°C)			
Fluid	32 (0)	68 (20)	140 (60)	212 (100)
Propane[a]	0.19	0.18	0.16	—
Water[a]	1.7	1.0	0.48	0.28
Methanol[a]	0.78	0.56	0.36	0.26
Ethylene glycol[b]	—	~25	5.1	2.0
Triethylene glycol[b]	170	49	9.7	3.6

Sources:
[a] Lemmon et al. (2017).
[b] Appendix B, Table B.5, and Figures B.14 and B.15.

TABLE 1.7
Viscosity of Some Gases in Gas Processing at Low Pressure, cP (mPa-s)

	Temperature, °F (°C)			
Fluid	32 (0)	68 (20)	140 (60)	212 (100)
Methane	0.0104	0.0110	0.0123	0.0135
Propane	0.0074	0.0080	0.0091	0.0101
Water vapor	0.0092	0.0097	0.011	0.0124

Source: Lemmon et al. (2017).

[6] The lower case *m* as a prefix denotes 10^{-3}.

1.3.3.7 Surface Tension and Interfacial Tension

Surface tension and interfacial tension are similar in that they address how the surface of a liquid differs from the bulk liquid (McCain, 1990). Surface tension makes a liquid droplet or gas bubble spherical. It is important when a pure fluid or mixture has two phases, such as in boiling. Interfacial tension is important when there are two different materials in contact, such as a liquid and solid, gas and liquid, or liquid and liquid because it affects how well the phases separate. The common units for surface tension and interfacial tension are dyn/cm and N/m, which equals 1,000 dyn/cm.

Interfacial tension is critically important in foam (gas–liquid) and emulsion (liquid–liquid) formation and stabilization. Bubbling pure methane through liquid water creates some frothing, depending upon the bubbling rate. However, the foam is unstable and the bubbles collapse almost instantly because the interfacial tension is low. The foam can be stabilized by adding surface active agents which are materials that concentrate at interfaces. Surface active agents can be very fine solids, e.g., iron sulfide particles, or liquid additives such as lubricating oils, detergents, and inhibitors. These agents raise the interfacial tension and make the bubbles more stable, possibly causing foaming problems. For mixtures containing liquid water and liquid hydrocarbons, surface active agents can stabilize emulsions.

Surface tension and interfacial tension decrease with increasing temperature. Heating foams and emulsions makes them less stable and quicker to decompose. The other common way to break foams and emulsions is to add other surface-active agents that decrease the interfacial tension.

1.3.4 Mixtures

Mixtures are much more common in gas processing than pure fluids. This section discusses the common ways compositions are reported and then discusses simple ways to estimate mixture physical properties from pure fluid data.

1.3.4.1 Composition

There are various ways compositions are reported. This section first looks at gas compositions and then liquid compositions.

1.3.4.1.1 Gas Phase

The most common method for reporting gas composition is on a mole percent basis, denoted mol%. At low pressure where the gas is ideal, this is identical to volume percentage basis, vol%.

Often there is interest in trace amounts of a component. In these cases, compositions are frequently reported in parts per million. Because it is a gas analysis, the concentrations are on a volumetric or molar basis, and the low concentrations are denoted by ppmv. Other units used include mass per unit volume, i.e., lb_m/MMscf or kg/1,000 Nm^3, grains/scf and dew point temperature. While convenient from a processing perspective, dew point temperatures can be difficult to convert into other common units.

One other "composition" that is extremely valuable in separation processes is the concept of partial pressure. As noted above, for an ideal gas mixture, mol% and vol% are identical. The partial pressure of a component *i*, denoted by p_i, is extremely useful because it represents a driving force in separation processes (see Chapter 4). The partial pressure (p_i) is given by

$$p_i = y_i P \tag{1.9}$$

where

y_i is the mole fraction (mol%/100) of component *i*

P is the total pressure

Example 1.6

A gas contains 80 vol% methane and 20 vol% ethane. If the pressure is 85 psig, what are the partial pressures of the two components?

Solution

The absolute pressure of the gas mixture is 85 + 14.7 = 100 psia. For gases, the vol% equals the mol%. Therefore, using Equation 1.9 the partial pressures are

$$p_{C_1} = y_{C_1} P = 0.80 \times 100 = 80\,\text{psia}$$

$$p_{C_2} = y_{C_2} P = 0.20 \times 100 = 20\,\text{psia}$$

1.3.4.1.2 Liquid Phase

For liquids, the common ways to express composition are volume percent (LV%), weight[7] percent (wt%), and mole percent. Unlike gas mixtures, mole percent will not equal volume percent. Mole percent equals weight percent only if all components have the same molar mass. Example 1.7 shows a comparison of the three different compositions. For liquid trace quantities, parts per million values typically are on a weight basis and denoted by ppmw.

Example 1.7

One gallon (or one liter) of methanol (MeOH) is mixed with one gallon (or one liter) of water. Compute the volume fraction, weight fraction, and mole fraction of methanol in the mixture. Table 1.8 gives the needed properties for the two liquids.

Solution

$$\text{The volume fraction MeOH} = \frac{\text{Volume MeOH}}{\text{Total volume}} = \left(\frac{1}{2}\right) = 0.5$$

For weight fraction:

$$\text{Mass of MeOH}, m_{\text{MeOH}} = \rho V = 6.63\,\text{lb}_\text{m}/\text{gal} \times 1\,\text{gal} = 6.63\,\text{lb}_\text{m}\left(0.79\,\text{kg}\right)$$

$$\text{Mass of water}, m_{\text{Water}} = \rho V = 8.34\,\text{lb}_\text{m}/\text{gal} \times 1\,\text{gal} = 8.34\,\text{lb}_\text{m}\left(0.999\,\text{kg}\right)$$

$$\text{Weight fraction MeOH} = \frac{m_{\text{MeOH}}}{\left(m_{\text{MeOH}} + m_{\text{Water}}\right)} = \frac{6.63}{\left(6.63 + 8.34\right)} = 0.44$$

TABLE 1.8
Properties of Methanol and Water at 60°F

	Methanol (MeOH)	Water
Density, ρ, lb_m/gal (kg/L)	6.63 (0.795)	8.34 (0.999)
Molar mass (MW), lb_m/lb-mole (g/g-mole)	32.04	18.02

Source: Lemmon et al. (2017).

[7] The weight fraction should properly be called the mass fraction but this is uncommon.

For mole fraction:

$$\text{Moles of MeOH}, n_{\text{MeOH}} = \frac{m_{\text{MeOH}}}{\text{MW}_{\text{MeOH}}} = \frac{6.63}{32.04} = 0.207\,\text{lb-mol}\left(0.0248\,\text{kg-mol}\right)$$

$$\text{Moles of water}, n_{\text{Water}} = \frac{m_{\text{Water}}}{\text{MW}_{\text{Water}}} = \frac{8.34}{18.02} = 0.463\,\text{lb-mol}\left(0.0554\,\text{kg-mol}\right)$$

$$\text{Mole fraction methanol} = \frac{n_{\text{MeOH}}}{\left(n_{\text{MeOH}} + n_{\text{Water}}\right)} = \frac{0.207}{\left(0.207 + 0.463\right)} = 0.31$$

Compositions are important in meeting product specifications and maintaining proper operating conditions. Example 1.8 gives an example of compositions being used to maintain good operation.

Example 1.8

An MDEA solution is used to remove H_2S and some CO_2 from a natural gas stream. The process holds 50,000 gal (189 m^3) of a 50 wt% solution. A titration of the solution shows that the amine strength has increased to 53% due to water evaporation. How much high-purity water must be added to the system to return the concentration to 50 wt%? Assuming the volume is based upon 104°F (40°C), the density, ρ_{Sol}, of the 50 wt% solution is 8.63 lb/gal (1,034 kg/m^3).

Solution

Assuming no amine loss, the mass of amine present, m_{MDEA} is

$$m_{\text{MDEA}} = \text{wt\%}/100 \times \rho_{\text{Sol}} \times V = 0.50 \times 8.63\,\text{lb/gal} \times 50{,}000\,\text{gal} = 215{,}750\,\text{lb}\left(98{,}070\,\text{kg}\right).$$

The initial mass of water equaled that of the MDEA. The decreased mass of water, m_{Water}, is

$$m_{\text{Water}} = 47/53 \times 215{,}750 = 191{,}325\,\text{lb}\left(86{,}966\,\text{kg}\right)$$

The mass of water to be added = 215, 750 – 191,325 = 24,425 lb (11,102 kg)

Assuming a water density of 8.34 lb/gal (1 g/cm^3) the required amount of water is 25,425 lb/8.34 lb/gal = 2,930 gal (11.1 m^3)

1.3.4.2 Physical Properties

Accurately estimating physical properties of mixtures is a difficult task, usually involving complex models and computer programs. Poling et al. (2000) provide some relatively simple and accurate methods to obtain estimated values. For important binary mixtures, like aqueous glycol solutions, graphs like those found in Appendix B are adequate for many calculations. This section provides some guidelines for estimating mixture properties.

For any mixture calculation it is critically important to use only mole fractions. As a first approximation for a mixture property, Prop_{Mix}, use an average of the pure component properties based upon composition:

$$\text{Prop}_{\text{Mix}} = \sum y_i \text{Prop}_i \tag{1.10}$$

where

Prop is the property being computed

y_i is the mole fraction of component i

Prop_i is the pure component property of component i

Equation 1.10 is valid for properties based upon ideal gas, e.g., ideal gas heats of combustion. For gases at low pressure this usually works well for most other properties because the gas behaves like an ideal gas. For liquids, Equation 1.10 is used but can be in large error. For both nonideal gases and liquid mixtures there can be significant errors when there are differences in the chemical nature of the components, e.g., mixing polar and nonpolar fluids. When making density calculations the calculations must be done using volumes.

Some mixture properties are easier to predict than others. For example, heat capacities of both gases and liquids can be estimated relatively accurately unless components are near the critical point. Liquid densities are less accurate and unfortunately, vapor pressures can have a large error. This is discussed more in Chapter 4. Heating values are routinely computed from gas compositions. See Chapter 6 for details.

Example 1.9

The ideal gas heat capacity is important in estimating compressor workloads. Calculate the heat capacity at constant pressure at 60°F (15.6°C) for a hypothetical gas mixture with the following composition:

Component	mol% (vol%)
N_2	8.0
H_2S	2.0
CH_4	75.0
C_2H_6	10.0
C_3H_8	5.0

Solution

To compute the heat capacity of the ideal gas, C_P of each component is obtained from Table B.2 (B.3). Writing Equation 1.10 in terms of heat capacities gives:

$$C_{P,\text{mix}} = \sum_{i=1}^{n} y_i C_{P,i} \tag{1.11}$$

Table 1.9 shows the calculations. Heat capacity of the mixture is 9.13 Btu/lb-mol-°F (38.2 kJ/kmol-°C). Note that the heat capacity is computed on a molar basis. Liquid compositions

TABLE 1.9
Example Computation of Heat Capacity of Mixture at 60°F (15.6°C)

Component	Mole Fraction, y_i	$C_{P,i}$, Btu/lb-mol-°F (kJ/kmol-°C)	$y_i\ C_{P,i}$, Btu/lb-mol-°F (kJ/kmol-°C)
N_2	0.08	6.96 (29.1)	0.56 (2.33)
H_2S	0.02	8.14 (34.1)	0.16 (0.68)
CH_4	0.75	8.44 (35.3)	6.33 (26.50)
C_2H_6	0.10	12.23 (51.2)	1.22 (5.12)
C_3H_8	0.05	17.08 (71.5)	0.85 (3.58)
Total	1.00		9.13 (38.2)

Source: Appendix B, Table B.2 (B.3).

Note that the heat capacity is computed on a molar basis. Liquid compositions commonly are reported on a liquid volume basis. To obtain a good estimate of a mixture property, the concentration must be converted to a molar basis and liquid molar properties must be used.

commonly are reported on a liquid volume basis. To obtain a good estimate of a liquid mixture property, the concentration must be converted to a molar basis and liquid molar properties must be used.

1.4 SPECIFICATION TEST METHODS

This section briefly discusses two important test methods commonly used in the gas industry: Copper strip test and RVP. Both test methods are maintained and updated by the American Society of Testing Materials (ASTM).

1.4.1 Copper Strip Test

As noted in Section 1.3.2 several compounds are reactive with metals and can cause corrosion. To protect the pipeline, storage facilities, and processing equipment, specifications on reactive contaminant concentrations in gas plant products are usually required. The common specification standard for corrosive materials in liquefied petroleum gas (LPG) is the ASTM copper strip test (ASTM D1838-16, 2016). For natural gasoline a similar test (ASTM D130-18, 2018) is used. (Chapter 6 gives descriptions of the liquid products produced in gas plants.) The test consists of placing a clean, polished copper strip into approximately 100 mL of the liquid in a test cylinder for 1 h at 100°F (37.8°C). The strip is removed and compared against a color chart. There are four classifications. If the strip shows no indication of corrosion the test result is #1. High concentrations of corrosive compounds turn the copper strip black, giving a test result of #4. For a more detailed discussion of the copper strip tests, refer to Clark and Lesage (2004).

1.4.2 Reid Vapor Pressure

There are two "vapor pressures" used in the gas industry. The first is the "true" vapor pressure or bubble point of a mixture. This is discussed in detail in Chapter 4. The second is RVP. This value, originally designed to determine the potential for vapor locking in automobile carburetors, provides an indication of the concentration of volatile components in a liquid. The RVP value will always be less than the true vapor pressure.

The ASTM D1267-18 (2018) test is used to measure RVP of LPG products. The test requires filling a vessel of specified volume. The vessel is connected to another chamber having a pressure gauge. These two vessels are immersed into a liquid bath maintained at a temperature of 100°F (37°C) or optionally at a temperature up to 158°F (70°C), until the observed pressure becomes constant. The observed pressure is the RVP.

1.5 THERMODYNAMICS

1.5.1 Introduction

To understand the principles behind many gas processing steps requires a basic understanding of changes in energy, e.g., heat and work that are involved in the process. Thermodynamics provides the means for this understanding. This discussion introduces the reader to the relevant elements of thermodynamics. This section provides only a simple discussion of a complex subject. It then provides brief thermodynamic analyses of two important operations in gas processing: compression and expansion.

Thermodynamics involves rigorous mathematics. However, this discussion minimizes the math and stresses physical concepts. To obtain a more thorough understanding the reader should consult any good chemical engineering thermodynamics book, e.g., Smith et al. (2018).

1.5.2 First Law of Thermodynamics

Simply defined, the first law states that energy can be neither created nor destroyed. This empirical observation has held in all cases except one, processes involving nuclear reactions, which are unimportant in gas processing. The first law is valid for all systems, regardless of scale. It applies to a pump as well as an entire gas plant.

Unlike mass, energy is not obvious although results from changes in energy frequently are, e.g., converting electrical energy to heat or light. To make the first law more understandable, consider the analogy with finance. A household has various incomes (money) coming in each month. Likewise, it has numerous expenses (money) going out during the month. How much money is saved (which can be positive or negative) each month depends upon the difference between income and expenses. The monthly savings is calculated by

$$\text{Savings} = \sum \text{incomes} - \sum \text{expenses}$$

However, the following equation is more appropriate:

$$\Delta\text{Savings} = \sum \text{incomes} - \sum \text{expenses}$$

because the amount of savings changes monthly. The equation is true for any one household and thus for the sum of any number of households. The magnitude of the numbers depends upon how many households are included. To make the numbers meaningful, the "system," i.e., how many, and possibly which, households, must be clearly stated.

A similar equation is valid for any physical system if energy (Btu or J) replaces money,

$$\Delta\text{Total energy} = \sum \text{heat} - \sum \text{work}$$

which states that the total energy (yet to be defined) of a system will change based upon heat added from outside the system and net work generated for use outside the system. This is the first law of thermodynamics. It most often is in the form of

$$\Delta\text{Total energy} = Q - W_s \tag{1.12}$$

where

Q symbolizes the total heat added

W_s is the shaft work,[8] i.e., net mechanical work, done by the system on the outside world.

Note that by convention, Q is positive when heat is added to system and W_s is positive when the system produces work.[9] Equation 1.12 shows both q and w_s capitalized which means that the values are for the total system. Lower case terms denote the quantities are on a per unit mass basis. This nomenclature applies to all thermodynamic properties discussed below.

1.5.3 Forms of Energy

While there are many forms of energy, this section discusses only those relevant to understanding material in later chapters. To explain some energy forms some simpler examples are used.

[8] There are many different forms of work. Zemansky and Dittman (1979) give a detailed discussion of various forms of work.

[9] Some thermodynamics texts define W_s to be positive when work is done on the system. In this case, the sign in front of W_s is positive instead of negative.

1.5.3.1 Work (W_s)

Physicists define work as force times distance. Simple examples of work would be moving a piston in a cylinder and a rotating shaft driving a mechanical device. It is important to note that a system, e.g., a gas turbine, can have work occurring inside the system but W_s represents the *net* work done by or on the system. As noted earlier, W_s is positive when work is done by the system.

1.5.3.2 Heat (Q)

Heat represents the energy transferred from a warmer body to a cooler body when the two come into contact. Heat is generated by many ways including chemical reactions, such as combustion, and changes in physical state, such as condensation. Unfortunately, heat is generated, although the amount may be small, in most conversions from one energy form to another. One common "hidden," and unwanted, source of heat generation is friction. Heat is a positive term when being added to the system.

1.5.3.3 Potential Energy (PE)

Potential energy is commonly a result of relative vertical position. The name comes from the potential for an object to generate another form of energy as it moves to a lower position. The potential energy for a mass, m, is

$$\Delta \text{PE} = gm\Delta Z \tag{1.13}$$

where

g is the gravitational constant
ΔZ represents the change in vertical position

Changing the potential energy requires or generates work.

Example 1.10

How much energy is required to move 100 lb_m (45 kg) of water from sea level to 40 ft (12 m) above sea level?

Solution

The only change in the water is a change in elevation so using Equation 1.13 is appropriate. However, when using USES units lb_m must be converted to lb_f using g_c. The energy change is then

$$\Delta \text{PE} = \frac{g}{g_c} m\Delta Z = \frac{32\,\text{ft/s}^2}{32\,\text{ft-lb}_\text{m}/\text{s}^2\text{-lb}_\text{f}} \times 100\,\text{lb}_\text{m} \times 40\,\text{ft} = 4{,}000\,\text{ft-lb}_\text{f} \times \frac{\text{Btu}}{778\,\text{ft-lb}_\text{f}} = 5.1\,\text{Btu}$$

In SI units

$$\Delta \text{PE} = gm\Delta Z = 9.80\,\text{m/s}^2 \times 45\,\text{kg} \times 12\,\text{m} = 5{,}290\,\text{J}$$

1.5.3.4 Kinetic Energy (KE)

Changes in kinetic energy denote changes in velocity

$$\Delta \text{KE} = \tfrac{1}{2} m\Delta u^2 \tag{1.14}$$

where u is the linear velocity. Note that the energy change is proportional to the difference in the square of the velocity. Kinetic energy changes tend to be less important in gas processing. Changes in kinetic energy can be important in fluid flow calculations where there is a change in pipe diameter.

1.5.3.5 Pressure Head (P_H)

Pressure head is important primarily in the pumping of liquids. It is computed using

$$\Delta P_H = \frac{m(P_2 - P_1)}{\rho} \tag{1.15}$$

where

P_1 and P_2 denote the inlet and outlet pressure
ρ is the liquid density

Chapter 2 discusses pressure head in more detail.

1.5.3.6 Internal Energy (U)

Consider a metal block placed on the floor and at room temperature. Heat is added to the block to bring it to some higher temperature. According to Equation 1.12 Q is positive but W_s is zero. Thus, the total energy of the block is increased. All of the other energy forms mentioned above are unchanged indicating another form of energy is present. This energy is called internal energy because the energy resides within the block. Changes in internal energy are detectable by changes in temperature or by knowing how much the other energy forms changed. If only heat is being added to the system then the internal energy change is calculated using

$$\Delta U = mC_V \Delta t \tag{1.16}$$

1.5.3.7 Enthalpy (H)

Internal energy is convenient for calculations when the system is at constant volume and materials are not continually flowing in and out of the system. Most applications in gas processing involve fluid flow and are continuous. To easily apply thermodynamics to these processes another energy term, enthalpy, is defined:

$$H \equiv U + PV \tag{1.17}$$

where PV, pressure times volume, is added to internal energy. The PV term represents the work to move fluid into or out of a system. If only heat is being added to the system then the enthalpy change is calculated using

$$\Delta H = mC_P \Delta t \tag{1.18}$$

Example 1.11

A variable volume vessel contains 1 lb-mol (0.45 kg-mol) of a gas with an equimolar mixture of methane and ethane gas at 60.0°F (15.6°C) and 14.7 psia (1.01 bara). Compute how much heat must be added to warm the gas to 100.0°F (37.8°C) heated at constant volume and at constant pressure.

Solution

First consider process of heating at constant pressure, which is the most common path in gas processing. In this case, the gas is being heated but no work is being done so $Q = \Delta H$ and Equation 1.18 is appropriate. At these temperatures and pressure the gas can be assumed to be ideal. Tables B.2 and B.3 give the following values of the molar ideal gas heat capacities at constant pressure, C_P, for methane and ethane.

	C_p, Btu/(lb-mol-°R) (kJ/(kg-mol-°C)		
Component	60.0°F (15.6°C)	100.0°F (37.8°C)	Average
Methane	8.44 (35.3)	8.64 (36.2)	8.54 (35.8)
Ethane	12.23 (51.2)	12.90 (54.0)	12.56 (52.6)

The values in the last column are averages over the temperature range. Using Equation 1.10 C_P for the mixture is

$$C_{P\,\text{mix}} = y_{C_1}C_{PC_1} + y_{C_2}C_{PC_2} = 0.5\times 8.54 + 0.5\times 12.56 = 10.55\,\text{Btu/lb-mol-°R}(44.2\,\text{kJ/kmol-°C})$$

which is then inserted into Equation 1.18 to give

$$\Delta H = Q = mC_P\Delta t = 1\,\text{lb-mol}\times 10.55\,\text{Btu/(lb-mol-°F)}\times(100-60)\,°\text{F} = 422\,\text{Btu}\left(445\,\text{kJ}\right)$$

If heat is added to the gas at constant volume and no work is done then $Q = \Delta U$ and Equation 1.16 applies. The values of C_V are not commonly tabulated but for an ideal gas they can be computed using Equation 1.8 and the gas constant from Appendix B.2.1

$$C_V = C_P - R = 10.55 - 1.99 = 8.56\,\text{Btu/lb-mol-°R}\,(35.8\,\text{kJ/kg-mol-°C})$$

Therefore, the amount of heat added at constant volume is

$$\Delta U = Q = mC_V\Delta t = 1\,\text{lb-mol}\times 8.56\,\text{Btu/(lb-mol-°F)}\times(100-60)\,°\text{F} = 342\,\text{Btu}\left(361\,\text{kJ}\right)$$

Heating the gas at constant pressure requires more energy because the gas expands on warming and thus the gas is doing work as it pushes against the atmosphere. Although some work is done by the gas but on itself and W_s remains zero. Note that heating a liquid usually results in a small density change. Therefore, C_P and C_V are essentially equal. The one exception is when the liquid is near its critical point.

1.5.3.8 Overall Energy Equation

Referring to Equation 1.12 there are two forms of the first law of thermodynamics that are extensively used in gas processing. Both are for steady-state flow processes. The first is

$$\Delta h + \frac{\Delta u^2}{2g_c} + \frac{g\Delta Z}{g_c} = q - w_s \tag{1.19a}$$

$$\Delta h + \frac{\Delta u^2}{2g} + g\Delta Z = q - w_s \tag{1.19b}$$

which is on a unit mass basis and g_c is included to account for the difference between lb_m and lb_f in USES units. For many applications of Equation 1.19, the potential and kinetic energy terms are often neglected. In addition, for heat transfer calculations the work term is not needed and for compressor work calculations the heat term is ignored (see Chapter 9).

The second form, called the mechanical energy balance is invaluable for liquid flow calculations.

$$\frac{\Delta P}{\rho} + \frac{\Delta u^2}{2g_c} + \frac{g\Delta Z}{g_c} + w_s = 0 \tag{1.20a}$$

$$\frac{\Delta P}{\rho} + \frac{\Delta u^2}{2} + g\Delta Z + w_s = 0 \tag{1.20b}$$

The equation assumes that there is no frictional loss and that the liquid is incompressible.

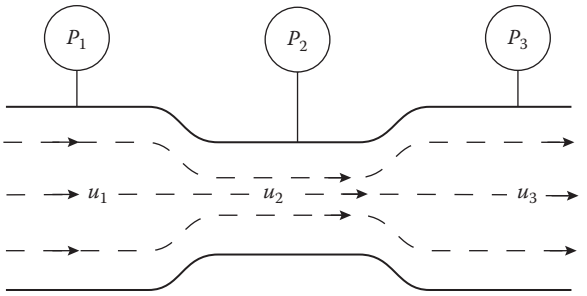


FIGURE 1.5 Flow geometry for Example 1.12.

Example 1.12

An incompressible fluid flows through a restriction where the inner diameter of the pipe is reduced by 25%. The fluid pressure and velocity is P_1 and u_1 as shown in Figure 1.5. What are the values of P_2, P_3, u_2, and u_3 in terms of the initial values?

Solution

First consider the velocity u_2, which is computed using $u = Q/A$ where Q is the volumetric flow rate (ft^3/s, m^3/s) and A is the cross-sectional area (ft^2, m^2). The area is computed using $\pi d^2/4$ and the ratio of the two areas is

$$\frac{A_2}{A_1} = \left(\frac{d_2}{d_1}\right)^2 = (0.75)^2 = 0.56$$

Because the volumetric flow rate remains constant the velocity increases by 1/0.56 or 78%.

Using Equation 1.20 and noting that there is no change in elevation and no work is added to the liquid, the change in pressure is

$$\frac{\Delta P}{\rho} = -\frac{\Delta u^2}{2} = -\frac{(1.78u_1)^2 - u_1^2}{2} = -\frac{(3.17-1)u_1^2}{2} = -1.08u_1^2$$

Therefore, P_2 is *lower* than P_1 and the pressure drop depends upon liquid density and inlet velocity. This is the principle used in venturi meters to measure flow rates.

Assuming there are no friction losses in the system, $P_3 \approx P_1$ and $u_3 \approx u_1$ although the values will be lower because there are inherent losses when a fluid flows through an expansion or contraction.

Finally, note that when a fluid flows through an expansion the pressure increases as the velocity decreases. If energy is added to the fluid to increase u_2, this will increase the discharge pressure P_3. Both centrifugal pumps and compressors utilize this principle.

1.5.4 State and Path Functions

Thermodynamic functions are either "State Functions" or "Path Functions." State functions require knowing only the initial and final states of a system to determine the change in the function. All energy forms, excluding heat and work, mentioned in Section 1.5.3 are state functions. Potential energy provides a simple example. Moving a block from the floor to a table changes the potential energy, and thus the total energy, of the block. This change in potential energy depends *only* upon the change in elevation. The route taken by the block in going to the table is not relevant. State functions are extremely useful; being independent of path permits state functions to be displayed in charts and tables. An important example is given in the next section.

There are only two path functions: heat and work. These are independent of the system properties and represent energy moving between the system and its surroundings. They depend upon the "path," or exact steps, used to add or remove heat and work. Consider a cylinder with a piston containing a gas to be heated from temperature t_1 to t_2. The gas in the cylinder is at ambient pressure. Two obvious ways to heat the gas are

1. At constant volume by preventing the piston from moving, which increases the pressure.
2. At constant pressure by allowing the piston to move, which increases the volume.

The heat added in the two cases will not be the same. Adding heat at constant pressure will be greater because the gas had to do work to move the piston. According to Equation 1.8, for an ideal gas the difference in heat added will be $R(t_2 - t_1)$.

Note that work can, in theory, be converted 100% into heat and all other energy forms. The second law of thermodynamics (see, e.g., Smith et al. (2018)) states that only a fraction of heat can be converted to other energy forms. The maximum possible amount converted depends on operating temperatures. Further discussion of the second law is beyond the scope of this introduction.

1.5.5 Important Thermodynamic Paths

There are infinite combinations of adding heat and work in a process. However, there are only a few commonly used to calculate changes in state functions, which are independent of path chosen. Those paths that include both heat and work occur at

- Constant volume ($\Delta V = 0$) which is called an isochoric process
- Constant pressure ($\Delta P = 0$) which is called an isobaric process
- Constant pressure ($\Delta T = 0$) which is called an isothermal process

Another useful path is where there is no heat exchange. For this path $Q = 0$ and the process is called adiabatic.

There are two other important paths that define changes in heat and work. These are discussed in the following two sections.

1.5.5.1 Joule–Thomson Expansion

A Joule–Thomson (J–T) expansion involves a fluid expanding through a restriction with no heat exchange or work occurring and where kinetic and potential energy effects are insignificant. For this process $\Delta H = 0$ and the path is called isenthalpic. The J–T expansion is an important means of providing cooling in refrigeration (see Chapters 12 and 18).

Fluids have a Joule–Thomson coefficient, μ, which is both temperature and pressure dependent.[10] For an ideal gas $\mu = 0$, and thus no temperature change occurs when an ideal gas undergoes a J–T expansion. For a real gas, the Joule–Thomson coefficient may be positive (the gas cools upon expansion), negative (the gas warms upon expansion), or zero.

Table 1.10 shows the behavior of several gases upon expansion from 1,470 psia (101 bara) to 14.5 psia (1 bara). Two items should be noted. First, for both methane and nitrogen, the cooling effect upon expansion when started at −40°F (−40°C), is relatively small. Second, the cooling effect increases significantly as the initial temperature is lowered.

For helium, the expansion results in heating the gas rather than cooling. The temperature increase remains constant for helium because the Joule–Thomson coefficient remains nearly constant over the temperature range considered. Contrast this with methane where the temperature change from expansion increases by 37% from one initial temperature to another.

[10] The J–T coefficient is defined as $\mu = (\partial T/\partial P)_h$. It is computed using the following thermodynamic relationship $\mu = -1/C_P (V - T(\partial V/\partial T)_p) = -1/C_P (\partial H/\partial P)_T$.

TABLE 1.10
J–T Expansion from 1,470 psia (101 bara) to 14.5 psia (1 bara)

	Initial Temperature, °F (°C)	Final Temperature, °F (°C)	$t_{final} - t_{initial}$ °F (°C)
Nitrogen	0 (–18)	–49 (–45)	–49 (–27)
	–40 (–40)	–100 (–73)	–60 (–33)
Methane	0 (–18)	–129 (–89)	–129 (–71)
	–40 (–40)	–217 (–138)	–177 (–98)
Helium	0 (–18)	12 (–11)	12 (7)
	–40 (–40)	–29 (–34)	11 (6)

Source: Lemmon et al. (2017).

1.5.5.2 Isentropic Process

This is a special case of the adiabatic process. All real processes require a finite driving force to make the process proceed at a finite rate. For example, to add heat to a metal block requires contacting the block with a heat source that is at a higher temperature than the block. However, having a finite driving force generates heat which is lost. This lost energy is determined using a thermodynamic state function called entropy (usually given the symbol S). The amount of lost energy, and entropy generated, increases with increasing driving force. Mathematically, work can be calculated for an adiabatic process with an infinitesimal driving force. This hypothetical path is isentropic because the change in entropy is zero ($\Delta S = 0$). Equation 1.19 then reduces to

$$\Delta h = -w_s \tag{1.21}$$

The isentropic path is important in compressor and turboexpander calculations in Chapters 8 and 12, respectively. The isentropic process is the maximum amount of theoretical work required for compression. Conversely, it is the maximum amount of work, and therefore, cooling, obtainable from an expansion. Table 1.11 shows results from an isentropic expansion for the same conditions given in Table 1.10. Note that the cooling is significantly more than for a J–T expansion and that liquid is formed for both nitrogen and methane. Chapter 18 discusses liquefaction processes. Table 1.10 showed helium warming in a J–T process while there is substantial cooling in the isentropic process.

1.5.6 Pressure-Enthalpy (PH) Diagrams

For all fluids there is a relationship, called an equation of state, between volume, temperature, and pressure. The simplest is that for an ideal gas (see Section 1.3.3.1). Accurate equations of state are

TABLE 1.11
Isentropic Expansion from 1,470 psia (101 bara) to 14.5 psia (1 bara)

	Initial Temperature, °F (°C)	Final Temperature, °F (°C)	$t_{final} - t_{initial}$ °F (°C)
Nitrogen	0 (–18)	–320 (–195) (7% liquid)	–320 (–177)
	–40 (–40)	–320 (–195) (12% liquid)	–280 (–137)
Methane	0 (–18)	–259 (–162) (23% liquid)	–259 (–144)
	–40 (–40)	–259 (–162) (32% liquid)	–219 (–144)
Helium	0 (–18)	–391 (–235)	–391 (–217)
	–40 (–40)	–387 (–232)	–347 (–193)

Source: Lemmon et al. (2017).

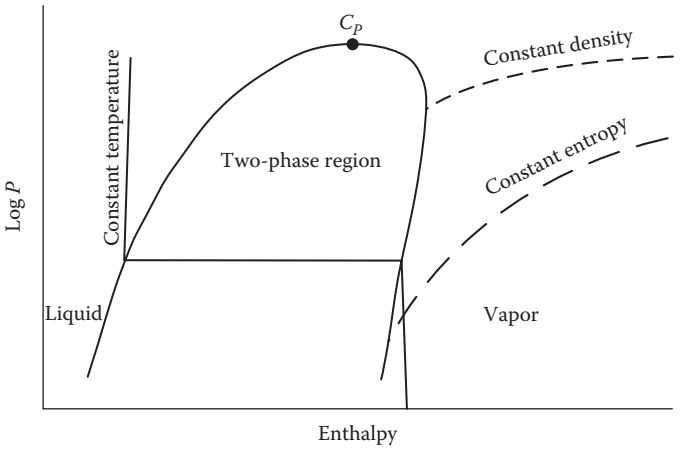


FIGURE 1.6 Pressure-enthalpy diagram.

complex empirical equations. These equations are powerful tools because they are used to compute useful thermodynamic state functions, including enthalpy and entropy as a function of temperature and pressure. State functions of pure fluids and constant composition mixtures can be plotted as a function of any two variables. Figure 1.6 shows a PH plot which is extremely useful for both isenthalpic and isentropic processes. There are four important features denoted on the figure:

1. Phase envelope—the region to the left of the envelope is the liquid region while that to the right is the vapor region. Properties on the phase envelope are where liquid is in equilibrium with vapor (saturation conditions).
2. Lines of constant temperature.
3. Lines of constant entropy.
4. Lines of constant density.

The PH diagram makes it simple to determine the exit temperature of a J–T expansion. The isenthalpic process follows a vertical line on the PH diagram. Chapter 12 shows examples of using PH diagrams for J–T expansion.

Lines of constant entropy are valuable for determining compressor and expander work requirements and exit temperatures. See Chapters 9 and 12, respectively, for more details.

DISCUSSION QUESTIONS

1. What is the difference between atom, compound, molecule, and mole?
2. Why does Table 1.1 have force as a basic unit in USES while it is a derived unit in Table 1.2?
3. Why is using the prefix "M" confusing when used in the gas industry?
4. What is the difference between density and relative density for a gas and a liquid?
5. Which has the higher NBP, ethanol or ethyl mercaptan?
6. What is the difference between the two heating values?
7. Are mol percent and volume percent the same in both liquids and gases? If not, why?
8. Give a good example of the first law of thermodynamics as applied to your training and experience.
9. Why are there charts and tables showing relationships between temperature, pressure, volume, and enthalpy but none showing similar relationships involving work and heat?
10. What are the major differences between Joule–Thomson expansion and turboexpansion?

EXERCISES

1.1 An unstabilized condensate enters a stabilizer at 48°F. What is the temperature in °R, °C, and K?
1.2 A pressure gauge reads 13 psig. The atmospheric pressure is 12 psia. What is the pressure in psia, barg, and bara?
1.3 A small compressor has a 500 W electric motor. How much energy does the motor consume in 1 h in units of Btu and ft-lb_f?
1.4 A condensate has a molar mass of 71 and a relative density of 0.68 (relative to water at 60°F). What is the absolute density in lb_m/gal, lb_m/ft^3, lb-mol/gal, lb-mol/ft^3, mol/m^3, and kg/m^3? Use a water density of 62.36 $lb_{m/ft}{}^3$.
1.5 In USES, the standard cubic foot of a gas is based on 60°F and 14.6959 psia while Standard conditions in SI are 15°C and 1.01325 bara and Normal conditions are 0°C and 1.01325 bara. Using the conversion of 1 m^3 = 35.31467 ft^3, what are the conversions between scf, Sm^3, and Nm^3?
1.6 A gas flowing at 75 MMscfd (2.1×10^6 Nm^3/d) enters a cold section of the plant at 750 psig (51.7 barg) and −40°F (−40°C). Assuming ideal gas behavior, what is the actual flow rate?
1.7 Assume the gas relative density in previous problem is 0.8. Obtain a more accurate estimate of actual flow rate in previous problem using the compressibility factor, *z*, given in Appendix B.4[11].
1.8 A liquid mixture contains 50 wt% liquid propane in *n*-butane at 60°F (15.6°C). Using data from Table B.1 estimate the liquid density in lb_m/gal (kg/m^3).

REFERENCES

ASTM D130-18, *Standard Test Method for Corrosiveness to Copper from Petroleum Products by Copper Strip Test*, ASTM International, West Conshohocken, PA, 2018. www.astm.org/Standards/D130.htm (Retrieved April 2019).

ASTM D1267-18, *Standard Test Method for Gauge Vapor Pressure of Liquefied Petroleum (LP) Gases (LP-Gas Method)*, ASTM International, West Conshohocken, PA, 2018. www.astm.org/Standards/D1267.htm (Retrieved April 2019).

ASTM D1838-16, *Standard Test Method for Copper Strip Corrosion by Liquefied Petroleum (LP) Gases*, ASTM International, West Conshohocken, PA, 2016. www.astm.org/Standards/D1838.htm (Retrieved April 2019).

Clark, P.D., and Lesage, K.L., The copper strip test: A review of existing procedures for the assessment of the quality of propane and LNG, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2004.

Engineering Data Book, Section 1, General information, GPSA Midstream Suppliers, Tulsa, OK, 2016.

Gas Processors Association, GPA Standard 2172-14, Calculation of gross heating value, relative density, compressibility and theoretical hydrocarbon liquid content for natural gas mixtures for custody transfer, *API Manual of Petroleum Measurement Standards Chapter 14.5*, Tulsa, OK, 2014.

GPA Midstream Association, GPA Midstream Standard 2145-16, Table of physical properties for hydrocarbons and other compounds of interest to the natural gas and natural gas liquids industries, Tulsa, OK, 2016.

Klinkenberg, A., The American engineering system of units and its dimensional constant gc, *Ind. Eng. Chem*., *61*(4), 53, 1969.

Lemmon, E.W., et al., Thermophysical properties of fluid systems, *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, Linstrom, P.J. and W.G. Mallard (eds.), National Institute of Standards and Technology, Gaithersburg MD, 2017. http://webbook.nist.gov (Retrieved April 2019).

McCain, W.D., *The Properties of Petroleum Fluids*, 2nd edn. Penwell Corporation, Tulsa, OK, 1990.

National Institute of Standards and Technology, The NIST reference on constants, units and uncertainty, 2017. http://physics.nist.gov/cuu/index.html (Retrieved April 2019).

Poling, B.E., et al., *The Properties of Gases and Liquids*, 5th edn. McGraw Hill, New York, 2000.

[11] See Appendix B on publisher website: www.crcpress.com/Fundamentals-of-Natural-Gas-Processing-Third-Edition/Kidnay-Parrish-McCartney/p/book/9781138612792

Prausnitz, J.M., et al., *Molecular Thermodynamics of Fluid-Phase Equilibria*, Prentice-Hall Publishers, Englewood Cliffs, NJ, 1999.

Smith, J.M., et al., *Introduction to Chemical Engineering Thermodynamics*, 8th edn. McGraw-Hill Higher Education, New York, 2018.

Speight, J.G., *Lange's Handbook of Chemistry*, 17th edn. McGraw-Hill, New York, 2017.

Zemansky, M.W., and Dittman, R.H., *Heat and Thermodynamics*, 6th edn. McGraw-Hill, New York, NY, 1979.

Taylor & Francis
Taylor & Francis Group
http://taylorandfrancis.com

2 Pumps

2.1 INTRODUCTION

Pumps are devices for moving liquids and modern life would be extremely difficult without them. This chapter provides a brief introduction to pumps in natural gas processing. Following a short discussion of the various energy terms and equivalent hydraulic heads, the discussion focuses primarily on centrifugal, reciprocating, and rotary pump performance. Little attention is given to theory, construction, installation, maintenance, and diagnostics. For more comprehensive, in-depth presentations see other references such as Karassik et al. (2008), Karassik and McGuire (1998), the *Engineering Data Book* (2016), Hydraulic Institute (undated), and Heald (2002).

Pumps are ubiquitous in the industrialized world, and the myriad applications have led to the development of many distinct types of pumps. There are many methods of grouping pumps to facilitate discussion and study. Figure 2.1 shows a modified version from Karassik et al. (2008). In this classification, pumps are divided according to the principle used to add energy to the liquid, and further subdivided according to the geometries employed.

Figure 2.2 shows the approximate ranges of applicability for the various pumps discussed. The figure is a general guide; a more detailed selection graph is presented in the *Engineering Data Book* (2016).

The subdivisions shown (e.g., centrifugal) can be further divided into many additional subclasses, but only three types of pumps will be discussed in this chapter: centrifugal (radial flow), reciprocating (piston), and rotary (screw). Centrifugal pumps are by far the most common in gas processing applications with few reciprocating pumps and even fewer rotary screw pumps used. Positive displacement reciprocating and rotary screw pumps are usually reserved for high-discharge pressure, low-flow applications.

In gas processing, the practice is to use centrifugal pumps wherever possible because they are usually less costly while requiring both less maintenance and space. Exceptions are small-flow, high-discharge pressure applications such as TEG circulation pumps (Chapter 11) and metering pumps. Consequently, this chapter focuses on radial flow centrifugal pumps, with secondary consideration given to reciprocating and rotary pumps. Specialty pumps are discussed in the later chapters where they are applied.

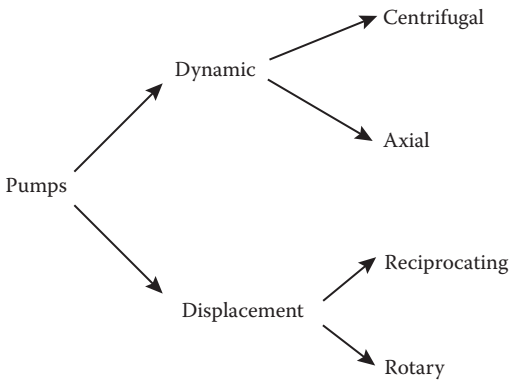


FIGURE 2.1 Pump classifications. (Adapted from Karassik et al., 2008.)

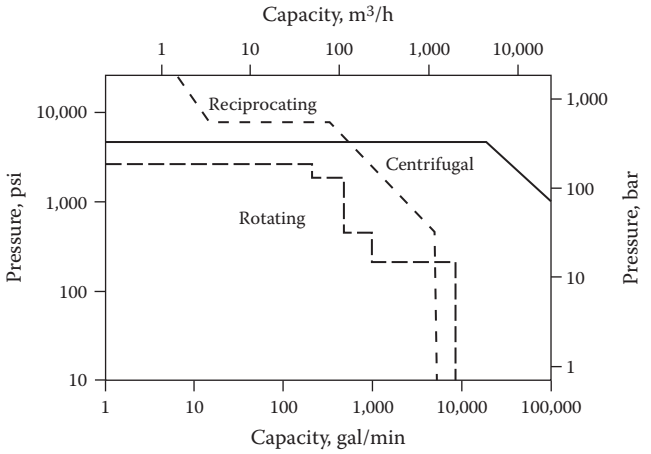


FIGURE 2.2 Typical operating ranges of three kinds of pumps. (Adapted from Karassik et al., 2008.)

2.2 PUMP FUNDAMENTALS

2.2.1 Energy Balance

The basic relation governing liquid flow is the modified Bernoulli equation or mechanical energy balance as shown in Equation 2.1 written per unit mass of fluid (Bird et al., 2007; McCabe et al., 2018; Wilkes, 2005):

$$\frac{\Delta u^2}{2} + g\Delta Z + \frac{\Delta P}{\rho} + w_s + gh_f = 0 \tag{2.1}$$

where

u is liquid velocity
g is acceleration due to gravity
Z is elevation
P is pressure
ρ is liquid density
w_s is pump shaft work per unit mass of liquid
h_f is friction loss

This is Equation 1.20 with the additional term for friction loss. The equation has consistent units in the SI system. When using USES, the first, second, and last terms must be divided by g_c (see Chapter 1). In developing this equation, the liquid is assumed incompressible, which for the liquids encountered in gas processing plants over typical operating pressure is normally an acceptable assumption. For the pressure range shown in Figure 2.3 using an average density would be satisfactory for most engineering calculations with Equation 2.1. The *Engineering Data Book* (2016) discusses pump calculations for compressible liquids and techniques for calculating the densities of liquid mixtures, including liquids containing dissolved gases.

2.2.2 Head

Pressure and head are directly related. The concept of head is important for two reasons. First, it has a simple physical meaning whereas pressure does not. Second, dynamic pumps (and compressors) generate head instead of pressure.

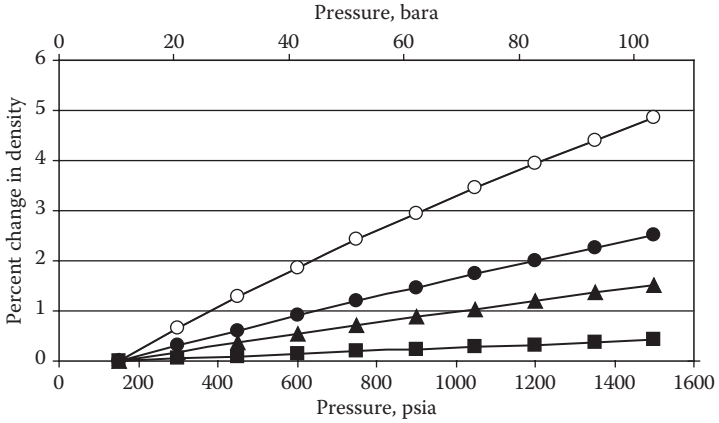


FIGURE 2.3 Percent change in liquid density relative to density at 150 psia (10 bara) and 80°F (27°C). The symbols, ○, ●, ▲, and ■ denote propane, *n*-butane, *n*-hexane, and water, respectively. (Data from Lemmon et al., 2017.)

Figure 2.4 shows a simple U-tube containing a liquid where the pressure over the left leg, P_2, is greater than that on the right leg, P_1. This pressure difference forces the liquid levels in the two legs to differ by Δz, which is called the head, h. The level difference in the two legs depends upon two factors: pressure difference and liquid density. Increasing the pressure difference or decreasing the liquid density increases Δz. The relationship between pressure and head from Equation 2.1 is

$$P_2 - P_1 = \Delta P = \rho g \Delta Z = \rho g h \tag{2.2}$$

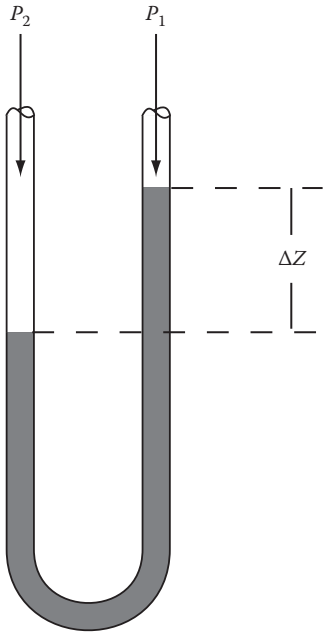


FIGURE 2.4 U-tube illustrating relationship between pressure and liquid level (head) differences.

Example 2.1

A centrifugal pump generates a 328 ft (100 m) head of water. What is the pressure difference across the pump when pumping water at 60°F (15°C)?

Solution

Using consistent units in any equation is critical and unfortunately, sometimes, confusing. First, calculate the pressure difference using SI and then USES. The density of water is ~1,000 kg/m^3. Using Equation 2.2

$$\Delta P = \rho g h = 1{,}000\,\text{kg/m}^3 \times 9.8\,\text{m/s}^2 \times 100\,\text{m}$$

$$= 0.98 \times 10^6\,(\text{kg-m/s}^2)/\text{m}^2 = 0.98\,\text{MPa} = 9.8\,\text{bar}$$

For USES, the conversion factor, g_c (see Chapter 1) is required to have consistent units. For USES, the water density is 62.4 lb_m/ft^3 and Equation 2.2 gives

$$\Delta P = \frac{\rho g h}{g_c} = 62.4\,\frac{\text{lb}_\text{m}}{\text{ft}^3} \times \frac{32.2\,\text{ft/s}^2}{\dfrac{32.2\,\text{ft-lb}_\text{m}}{\text{lb}_\text{f}\text{-s}^2}} \times 328\,\text{ft} \times \frac{\text{ft}^2}{144\,\text{in}^2} = \frac{142\,\text{lb}_\text{f}}{\text{in}^2} = 142\,\text{psi}$$

2.3 CENTRIFUGAL PUMPS

Centrifugal pumps are conceptually simple devices. They consist of a driver and an impeller. The sequence of events occurring in the centrifugal pump is:

- The driver adds energy (shaft work) to the impeller.
- The impeller increases the velocity of the liquid thus increasing its kinetic energy.
- The kinetic energy of the liquid is converted into pressure, as the liquid velocity is reduced in the volute.

Figure 2.5 is a cut-away view of a small centrifugal pump. Volute and impeller design are complex and not discussed in this book; interested readers should consult pump references such as Karassik and McGuire (1998) or Karassik et al. (2008).

For centrifugal pumps, blowers, and compressors, it is common practice to discuss performance in terms of head. As stated by Stepanoff (1955), "The fundamental property of head in feet as applied to turbomachinery (pumps, blowers, compressors) is that, for a given machine at a selected speed the head produced does not depend on the nature of the liquid, its inlet temperature, or whether it is cooled or not in the process of compression."

To illustrate this important point, refer again to Equation 2.1. The only term involving pressure and liquid properties is $\Delta P/\rho$.

Consider an energy balance around a pump using Equation 2.1. The potential energy change across a pump is negligible because the entrance and exit ports are near the same elevation. Usually, inlet and outlet lines on the pump are close to the same diameter so there will be little change in linear velocity of the liquid and thus, negligible kinetic energy change. If the friction term is ignored, the work per unit mass is

$$w_s = \frac{\Delta P}{\rho} \tag{2.3}$$

Note that in Equation 2.1 the sign convention is that work done by a system is a positive quantity and work done on the system is negative. In Equation 2.3, the sign convention has been reversed so that work done on the pump is considered positive. Equation 2.3 shows that the work required to pump

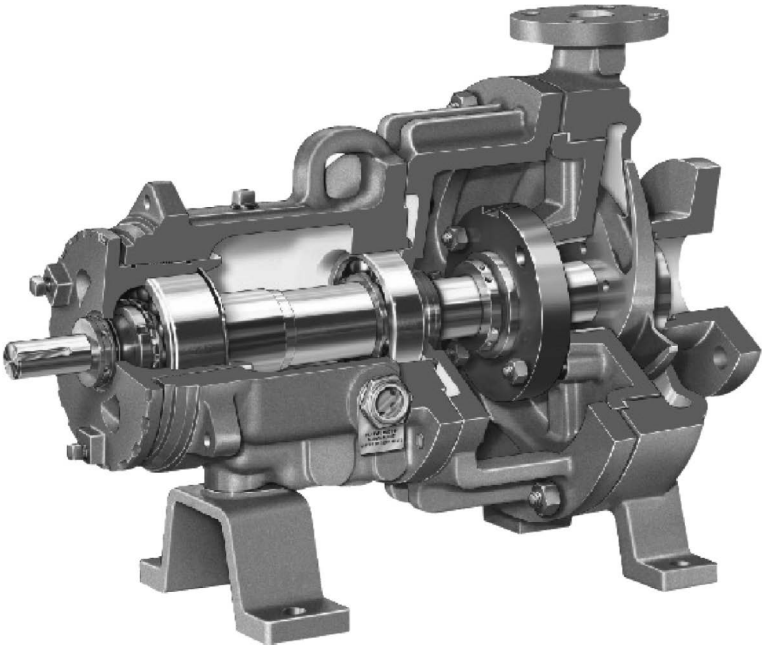


FIGURE 2.5 Cutaway of a centrifugal pump. (Courtesy of Flowserve Corporation.)

a liquid depends upon the pressure difference. Equation 2.3 applies not only to centrifugal but to all pump types. By comparison, work required to compress a gas depends upon pressure ratio rather than pressure difference (see Chapter 9).

Example 2.2

What will be the pressure differential across the pump in Example 2.1 if the fluid is changed from water to propane? Use density data from Table B.1[1].

Solution

The pump in Example 2.1 is a centrifugal and the head of 328 ft (100 m), is independent of the liquid. Therefore, the pump creates a column of liquid whose height is independent of liquid density. However, liquid density does affect the pressure difference (and consequently w_s) for the pump.

Applying Equation 2.2 to propane and water and taking the ratio gives

$$\frac{\Delta P_{C_3} = \left(\rho g h\right)_{C_3}}{\Delta P_{H_2O} = \left(\rho g h\right)_{H_2O}}$$

or

$$\Delta P_{C_3} = \left[\frac{\rho_{C_3}}{\rho_{H_2O}}\right] \Delta P_{H_2O}$$

[1] See Appendix B on publisher website: www.crcpress.com/Fundamentals-of-Natural-Gas-Processing-Third-Edition/Kidnay-Parrish-McCartney/p/book/9781138612792

$$\Delta P_{C_3} = \frac{4.2301}{8.3372} \times 142 = 72\,\text{psi}$$

Example 2.2 points out the usefulness of head when calculating pump requirements for different liquids because it is independent of liquid. Note that the head is the same in both cases but the ΔP across the pump is not.

2.3.1 Power, Pump Efficiency, and Temperature Rise

Power is the rate of energy consumed or generated. In the case of pumps, it is the product of the flow rate and pump work required. This section first determines the pump work required and then discusses power. It then briefly discusses efficiency and the temperature rise due to the inefficiency.

Referring to Equation 2.1 and considering only the driver and the impeller as the system, the work added by the driver (shaft work) is converted into kinetic energy of the liquid by the impeller, thus

$$w_s = \frac{\Delta u^2}{2} \tag{2.4}$$

This shows that the head depends only on the diameter and rotational speed of the impeller and is independent of the type of liquid (e.g., water or butane). Centrifugal pumps are constant head pumps. Once the impeller diameter and speed are selected, the characteristics of a pump are defined entirely by the head curve. (See Section 2.3.4 for more details.)

There are two types of power that need to be considered:

- The power the pump delivers to the liquid being pumped, commonly referred to as hydraulic horsepower, hhp, hkW
- The power the pump driver delivers to the pump shaft, commonly referred to as brake horsepower, bhp, bkW

Hydraulic power is the product of the mass flow rate and work given by Equation 2.5:

$$\text{hhp} = \frac{\dot{m}\Delta P}{229.2\rho} = Q\Delta P/1,714 \tag{2.5a}$$

$$\text{hkW} = \frac{1.67\dot{m}\Delta P}{\rho} = Q\Delta P/36.00 \tag{2.5b}$$

where

the mass flow rate, $\dot{m}$, is lb_m/min (kg/min)
the volumetric flow rate, Q is gallons per minute, gpm (m^3/h)
pressure, P, is lb_f/in^2 (bar)
density, ρ, is lb_m/ft^3 (kg/m^3)

The efficiency of a pump, η, which excludes driver efficiency, is defined as

$$\eta = \frac{\text{Hydraulic power}}{\text{Power input to the pump shaft}} \tag{2.6}$$

Consequently, brake power is

$$\text{bhp} = \frac{\text{hhp}}{\eta} \tag{2.7a}$$

$$\text{bkW} = \frac{\text{hkW}}{\eta} \tag{2.7b}$$

The power input to the liquid is larger than ideally required because of pump inefficiencies. Therefore, a fraction of the power delivered is converted into heat. The total power input to the driver and pump must include driver inefficiencies.

Under some circumstances, the temperature rise that occurs in a pumping operation may be significant. The difference between the energy delivered to the pump (brake power) and the energy the pump delivers to the liquid (hydraulic power) is the mechanical energy converted into heat in the pump. Some of these "losses" are due to friction in pump bearings but the majority of the loss is due to the action of the pump on the liquid. The equation for estimating the liquid temperature rise is

$$\Delta t(^\circ\text{F}) = \frac{h(1-\eta)}{778 C_P \eta}\left(\frac{g}{g_c}\right) \tag{2.8a}$$

$$\Delta t(^\circ\text{C}) = \frac{9.81 h(1-\eta)}{C_P \eta} \tag{2.8b}$$

where

h is the total pump head, ft (m)
η is the pump efficiency, dimensionless
C_P is the average heat capacity of the liquid, Btu/lb_m-°F (J/kg-°C)
the constant is 778 ft-lb_f/Btu (9.81 m/s^2)

Equation 2.8 assumes that all the energy is transferred to the liquid and none to the pump casing or impeller, that C_P is constant, and that no vaporization of the liquid occurs inside the pump. Note that the equation applies to flow rates that are sufficiently high to remove all heat. Lower flow rates could cause vaporization and pump damage. The manufacturer should be consulted for minimum safe flow rates. Overheating can be a major problem, especially on large, multistage pumps (*Engineering Data Book*, 2016).

Readers desiring more detailed discussions of pump efficiencies, power "losses," and temperature rise in pumps should consult books such as Karassik et al. (2008) and Karassik and McGuire (1998).

Example 2.3

What is the temperature rise for a pump with an efficiency of 75% pumping water 500 ft (152 m) up a hill?

Solution

Using Equation 2.8, the temperature rise is

$$\Delta t(^\circ\text{F}) = \frac{h(1-\eta)}{778 C_P \eta}\left(\frac{g}{g_c}\right) = \frac{500\,\text{ft}(1-0.75)}{\left(\frac{778\,\text{ft-lb}_\text{f}}{\text{Btu}}\right)\times\left(\frac{1\,\text{Btu}}{\text{lb}_\text{m}\text{-°F}}\right)\times 0.75}\left[\frac{32.2\,\text{ft/s}^2}{\left(\frac{32.2\,\text{ft-lb}_\text{m}}{\text{lb}_\text{f}\text{-s}^2}\right)}\right] = 0.2^\circ\text{F}(0.1^\circ\text{C})$$

This example points out the small temperature rises normally present when pumping liquids. By contrast, compressing a gas generates a significant temperature rise (see Chapter 9).

2.3.2 Suction Head, Suction Lift, Total Head

The previous sections discussed head in terms of the various forms of energy. This section considers head in terms of overall piping systems. For pump selection or evaluation, it is necessary to view the pump as one piece in a larger system. Consequently, it is vital to understand both pump suction characteristics as well as the piping system. Net positive suction head (NPSH) and cavitation are presented in the next section, followed by a discussion of pump characteristic curves and system curves. For in-depth presentations, the reader is referred to references such as Karassik and McGuire (1998), Hicks and Edwards (1971), Karassik et al. (2008), and Heald (2002).

Figure 2.6 illustrates various configurations involving static suction and discharge heads. The term "static head" denotes the vertical distance between pump impeller centerline and liquid level. (Note that some standards define the reference point as the centerline of the suction flange rather than the impeller.) Static heads are expressed in terms of height or pressure.

Below are important head terms commonly used with pumps:

- Suction head, h_s—the static suction head minus all frictional losses on the suction side of the pump when liquid supply level is above pump centerline.
- Suction lift head, h_l—the static suction head plus all frictional losses on the suction side of the pump when liquid supply level is below pump centerline. Suction lift is a negative value.
- Total discharge head, h_d—the sum of the static discharge head plus all frictional losses on the discharge side of the pump.
- Total head, h—the total discharge head minus the total suction head ($h = h_d - h_s$) or the total discharge head h_d plus the total suction lift h_l ($h = h_d + h_l$).

2.3.3 Net Positive Suction Head and Cavitation

NPSH is the suction head at the entrance of a pump. There are two important NPSH terms: the NPSH required (NPSHR) and the NPSH available (NPSHA). The NPSHR is determined by the pump design and is given as part of the characteristic curves supplied by the manufacturer. The NPSHA is a function of the piping system and liquid properties. It is important that the NPSHA always be

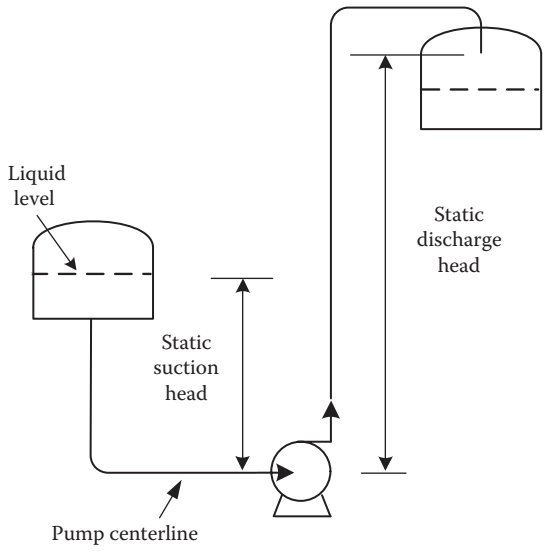


FIGURE 2.6 Example of static head terms. (Adapted from Hicks and Edwards, 1971.)

greater than the NPSHR. Otherwise, mechanical damage and poor pump performance can occur. More pump troubles result from misunderstanding of the NPSH than from any other single cause.

The NPSHA is the sum of suction heads:

$$\text{NPSHA} = h_T - h_{VP} + h_S - h_f \tag{2.9}$$

where

- h_T is the pressure above the liquid in the supply tank. For an open tank, this is atmospheric pressure. For use in Equation 2.9, pressure is converted to head of liquid using the density at suction conditions
- h_{VP} is the vapor pressure of the liquid being pumped
- h_S is the static suction head (see Section 2.3.2)
- h_f is the sum of all frictional losses (entrance and exit losses, pipe friction, valves and fittings, etc.) in the suction piping to the pump

The NPSHA and all head values in Equation 2.9 are in units of length (ft, m).

The NPSHR determined by the pump manufacturer is normally based on water as the pumped liquid. Data shows that for many organic and hydrocarbon liquids the NPSHR may be lower. Charts for determining the NPSHR correction for some liquids are available (Heald, 2002; Hydraulic Institute, undated; Karassik and McGuire, 1998; Karassik et al. 2008) along with cautions on the use and limitations of the corrections. However, in the gas processing industry it is common practice to ignore this correction.

If the NPSHA falls below the NPSHR, the pressure at some point in a pump may fall below the vapor pressure of the liquid, causing local vaporization and bubble formation in the liquid. When these bubbles move to a higher pressure part of the pump they collapse, with the mechanical energy created on collapse potentially inflicting physical damage to the pump. This process is known as cavitation. Figure 2.7 shows impeller damage due to cavitation.

In order to avoid cavitation, it is essential that NPSHA be greater than NPSHR. A safety margin of 10% is normally adequate (*Engineering Data Book*, 2016).

2.3.4 Characteristic Curves

The principal variables governing pump performance are power, head, flow rate, efficiency, impeller design, and speed. The most common way of showing the relationships is a plot of head, efficiency, and power against flow rate for a given impeller and speed. Figure 2.8 shows the typical shape of head, efficiency, and power curves as a function of flow rate.

The shape of the head–flow rate curves can vary significantly depending on the impeller design; three common shapes are shown in Figure 2.9. Note that the effect of pump flow rate on head is strongly dependent on the type of characteristic curve, ranging from small (drooping curve) to significant (steep). It is common practice to specify a rise in the order of 10% in the head curve from the rated capacity point to achieve proper control. If the curve is too flat or droops, it may be very

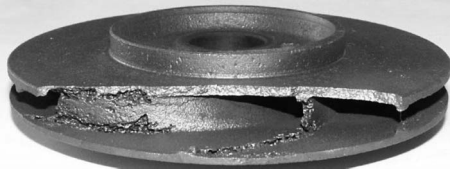


FIGURE 2.7 Centrifugal pump impeller showing cavitation damage. (https://commons.wikimedia.org/wiki/File:Kavitation_at_pump_impeller.jpg.)

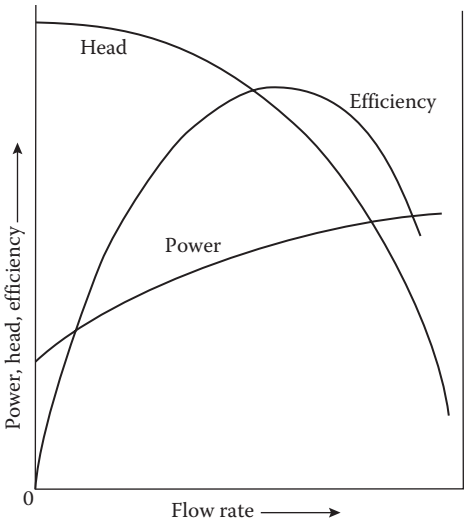


FIGURE 2.8 Typical centrifugal pump performance curves as a function of flow rate.

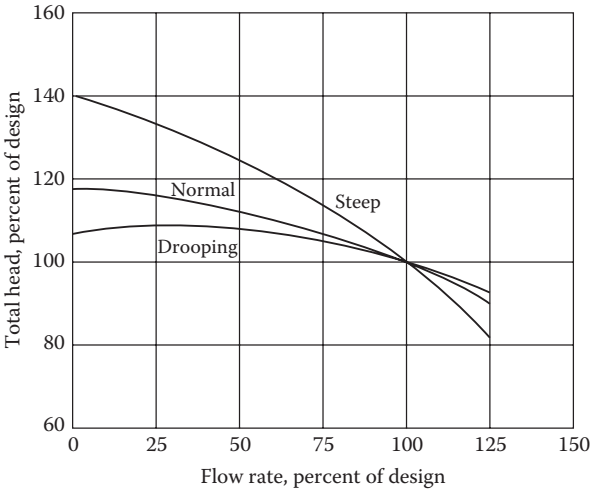


FIGURE 2.9 Three representative characteristic head-capacity curves as a function of flow rate.

difficult to control the system flow at the desired value. A pump should always be operated above the manufacturer's stated minimum flow rate.

Figure 2.10 shows a qualitative composite graph showing the effect of pump speed on developed head and efficiency. The design point is usually around maximum efficiency for the designed speed. Note that both developed head and efficiency drop at the higher flow rates.

The following example illustrates many of the principles discussed above.

Example 2.4

Saturated liquid propane at 90°F (32°C) is pumped from a reflux drum to a depropanizer at a maximum flow rate of 360 gpm (82 m^3/h). Assume pump nozzle elevations are at the same level and velocity heads are negligible. The vessel elevations are shown in Figure 2.11. Friction losses on

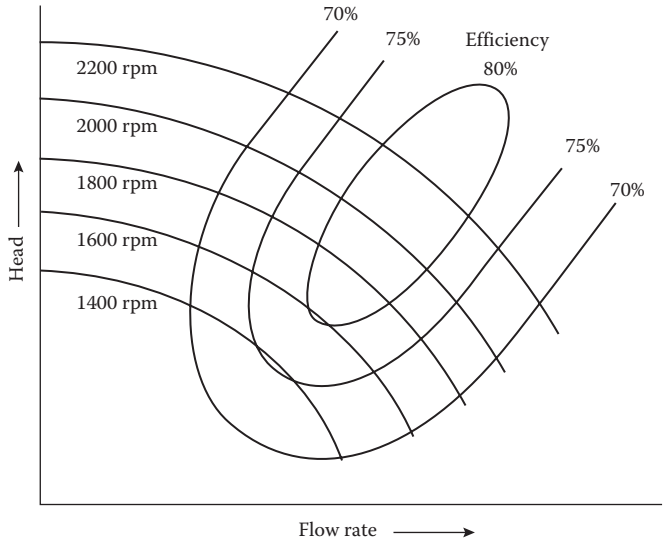


FIGURE 2.10 Effect of speed on head and efficiency.

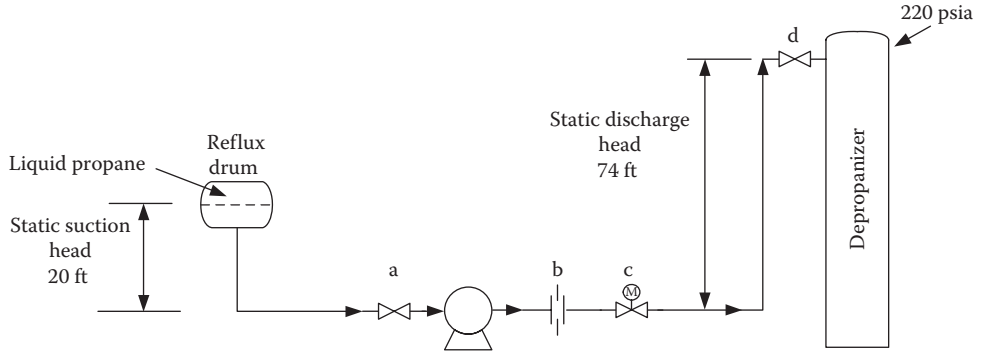


FIGURE 2.11 Piping diagram of propane reflux system.

the suction line consist of a valve (a) and piping which total 0.7 psi (0.05 bar) at 360 gpm (82 m^3/h). Friction losses on the discharge line consist of an orifice plate (b), piping and valves (c) and (d) which total 16.2 psi (1.12 bar). The vendor-provided performance curve is given in Figure 2.12.

Calculate the NPSHA and the brake horsepower for the pump.

Solution

CALCULATION OF NPSHA

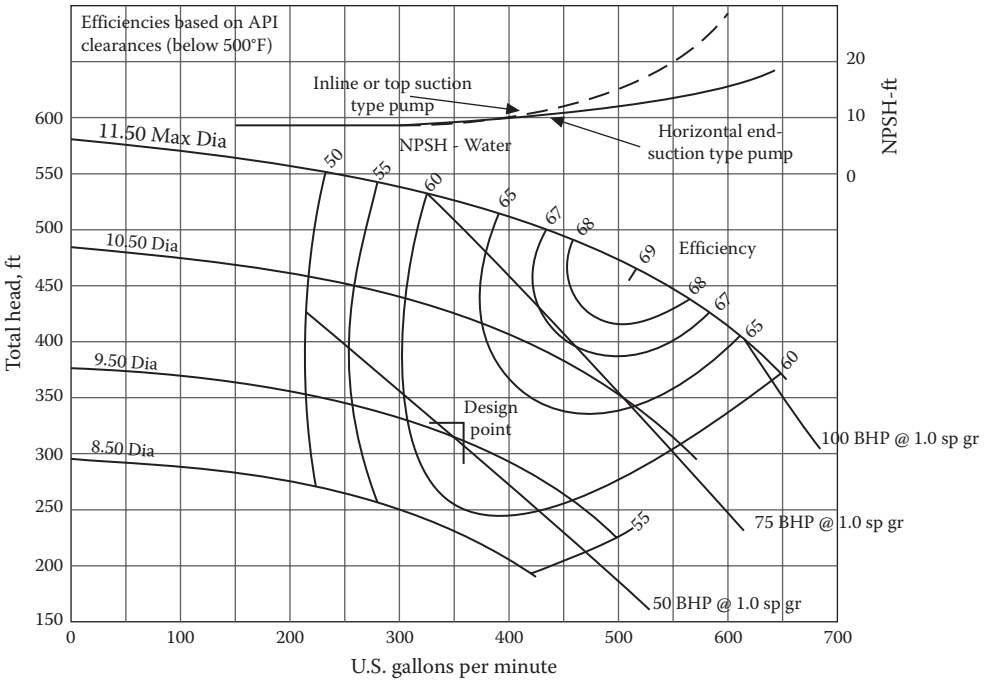
The NPSHA (Equation 2.9) is NPSH = $h_T - h_{VP} + h_S - h_f$

The propane vapor pressure and density at 90°F (32°C) are 165.3 psia (11.4 bara) and 30 lb_m/ft^3 (480 kg/m^3), respectively.

First, convert all terms to a common unit, ft (m) or psia (bara) using Equation 2.3 $h = P/\rho g$.

$$h_T = \frac{(165.3\,\text{psi})(144\,\text{in.}^2/\text{ft}^2)(32.2\,\text{ft-lb}_m/\text{s}^2\text{-lb}_f)}{(30\,\text{lb}_m/\text{ft}^3)(32.2\,\text{ft/s}^2)} = 793.4\,\text{ft}\,(242\,\text{m})$$

$$h_{VP} = 165.3\,\text{psia} = 793.4\,\text{ft}\,(242\,\text{m})$$



Depropanizer reflux pump				
Impeller Max Dia	11.50 In	2 × 4 × 11.5 Single stage pump		
Min Dia	8.50 In	Dia impeller 9.75 In	Impeller patt	3560 RPM
Eye Area	14.2 Sq In	NPSH required 9 Ft	Reference	Curve No.

FIGURE 2.12 Pump performance curves. (Adapted from *Engineering Data Book*, 2016, with permission.)

$$h_S = 20\,\text{ft}\,(6.1\,\text{m})$$

$$h_f = \frac{\left(0.7\,\text{psia}\right)\left(144\,\text{in.}^2/\text{ft}\right)\left(32.2\,\text{ft-lb}_m/\text{s}^2\text{-lb}_f\right)}{\left(30\,\text{lb}_m/\text{ft}^3\right)\left(32.2\,\text{ft/s}^2\right)} = 3.4\,\text{ft}\,(1.0\,\text{m})$$

$$\text{NPSHA} = 793.4 - 793.4 + 20 - 3.4 = 16.6\,\text{ft}\,(5.1\,\text{m})$$

Note: By definition, for a saturated liquid (bubble point) h_T and h_{VP} are equal and provide a net of zero positive head. This is a very common situation in gas processing and allows one to eliminate calculation of h_T and h_{VP} and eliminates the need to know the liquid vapor pressure if the suction pressure is otherwise known.

Referring to the pump manufacturer's data (Figure 2.12), the pump under consideration requires 9 ft (3 m) of NPSH (based on water) at 360 gpm (82 m^3/h). The available head is 16.6 ft (5.1 m). Allowing for a safety factor of 10% as recommended (*Engineering Data Book*, 2016), the NPSHA is more than 6 ft (2 m) greater than the NSPHR.

CALCULATION OF PUMP POWER

The required pressure increase across the pump is the net pressure difference between suction and discharge plus friction losses plus the net elevation change.

The net pressure increase is 220 – 165.3 = 54.7 psi (3.37 bar)
The friction losses are 0.7 + 16.2 = 16.9 psi (1.16 bar)
The net elevation change is 74 – 20 = 54 ft (16.4 m)
Converting the elevation term to pressure units:

$$\Delta P = \frac{\rho \Delta Z}{g_c} = \frac{\left(30\,\text{lb}_\text{m}/\text{ft}^3\right)\left(32.2\,\text{ft/s}^2\right)\left(54\,\text{ft}\right)\left(1\,\text{ft}^2/144\,\text{in.}^2\right)}{32.2\,\text{ft-lb}_\text{m}/\text{s}^2\text{-lb}_\text{f}} = 11.3\,\text{psi}\,(0.78\,\text{bar})$$

Required pressure increase is 54.7 + 16.9 + 11.3 = 82.9 psi. (5.72 bar)
Using Equation 2.5a, the required power is

$$\text{hhp} = \frac{(360)\times(82.9)}{1{,}714} = 17.4\,\text{hp}\,(13.0\,\text{kW})$$

Referring to Figure 2.12 at the design point the pump efficiency is approximately 62%. Thus,

$$\text{bhp} = 17.4/0.62 = 28\,\text{hp}(21\,\text{kW}).$$

2.3.5 System Curves

A system curve shows the head required to move the liquid through the piping system as a function of volumetric flow rate; it has three components:

- Static elevation head
- Pressure head
- Friction losses (pipe friction, valves, fittings, and entrance and exit losses)

The static head is only a function of elevation changes and usually remains relatively constant because liquid levels usually do not vary significantly. The pressure head is dictated by plant operating conditions and usually remains relatively constant. However, friction losses increase with increasing flow rate.

It is important to know the system curve for the application, because the pump will operate at the intersection of the pump characteristic curve and the system curve, as shown in Figure 2.13. The system curve is calculated by summing all the head losses in the system. It is relatively straightforward and will not be covered here; interested readers should consult references such as Crane Company (1988) and Heald (2002). Kumana and Suarez (2018) give a good review of using system curves.

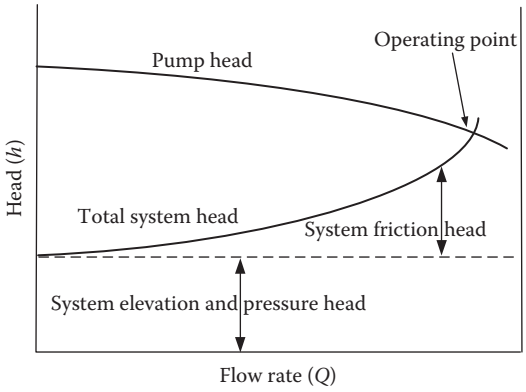


FIGURE 2.13 Combined system curve–pump curve.

2.3.6 Affinity Laws

For centrifugal pumps with radial flow impellers, there is a set of approximate relations between brake horsepower (bhp), impeller diameter (d), head (h), volumetric flow rate (Q), and speed (n). The relations may be expressed as (Heald, 2002):

For small variations in impeller diameter at constant speed

$$\frac{d_1}{d_2} = \frac{Q_1}{Q_2} = \frac{\sqrt{h_1}}{\sqrt{h_2}} \qquad \frac{\text{bhp}_1}{\text{bhp}_2} = \frac{d_1^3}{d_2^3} \tag{2.10}$$

For variations in speed at constant impeller diameter

$$\frac{n_1}{n_2} = \frac{Q_1}{Q_2} = \frac{\sqrt{h_1}}{\sqrt{h_2}} \qquad \frac{\text{bhp}_1}{\text{bhp}_2} = \frac{n_1^3}{n_2^3} \tag{2.11}$$

The affinity laws are generally used only as a quick guide to a change of operation; the pump vendor should be consulted before using. The results for changes in impeller diameters may be made less reliable due to differences in impeller configurations. The *Engineering Data Book* (2016) discusses limitations of using the affinity laws.

2.3.7 Coordinating Pump and System

Pump selection depends on the requirements of the overall piping system. Three of the more important system features have been discussed: NPSH, characteristic curves, and system curves. This section introduces five more:

- Series and parallel operation
- Flow control
- Drivers
- Speed control
- Pump priming

2.3.7.1 Series and Parallel Operation

To meet system requirements, multiple centrifugal pumps can be configured to operate in either series or parallel. In parallel operation, the capacities are added; in series operation, the heads are added. It is not necessary for the pumps to be identical, but the operating characteristics should be similar to provide balanced loads on the pumps.

2.3.7.2 Flow Control

Flow control in centrifugal pumps is most easily obtained by throttling the discharge. Depending on the shape of the pump head–flow rate curve (refer to Figures 2.8 and 2.9) the throttling effect on pump head may not be significant. Recall that the pump operates at the intersection of the pump head–flow rate curve and the system curve (Figure 2.13). Therefore, throttling not only moves the operating point to the left on the pump head curve but also changes the shape of the total system head–flow rate curve, so a new operating point will be obtained. Note that the new operating point may move the pump away from the maximum efficiency point (refer to Figure 2.8).

Flow control can also be achieved by recycling a portion of the pump discharge to the pump suction, maintaining the pump operating conditions while lowering the net liquid flow. The *Engineering Data Book* (2016) recommends using this technique with caution, because wide-open recirculation may result in a flow to the pump suction high enough to cause unacceptable liquid temperature rise and possible cavitation.

2.3.7.3 Drivers

Drivers for centrifugal pumps include electric motors, internal combustion engines, gas turbines, steam turbines, and hydraulic power recovery turbines. In gas processing, however, the most common driver is an alternating current (AC) electric induction motor, fixed or variable speed. This type of motor is relatively simple in construction, easy to install, and has a high availability. Most recent motor installations and many maintenance replacements have selected premium, higher efficiency motors to reduce power consumption at minimal additional initial cost.

The subject of driver selection for pumping systems is complex and beyond the scope of this book.

2.3.7.4 Speed Control

It is often desirable to have the ability to vary the speed of a pump because many applications require operation at varying flow rates and head. If a pump operates at constant speed, it is necessary to alter the system curve by throttling the flow to adjust the intersection of the two curves. However, it may be more economical to use a variable speed drive to adjust the system operating point.

There are various techniques for adjusting the speed of a pump; the more common are summarized in the *Engineering Data Book* (2016). The vast majority of variable speed pumps use variable frequency devices (VFD) with an AC motor drive. Variable frequency speed control has been applied to pump drivers of over 2,500 bhp (1.9 MW) and with the added advantage of controlling start-up power demand from the electrical system. It should be noted that some motors are not rated for variable frequency operation and the motor manufacturer should be consulted regarding VFD use. A few pumps have steam turbines drivers to vary speed and fewer still use other means of speed control.

2.3.7.5 Pump Priming

If the pump is elevated relative to the suction source (see Figure 2.6), suction lift is required. The pump must be capable of creating enough of a vacuum at its suction to create the necessary head to draw the liquid into the pump. If the pump and suction lines are filled with a gas at pump start-up, a centrifugal pump cannot create the necessary suction lift and the pump cannot function. If the pump is not designed to be self-priming, there are methods available to address the problem. Suction lift is uncommon in gas processing applications except for water pumps and sumps. For these applications, a manual priming arrangement is most often used.

2.4 RECIPROCATING PUMPS

Centrifugal pumps act by converting the shaft work into kinetic energy of the liquid, which is then converted into pressure head. Reciprocating pumps are positive displacement pumps and act by using the motion of a piston, plunger, or diaphragm to force the liquid from the pump. This chapter considers only piston pumps because they are the most widely used reciprocating pumps in gas processing. Figure 2.14 is a schematic of a single-acting piston pump, which is similar to a single-acting reciprocating compressor. It is called single-acting because it discharges liquid only when piston moves in forward direction. The pump would be double-acting if another set of valves were on the back side of the piston.

Figure 2.14 shows the pump in the discharge mode; the suction valve is closed and the piston is moving forward in the cylinder forcing the liquid out the open discharge valve into the discharge pipe. At the end of the piston stroke, the piston motion reverses, the discharge valve closes, the suction valve opens, and new liquid enters the cylinder. Liquid flows into the cylinder through the suction valve because the retreating piston creates a lower pressure in the cylinder. When the piston reaches the end of its intake stroke, the motion again reverses and the cycle repeats with the piston now forcing liquid out the discharge.

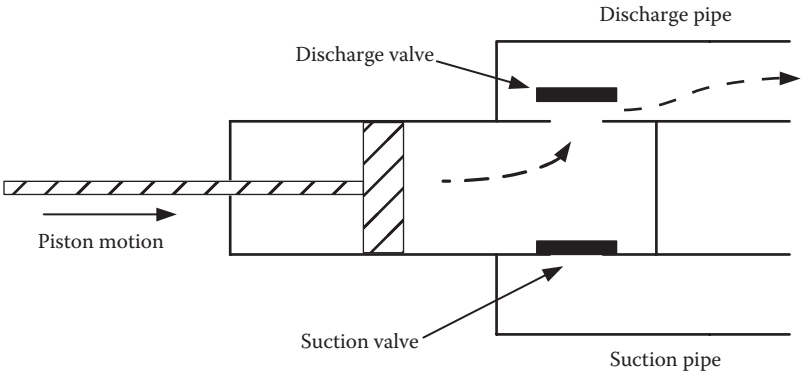


FIGURE 2.14 Single-action reciprocating pump in discharge mode.

2.4.1 Pump Fundamentals

The basic relations in Section 2.2 apply to reciprocating as well as centrifugal pumps. Although the two differ in mechanical design, there are no significant differences in the working equations used to calculate performance.

2.4.1.1 Flow Rate

The pump flow rate, Q (gpm, m^3/h), depends on the speed, n (rpm), the displacement volume of the cylinder, V (ft^3, m^3), and the pump stroke. In addition, reciprocating pumps have a volumetric efficiency. There are two major sources of volumetric inefficiency:

- Leakage, or slip, through the suction and discharge valves
- Changes in the liquid density due to compressibility of the liquid

The *Engineering Data Book* (2016) reports the combination of mechanical and volumetric efficiency of incompressible liquids is normally 90% or higher. Then, as a first approximation:

$$Q = \eta_V nV = 0.90nV \tag{2.12}$$

Equation 2.12 is for single-acting pumps and must be modified for double-acting pumps because there are two volumes swept for every crankshaft revolution.

For reciprocating pumps, flow varies directly with speed. Doubling the rotational speed doubles the flow. Doubling the rotational speed doubles the required power. More detailed discussions of flow rate calculations are available in the *Engineering Data Book* (2016) and Karassik et al. (2008).

2.4.1.2 Pulsating Flow

The flow from a centrifugal pump is uniform whereas flow from a positive displacement pump is pulsating. The severity and frequency of pulsation depends on pump design and speed. If necessary, there are techniques available for reducing pulsations, the most common being the use of gas bladders normally filled with nitrogen gas at 50%–70% of the discharge pressure (Karassik et al., 2008).

2.4.1.3 Net Positive Suction Head

NPSH calculations for reciprocating pumps are the same as those for centrifugal pumps with one important difference, the addition of an acceleration head term. The acceleration head must be added at each suction stroke to ensure that the liquid entering the pump remains a liquid and does not partially vaporize, resulting in pump cavitation. The calculation of acceleration head is quite

complex and beyond the scope of this chapter. Interested readers should refer to Heald (2002) or the *Engineering Data Book* (2016) for a discussion of an approximate method.

2.4.1.4 Flow Control

There are several methods for controlling the flow of a positive displacement pump with liquid recirculation to suction being the most common. Other methods include varying the driver speed, having speed reduction between the driver and the pump, and changing the pump stroke. Due to the mechanical complexity involved in building a pump with a variable pump stroke, this control method is normally reserved for small metering pumps. Note that pressure is independent of speed. At any speed, the pressure generated will be that required to support flow.

Recirculating part of the discharge flow to the suction of the pump is an effective method of control, but inefficient because a substantial portion of the work added is wasted. In addition to being inefficient, this method may cause vaporization in the pump suction. See Section 2.3.7.2 for a discussion of temperature rise and heat buildup in pumps with this type of control. Section 2.3.7.4 outlines the various methods commonly used for controlling the speed of electric motors.

The most common method of speed reduction is by using belts with different diameter sheaves. Note that this method of control requires manually changing of the sheave to achieve operation at different flow rates.

2.5 ROTARY PUMPS

There are many types of rotary pumps but the discussion here is limited to screw pumps; detailed discussions of vane, gear, lobe, and diaphragm as well as screw pumps are available in Karassik et al. (2008). In gas processing, most applications are at low flow rates, e.g., lubrication pumps and chemical injection pumps.

Screw pumps are positive displacement, axial-flow pumps that operate by trapping the liquid between rotating screw threads. A number of designs are available, generally divided into single rotor and multiple rotor, with multiple rotor units subdivided into timed and untimed categories for synchronizing the rotors.

The single screw pump, as the name implies, has a single rotating screw that meshes with threads on the stationary pump housing. Clearances are close and the threads form seals that trap liquid. Clearances decrease smoothly as the liquid moves through the pump.

Figure 2.15 shows a cutaway of a twin screw pump. In this design, there are two rotating screws, one right-hand thread and the other left-hand thread, on parallel shafts. One shaft is driven;

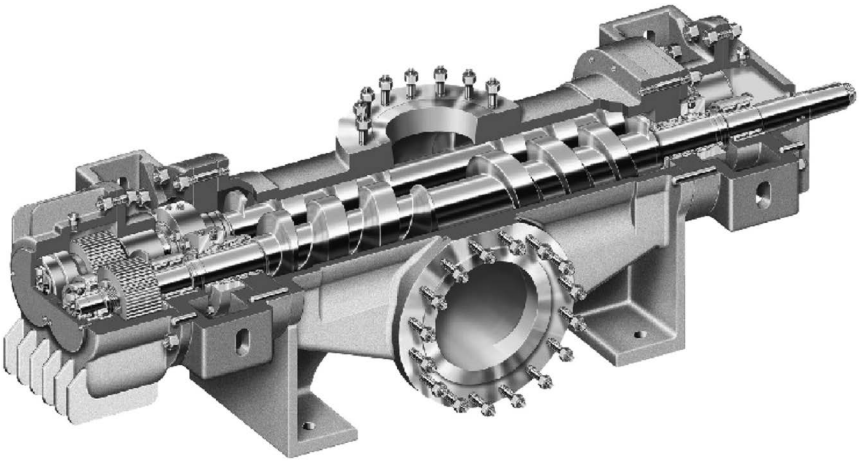


FIGURE 2.15 Cutaway of a twin screw pump. (Courtesy of Flowserve Corp.)

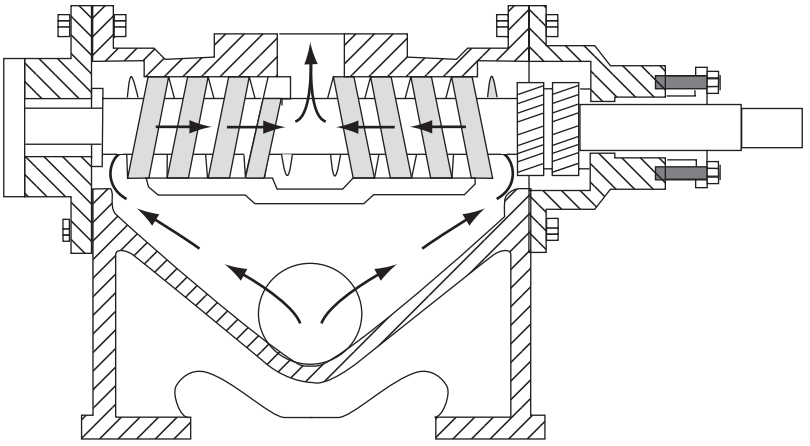


FIGURE 2.16 Flow pattern of twin screw pump.

the other is coupled to the drive shaft by gears making it a timed pump. Figure 2.16 shows the flow pattern of a twin screw pump (only one screw is visible). In the design shown, the entering liquid splits and flows to both ends of the pump and exits at the middle, thus, balancing the hydraulic thrust.

2.6 PUMP COMPARISONS

As mentioned earlier, centrifugal pumps are the most widely used pump type in gas processing. Therefore, it is appropriate to summarize the pros and cons of centrifugal pumps and the corresponding terms for positive displacement pumps. (Adapted from Coulson and Richardson (1977).)

2.6.1 Centrifugal

Pros

- Large variety in flow rates and head available
- Construction is simple
- Operation at high speed allows direct connection to electric motor
- Liquid delivery is steady, no pulsations
- Maintenance costs are generally lower than other pump types
- Pump may run for short periods of time with discharge line blocked
- Pumps are generally smaller than other pump types of the same capacity
- Liquids containing a percentage of solids can be handled

Cons

- Single stage pump will not develop a high head
- High efficiency possible only over a limited range of operating conditions
- Not self-priming unless specially designed

2.6.2 Positive Displacement

Pros

- Relatively simple construction
- High efficiency over wide range of operating conditions

- Will operate against a high head
- Can provide highly precise flow rates

Cons

- Pulsating delivery
- Uneven load on driver for reciprocating pumps

It is important to remember that centrifugal pumps produce a constant head dependent on flow rate while positive displacement pumps produce head limited only by the pumping energy available. It is good safety practice to place a pressure safety valve (PSV) on a positive displacement pump discharge to protect the pump, piping, and downstream equipment from incurring excessive pressures.

DISCUSSION QUESTIONS

1. Give a physical definition of head and pressure.
2. Which variables in Equation 2.1 are the most important when making an energy balance around just the pump?
3. For a given centrifugal pump, how do the generated head and generated discharge pressure vary with the density of the liquid being pumped?
4. What is the difference between hydraulic and brake power and which will always be larger?
5. What factors determine the value of NPSHR and NPSHA and which should always be larger than the other?
6. What is cavitation and why can it be harmful to pumps?
7. What are static suction head and static discharge head?
8. Referring to Figure 2.13, which of the lines will vary with flow rate and how will the operating point vary as the flow rate changes?
9. For the three types of pumps discussed, will they have to be primed if the static suction head is negative?
10. Of the pump types discussed, which will be most applicable to metering small liquid flows, such as in additive injection?

EXERCISES

2.1 Note the position of the pump in Figure 10.4. What horsepower (bhp) will be required to pump the lean amine to the top of the contactor? Assume:
- The top of the contactor is 50 ft (15 m) above the pump outlet.
- The pressure drop through each heat exchanger is 5 psi (0.3 bar).
- The pressure drop through all piping, filters, valves, and fittings is 10 psi (0.69 bar).
- The pump efficiency is 60%.
- The pressure at the pump suction is 10 psig (0.69 barg).
- The pressure at the contactor is 800 psig (55.2 barg).
- The density of the lean amine solution is 61.3 lb_m/ft^3 (982 kg/m^3).
- The lean amine flow rate is 300 gpm (1.13 m^3/min), which includes the slip stream going to the lean amine flash tank.

2.2 Liquid methane is pumped from a pressurized cryogenic vessel to a second pressurized vessel. The liquid enters the pump at 50 psia (3.4 bara) and –250°F (–157°C) and exits at 100 psia (6.89 bara). The liquid flow rate is 2,000 gpm (454 m^3/h). The pump is well insulated so the pumping process is approximately adiabatic. The pump efficiency is 70%. Estimate the temperature rise in the liquid methane.

The density of the liquid methane is 25.95 lb_m/ft^3 (415.7 kg/m^3) and $C_p = 0.845$ Btu/lb_m-°R (2.99 kJ/kg-K).

2.3 Liquid propane is withdrawn from one storage tank and transferred to a second tank. The temperature is constant at 80°F (27°C). The pump suction is located 10 ft (3.0 m) below the liquid level in the first tank. The pressure drop in the valves and fittings from the first tank to the pump suction is 1.0 psi (0.069 bar). What is the *NPSH* available in ft(m)? The vapor pressure of propane at 80°F (27°C) is 144.1 psia (9.928 bara).

REFERENCES

Bird, R.B., Stewart, W.E., and Lightfoot, E.N., *Transport Phenomena*, Revised 2nd edn. John Wiley & Sons, New York, 2007.

Coulson, J.M., and Richardson, J.F., *Chemical Engineering*, Vol 1, 3rd edn. Pergamon Press, Oxford, 1977.

Crane Company, Flow of fluids through valves fittings and pipe, Technical Paper Number 410, 1988.

Engineering Data Book, Section 12, Pumps & hydraulic turbines, GPSA Midstream Suppliers, Tulsa, OK, 2016.

Heald, C.C. (ed.), *Cameron Hydraulic Data*, Flowserve, Irving, TX, 2002.

Hicks, T.G., and Edwards, T.W., *Pump Application Engineering*, McGraw-Hill, New York, 1971.

Hydraulic Institute, undated. www.pumps.org (Retrieved April 2019).

Karassik, I.J., and McGuire, T., *Centrifugal Pumps*, 2nd edn. Chapman and Hall, New York, 1998.

Karassik, I.J., et al. (eds.), *Pump Handbook*. McGraw-Hill, New York, 2008.

Kumana, J.D., and Suarez, M.R., Analyzing the performance of pump networks, *Chem. Eng. Progr.*, *114*(1), 34, 2018.

Lemmon, E.W., McLinden, M.O., and Friend, D.G., Thermophysical properties of fluid systems, *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, Linstrom, P.J. and W.G. Mallard (eds.), National Institute of Standards and Technology, Gaithersburg MD, 2017. http://webbook.nist.gov (Retrieved April 2019).

McCabe, W., et al., *Unit Operations of Chemical Engineering*, 8th edn. McGraw-Hill, New York, 2018.

Stepanoff, A.J., *Turboblowers, Theory, Design, and Application of Centrifugal and Axial Flow Compressors and Fans*, John Wiley & Sons, New York, 1955.

Wilkes, J.O., *Fluid Mechanics for Chemical Engineers with Microfluidics and CFD*, Prentice Hall PTR, Upper Saddle River, NJ, 2005.

3 Heat Transfer

3.1 INTRODUCTION

Maximizing plant efficiency requires extensive use of heat exchange for energy recovery. Thus, heat transfer plays an important role in most gas processing steps. Next to compression, heat exchangers commonly are the largest capital expense in a gas plant. This chapter gives:

- An overview of the three ways heat flows from a higher temperature to a lower temperature
- A brief discussion of sources for cooling and heating
- A brief description of commonly used heat exchanger types
- A discussion of condensers
- A discussion of reboilers

Only the briefest introduction to heat transfer is given. For more details on heat transfer in general, the reader should refer to heat transfer or unit operations books, e.g., Cengal (2007), Holman (2002), Bergman et al. (2011), and McCabe et al. (2018). The *Engineering Data Book* (2016a–c) provides more detail and design guidelines for several types of heat exchange equipment.

3.2 MODES OF HEAT TRANSFER

There are three ways heat flows from a high temperature to a low temperature:

1. Conduction
2. Convection
3. Radiation

All may play a role in a heat transfer process. However, one mode usually dominates. A brief description of each mode is given along with the applications where they are important.

3.2.1 Conduction

Heat moves through solids by conduction. Although it occurs in stagnant liquids and gases, conduction usually is overwhelmed quickly by fluid motion due to density differences caused by the temperature difference. This effect, called natural convection, is discussed in the next section. We concentrate on conduction through solids, such as heat exchanger tubing and insulation.

Figure 3.1 depicts heat flowing through a solid media. The rate of heat flow, Q, has units of energy per unit time (e.g., Btu/h or W). The heat flow rate is determined by four factors:

1. Temperature difference, $t_2 - t_1$ (°F or °C)
2. Cross-sectional area, A (ft^2 or m^2)
3. Solid thickness, L (ft or m)
4. Thermal conductivity of the solid, k (Btu/h-ft-°F[1] or W/m-°C)

[1] Some tables present thermal conductivity in units of Btu-in/ft^2-h-°F.

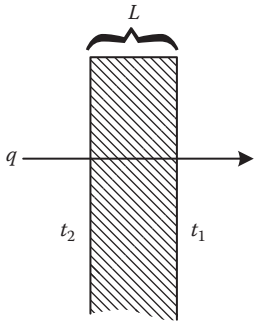


FIGURE 3.1 Flow of heat through solid by conduction.

Heat flow increases with increasing temperature difference and surface area but decreases with increasing solid thickness. Thus, the equation for conduction through a flat slab of thickness L, e.g., furnace wall, is given by

$$\dot{Q} = \frac{k(t_2 - t_1)A}{L} \tag{3.1}$$

where $\dot{Q}$ is the heat flux and the proportionality constant, k, is the thermal conductivity. For conduction through a cylinder of length L the equation[2] is

$$\dot{Q} = \frac{2\pi Lk\Delta t}{\ln\left(d_o/d_i\right)} \tag{3.2}$$

and for conduction through a sphere the equation is

$$\dot{Q} = \frac{2\pi k\Delta T}{(1/d_i) + (1/d_o)} \tag{3.3}$$

where d_i and d_o represent inner and outer diameters.

Thermal conductivity is a property of the solid and normally increases with increasing temperature. The above equations assume that the temperature difference is small enough to ignore this effect or that an average value is used. Table 3.1 gives representative thermal conductivities of various materials. Included for comparison are thermal conductivities of several fluids.

Frequently, the temperature difference and area are set so that the only variables that can be changed are thickness and thermal conductivity. For heat exchangers, high thermal conductivities and thin walls are desired to maximize heat transfer through the walls. However, wall thickness usually is determined by operating pressures and metal mechanical properties.

For insulation, materials with low thermal conductivities and thick walls are used. Insulating materials commonly have "*R*-values," which are the thickness divided by the thermal conductivity. While this is true for solids like metals, insulating materials commonly contain voids. Therefore, *R*-values represent the overall apparent thermal conductivity, which combines all three modes of heat transfer. The above equations are still appropriate when using *R*-values if the *k/L* term is replaced by 1/*R*-value. For example, Equation 3.1 becomes

$$\dot{Q} = \frac{\Delta tA}{R\text{-value}} \tag{3.4}$$

Note that commercial insulations are given as a number (e.g., *R*-24) without units. The units are implied and in USES units, they are h-ft^2-°F/Btu. In SI, the units are m^2-°C/W.

[2] The "ln" denotes the "natural" logarithm. It is equal to 2.303 log10 or "common" logarithm.

TABLE 3.1
Thermal Conductivities of Various Materials

Substance	Temperature, °F (°C)	Thermal Conductivity Btu/h-ft-°F (W/m-K)
Methane,[a] gas at low pressure	60 (15.6)	0.019 (0.033)
Propane,[a] liquid	–40 (–40)	0.058 (0.10)
vapor		0.0092 (0.016)
Triethylene glycol,[a] liquid	140 (60)	0.12 (0.20)
Carbon steel[b]	200 (93)	29 (50)
	600 (315)	26 (45)
304 Stainless steel[b]	200 (93)	9.3 (16)
	600 (315)	11 (19)
Aluminum, 3,003 tempered[b]	200 (93)	104 (180)
	400 (205)	106 (183)
Titanium[b]	200 (93)	12 (21)
	600 (315)	11.2 (19)
Copper[b]	200 (93)	225 (389)
	600 (315)	223 (386)
Firebrick[c]	500 (260)	0.7–2 (1–4)
Insulating brick[c]	500 (260)	0.08–0.2 (0.1–0.4)
Cellular glass[d]	100 (38)	0.028–0.031 (0.048–0.054)
Perlite[e]	100 (38)	0.027 (0.048)
Mineral wool[f]	100 (38)	0.023–0.032 (0.040–0.056)
Calcium silicate[g]	100 (38)	0.038–0.045 (0.065–0.078)

[a] Figures 23.38 & 23.39, *Engineering Data Book* (2016e).
[b] Figure 9.8, *Engineering Data Book* (2016b).
[c] Range of values for grades of brick; values given at mean temperature. Figure 8.3, *Engineering Data Book* (2016a).
[d] ASTM C552-17e1 (2017).
[e] ASTM C549-18 (2018).
[f] ASTM C553-13 (2013).
[g] ASTM C533-17 (2017).

Example 3.1

A mole sieve regeneration gas furnace has 2 in. (51 mm) of fire brick with a thermal conductivity of 1.0 Btu/h-ft-°F (1.7 W/m-°C). The inside wall temperature is 1,250°F (677°C) and outside wall temperature is 77°F (25°C).

a. What is the heat loss through the wall on a Btu/h-ft^2 (W/m^2) basis?
b. If 1 in. (25 mm) of insulating brick with a thermal conductivity of 0.14 Btu/h-ft-°F (0.24 W/m-°C) is added, what would be heat loss?

Solution

a. Rearranging Equation 3.1 to give heat flux on Btu/h-ft^2 basis gives

$$\frac{\dot{Q}}{A} = \frac{k(t_2 - t_1)}{L}$$

$$= 1\,\text{Btu/h-ft-°F}\,\frac{(1{,}250 - 77)\,°\text{F}}{(2/12\,\text{ft})}$$

$$= 7{,}040\,\text{Btu/h-ft}^2\,(22.2\,\text{kW/m}^2)$$

b. In analogy to electrical resistances, thermal resistances, R (L/k), must be added

$$\frac{1}{R_{\text{Total}}} = \frac{L_1}{k_1} + \frac{L_2}{k_2} = \frac{(2/12\,\text{ft})}{1.0\,\text{Btu/h-ft-°F}} + \frac{(1/12\,\text{ft})}{0.14\,\text{Btu/h-ft-°F}} = 0.167 + 0.595$$

$$= 0.762\,\text{Btu}^{-1}\,\text{h-ft}^2\text{-°F}\left(0.440\,\text{W}^{-1}\text{m}^2\text{-°C}\right)$$

Then,

$$\frac{\dot{Q}}{A} = \frac{(t_2 - t_1)}{R_{\text{Total}}} = \frac{(1{,}250 - 77)\,°\text{F}}{0.762\,\text{Btu}^{-1}\,\text{h-ft}^2\text{-°F}} = 1{,}540\,\text{Btu/h-ft}^2\left(4.86\,\text{kW/m}^2\right)$$

which represents a 78% reduction in heat loss.

3.2.2 Convection

Convection is the flow of heat caused by movement of fluid. It is the dominant mode of heat transfer in most gas processing steps. There are two kinds of convection:

- Natural (or free) convection
- Forced convection

As noted above, natural convection occurs in stagnant fluids because density differences, created by temperature differences, create fluid motion.

The general equation for heat transfer by forced or free convection is

$$\dot{Q} = hA\Delta t \tag{3.5}$$

where h is the heat transfer coefficient for either forced or natural (free) convection, in Btu/ft^2-h-°F or W/m^2-°C.

Natural convection is a complex process and, typically, empirical equations are used to compute the heat flow. The above-mentioned heat transfer books and *Engineering Data Book* (2016a) discuss predicting natural convection. However, it is obvious that larger area and temperature differences enhance natural convection. Less obvious but still important is how much the fluid expands with temperature (thermal expansion), fluid thermal conductivity, and fluid viscosity. Compared to liquids, gases have a higher thermal expansion but a lower thermal conductivity and viscosity. For the same temperature difference, there will be more natural convection in a gas than in a liquid. Natural convection is most important when natural drafts are used, like stacks, and in essentially stagnant fluids, such as storage tanks. Natural convection causes "turnover" when heating tanks. It also plays a major role in "rollover" of liquified natural gas (LNG) tanks (see Chapter 18). Natural convection occurs in gas filled or porous insulation, which reduces insulation effectiveness. However, R-values cited by the manufacturer include this effect.

Forced convection is the dominant mode of heat transfer in heat exchangers as well as the heat transfer between a flowing fluid and pipe wall. Like natural convection, forced convection is a complex process requiring empirical equations to correlate the variables affecting the heat transfer. In analogy to Equation 3.1, heat transfer coefficients replace k/L. Section 3.2.4 discusses heat transfer coefficients.

3.2.3 Radiation

Conduction and convection transfer heat with the help of solid, liquid, or gas. Radiant heat is electromagnetic wave energy in the ultraviolet to infrared region, which includes visible light. It travels in a vacuum as well as through a gas, poorly through liquids, but not through solids. Like light, it

is both reflected and absorbed. All bodies both emit and absorb thermal radiation. A mirrored surface absorbs little radiant heat while a black surface absorbs most of the incident radiant heat.

An equation similar to Equation 3.1 for radiation is

$$\dot{Q} \propto A\left(T_2^4 - T_1^4\right) \tag{3.6}$$

where T is the absolute temperature (°R, K), and temperatures to the fourth power are used.[3] Whereas Equation 3.1 had thermal conductivity as the proportionality constant, the proportionality constant for radiation heat transfer is a combination of the bodies' ability to absorb and transmit radiant energy along with geometrical factors. Radiation heat transfer is a complex subject and for more information, the reader is referred to previously mentioned heat transfer texts and the *Engineering Data Book* (2016a).

Radiation plays an important role whenever temperature differences are large. It dominates the rate of heat transfer in the exchange of heat between flames, furnace tubes, and walls. It is important in cryogenic processes. Low temperature distillation towers and vessels have highly reflective outer shells to minimize radiant solar heating.

3.2.4 Heat Transfer Coefficients

This section considers only forced convection because it is the dominant mode of heat transfer in most applications. Heat exchange with no change of phase is discussed first, followed by heat exchange involving condensation or boiling.

3.2.4.1 Heat Transfer with No Phase Change

Consider first the simple case of a flowing fluid inside an electrically heated tube. Figure 3.2 shows the temperature profile near the wall. In this case, heat is transferred to the fluid through a metal wall or tubing. Heat exchangers are usually designed to have high flow rates through the tubes so that the flow is turbulent. The turbulence ensures that the bulk fluid temperature is uniform in the radial direction except very near the wall. This very thin layer, where the fluid temperature changes from wall temperature to bulk temperature, is called the boundary layer. Using Equation 3.5 the heat going into the liquid is

$$\dot{Q} = h_i A\left(t_2 - t_1\right) \tag{3.7}$$

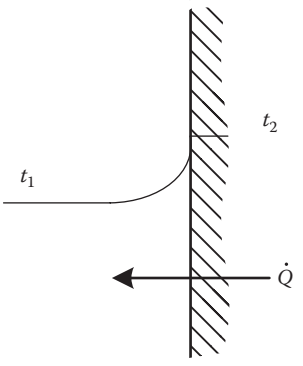


FIGURE 3.2 Temperature profile of a flowing fluid in highly turbulent flow moving through an electrically heated tube. Heat transfer occurs close to wall.

[3] The symbol ∝ denotes "is proportional to."

where h_i is the inside heat transfer coefficient. The most important fluid property affecting the heat transfer coefficient is the thermal conductivity. Heat capacity and viscosity are less important. The flow rate is also important because an increasing linear velocity increases heat transfer rate by reducing the thickness of the boundary layer. Unfortunately, increased flow rate also increases pressure drop. Table 3.2 shows the orders of magnitude for heat transfer coefficients in forced convection.

Direct electrical heating is rarely used in forced convection; typically, heat is exchanged between hot and cold fluids through a metal wall. Figure 3.3 depicts the temperature profile for this case. The total heat transfer is calculated from

$$\dot{Q} = UA(t_4 - t_1) \tag{3.8}$$

where U represents the local, overall heat transfer coefficient with t_1 and t_4 denoting the bulk cold and hot fluid temperatures. Heat transfer books provide details for estimating the local overall heat transfer coefficient, which accounts for the resistance to heat flow through the boundary layer. The overall heat transfer coefficient is a combination of heat transfer coefficients on each side of the wall plus the tube geometry and its thermal conductivity (see, e.g., McCabe et al., 2018).

Equation 3.8 tells how much heat is transferred at a given point along the tube. However, it is of little practical use because only entrance and exit temperatures in heat exchangers are known. Also, the temperature difference rarely remains constant along the heat exchanger. Figure 3.4 characterizes the temperature profile in countercurrent (i.e., hot and cold fluids flow in opposite directions) and cocurrent exchangers, where hot and cold fluids flow in the same direction. To determine heat flow in heat exchangers, Equation 3.8 must be revised to

$$\dot{Q} = U_o A \Delta t_{lm} \tag{3.9}$$

TABLE 3.2
Typical Orders of Magnitude for Heat Transfer Coefficients

Fluid	h, Btu/ft²-h-°F (W/m²-°C)
Gases in forced convection	2–20 (10–100)
Liquids in forced convection	10–100 (50–500)
Water	100–2,000 (500–10,000)
Boiling water	200–4,000 (1,000–20,000)
Condensing vapors	200–20,000 (1,000–100,000)

Source: Bird et al. (2007).

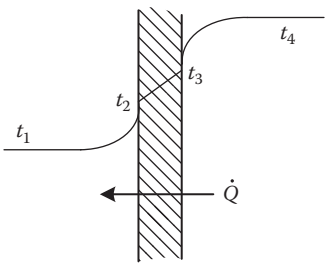


FIGURE 3.3 Temperature profiles of cold and warm fluids next to tube wall. Actual film thickness is much smaller than tube wall.

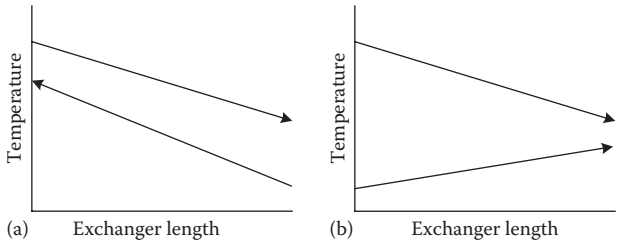


FIGURE 3.4 Temperature profile in (a) countercurrent and (b) cocurrent heat exchangers where there is no change of phase.

where U_o represents the overall heat transfer coefficient and Δt_{lm} is the log mean temperature difference given by

$$\Delta t_{lm} = \frac{(\Delta t_2 - \Delta t_1)}{\ln(\Delta t_2 / \Delta t_1)} \tag{3.10}$$

where Δt_1 and Δt_2 represent the temperature differences (approach temperatures) between the hot and cold fluids at each end of the heat exchanger. Equation 3.10 accounts for the temperature difference not remaining constant. The overall heat transfer coefficient is a function of fluid properties, flow rates, and heat exchanger geometry.

Heat exchangers often accumulate solid deposits on the tube walls. These may be degradation products, suspended solids, solids such as scale from water or material left from incomplete cleaning after construction. The solids increase the resistance to heat flow, which lowers the overall heat transfer coefficient. Using Equation 3.9 to determine U_o on a periodic basis can be extremely useful in monitoring exchanger fouling. (Commonly, the *UA* is computed because the area remains constant and need not be known to track fouling.) This method detects fouling before there is an obvious change in temperature differences and well before pressure drop indicates problems.

Example 3.2

The table below shows operating data taken for a countercurrent heat exchanger cooling lean MEA with water. The second data set was taken 6 months after the first set. The MEA concentration is 25 wt%., the average heat capacity over the temperature range is 0.91 Btu/lb_m-°F (3.8 kJ/kg-°C) and the density is 8.4 lb_m/gal at 60°F (1.01 kg/L), which is the reference temperature for the liquid flow meter. Determine if the data suggest that the exchanger shows signs of fouling.

	Data Set 1	Data Set 2
Lean amine flow rate	200 gal/min (12.6 L/s)	210 gal/min (13.2 L/s)
Lean amine inlet temperature	140°F (60°C)	140°F (60°C)
Lean amine exit temperature	100°F (38°C)	102°F (39°C)
Water inlet temperature	60°F (15.5°C)	59°F (15.0°C)
Water exit temperature	90°F (32°C)	91°F (33°C)

Solution

Although the lean amine exit temperature is slightly higher in the second data set, so is the amine circulation rate, and fouling is not obvious. Use Equation 3.9 to compute *UA* for both data sets. To determine $\dot{Q}$, we need the density and heat capacity, and $\dot{Q}$ is

$$\dot{Q} = 200\,\text{gal/min} \times 8.4\,\text{lb}_m/\text{gal} \times 60\,\text{min/h} \times 0.91\,\text{Btu/lb}_m\text{-°F} \times (140°\text{F} - 100°\text{F})$$
$$= 3.67\,\text{MMBtu/h}\,(1.07\,\text{MW})$$

$$\Delta t_1 = (140°\text{F} - 90°\text{F}) = 50°\text{F}(27.8°\text{C})$$
$$\Delta t_2 = (100°\text{F} - 60°\text{F}) = 40°\text{F}(22.2°\text{C})$$

$$\Delta t_{\text{lm}} = \frac{(\Delta t_1 - \Delta t_2)}{\ln(\Delta t_1/\Delta t_2)} = \frac{(50-40)}{\ln(50/40)} = 44.8°\text{F}\,(24.9°\text{C})$$

$$UA = \frac{\dot{Q}}{\Delta t_{\text{lm}}} = 3{,}670{,}000\ \text{Btu/h}/44.8°\text{F} = 81{,}900\ \text{Btu/h-°F}\left(43.0\ \text{kW/°C}\right)$$

Repeating the calculations for the second data set gives

$$\dot{Q} = 3.66\ \text{MMBtu/h}\,(1.07\ \text{MW}), \quad \Delta t_{\text{lm}} = 45.9°\text{F}\,(25.5°\text{C}), \quad \text{and} \quad UA = 79{,}700\ \text{Btu/h-°F}\left(42.0\ \text{kW/°C}\right)$$

The decreasing *UA* indicates that fouling might be occurring. Future data sets will be needed to confirm the trend. With only 3% decrease in *UA* the exchanger does not require cleaning.

3.2.4.2 Heat Transfer with Phase Change

As noted above, forced convective heat transfer takes place through the thin film at the wall. However, condensation and boiling disrupt the film and increase the heat transfer coefficient. The *Engineering Data Book* (2016b) gives an example for condensing propane with cooling water; the overall heat transfer coefficient for condensing is double that of cooling the gas phase and 20% higher than that for liquid–liquid exchange. Table 3.2 shows typical orders of magnitude for heat transfer coefficients when there is a phase change.

Boiling heat transfer rates are a complex function of the temperature differences between the wall and fluid. Figure 3.5 qualitatively shows the heat transfer coefficient in the boiling regions:

a. No boiling—Wall temperature is too low to cause boiling. The heat transfer coefficient changes little with temperature difference.
b. Nucleate boiling—As the temperature difference increases, boiling begins and the heat transfer coefficient increases rapidly with increasing temperature difference. This is because bubbles form at the nucleate sites and leave the surface, which disrupts the boundary layer.

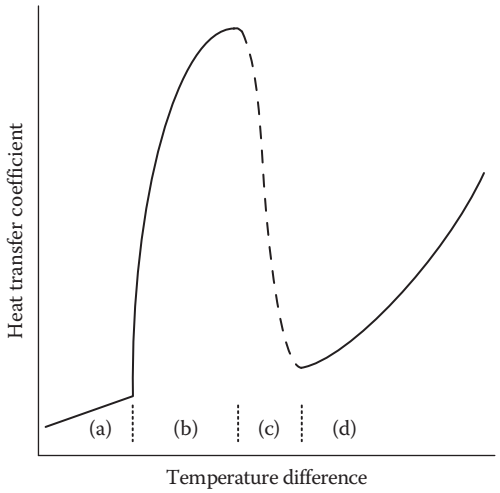


FIGURE 3.5 Heat transfer coefficient as function of temperature difference between liquid and hot surface. Region (a) no boiling, (b) nucleate boiling, (c) transition region, and (d) film boiling.

c. Transition—At some high temperature difference the amount of vapor formation begins to insulate the liquid from the wall and dramatically lowers heat transfer rate.
d. Film boiling—At higher temperature difference the surface is covered with only vapor and the heat transfer will again increase with increasing wall temperature. An example of film boiling is when water droplets dance on a very hot surface; the drop is separated from the surface by a thin vapor film.

The maximum temperature difference for nucleate boiling is a function of the fluid and surface conditions. While operating near the top of the curve in Figure 3.5 provides excellent heat transfer, the region is avoided because slight changes in temperatures or pressures can put the system into an unstable transition region.

3.3 COOLING AND HEATING SOURCES

This section provides a brief overview of the common sources for providing cooling and heating of process streams in gas plants. Cooling and heating fluids provide the means to bring a process stream to the required temperature.

3.3.1 Cooling Sources

As discussed in later chapters, major sources of cooling or refrigeration are by exchange with colder process streams, compression and expansion of the process streams themselves, or by propane refrigeration. Two additional common cooling fluids are ambient air and cooling water. Air-cooled exchangers are discussed later in Section 3.4.3.

Cooling water is obtained using evaporative cooling towers. The *Engineering Data Book* (2016d) provides a discussion on designing the various types of towers. This is beyond the scope of this book. Although the cooling water concept is simple, the "water chemistry" is not. Additives are required to avoid problems including the controlling of pH, minimizing solids deposits (scale), and preventing algae, bacteria, and fungi growth. Reputable chemical suppliers provide an excellent resource for additives when cooling water is used.

3.3.2 Hot Fluids

Electrical heating is sometimes used for pipe heat tracing and smaller heaters. However, its use is limited because it is expensive and because of safety concerns. As noted above, heat transfer coefficients for condensing fluids are high, making them excellent sources of heat. Steam is an ideal fluid and used extensively in refineries. However, it is little used in gas plants. There are two reasons for this:

1. The problems of maintaining a steam system
2. The limited need for high-temperature fluids

Like cooling water, water in steam systems must be carefully monitored and treated for pH and solids. Solids formation in exchangers can cancel the benefits of higher heat transfer coefficients due to condensation. Often steam is not an attractive option because gas processing facilities are in areas where makeup water is not readily available. The most common source of steam in modern gas plants is in heat recovery from sulfur recovery units (see Chapter 16); the steam is usually used in driving steam turbines on the units, not as a high-temperature energy source.

New gas plants and retrofitted older plants use hot oil (thermal fluid) instead of steam. While the heat transfer coefficients are lower than for steam, the simplicity of maintaining the hot oil system makes them attractive. For lower temperature applications (<~300°F (~150°C)) glycol-based oils

are often used. One common application is in wellhead separators (see Chapter 8). Hydrocarbon-based oils, polyethers, and inhibited glycols are used at temperatures up to ~700°F (~380°C). They are extensively used in reboilers. While less expensive, the hydrocarbon-based oils are more prone to fouling, especially by air. Areneault (2008) provides a good discussion of several hydrocarbon-based oils. The most stable and expensive are synthetic silicone-based oils. These oils come in various molecular weights, which determine their viscosity and flash point.[4] The flash point limits the maximum operating temperature while oil viscosity and freezing point limit the minimum operating temperature.

Furnaces, which are direct fired units, have combustion gases directly contacting tubes containing the process fluid or hot oil. Both radiant and convective transfer is important. "Convective furnaces" flow hot combustion gas over furnace tubes, which are not exposed to radiant heat from the burners. Convective furnaces are used when fluid temperatures must be controlled. Furnaces have high thermal efficiencies and are well insulated to have low (~2%) heat losses through the walls. To maximize efficiencies the exhaust gas from the furnace is often used to preheat the incoming oil or process fluid. Also, the most efficient designs include preheating the combustion air with exhaust gas. The *Engineering Data Book* (2016a) provides an extensive discussion on design, thermal calculations, and ways to improve furnace thermal efficiency.

3.4 HEAT EXCHANGER TYPES

3.4.1 Shell and Tube

Shell and tube exchangers have been the mainstay of heat exchangers since the beginning of gas processing. The exchangers are relatively rugged and simple to maintain. Therefore, they are frequently used in applications where fouling occurs. However, they are relatively heavy and compared to some other types, have a low heat transfer surface area for their size and weight. They are widely used with hot oil or steam as the heating medium. Figure 3.6 shows a schematic of two commonly used exchangers. The exchangers have baffles on the shell-side to force flow across the tubes.

The single tube-pass exchanger is easier to maintain when fouling occurs inside the tubes because the tubes can be mechanically cleaned without removing the tube bundle. However, the two tube-pass exchanger is widely used to conserve space and it requires no thermal expansion joints on the tube-side. Depending upon the type of service and plant layout requirements, exchangers with four-, six-, or eight-tube passes and up to four shell passes are used. If little heat transfer area is required a simple finned tube inside a pipe is used.

Regardless of the number of passes, Equation 3.9 can be used for checking for fouling. A correction factor is required for the temperature difference when sizing a multipass shell and tube heat exchanger (*Engineering Data Book*, 2016b). Often the heat transfer is "controlled" by either tube- or shell-side because one side has a much lower heat transfer coefficient. If this is the case, slight fouling on the controlling side will have a greater effect on the overall heat transfer coefficient than slight fouling on the other side.

3.4.2 Kettle Exchangers

Shell and tube heat exchangers are usually designed to have high linear velocities on both the shell- and tube-side to increase heat transfer coefficients. This reduces capital cost by reducing required heat transfer area. The one exception is the kettle, where the tube bundle is submerged in a boiling liquid. The main resistance to heat transfer is on the tube-side, because boiling occurs on the shell-side. Tube bundles are similar to those of the two-pass exchanger mentioned above.

[4] The flash point is the lowest temperature where a combustible liquid will ignite in ambient air. It is a function of both the liquid vapor pressure and combustion characteristics.

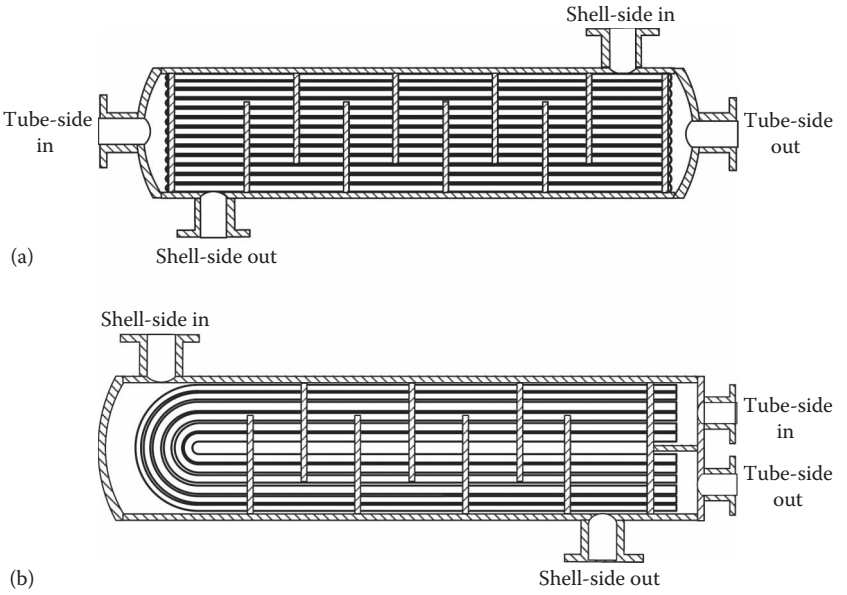


FIGURE 3.6 Two commonly used heat exchanger types. (a) Single-pass, tube- and shell-side. (b) Single shell pass, two-tube pass.

Some new units replace tube bundles with plate-fin exchangers (described below). The cores can provide a *UA* that is up to 20 times that of traditional tube bundles (Chart Energy & Chemicals, 2018), but they are limited in application because of maximum temperature limits on the aluminum materials used.

Kettle exchangers are used as reboilers, chillers, and heat recovery exchangers in Claus sulfur recovery units. For comparable heat exchanger area, the larger shell diameter makes kettles more expensive than shell and tube exchangers.

The heat source for reboilers can be a warmer process stream (e.g., demethanizer reboiler and side reboiler), steam, hot oil, or a firetube heater.

In contrast to direct fired furnaces, firetube heaters (Figure 3.7) contain the burner in a U-tube, which is immersed in a liquid bath. The liquid may be the process fluid (direct heating) or a heat

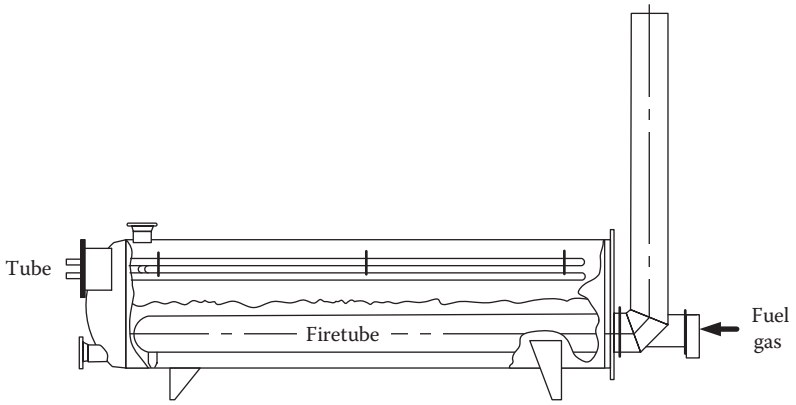


FIGURE 3.7 Firetube heater. Heater is indirect fired if the process stream is in the tube; directly fired if the bath fluid is the process stream. (Adapted from *Engineering Data Book*, 2016a, with permission.)

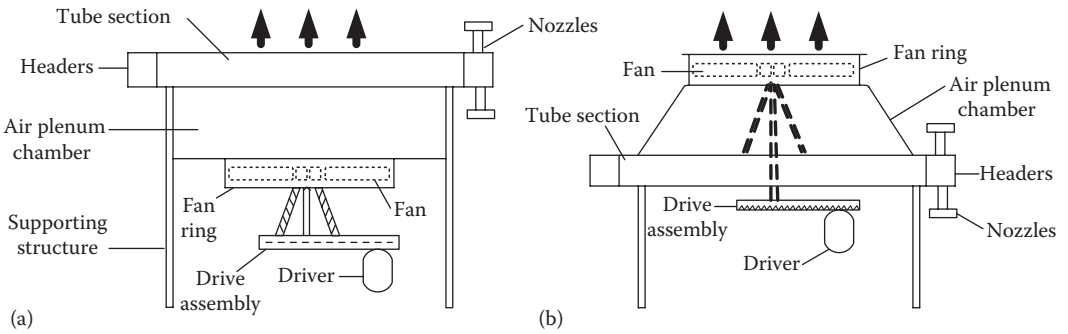


FIGURE 3.8 Typical side elevations of air coolers. (a) Forced draft and (b) induced draft. (Adapted from *Engineering Data Book*, 2016c, with permission.)

transfer fluid exchanging heat with the process fluid in tubes above the bath (indirect heating). Having the firetube immersed in liquid reduces the chance of hot spots. The firetube heat transfer area can be relatively small because the bath liquid boils on the firetube surface. Reboilers on glycol dehydration regenerators frequently are direct heating firetube units.

Indirectly heated firetube units have a tube containing the process fluid. The tube is "folded" several times to increase heat transfer area. Locating the tube above the boiling liquid allows hot vapors to condense on the tube and provide excellent heat transfer on the shell-side.

Firetube units can be small and skid mounted. Chapter 8 discusses their use in field operations.

3.4.3 Air-Cooled Exchangers

The *Engineering Data Book* (2016c) provides an extensive discussion of air-cooled exchangers. Air-cooled exchangers use ambient air to cool a process stream. The exchangers consist of a fan to force air across banks of tubes containing the process stream. To increase heat transfer on the air side, tubes usually have aluminum fins. The tubes are normally horizontal, although they may have a slight slope or be vertical to permit condensed liquid to drain. Both the fan and tubes can be vertical or sloped if a small footprint is needed.

Figure 3.8 shows that the air can be either pushed (forced draft) or drawn (induced draft) over the tube bundles. Induced draft provides better air distribution over the entire tube bundle. However, energy costs are slightly higher than forced draft because the fan moves warmer air. Also, the maximum effluent air temperature is 200°F (90°C) to prevent damage to the fan blades and drive components. If the process inlet temperatures exceed 350°F (175°C), forced draft should be used (*Engineering Data Book*, 2016c).

Besides handling higher temperatures and being slightly more efficient, forced draft has the advantage of being adaptable for warm air recirculation in cold climates. However, compared to the induced draft, there will be less natural draft caused by the stack effect if the fan is not operating. Induced draft fans also tend to be quieter than forced draft because the fan is farther from where personnel are present.

There often are multiple fan bays to provide redundancy and turndown capability. However, single-unit systems are used. The fan usually is driven by an electric motor. Air flow control is important when there are large seasonal temperature differences. Techniques to adjust air flow to accommodate variable air temperatures include

- Variable-speed drives
- Two-speed motors
- Louvers
- Variable blade pitch

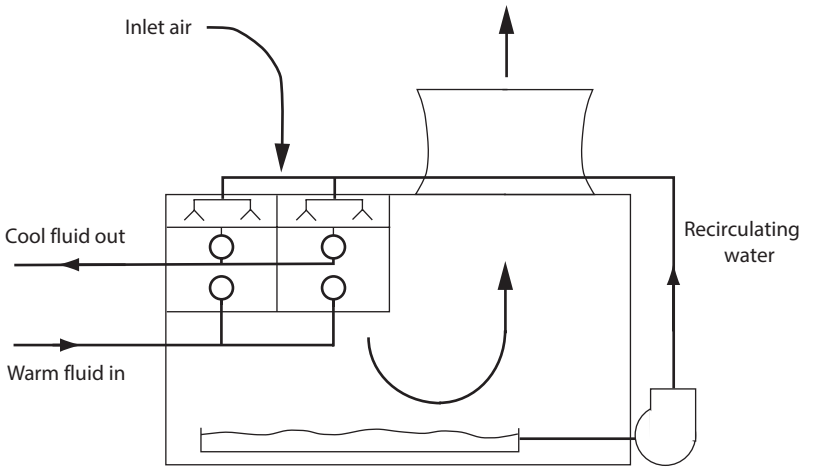


FIGURE 3.9 Wet surface air-cooled cooler. (Adapted from www.niagarablower.com/Resources/WSAC/Literature, with permission.)

All of the above methods reduce energy consumption when lower air flow rates are needed.

Cold climates may require air recirculation to prevent freezing the process fluid. Using louvers on forced draft systems, a portion of the warmer air returns to the air intake and raises the air temperature going past the tube bundles.

Hot summer temperatures also can be a problem. As an emergency measure to enhance cooling, water can be sprayed into the intake air to provide evaporative cooling. This is not considered good practice in the long term because scale from the evaporating water deposits on the tubes and lowers the heat transfer rate. Most coolers which have had water sprayed on them for extended periods have to be replaced or thoroughly cleaned. An alternative is the wet surface air cooler discussed in the following section.

Air-cooled exchangers are frequently used for interstage cooling on compressors and on condensers when condensation occurs above ambient temperatures. When cooling process streams to near ambient temperature the units must be located away from other processes to maximize cooling. Careful placement of air-cooled exchangers is a must. Factors that need to be considered include hot air plumes from other exchangers and the prevailing wind at the site.

3.4.4 Wet Surface Air Coolers

If process temperatures routinely need to be below 10°F–15°F (5°C–8°C) of the web-bulb air temperature,[5] wet surface air-cooled (WSAC) coolers shown in Figure 3.9 can be used. Approach temperatures can be as small as 5°F (3°C) to web-bulb temperature (Demakos, 2008). The units use induced draft to draw air down over horizontal tubes with no fins. Water is sprayed downward into the inlet air, collected at the bottom and then recirculated. This flow configuration prevents scale formation, even when turbidity is high. Water losses are far less than using a cooling tower and power requirements are less than with air coolers. The *Engineering Data Book* (2016c) provides more details.

3.4.5 Plate Frame Exchangers

Figure 3.10 shows an exploded view of a plate frame exchanger, often called gasketed plate exchanger. It consists of a series of metal plates, separated by gaskets, bound by two endplates and

[5] Web-bulb temperature is the lowest temperature obtainable at sampled air temperature and humidity.

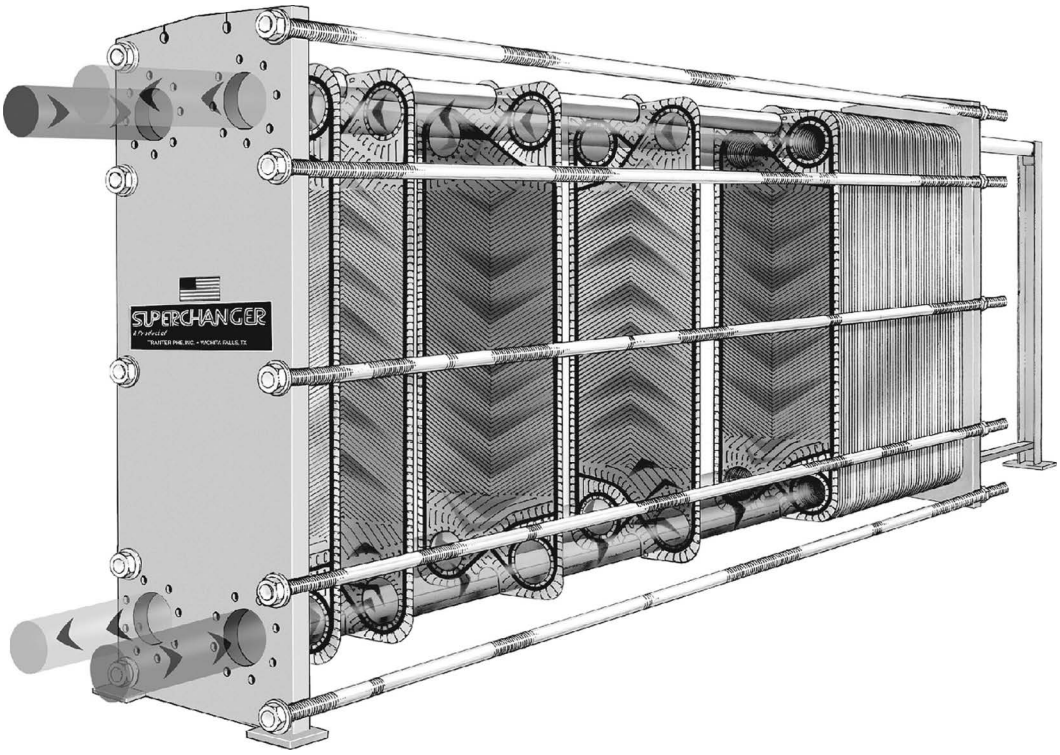


FIGURE 3.10 Exploded view of plate frame heat exchanger. (Courtesy of Tranter, Inc.)

held together by compression bolts. The metal plates have corrugated flow channels to provide high heat transfer surface area. Various plate patterns are available. One fluid enters at the top of the end plate, flows down between alternate plates, and exits at the bottom. The other fluid enters at the bottom, flows up, and out at the top. Thickness of the flow channels is 0.2–0.6 in. (5–15 mm). The exchanger is essentially a number of heat exchange units in parallel. Having all ports at one end facilitates disassembly.

The plate frame exchanger offers a number of advantages including (*Engineering Data Book*, 2016b):

- Easy disassembly for cleaning and adding or removing plates as heat duties change
- Close temperature approaches of 2°F (1°C) (Tranter, Inc, 2016)
- Short residence times
- High heat transfer coefficients because of high velocities
- Small footprint compared to comparable shell and tube exchanger
- Relatively low heat loss to surroundings, which reduces the need for insulation
- Fluid leakage between steams unlikely
- Leakage due to gasket failure is external and readily detectable

There are also some disadvantages:

- Gaskets limit operating temperatures to noncryogenic service and maximum temperatures of around 370°F (185°C) and maximum pressures of 400 psig, (28 barg) (Tranter, Inc, 2016).
- Care and patience is required when handling gaskets during assembly and disassembly to avoid leaks.

- Gasket material must be compatible with process fluid.
- Exchangers have relatively high pressure drop.
- Exchangers have poor turndown and are more susceptible to fouling at low rates.

Vendors offer plate frame exchangers with the plates welded together. This eliminates the gaskets and permits higher operating temperatures and pressures but eliminates the advantage of easy disassembly. For relatively clean service the high surface area, close approach temperatures, and small size make welded plate frame exchangers attractive.

The gasketed exchangers are used primarily for liquid service such as lean-rich amine exchange. Although more expensive than shell and tube exchangers, they are often competitive whenever alloys are required or where space is important such as skid mounts and offshore installations.

3.4.6 Plate-Fin Exchangers

Cryogenic facilities have made extensive use of brazed aluminum plate-fin heat exchangers since the 1950s. Figure 3.11a shows a cutaway of an element of a plate-fin exchanger. Instead of a shell and tube configuration, these units consist of channels formed by a thin sheet of aluminum pressed into a corrugated pattern (the fin) sandwiched between two aluminum plates. Each layer resembles the end view of corrugated cardboard. The fin channels may be straight or may have a ruffled or louvered pattern to interrupt the straight flow path. The entire unit is brazed together to form a single unit. Figure 3.11b shows a cutaway of a complete exchanger where multiple streams are being heated and cooled. Figure 3.12 shows the heat transfer bundle (core) prior to adding insulation and outer jacket.

Advantages of plate-fin exchangers include (*Engineering Data Book*, 2016b):

- Light weight.
- Excellent mechanical strength at subambient temperatures (used in liquid helium service [–452°F (–268°C)]). Can operate at pressures up to 1,400 psig (96 barg).
- High heat transfer surface area. Up to 6 times the surface area per unit volume of shell and tube exchanger and 25 times the area per unit mass.
- Complex flow configurations. Can handle more than ten inlet streams with countercurrent, crossflow, and counter crossflow configurations.

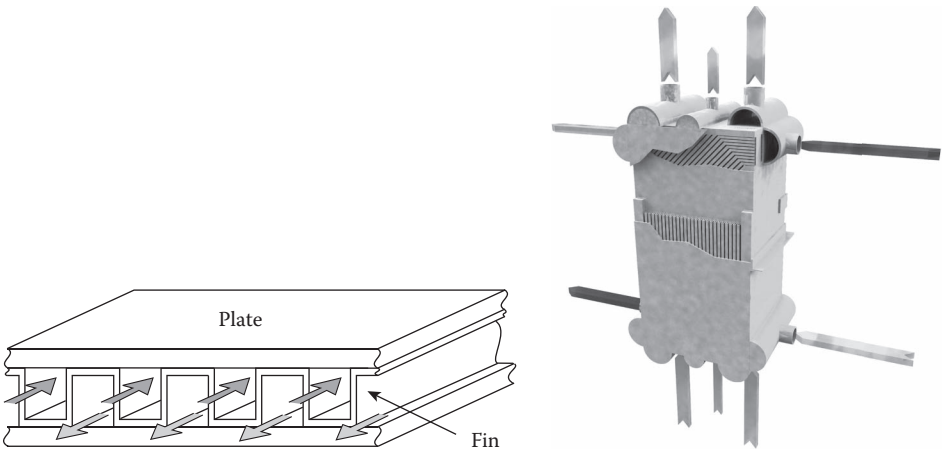


FIGURE 3.11 (a) Cutaway view of a plate-fin exchanger element. (b) Cutaway of view of plate-fin exchanger. (Courtesy of Chart Industries, Inc.)

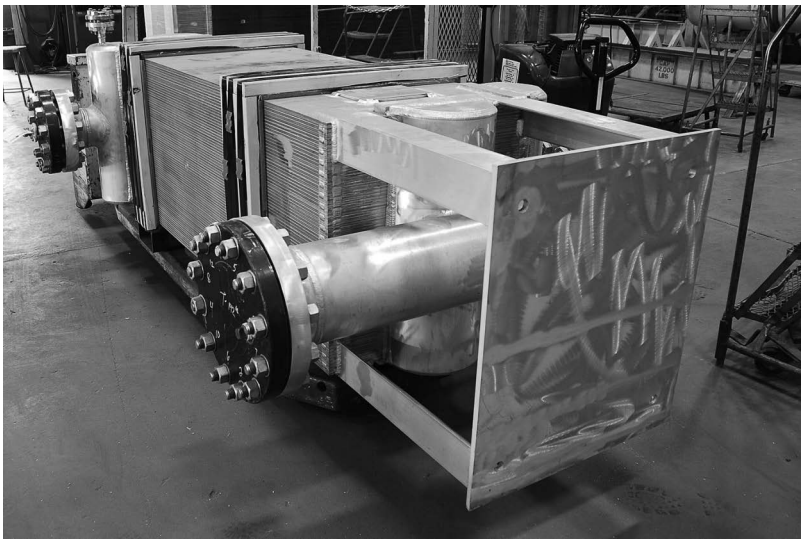


FIGURE 3.12 Uninsulated plate-fin heat exchanger ready for shipment (Courtesy of Chart Industries, Inc.)

- Close temperature approaches. Temperatures of 3°F (1.7°C) for single-phase fluids compared with 10°F–15°F (6°C–9°C) for shell and tube exchangers and 5°F (2.8°C) for two-phase systems.

Drawbacks and limitations of the exchangers include:

- Specialized maintenance required. Repair can be more costly and time-consuming than with shell and tube exchangers.
- Limited high-temperature operation. The maximum operating temperature is ~150°F (~85°C), although special designs go up to 400°F (200°C).
- Narrow channels. This makes them susceptible to plugging, and fine mesh screens are needed where solids may enter. The exchangers can be difficult to clean if plugging occurs. The exchangers are frequently located immediately downstream of molecular sieve dehydration units and fine accumulations can plug the exchanger. Often the blockage can be removed by back flowing gas through the exchanger.
- Less rugged. They do not tolerate rough handling or high pipe stress on nozzles.
- Limited to fluids noncorrosive to aluminum. Caustic chemicals are corrosive but acid gases are not, unless free water is present.
- Susceptible to mercury contamination. Mercury amalgamates with aluminum to destroy mechanical strength.
- Susceptible to thermal overstress. Maximum rate of temperature change and maximum difference between streams is limited and is set by manufacturer.
- Susceptible to thermal fatigue. Thermal stresses from changing thermal gradients are a major cause of external leaks (McNeilly and Shields, 2018).

Failures have occurred that are related to liquid slugging. These fluctuations are due to improper pipe geometry or improperly sized units (Vallee et al., 2018). To help operators address issues with brazed aluminum heat exchangers, the Gas Processors Association developed a technical bulletin (GPA-TB-M-001) on exchanger application and operation. This bulletin contains an extensive list of references on these exchangers. McNeilly and Shields (2018) provide a good explanation of the component terminology and functions.

The *Engineering Data Book* (2016b) provides additional information on plate-fin exchangers, including fin geometries. Lunsford (1996) provides guidelines on designing plate-fin exchangers. However, because of the complex design, heat exchanger vendors should be contacted for details on a specific application. Most often, heat transfer surface areas will be given for both hot and cold sides. This practice is comparable in adding both the shell and tube heat transfer surface areas together in a conventional shell and tube exchanger.

Plate-fin exchangers are extensively used in cryogenic service as gas–gas exchangers. Demethanizer columns have them for side reboilers and reboilers. As noted before, they are now used in propane chilling service.

3.4.7 Printed Circuit Heat Exchangers

Another heat exchanger type, the printed circuit heat exchanger (PCHE) is used in clean service (*Engineering Data Book*, 2016b). This technology is relatively new, commercialized in the 1980s, but hundreds of units are in service (Pua and Rumbold, 2003). Like electronic printed circuits, heat transfer passages are etched in plates, and the plates are sealed together by diffusion bonding. Unlike the brazed aluminum exchangers, they are rugged and, depending on materials of construction, go to high temperatures and pressures but can still handle complex flow schemes that involve many streams. The sizes of heat transfer passage range from "microchannels" (<8 mil, 200 μm) to "minichannels" (0.12 in., 3 mm) to provide high heat transfer surface areas. Like plate-fin exchangers, vendor design is required.

Offshore operations employ PCHEs in many applications because they offer comparable heat transfer at comparable pressure drops while being significantly smaller and lighter, one-fifth the weight of a shell and tube exchanger (Pua and Rumbold, 2003). One example of a high-temperature onshore application is in gas turbine-driven compressor stations, where hot lube oil is used to preheat fuel gas to the gas turbine to avoid condensation problems (Sell et al., 2004). Yoon et al. (2017) discuss their design for LNG Floating Storage Regasification Units (FSRU). Haynes and Johnson (2002) discuss exchanger performance characteristics.

3.5 CONDENSERS

Figure 3.4 showed temperature profiles, where there is negligible condensation or boiling in either warm or cold fluids. Figure 3.13a is typical of a refrigeration propane condenser. Superheated propane enters and cools to its dew point temperature, which is determined by the operating pressure. The majority of the heat is removed during condensation. Because it is a pure liquid, the temperature remains constant during condensation. There normally is some additional subcooling of the liquid. The heat transfer coefficient in each of the three sections of the exchanger will be quite different.

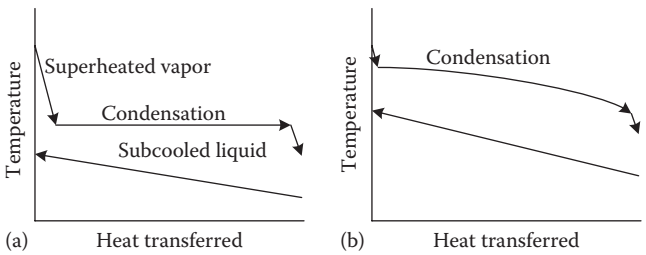


FIGURE 3.13 Temperature profiles in condensers. (a) Profile typical of pure warm vapor cooled, condensed, and sub-cooled. (b) Profile typical of overhead condenser on distillation column with impure overhead product. Lower line represents cooling fluid.

Condensers on distillation columns extract the heat from the overhead vapor to give a liquid product and to provide reflux back to the column. Figure 3.13b shows a typical temperature profile for an overhead condenser on a distillation column. In this case, there is little superheating and subcooling. The temperature profile during condensation will curve if a mixture is being condensed.

Most condensers on distillation columns are external to the column. Commonly these are either shell and tube or air-cooled exchangers. If condenser heat loads are very low the condensers may be internal. For example, in TEG regenerators the cold rich glycol feed to the regenerator is used to cool the top of the column. This reduces glycol losses overhead and preheats the rich glycol. See Chapter 11 for more details.

3.6 REBOILERS

Reboilers are the primary sources of heat in a distillation column and generate a liquid–vapor mixture by heating the liquid leaving the bottom mass transfer stage or tray. Side reboilers are normally used on demethanizer columns. Their main function is to recover refrigeration over a wider range of temperatures than would be possible with a single bottom reboiler. The *Engineering Data Book* (2016b) describes four reboiler types:

1. Kettle
2. Recirculating thermosyphon
3. Pump-through
4. Once-through

This section briefly describes each one. Finally, the section discusses internal reboilers.

The heat source in reboilers depends upon the bottoms column temperature and heat duty. Demethanizers often use gas exiting the dehydration unit. Stabilizers and reboilers on amine and glycol regenerators use steam, hot oil, or fired units. Field amine treaters, TEG dehydrators, and stabilizers frequently use directly heated firetube reboilers.

3.6.1 Kettle Reboiler

Kettle reboilers are attractive because they tolerate variable flow rates or when the return stream to the column must be vapor. As Figure 3.14 shows, they also provide an additional fractionation stage. Their major drawbacks are capital cost and small volume downstream of the weir. The small volume makes the reboiler sensitive to column upsets, which can cascade downstream to columns using the bottoms as feed. Kettles are used when fouling rates are low to moderate and when large heat transfer areas are required. Some columns, like glycol regenerators, often incorporate the reboiler into the bottom of the column.

3.6.2 Recirculating Thermosyphon

Whenever the bottoms product rate is essentially constant and fouling is not critical, thermosyphon reboilers are attractive because they are relatively inexpensive. Figure 3.15 gives a typical configuration. Liquid flows to the reboiler because of the difference in liquid levels and density. They often are vertical shell and tube exchangers with the process fluid on the tube-side. Because fluid velocities are high, thermosyphon reboilers are less prone to fouling. Unlike kettle reboilers, a full stage of separation is not provided. These exchangers often require a taller tower skirt[6] for proper operation when compared to some other configurations.

[6] The tower skirt is the mechanical support for the column; skirt height is the vertical distance between the column bottom and ground level.

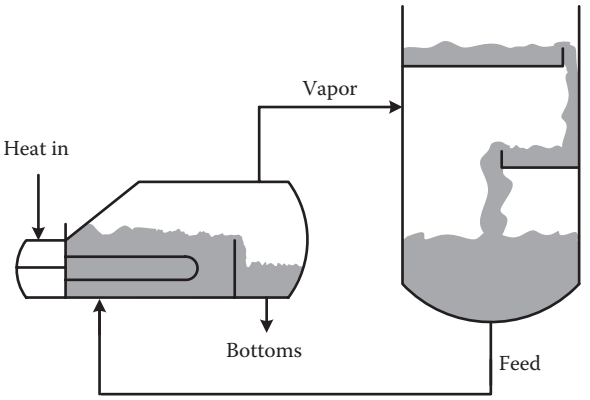


FIGURE 3.14 Kettle reboiler on column bottoms. (Adapted from *Engineering Data Book,* 2016b, with permission.)

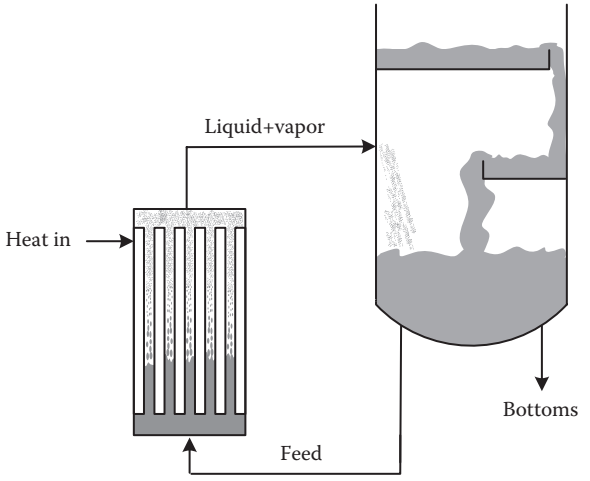


FIGURE 3.15 Recirculating thermosyphon. (Adapted from *Engineering Data Book,* 2016b, with permission.)

3.6.3 Pump-through Reboiler

Figure 3.16 shows that the pump-through reboiler is similar to the thermosyphon. However, it is required whenever there is insufficient liquid head, heavy fouling, or when the liquid is very viscous. The stream returning to the column usually is partially vaporized. Because a pump is present to overcome pressure drop, these units can be designed for a higher exchanger pressure drop and lower tower skirt height. The obvious disadvantage is that a high-temperature pump is required if bottoms temperature is well above ambient.

3.6.4 Once-through Reboiler

Figure 3.17 shows a once-through reboiler. They are similar to recirculating thermosyphon except that they allow a higher pressure drop though the tubes. Like a recirculating type, they do not require a pump. They do provide a full stage of separation and are less susceptible to fouling because they can be designed with higher tube velocities. They require more skirt height than a kettle reboiler but somewhat less than a recirculating thermosyphon.

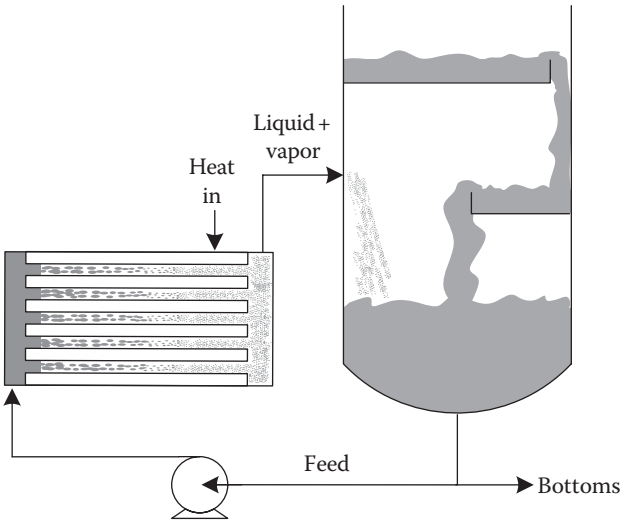


FIGURE 3.16 Pump-through reboiler on column bottoms. (Adapted from *Engineering Data Book,* 2016b, with permission.)

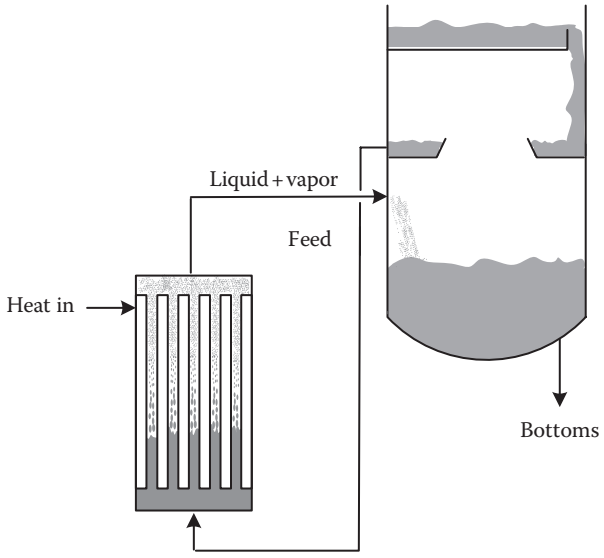


FIGURE 3.17 Once-through reboiler. (Adapted from *Engineering Data Book*, 2016b, with permission.)

3.6.5 Internal Reboilers

The above reboilers are external to the column. If reboiler duty is low, the reboiler can be inside the column. If the column operating pressure is near ambient, high reboiler duties are possible by essentially attaching a kettle reboiler as shown in Figure 3.18. They are commonly used on amine and glycol regenerators. Internal reboilers in gas plants may use steam, hot oil, or direct fired firetube heaters. Firetube heaters are used in nearly all field units.

Internal reboilers are ideal for small units where the kettle forms the bottom of the column and they are less expensive than a separate reboiler shell. Firetube reboilers also have the advantage of easy removal and replacement of the firetube.

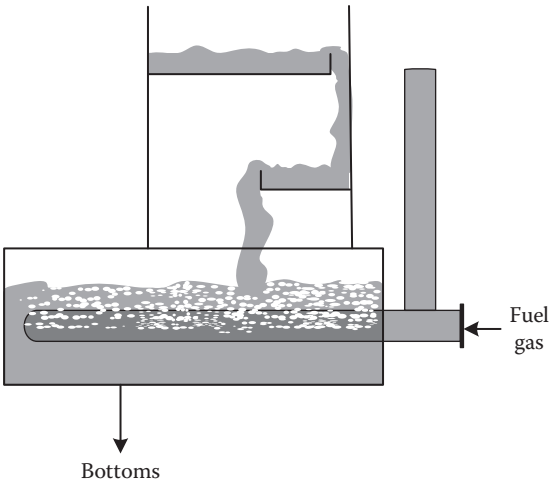


FIGURE 3.18 Internal reboiler with direct fired heating.

DISCUSSION QUESTIONS

1. Which of the three heat transfer modes dominate in most gas processing steps?
2. Why is conduction most important in solids but less important in fluids?
3. What modes of heat transfer are important in the "R-value" of wood and fiberglass insulation?
4. Give some examples where natural convection is important.
5. Give some examples where radiation is important.
6. What is meant by having one side "controlling" the heat transfer and why is this concept important?
7. How does boiling at a surface affect the heat transfer coefficient?
8. What are the relative merits of the types of the heat exchangers discussed in Section 3.4?
9. What are the advantages and disadvantages of using water as a heating or cooling fluid?
10. Figure 3.12 shows the temperature profiles in a condenser. What would the temperature profiles look like in a reboiler with the heating source being steam or hot oil?

EXERCISES

3.1 What is the heat loss, in Btu/h-ft (W/m) from a 40 psig (2.76 barg) saturated steam line assuming an outer wall temperature of 100°F (37.8°C)? The line has an outer diameter of 8.625 in (219 mm) and there are 2 in. (50.8 mm) of insulation with a thermal conductivity of 0.03 Btu/h-ft-°F (0.05 W/m-K). Assume the inside and outside pipe wall temperatures are the same.

3.2 A heat exchanger is being designed to cool a gas stream from 140°F (60°C) to 80°F (27°C) using cooling water that enters at 60°F (15.6°C) and exits at 70°F (21°C). Assuming heat duty and overall heat transfer coefficients are constant over the temperature ranges for both gas and water, what will be the relative difference in heat transfer area required if cocurrent flow is selected instead of countercurrent flow?

3.3 A condensate stabilizer column has a 300°F (149°C) bottoms temperature and the partially vaporized condensate leaves the reboiler at 350°F (176°C). The designed hot oil rate to the reboiler is 500,000 lb_m/h (63 kg/s) and the oil temperature changes from 450°F to 360°F (232°C to 182°C). The heat capacity of the hot oil is 0.55 Btu/lb_m-°F (2.3 J/g-°C). After 6 months in service the condensate inlet and outlet temperatures are 305°F and 350°F

(153°C and 177°C) and hot oil inlet and exit temperatures are 450°F and 370°F (232°C and 188°C) with a hot oil flow rate of 527,000 lb_m/h (66.5 kg/s). What is the percentage change in the *UA* for the reboiler? Assume countercurrent flow.

REFERENCES

Areneault, G., Safe handling of heat-transfer fluids, *Chem. Eng. Progr., 104*(3), 42, 2008.

ASTM C533-17, *Standard Specification for Calcium Silicate Block and Pipe Thermal Insulation*, ASTM International, West Conshohocken, PA, 2017. www.astm.org/Standards/C533.htm (Retrieved April 2019).

ASTM C549-18, *Standard Specification for Perlite Loose Fill Insulation*, ASTM International, West Conshohocken, PA, 2018. www.astm.org/Standards/C549.htm (Retrieved April 2019).

ASTM C552-17e1, *Standard Specification for Cellular Glass Thermal Insulation*, ASTM International, West Conshohocken, PA, 2017. www.astm.org/Standards/C552.htm (Retrieved April 2019).

ASTM C553-13, *Standard Specification for Mineral Fiber Blanket Thermal Insulation for Commercial and Industrial Applications*, ASTM International, West Conshohocken, PA, 2013. www.astm.org/Standards/C553.htm (Retrieved April 2019).

Bergman, T.L., et al., *Fundamentals of Heat and Mass Transfer*, 7th edn. John Wiley & Sons, New York, 2011.

Bird, R.B., Stewart, W.E., and Lightfoot, E.N., *Transport Phenomena*, Revised 2nd edn. John Wiley & Sons, New York, 2007.

Cengal, Y.A., *Heat and Mass Transfer: A Practical Approach*, 3rd edn. McGraw-Hill, New York, 2007.

Chart Energy & Chemicals, Core-In-Kettle® heat exchangers, 2018. www.chartindustries.com/Energy/Brazed-Aluminum-Heat-Exchangers (Retrieved April 2019).

Demakos, P.G., Wet surface air coolers minimize water use by maximizing heat transfer efficiency, *Power*, 2008. www.powermag.com/wet-surface-air-coolers-minimize-water-use-by-maximizing-heat-transfer-efficiency/?printmode=1 (Retrieved April 2019).

Engineering Data Book, Section 8, Fired equipment, GPSA Midstream Suppliers, Tulsa, OK, 2016a.

Engineering Data Book, Section 9, Heat exchangers, GPSA Midstream Suppliers, Tulsa, OK, 2016b.

Engineering Data Book, Section 10, Air-cooled exchangers, GPSA Midstream Suppliers, Tulsa, OK, 2016c.

Engineering Data Book, Section 11, Cooling towers, GPSA Midstream Suppliers, Tulsa, OK, 2016d.

Engineering Data Book, Section 23, Physical properties, GPSA Midstream Suppliers, Tulsa, OK, 2016e.

Gas Processors Association, GPA technical bulletin brazed aluminum heat exchangers GPA-TB-M-001, Tulsa, OK, 2015.

Haynes, B.S., and Johnson, A.M., High-effectiveness micro-exchanger performance, *Proceedings of the AIChE 2002 Spring National Meeting*, New Orleans, LA, 2002. www.heatric.com/app/uploads/2018/04/High-effectiveness-micro-exchanger-performance.pdf (Retrieved April 2019).

Holman, J.P., *Heat Transfer*, 9th edn. McGraw-Hill, New York, 2002.

Lunsford, K.M., Understand the use of brazed heat exchangers, *Chem. Eng. Progr., 92*(11), 44, 1996.

McCabe, W., et al., *Unit Operations of Chemical Engineering*, 8th edn. McGraw-Hill, New York, 2018.

McNeilly, A., and Shields, P., A smarter system, *Hydroc. Eng., 23*(12), 45, 2018.

Pua, L.M., and Rumbold, S.O., Industrial microchannel devices -where are we today? *First International Conference on Microchannels and Minichannels*, Rochester, NY, 2003. May 2006.

Sell, K.T., Langston, P.R., and Mitchell, R.H., Compressor station fuel gas superheating using lube oil waste heat, *Proceedings of the International Pipeline Conference*, Calgary, Alberta, Canada, 2004.

Tranter, Inc, Bringing efficiency to heat transfer, 2016. www.tranter.com/products/superchanger-plate-frame-heat-exchanger/ (Retrieved April 2019).

Vallee, S., Decker, D., and McNeilly, A., Reboilers with plate-fin brazed aluminum heat exchangers: Best practices and considerations for design and operation, *Ninety-Seventh GPA Midstream Convention*, Tulsa, OK, 2018.

Wet surface air coolers minimize water use by maximizing heat transfer efficiency. www.powermag.com/wet-surface-air-coolers-minimize-water-use-by-maximizing-heat-transfer-efficiency/?printmode=1 (Retrieved April 2019).

Yoon, S.H., et al., Design of Printed Circuit Heat Exchanger (PCHE) for LNG re-gasification system, *ASME 2017 International Mechanical Engineering Congress and Exposition*, ASME, Tampa, FL, 2017. http://proceedings.asmedigitalcollection.asme.org/proceeding.aspx?articleid=2669343 (Retrieved April 2019).

4 Separation Processes

4.1 INTRODUCTION

Gas plants take natural gas from the field and produce products to meet customer requirements. This requires separation processes, such as removing natural gas liquids (NGLs) and acid gases from the gas, and removal of trace components, such as mercury or arsenic.

Separation processes utilize differences in physical and chemical properties between components to obtain the desired outlet streams. These differences include:

- Volatility
- Solubility
- Chemical reactivity
- Molecular size
- Density

While most of these properties are strongly interrelated, usually one or two are considered the primary means for a separation.

All separation processes involve mass transfer from one phase to another. In analogy to heat transfer, there are two modes of mass transfer: diffusion and convection. Diffusion coefficients are similar to the thermal conductivity with the driving force being concentration differences instead of temperature differences and mass flow instead of heat flow. Convective mass transfer dominates most separation processes. Like heat transfer, mass transfer coefficients are used to describe separation processes. Equations for mass transfer are more complex than for heat transfer. The reader is referred to texts on mass transfer, such as Geankoplis et al. (2018) and McCabe et al. (2018) for more details.

This chapter provides a brief introduction to the separation processes used in gas processing. The basic principles along with the advantages and disadvantages of the general processes are discussed. Later chapters provide details of specific applications. Chapter 5 gives an overview of the types of equipment used to physically separate different phases.

4.2 DISTILLATION

This section considers the basic concepts of distillation. Later sections discuss the types of columns and column internals. The basic concepts are emphasized to provide an understanding of how distillation works.

Distillation uses the difference in volatility to separate components. However, solubility also is important. Volatility refers to the property of a component that causes it to distribute between two phases, generally vapor and liquid. Solubility refers to the ability of a component to mix with another component in a single phase.

Density differences between the liquid and vapor are required as well to ensure that the phases are properly separated. Fluid interfacial tension is also an important property in distillation because it affects how quickly the phases separate.

4.2.1 Basic Concepts

Understanding distillation requires a basic knowledge of vapor–liquid equilibria, which describes how pure fluids and mixture components distribute between a liquid and vapor when phases are in equilibrium. Pure fluids are discussed first, then mixtures.

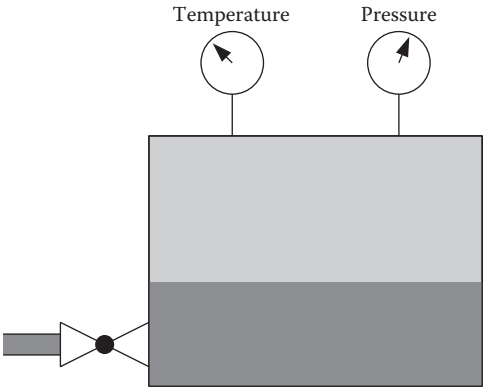


FIGURE 4.1 Vessel containing a pure volatile liquid. Pressure is independent of liquid level.

4.2.1.1 Pure Fluids

Consider the simple system shown in Figure 4.1, which consists of a feed line containing a pure volatile liquid, e.g., propane, connected through a valve to a vessel that is initially completely evacuated. If the valve is momentarily opened to allow a small amount of the liquid into the vessel while holding the temperature constant (isothermal process), the pressure increases each time the valve is opened and all the propane entering the vessel vaporizes. After repeated injections some propane begins to condense and the vessel pressure becomes constant. This pressure is the vapor pressure at the vessel temperature. Once it is reached, all added propane remains as a liquid. While the liquid level increases, the vessel pressure remains constant as long as the temperature remains constant. For a pure fluid, the pressure depends only on the temperature and not the liquid level. This follows the phase rule discussed in Chapter 1.

When the liquid and vapor are in equilibrium the two phases are "saturated" and any change in temperature or pressure will result in condensation or vaporization.

Process simulators provide vapor pressure data for propane and other components of natural gas as a function of temperature. They also have other physical properties needed for process design and operations. The NIST Chemistry WebBook (Lemmon et al., 2017) also provides high quality physical properties data.

Increasing the temperature increases the vapor density because of the higher pressure and decreases the liquid density because liquids expand with increasing temperature. At some temperature and pressure the liquid and vapor densities become equal; this is called the critical point. The critical point for propane is 206.13°F (96.74°C) and 616.6 psia (42.51 bara) and is denoted as CP in Figure 4.2.

All pure fluids, in principle, have a measurable critical temperature, pressure, and density. At the critical point, the liquid and vapor phases become one phase and all properties are equal. Appendix B[1] tabulates critical point values for the common components in natural gas processing. However, some liquids used in gas processing may react or decompose before reaching the critical point, making measurements difficult or impossible. These include some heating oils and amines.

4.2.1.2 Mixtures

Next, consider a simple binary mixture (e.g., propane and isobutane) with both components having normal boiling points (the temperature at which the vapor pressure is 14.7 psia (1.01 bara)) relatively close together. For a pure fluid, which is all vapor or liquid, only temperature and pressure are

[1] See Appendix B on publisher website: www.crcpress.com/Fundamentals-of-Natural-Gas-Processing-Third-Edition/Kidnay-Parrish-McCartney/p/book/9781138612792

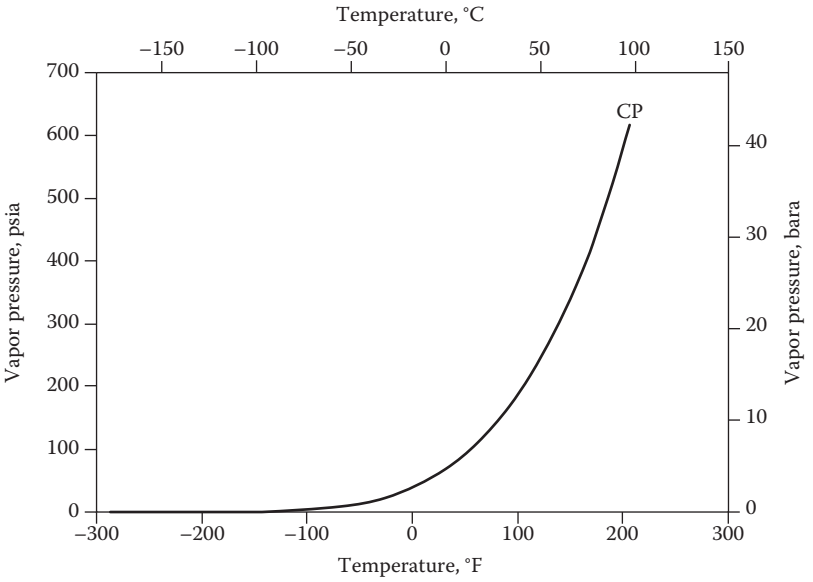


FIGURE 4.2 Vapor pressure curve for propane (Lemmon et al., 2017).

required to obtain any property. When both liquid and vapor are present, only the temperature or pressure is required (for example, see Tables B.19–B.32 or PH diagrams Figures B.24–B.35). According to the phase rule,[2] for a binary mixture there is one more variable—composition. Only two of the three variables can be plotted. Which two are selected depends on what is needed. Distillation columns run at nearly constant pressure so a plot of temperature versus composition at a fixed pressure is a common choice. Figure 4.4 is an example of a typical plot showing boiling point temperatures for the two pure fluids at a fixed pressure below the pure fluid critical points.

As discussed in Chapter 1, composition can be given in many ways including:

- Weight fraction or percent
- Volume fraction or percent
- Mole fraction or percent

Mole fraction is commonly used on plots of vapor–liquid equilibria. As shown in Figure 4.4 for components in the liquid phase, the mole fraction is denoted by x while vapor-phase concentrations are denoted by y. These plots are called "T–x–y diagrams."

Figure 4.3 shows how the temperature varies with composition for both the liquid and vapor phases. While the shape of the liquid and vapor line depends on the components, the liquid line will always be below the vapor line on temperature–composition plots.

Again, consider the evacuated vessel in Figure 4.1 with a connected liquid line. This time the liquid contains two components with a concentration, x_F, of the lighter component. As in the pure fluid case, adding a small amount of the mixture fills the vessel with only vapor until the pressure reaches a point where a liquid droplet forms. The pressure at which the liquid first forms is called the "dew point." This is the dew point temperature for the mixture at the given pressure. Figure 4.4 shows

[2] The phase rule from Equation 1.7 is $F = N - \varphi + 2$. For present case both the number of components, N, and number of phases, φ, are two, making the degrees of freedom, F, equal to two. Therefore, two of the three variables, temperature, pressure and composition must be stated to specify the third variable.

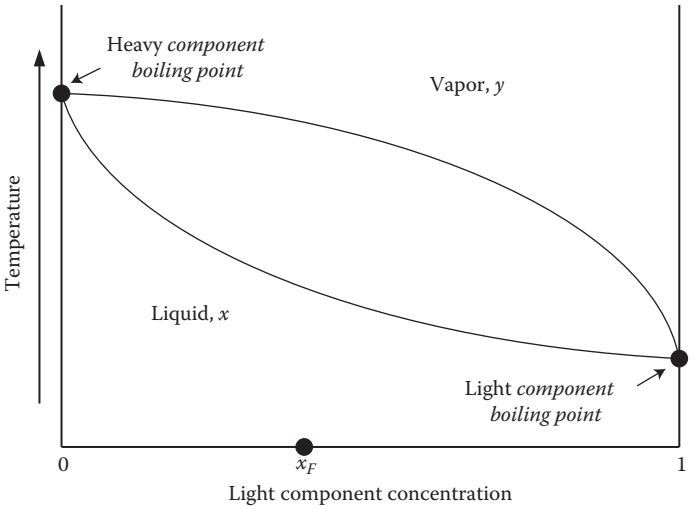


FIGURE 4.3 Temperature-composition (*T-x-y*) diagram at constant pressure for binary mixture with liquid and vapor composition lines shown.

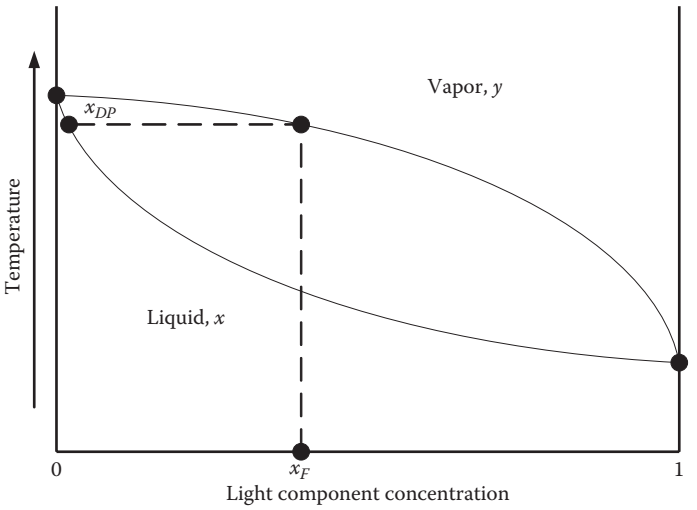


FIGURE 4.4 Binary mixture at the dew point.

that at the dew point the vapor-phase composition is x_F ($y_{DP} = x_F$). However, the liquid phase is more concentrated in the heavy component and has a composition of x_{DP}.

Unlike the pure fluid, to keep the pressure constant when adding more feed requires lowering the temperature. Figure 4.5 shows that on adding more mixture the liquid and vapor compositions both differ from the feed composition. The liquid composition, x_1, will be leaner in the light component and the vapor-phase composition, y_1, will be richer in the light component.

Adding more feed increases the liquid volume and makes the liquid composition richer in the heavy component. To keep the pressure constant the temperature must be adjusted after each addition. Once enough liquid is added to almost completely fill the vessel, the liquid composition equals the feed composition. Figure 4.6 shows this point, which is called the "bubble point." The bubble point pressure is also the true vapor pressure (TVP) of the mixture. Another way to think of the

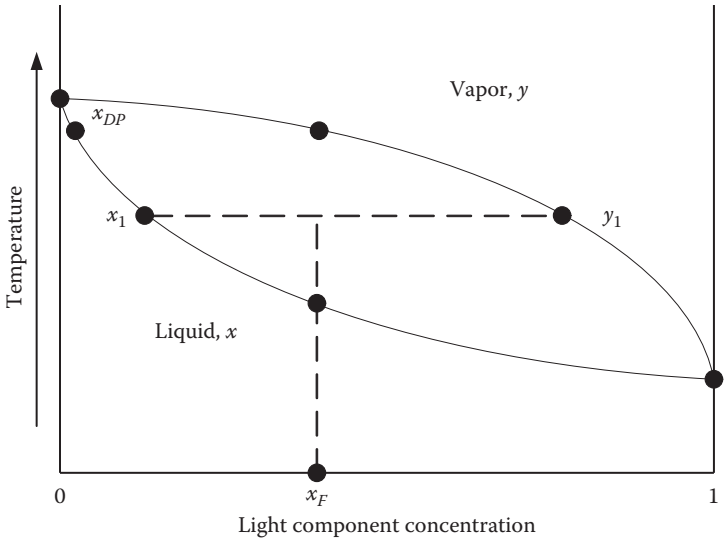


FIGURE 4.5 Binary mixture at some intermediate liquid volume at constant pressure.

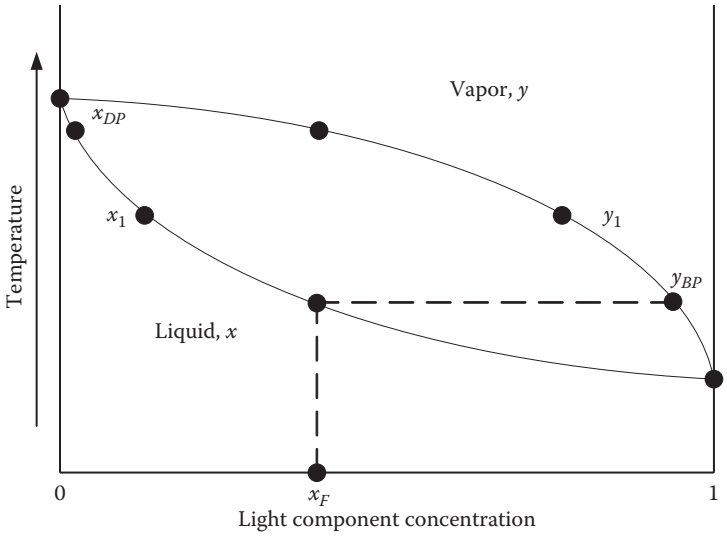


FIGURE 4.6 Binary mixture at bubble point at constant pressure.

bubble point is to have the vessel full of liquid, and slowly raise the temperature at constant pressure until the first "bubble" is formed. This is the bubble point temperature for the liquid with composition x_F at the given pressure.

Although calculating the liquid and vapor lines between the two endpoints will not be described, it is important to understand the factors that affect the distribution of a component between liquid and vapor. The vapor concentration of component i, y_i, depends on:

- The concentration of component i, x_i in the liquid phase; the higher the x_i, the higher the y_i.
- The vapor pressure of component i, P_i^{Sat}; the higher the P_i^{Sat}, the higher the y_i.
- The total pressure of the system, P; the higher the total pressure, the lower the y_i.

For similar fluids, these factors are related by the following equation:

$$y_i = \frac{x_i P_i^{\text{Sat}}}{P}, \tag{4.1}$$

which is called Raoult's law. (Raoult's law may be derived on a molecular level, see, e.g., Hildebrand (1963)). It provides a good estimation for simple hydrocarbon mixtures, like propane–isobutane mixtures. This is because it assumes that all components differ only in vapor pressure, a good assumption for very similar compounds, like propane and isobutane. The definition of the partial pressure (Equation 1.9) is $y_i P$; so, for an ideal mixture the partial pressure is $x_i P_i^{\text{Sat}}$.

However, mixture components also differ in their chemical nature. To account for this, the above equation requires another term:

$$y_i = \frac{\gamma_i x_i P_i^{\text{Sat}}}{P}, \tag{4.2}$$

where γ_i is called the activity coefficient. The activity coefficient for each component depends on the other components present, the composition, and the temperature. Similarly, there is usually nonideality in the vapor phase, which is accounted for by using a fugacity coefficient (for details see Prausnitz et al. (1999) or Smith et al. (2018)). For pure fluids the activity coefficient is unity; for mixtures where the components are similar, it ranges from slightly less than 1 to about 10. For very dissimilar compounds, e.g., water and pentane, the activity coefficient can be large. For immiscible mixtures, the activity coefficient can be estimated using

$$\gamma_i = \frac{1}{x_i}, \tag{4.3}$$

where x_i is the mole fraction of component *i*.

Example 4.1

For a binary mixture of water and propane estimate the activity coefficient for water in propane at 50°F (10°C) and compare the apparent vapor pressure of water in propane with that of pure propane.

Solution

The water solubility in propane at 50°F (10°C) is about 0.012 wt% (*Engineering Data Book, 2016*). The weight percent must be converted to mole percent to use Equation 4.3. The molar masses of water and propane are 18 and 44, respectively, so

$$x_{\text{water}} = \left(\frac{0.00012/18}{0.00012/18 + 0.99988/44} \right) = 2.9 \times 10^{-4}$$

Then, using Equation 4.3

$$\gamma_{\text{water}} = \frac{1}{x_{\text{water}}} = \frac{1}{2.9 \times 10^{-4}} = 3{,}400.$$

The vapor pressure of pure propane at 50°F (10°C) is 92.4 psia (6.37 bara). The vapor pressure of water at 50°F (10°C) is 0.178 psia (0.0123 bara). The apparent vapor pressure of water in propane will be roughly 3,400 times that of pure water or 600 psia (42 bara). Therefore, in distilling propane containing trace amounts of water, the water will be the more volatile component and go overhead. This shows that distillation could be used to dry propane (see Chapter 11).

The other extreme is where two components have a strong attraction for one another. In this case, the activity coefficient will be much smaller than unity. One example is the glycol–water system, where water and glycol have a strong affinity for one another. This is why glycols are used to remove water from hydrocarbon gases and liquids.

4.2.1.3 Flashes

The term "flash" originates from the simple concept of vapor "flashing" from a liquid on lowering the pressure on the liquid. However, in general usage a flash is a situation where two or more phases are in equilibrium. "Flash calculations" determine temperature, pressure, and phase compositions by assuming the phases are in true equilibrium.

The flash is an important component of gas processing. A common flash is through a restriction, which occurs at constant enthalpy, called a Joule–Thomson (J–T) expansion. (See Chapter 1 for discussion of J–T expansion.) Figure 4.7 shows a simple case where a two-component vapor–liquid mixture continuously flows into a vessel and splits into a liquid with composition x_1 and vapor with composition y_1.

The phases are assumed to come to equilibrium in temperature, pressure, and composition. While the temperature and pressure are the same for both phases, the phase compositions differ. The more volatile component preferentially leaves with the vapor phase while the less volatile component preferentially goes with the liquid phase. The phases are in equilibrium and are "saturated" because the vapor phase leaves at its dew point and the liquid phase at its bubble point.

Often, the exiting concentrations from the flash are the desired products, but consider the case where the concentration of the heavy product in the bottoms stream needs to be increased.

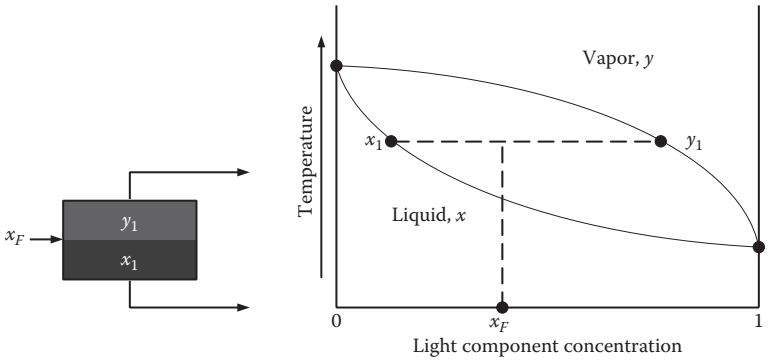


FIGURE 4.7 Simple continuous binary flash and corresponding *T-x-y* diagram.

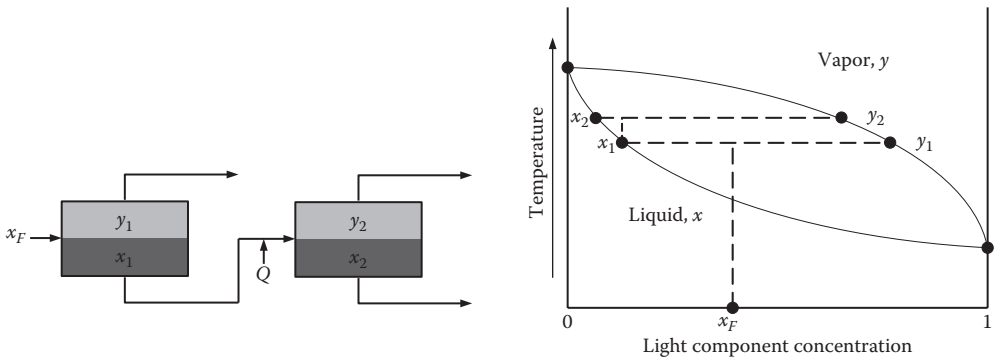


FIGURE 4.8 Two-stage flash and corresponding *T-x-y* diagram. Both vessels are at the same pressure.

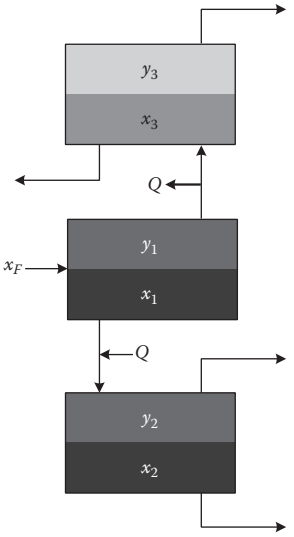


FIGURE 4.9 Three stage flash at constant pressure.

Figure 4.8 shows that this can be done by taking the liquid with concentration x_1 and flashing it into a second vessel. For this discussion, the vessels are assumed to be at the same pressure, so heat must be added to vaporize some of the liquid.

Likewise, the light component concentration in the vapor phase can be enriched by partially condensing it and flashing it into a third vessel. Figure 4.9 shows the three-stage flash along with indications of where heat (Q) is added or removed. There are several problems with this scheme. One is that unwanted intermediate streams are generated. A second problem is that heat transfer is required to add or remove heat from the various streams.

The most serious problem with the three-stage flash is that the product streams still may not be at the desired concentration. Then, more flash stages are required, with more unwanted side streams.

The solution to the problems is to combine the flash stages as shown in Figure 4.10. Heat removed from the vapor from the lower flash warms the liquid entering the lower flash. Similarly, heat is

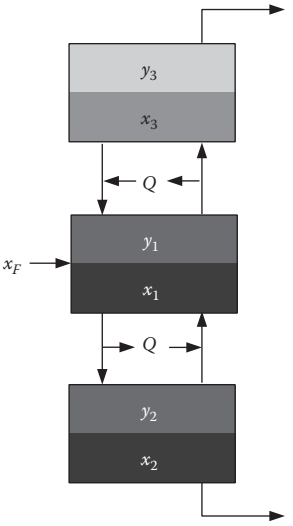


FIGURE 4.10 Combined three stage flash.

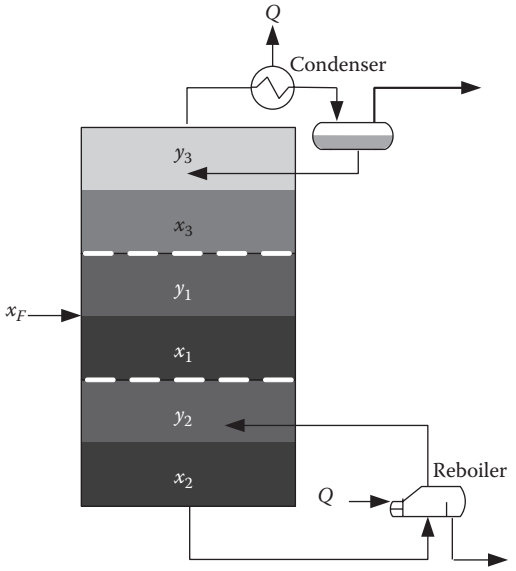


FIGURE 4.11 Elements of a distillation column with three equilibrium flash stages.

exchanged between the two streams on the upper flash. This eliminates the unwanted product streams but requires heat exchange between the stages. The process is simplified further by having the liquid and vapor exchange heat by direct contact and having the stages separated by a barrier with all stages in a single vessel. Figure 4.11 shows the combined flash stages, which is a simple distillation column. Section 4.4 discusses the various methods for separating the stages.

To obtain proper separation of components in a distillation column requires the correct balance of vapor and liquid flows. This usually requires heat addition in a reboiler to generate vapor at the bottom of the column and heat removal in a condenser to provide liquid reflux at the top.

Figure 4.11 shows a "partial" condenser. A vapor overhead product is taken off from the reflux drum and the liquid is returned as reflux. This partial condenser provides another stage of separation. In a "total" condenser, the vapor leaving the column is completely condensed. The condensed liquid leaving the overhead reflux drum splits with part returning to the top of the column as reflux. The rest is overhead product. Likewise, the figure shows one possible configuration where the reboiler (see Chapter 3) acts as another stage.

4.2.2 Types of Columns

There are several general types of columns. Figure 4.12 shows a conventional distillation column. The number of stages in the column depends on the mixture being distilled and the product purity required. The number of stages may be 100 or more when separating isobutane/*n*-butane. Columns may also have multiple feeds, multiple draw offs, and multiple reboilers, called side reboilers.

Figure 4.13 shows a type of column commonly found in gas processing called strippers or stabilizers. This column is simply the lower section of a conventional column. A condenser is not used because no reflux is needed. As the name implies, strippers remove light components from the liquid flowing down the column. Reboiler heat generates vapor flow to remove any remaining light ends. Sometimes a gas stream (stripping gas) is fed in near the column bottom to provide additional vapor flow to remove the more volatile components. One application for stripping gas is removal of H_2S from sour condensate and NGL streams. A major drawback of stripping gas is that it increases compressor duty if the overhead gas is recycled.

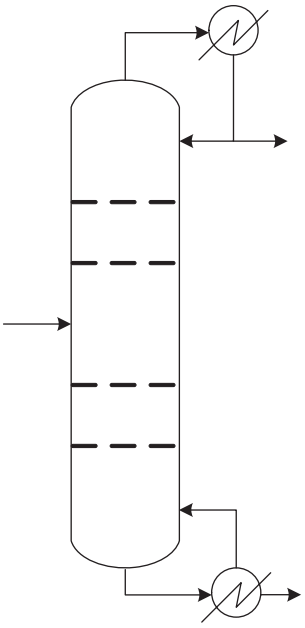


FIGURE 4.12 Conventional distillation column.

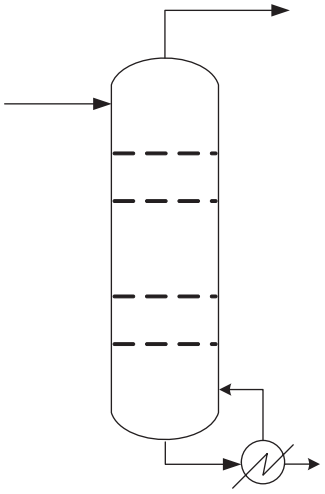


FIGURE 4.13 Stripper (stabilizer) columns have a reboiler but no condenser.

Stripper columns are common for removing light ends from NGL. In cryogenic plants, the demethanizer is a stripper column with some liquid fed to the top of the column to obtain better recovery. Demethanizers are striking in appearance because the top of the column has a larger diameter than the lower section (see Figure 12.7). This is needed to provide good gas–liquid separation in a stream that is mostly gas.

Distillation requires the density difference between vapor and liquid to be large enough so that the liquid and vapor disengage easily. This limits column operating pressure when the mixture is relatively near the critical conditions of the mixture (at the critical point the liquid and vapor phases have the same density). Demethanizer columns must be run at relatively low pressures for this reason.

4.3 ABSORPTION

4.3.1 Basic Concepts

Absorption involves contacting a gas or liquid stream with a liquid solvent to remove specific components. The process is "physical absorption" if there is no chemical reaction between the solvent and components of the stream. Absorption processes utilizing chemical reactions to enhance the separation are called "chemical absorption." For liquid–liquid systems the solvent density must be different than the process stream. The discussion below considers the case of gas absorption.

4.3.2 Physical Absorption

The basic principles of physical absorption are identical to those for distillation. While distillation uses heat and volatility differences to make the separation, absorption uses a solvent and volatility differences. The solvent usually enhances the volatility difference between various components.

All liquids absorb gases to some extent. First, consider a pure gas in contact with a pure nonvolatile liquid. Factors affecting how much gas is absorbed are:

1. The gas pressure—increasing pressure increases solubility
2. The solvent temperature—increasing temperature decreases solubility[3]
3. The chemical and physical properties of the gas and solvent

To obtain an effective separation of a gas mixture using physical absorption, there must be partial pressure (y_iP) and physical differences between the gaseous components. If the components are nonpolar hydrocarbons, the primary key for separation is vapor pressure. Lean oil absorbers use vapor pressure differences for C_2^+ (ethane and heavier hydrocarbons) recovery (see Chapter 12).

Physical absorption is most effective when differences in the chemical nature of the mixture components exist, such as water, a polar compound, in a nonpolar natural gas. A polar solvent, e.g., glycol, strongly attracts water and is a common dehydration process (see Chapter 11). Although the attraction between water and glycol is extremely strong, no chemical reaction takes place.

4.3.3 Chemical Absorption

Chemical absorption involves a two-step process for the component that is being removed:

1. Physical absorption of a gas into the solvent
2. Reaction of the dissolved gas with the solvent

Having the solvent react with a specific component provides a powerful separation technique that can reduce a component concentration to parts per million.

If the chemical reaction is irreversible, the solvent is consumed and must be discarded. Scavengers[4] offer an inexpensive way for removing trace amounts of components like hydrogen sulfide (see Chapters 10 and 15).

The most common chemical absorption processes in gas processing use reversible chemical reactions to reduce acid gas (carbon dioxide and hydrogen sulfide) levels to low concentrations

[3] For nearly ideal systems, e.g., nitrogen gas or propane vapor in hexane solvent, the gas or vapor solubility increases with increasing temperature if the gas or vapor partial pressure remains constant. This is because the solvent density decreases with increasing temperature. When the system is highly nonideal, e.g., water in glycol, the activity coefficient for water decreases rapidly with increasing temperature, making the water solubility decrease with increasing temperature. For more details, see Prausnitz et al. (1999) or Smith et al. (2018).

[4] A scavenger is a nonregenerative solid or liquid used to remove trace amounts of a compound from a process stream. It is attractive when the total amount of impurity is too low to justify a continuous regenerative process.

(see Chapters 10 and 15). For the physical absorption step, moderate temperatures and high pressures are used; pressure has a minor effect on the liquid phase chemical reactions in the second step. Too low an operating temperature can result in high viscosity, low reaction rates, or both. Because the reactions involved in this chemical absorption process generate heat (exothermic reactions), the solvent regeneration step requires the addition of significant quantities of heat to reverse the chemical reactions.

4.3.4 Solvent Selection

This section discusses some general guidelines for solvent selection. Specific applications are discussed in later chapters. Attributes of a good solvent include:

- Good selectivity between components being separated
- High capacity for component being absorbed
- Low volatility if gas/liquid, low solubility if liquid/liquid
- Low cost
- Low rates of corrosion
- Good chemical stability
- Low heat of reaction if chemical absorption
- Large density difference if liquid/liquid
- Low viscosity
- Low tendency to form foams or emulsions

If the solvent is being regenerated, the following additional attributes are important:

- Low energy consumption in regeneration
- Good thermal stability

Solvent selection is inevitably a compromise of the above attributes. The preferred solvent may even be a mixture of solvents. Mixtures containing both physical and chemical solvents are "hybrids." Hybrids typically are blends that reduce regeneration energy demands while keeping selectivity high.

In general, physical solvents are used when the feed concentration of components to be separated is relatively high and a high degree of separation is not required. They are most attractive when the partial pressure of the component(s) to be separated is high. Typically, chemical absorption is most attractive when lower levels of contaminants in the feed must be reduced to parts per million levels; then the much higher energy consumption in solvent regeneration is justified.

4.3.5 Regenerative Absorption Processes

Gas processing uses regenerative absorption processes for treating and dehydrating. Figure 4.14 shows an absorber, often called a contactor, for a gas being contacted with a solvent. An inlet scrubber (see Chapter 5) is used to remove entrained liquids to prevent possible foaming problems and solvent contamination. Lean solvent, which is cooled to increase capacity, enters the absorber near the top and flows downward, countercurrent to the gas stream. The term "lean" refers to a solvent that has been stripped of the component being removed from the process stream. The column space above the solvent entry provides a disengagement zone for liquid–vapor separation to reduce solvent carryover losses. Additional separators are used to minimize solvent losses (see Chapter 5).

The contactor internals provide good contact between the solvent and the gas. Absorption requires no heating so a reboiler and condenser are unnecessary. However, the top of the absorber is cooled by the lean solvent and the bottom is cooled by the entering feed gas. In the middle of the column, the temperature may be higher because the absorption process generates heat.

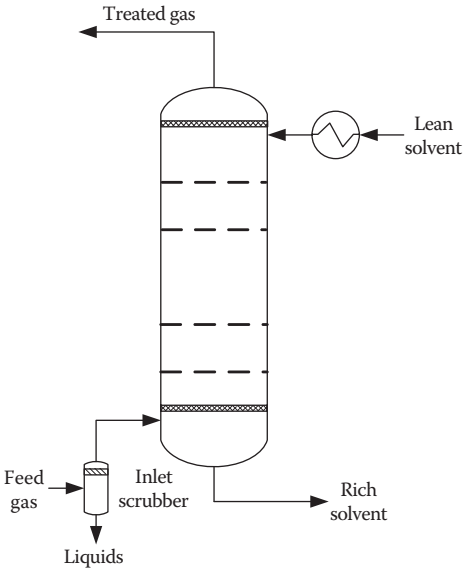


FIGURE 4.14 Absorber/contactor in absorption process.

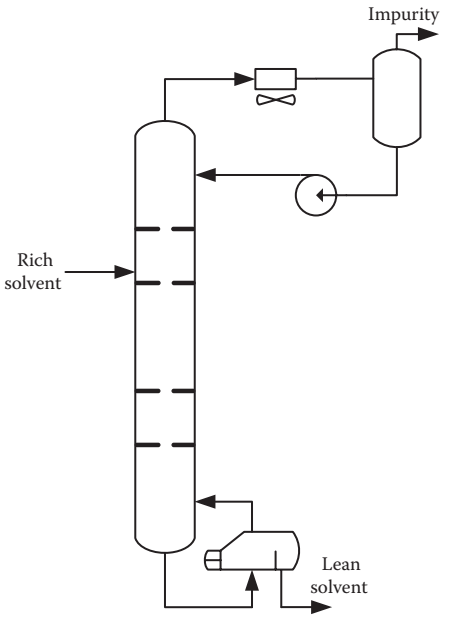


FIGURE 4.15 Solvent regenerator/stripper.

The temperature increase in physical absorption is lower than chemical adsorption. Contactors involving chemical absorption generally have a significant temperature increase and often exhibit a "temperature bulge" because the reaction is highly exothermic. To prevent the chemical reaction from reversing, intercoolers are sometimes added to the absorber to remove the heat of reaction and/or increase selectivity.

Figure 4.15 shows a solvent regenerator or stripper. Rich solvent enters near the top of the low-pressure column. The term "rich" refers to a solvent that has absorbed a quantity of the

component to be removed from the gas in the contactor. Most processes reduce the rich solvent pressure in a flash tank before it enters the regenerator. This allows the absorbed hydrocarbon in the solvent to be recovered and be used as fuel gas or be compressed and put back into the process upstream of the contactor. It also minimizes the quantity of hydrocarbon going with the overhead impurity stream from the regenerator.

In the regenerator, the overhead condenser removes reboiler heat and condenses vaporized solvent. Condensed solvent returns to the column as reflux. The reboiler provides the heat to reverse the chemical reaction if chemical absorption is used. It also heats the lean solvent to remove traces of absorbed species.

The contactor and solvent regenerator are not a distillation columns, but both use the same column internals as distillation columns.

4.4 COLUMN INTERNALS

Distillation columns, contactors, and regenerators use internals to provide the good contact between phases needed in separation. Column internals generally fall into one of the following types:

- Bubble cap trays
- Valve trays
- Sieve trays
- Random packing
- Structured packing

This section briefly discusses each type, and then describes where they are used in gas processing. Pilling and Holden (2009) provide a good overview of column internals useful for selecting trays and packing.

Early commercial distillation columns used bubble cap trays, as shown schematically in Figure 4.16. Liquid travels down from the downcomer of the previous tray and across the tray, which contains perforated caps that bubble upcoming vapor through the liquid. This crossflow/upflow configuration provides excellent contact between the liquid and vapor phases so that they will approach equilibrium. Vapor flow rates must be low enough so that the liquid is not entrained and carried up to the next tray. Similarly, liquid flow must be in the range to keep the proper level

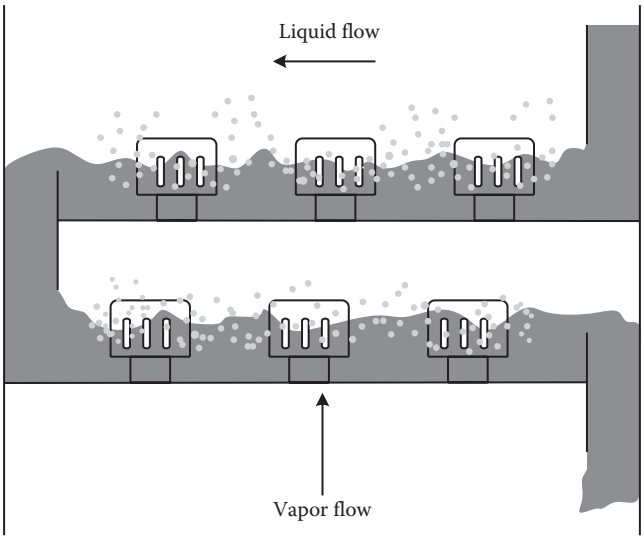


FIGURE 4.16 Schematic of bubble cap tray with liquid crossflow and vapor upflow.

(a) (b) (c)

FIGURE 4.17 (a) Bubble cap tray, (b) fixed valve tray, (c) moving valve tray. (Courtesy of Sulzer Chemtech.)

on the tray and keep vapor from rising through the downcomer. Weirs are included to maintain a minimum liquid level.

Figure 4.17 shows a bubble cap tray along with two kinds of valve trays. Valve trays replace the bubble cap with a simple, partially covered opening. The "valve" may be fixed (Figure 4.18b) or move up and down with vapor flow. Figure 4.17c shows a simple moving valve tray configuration. Compared to bubble caps, valve trays are much cheaper to construct and provide better mixing of the liquid and vapor. They also offer lower pressure drop than bubble cap trays. Sieve trays are even simpler as they contain only holes in the trays. The liquid is kept from falling through the holes by the upward flow of vapor. Bubble cap and moving valve tray designs have the largest turndown[5] ratio of the three tray types while sieve trays have the most limited turndown ratio.

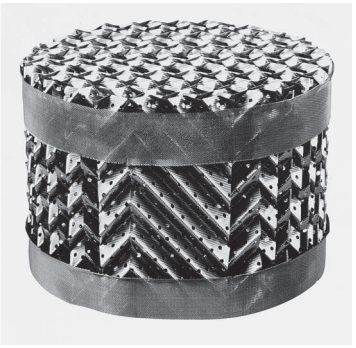
The crossflow of liquid on columns with trays provides good contact between liquid and vapor but requires large cross-sectional area for adequate liquid contact time. A large diameter increases cost of materials substantially for high pressure columns because of increased column wall thickness. For comparable liquid flow rates, packed columns can reduce the column diameter by over 50% because the liquid flow is downward instead of crossflow. For comparable throughputs, the pressure drop will be lower for packed columns and column heights will lower (Pilling and Holden, 2009). However, as a general rule packed columns work best when the liquid to vapor ratio (L/V) is low because it is easier to get good contact between the two phases when there is relatively more vapor present. Conversely, trayed columns work better at higher L/V ratios.

Figure 4.18 shows examples of random and structured packing. The random packing comes in a variety of shapes and sizes. Vendors offer packing in various materials, including specific metals and ceramics to handle corrosive systems. The packing is dumped into the empty column. Structured packing is a bundle of corrugated sheets, and comes in various heights. To enhance mixing, the bundles are stacked and rotated at 90° angles to force the fluids to move back and forth; structured packing is essentially a large static mixer. Both kinds of packing are susceptible to fouling in "dirty" systems, i.e., systems prone to solid deposits. Fouling causes channeling in random packing, which greatly reduces contact efficiency. Fouling in structured packing typically occurs at the interface between adjacent bundles, where the flow channels are reduced in size. This plugging can cause significant pressure drop. Newer packing designs have a less dramatic change in flow direction at the bundle interface which results in a lower pressure drop.

Table 4.1 compares the relative merits of trays and random packing. Overall, random packed towers are preferred over trayed columns because they usually have a smaller column diameter, shorter column height, and lower pressure drop. Where packing does not provide savings in column size, trays can be less expensive than packing. Column internals are a small fraction of the overall column cost so factors such as turndown ratios, flow regimes, and weight, especially offshore, are usually more important than cost of internals.

[5] Turndown denotes the minimum flow rate, relative to design conditions, at which the equipment still operates properly. A turndown ratio of 3 to 1, or 66% turndown both mean the equipment operates properly at one-third of design capacity.

(a)



(b)

FIGURE 4.18 Examples of random packing and structured packing. (Courtesy of Sulzer Chemtech, Ltd.)

TABLE 4.1
Comparison of Trays and Random Packing

	Trays	Random Packing
Pressure drop	Higher	Lower
Vapor/liquid ratio	Best at high values	Best at low values
Capital cost[a]	Higher	Lower
Corrosive systems	Expensive	Inexpensive
Turndown	Up to 85%	Up to 50%
Liquid distribution	Excellent	Good unless channeling present
Dirty systems	Better	Worse
Serviceability	Easier	More difficult

[a] Column internals constitute about 10% of total column cost. The overall column cost must be considered when selecting internals.

TABLE 4.2
Usage of Column Internals for Common Gas Processing Steps Revised

	Bubble Cap Trays	Valve Trays	Sieve Trays	Random Packing	Structured Packing
NGL fractionation	R	F	S	S	R
NGL stabilizers	R	F	S	R	R
TEG contactors	S	S	R	R	F
TEG regenerator	R	S	R	F	R
Amine contactor	R	F	F	F	R
Amine regenerator	R	F	F	S	R

Note: F, S, and R denote frequently used, sometimes used, and rarely used, respectively.

Table 4.2 shows the preferred column internals for the common gas processing operations. Note that bubble cap trays are now rarely used except for dehydrating gas with triethylene glycol (TEG). They are used here because liquid flows are low and bubble cap design keeps liquid from leaking onto lower trays (called weeping). However, structured packing has become the preferred internal for this application because the column diameter will be much smaller. Structured packing

is preferred offshore because of smaller column diameter (less weight and space) and because the structured packing tolerates some column motion.

4.5 ADSORPTION

4.5.1 Basic Concepts

Absorption is a vapor–liquid or liquid–liquid separation process. Adsorption is a gas–solid or liquid–solid separation process. In adsorption processes, differences in volatility, chemical nature, and molecular size drive the separation. Like absorption there is physical adsorption and chemical adsorption, chemisorption. In physical adsorption, the bonding between the adsorbed species and the solid phase is due to polar forces and van der Waals forces, the attractive and repulsive forces that hold liquids and solids together and give them their structure. In chemisorption, a much stronger chemical bonding occurs between the surface and the adsorbed molecules. This discussion considers only physical adsorption using adsorption from the gas phase. However, the concepts also apply to liquid–solid adsorption, with the major difference that concentrations are typically expressed as partial pressures for gases while mass or molar concentrations are used for liquid adsorption.

Adsorption is most often used to remove trace amounts of a component from the process stream. The one exception, pressure swing adsorption (PSA), is discussed later in this section.

Physical adsorption is an equilibrium process similar to vapor–liquid equilibria. For a given vapor-phase concentration (partial pressure) and temperature of the component being adsorbed (adsorbate), an equilibrium concentration of the adsorbed component exists on the adsorbent surface. Figure 4.19 shows the typical equilibrium behavior for a gas adsorbing on an adsorbent. The amount adsorbed decreases with both increasing temperature and decreasing partial pressure.

Generally, only a few layers of molecules adsorb on the solid surface. Consequently, industrial processes use adsorbents with extremely high internal surface-to-volume ratios (200–800 cm^2/cm^3) with almost the entire surface for adsorption inside of the adsorbent (Gabelman, 2017). Adsorbents resemble a sponge, and referring to an adsorbent as a molecular sponge is a good analogy. Adsorbents such as activated carbon, silica gel, and alumina are formed in large particles. One commercially important class of adsorbents, molecular sieves, consists of extremely small zeolite crystals[6] held together by a clay binder. Adsorbing species diffuse through the macropores of the binder into

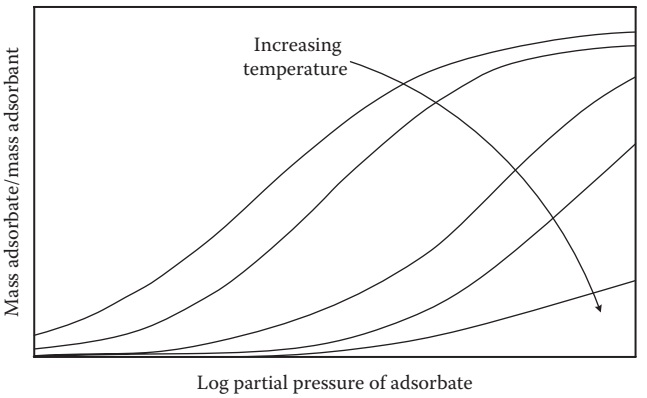


FIGURE 4.19 Typical gas adsorption isotherms which show the equilibrium conditions for adsorption at constant temperature as a function of partial pressure of adsorbing species. Adsorption increases with increasing partial pressure and decreasing temperature.

[6] Zeolites are aluminosilicate solids that contain uniform size micropores in the crystalline structure. Both natural and synthetic zeolites are used in applications ranging from adsorbents and catalysts to detergent additives.

the micropores of the zeolite. Pore openings leading to the *inside* of commercial adsorbents are of molecular size; they normally range from ~4 Å (1 Å = 10^{-10}m) to 100 Å. Molecular sieves have an extremely narrow pore size distribution, whereas other adsorbents have wide distributions. However, a molecular sieve binder, commonly about 20% of the weight of the total adsorbent, has large pores that adsorb heavier components. de Bruijn et al. (2002) show a clay binder that has pore distributions of ~200 and 5,000 Å. Chapter 11 provides properties of commonly used absorbents in dehydrating gases.

Adsorption of a component from a gas mixture is a two-step process. The first step involves moving the component through the gas to the outer surface of the adsorbent (gas-phase mass transfer). The second step involves the component diffusing through the adsorbent pores into the interior of the particle. Because the second step is relatively slow, solid adsorbents take longer to come to equilibrium with the gas phase than do absorption processes.

In addition to concentration (i.e., partial pressure for gases), two properties of the adsorbate dictates its concentration on the adsorbent surface: polarity and size. For polar adsorbents, such as those used to dehydrate a gas, polar molecules, like water, will be more strongly adsorbed than weakly polar or nonpolar compounds. Thus, methane is displaced by the weakly polar acid gases, which are displaced by the strongly polar water molecule. Nonpolar adsorbents such as activated carbon reject polar compounds and less volatile compounds displace more volatile compounds.

How size affects adsorption depends on the pore size of the adsorbent. A component too large to fit into the pores adsorbs only on the outer surface of the adsorbent, which is a trivial amount of surface area compared with the area inside the pores. If the pores are sufficiently large to pass more than one adsorbate, the less volatile, which usually correlates with size, adsorbates will displace the more volatile ones. Therefore, ethane will be displaced by propane.

Depending on the quantities of material being removed from a stream, adsorption can be either batch or semicontinuous. When the impurity amount being removed is very small, adsorbents can be replaced on a periodic basis. However, for large quantities of adsorbate removal, adsorption is a batch process using fixed beds that require regeneration. Regeneration is accomplished by flowing a gas containing little or no adsorbate through the loaded adsorbent bed. Regeneration occurs at either a higher bed temperature (temperature swing adsorption (TSA)) or at lower bed pressure (PSA) or both. Both PSA and TSA are discussed below.

In commercial practice, regenerative adsorption is carried out in a vertical, fixed adsorbent bed. The feed can enter either the top or bottom. For gases using TSA the gas usually flows down through the bed. For gas adsorption using PSA the feed usually flows up through the bed. Most liquid adsorption processes are upflow because it makes it easier to regenerate the bed (Richman, P., Private Communication, 2005).

Because the adsorption process is not instantaneous, a mass transfer zone (MTZ) forms in the bed. Figure 4.20 shows the three zones in an adsorbent bed:

1. The equilibrium zone, where the adsorbate in the gas phase is in equilibrium with the adsorbate on the bed and no additional adsorption occurs.
2. The MTZ, where mass transfer and adsorption take place.
3. The active zone, where no adsorption has yet taken place.

In the equilibrium zone, the gas-phase concentration equals the inlet concentration, y_{in} because the bed is saturated. In the MTZ, the gas-phase adsorbate concentration drops from the inlet value to the outlet value, y_{out}, in a smooth S-shaped curve. If the rate of diffusion of adsorbate into adsorbent pores was infinite, the MTZ would have zero thickness. The MTZ is usually assumed to form quickly in the adsorption bed and to have a constant length as it moves through the bed, unless the bed particle size or shape is changed. The value of y_{in} is dictated by upstream processes; the y_{out} value is determined by the regeneration gas temperature, pressure, and adsorbate content. The MTZ length depends on the adsorbent, particle size, and gas velocity. To maximize bed capacity, the MTZ

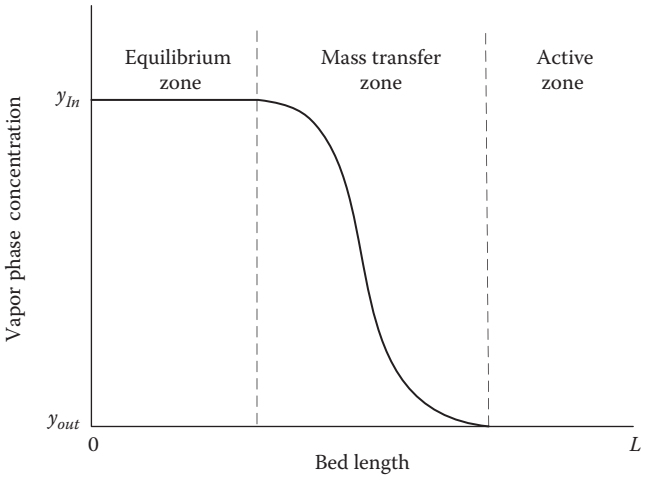


FIGURE 4.20 Vapor phase concentration profile of an adsorbate in the three zones of an adsorption bed.

needs to be as small as possible because the zone nominally holds only 50% of the adsorbate held by a comparable length of adsorbent at equilibrium. Tall, slender beds, which reduce the percentage of the bed in the MTZ, and smaller adsorbent particles make more of the bed effective. However, smaller particle size, deeper beds, and increased gas velocity increase bed pressure drop.

For a point in the bed, the bed adsorbate content increases over time from y_{out} to y_{in} in an S-shaped curve that mirrors the curve shown in Figure 4.20. In principle, beds can be run until the first sign of breakthrough. This practice maximizes cycle time, which extends bed life, because pressure and temperature cycling are major sources of bed degradation and minimizes regeneration costs. However, most plants operate on a set time cycle to ensure no adsorbate breakthrough.

When used as a purification process, adsorption has two major disadvantages:

- It is a fixed-bed process that requires two or more adsorption beds for continuous operation.
- It has limited capacity and is usually impractical for removing large amounts of impurity.

However, adsorption is very effective in the dehydration of hydrocarbon streams because water is much more strongly adsorbed than any of the alkanes, carbon dioxide, or hydrogen sulfide (see Chapters 10, 11, and 15). Generally, a higher degree of dehydration can be achieved with adsorbents than with physical absorption processes. Adsorption has the advantage of requiring no solvent removal downstream of the separation step. However, filters (see Chapter 5) are needed to remove adsorbent fines generated by attrition. By using PSA, it is feasible to purify gases containing high concentrations of adsorbate.

4.5.2 Adsorption Process

Regenerative adsorption processes require two or more adsorption beds to make the process continuous; one bed is active while the other beds are being regenerated. As noted above, both temperature swing and pressure swing regeneration processes are used. The two methods are discussed below along with their advantages and disadvantages.

4.5.2.1 Temperature Swing Adsorption

Traditionally, most adsorption processes in gas processing use high temperatures and low partial pressures of the adsorbate in the gas phase for regeneration. Dehydration is the most common

application although adsorption is used for acid gas removal as well. Chapters 10 and 11 discuss acid gas removal and dehydration in gas processing, respectively.

The basic process for adsorption in gases and liquids is the same. However, there are some important differences. Chapter 15 discusses adsorption processes for both acid gas removal and dehydration of liquids.

At the end of the adsorption cycle, the inlet gas flow is switched to a regenerated bed and the loaded bed begins the regeneration process. The bed first may be depressurized, at a low rate to minimize bed movement and mechanical stress. Next, the regeneration gas enters counter to the flow during adsorption. This ensures that the adsorbent at the bed outlet during the adsorption step is fully regenerated. The regeneration gas commonly is a slipstream from the gas exiting the active bed.

Figure 4.21 shows the inlet and outlet temperature profiles for the regeneration gas. Regeneration starts with heating the bed using hot gas from a regeneration gas heater (usually a direct fired furnace). Initially, the exit temperature is nearly constant as the regeneration gas desorbs the adsorbate and warms the bed. The adsorbate concentration in the exiting gas is also constant. As the temperature of the bed exit starts increasing, the bed adsorbate concentration drops to a very low level. Once the exit temperature reaches a desired value, the regeneration gas furnace is turned off and cool regeneration gas lowers the bed temperature so that it can be placed into service again.

TSA is ideal for removing trace amounts of impurities. It is the only feasible adsorption process if the heat of adsorption is high, e.g., water on molecular sieve, because high temperatures are required to drive off the adsorbate. Long cycle times make it possible to have a two-bed process because there is adequate time to heat and cool the bed.

Some processes employ more than two beds. If four beds are used two beds may adsorb in parallel. Beds may also be in series. In this case, gas from the first bed in series enters a second, freshly regenerated, bed. The second bed is a guard bed insuring no adsorbate breakthrough and becomes the next active bed. This "lead-guard" system is used when the MTZ is long to better utilize the lead bed adsorbent. However, the second bed doubles the pressure drop across the process.

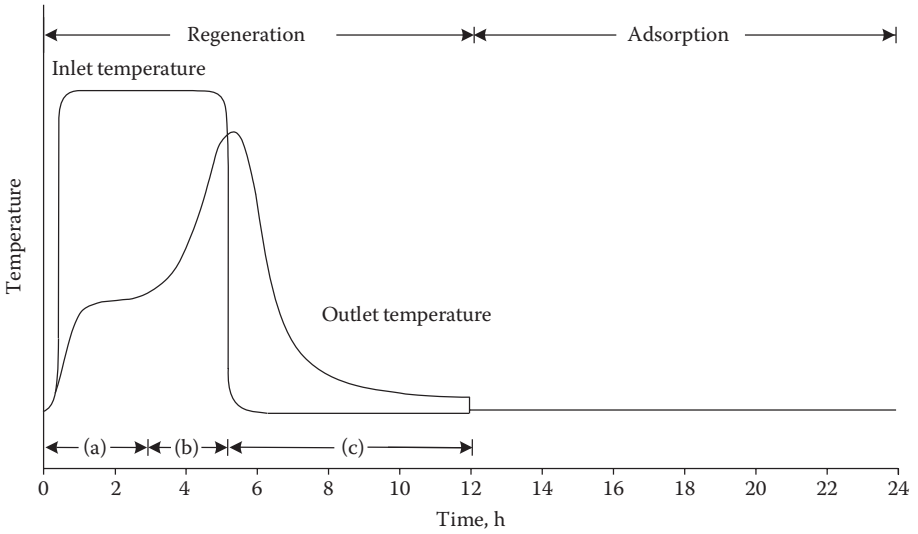


FIGURE 4.21 Gas inlet and outlet temperature time profiles for regeneration and adsorption for a bed recycled once per day. Region (a) is desorption, (b) is bed heating, and (c) is bed cooling. (Adapted from *Engineering Data Book*, 2016, with permission.)

High temperature regeneration presents a number of drawbacks, including:

- High energy cost for heating regeneration gas
- Adsorbent degradation caused by temperature cycling
- Possible undesirable reactions occurring during regeneration

Chapter 11 discusses these drawbacks when using TSA for gas dehydration.

4.5.2.2 Pressure Swing Adsorption

PSA was commercially developed in the 1960s as an alternative to cryogenic distillation for enriching gases. Hydrogen enrichment of gas generated by steam reforming natural gas in refineries was one of the first applications.

This section provides only an introduction to the process. A number of books provide details on the various processes being used (Ruthven, 1984; Yang, 1997, 2003). Figure 4.22 shows a plot of adsorbent bed capacity as a function of adsorbate composition for two pressures. The temperature is constant and pressure P_1 is greater than P_2. The basic PSA cycle involves the following steps:

1. Adsorption—freshly regenerated bed at Point 1 is at P_1 and has n_1 moles of adsorbate on the adsorbent. Feed gas with concentration y_F passes over the bed, loading the bed to n_2 moles. At Point 2, the bed is saturated at these conditions and can adsorb no more material at P_1 with gas composition y_F.
2. Blowdown—bed pressure is lowered from P_1 to P_2 at Point 3. Ideally, there is no loss of adsorbate in vented gas but in practice some adsorbate is lost.
3. Purge—the bed is regenerated by passing a gas of composition y_3 over the bed, which reduces adsorbate concentration to n_1 at Point 4.
4. Pressurization—bed is pressurized to P_1 at Point 1. Ideally, the loading will not increase but some adsorbate is added during the step.

There are $n_1 - n_2$ moles of adsorbate removed from the gas in the adsorption step. During purge, the exit composition of the regeneration gas is between y_2 and y_F.

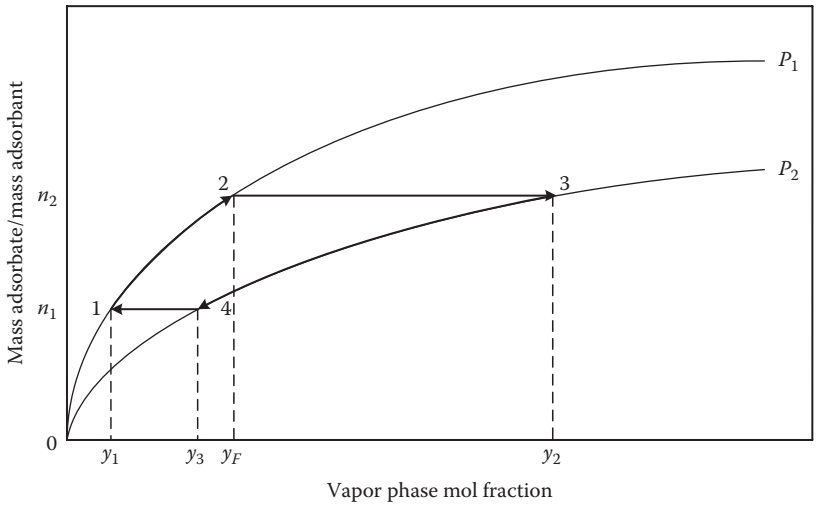


FIGURE 4.22 Absorbent capacity as a function of gas phase composition at two pressures with pressure P_1 being greater than P_2. See text for details.

In the adsorption step, the exiting stream concentration is constant at y_1 until the bed breaks through. At this point, the exit gas composition increases to y_F. Note that the lowest possible adsorbate concentration in the exit gas is y_1. Assuming complete bed regeneration, the value of y_1 depends on the purity of the purge gas, y_3, and the difference between P_1 and P_2.

While the adsorption step is the same for both TSA and PSA, there are several major differences between the processes other than temperatures, including:

- Feed gas usually enters the top of the bed in TSA units but bottom of PSA units.
- Cycle times range from less than 1 min to about 10 min for PSA units compared to 4–16 h for TSA units.
- Flow patterns are complex with up to 16 beds for PSA units whereas two or three beds are common for TSA units.

PSA is attractive compared to cryogenic separation, especially when gas flow rates are too low to justify the capital cost of distillation. It is most attractive when the major component is the most volatile component. Economics dictate how it compares with other noncryogenic processes such as membranes and absorption. However, PSA can obtain a 99.999% purity product from a low-purity feed stream. The process can be fully automated, so there is little operator attention required. Noncycling temperature reduces adsorbent attrition and eliminates unwanted high-temperature reactions. Pressure changes are sufficiently slow to avoid bed degradation.

Drawbacks of PSA include:

- Compression costs
- Only gas phase applications
- Limited flexibility in feed composition
- Difficulty in obtaining high purity if the product component is heavier than the impurity being removed
- Potential loss of product when it is the heavier component

However, PSA offers an attractive option to other separation processes including nitrogen rejection (Chapter 13) and helium purification (Chapter 14).

4.6 MEMBRANES

Membranes utilize differences in solubility and molecular size, i.e., diffusion, to make a separation. They have been used in liquid systems for many years, e.g., water purification using reverse osmosis. This discussion focuses on membrane applications for separating gas mixtures. Membranes are used in natural gas processing for dehydration, fuel-gas conditioning, nitrogen removal, and bulk CO_2 removal, but CO_2 removal is by far the most important application (Baker, 2002). This chapter presents the fundamentals of membranes for gas separations. Chapters 10, 11, and 13 discuss membrane applications.

4.6.1 Basic Concepts

Assuming ideal gas behavior, the driving force for transport through the membrane is the difference in partial pressure,[7] $y_i P$, for component i on the two sides of the membrane. If component i is the diffusing component, then

$$y_{i,\text{feed}} P_{\text{feed}} > y_{i,\text{permeate}} P_{\text{permeate}}, \tag{4.4}$$

[7] The thermodynamically correct driving force for a component moving across a membrane is the chemical potential. Partial pressure differences are equal to chemical potential differences if the gases follow the ideal gas law. For convenience ideal gas behavior is commonly assumed.

where the material moves from feed side to the permeate side. (Gas not permeating the membrane is called the residue.) This equation shows what terms affect the driving force across the membrane. The equation can be rearranged to obtain

$$\left(\frac{y_{i,\text{permeate}}}{y_{i,\text{feed}}}\right) \leq \left(\frac{P_{\text{feed}}}{P_{\text{permeate}}}\right) \tag{4.5}$$

This relation shows that the separation achieved ($y_{i,\text{ permeate}}/y_{i,\text{ feed}}$) can never exceed the pressure ratio ($P_{\text{feed}}/P_{\text{permeate}}$).

Because the discussion above was based on classical thermodynamics, it states nothing about the rate at which the diffusion processes take place. A discussion of diffusion rate requires use of Fick's law. Fick's law for solution-diffusion membranes in rectangular coordinates is (Echt et al., 2002)

$$J_i = \frac{S_i \boldsymbol{D}_i \Delta p_i}{L}, \tag{4.6}$$

where

J_i is the flux of component i, i.e., the molar flow of component i through the membrane per unit area of membrane
S_i is the solubility term
$\boldsymbol{D}_i$ is the diffusion coefficient
Δp_i is the partial pressure difference across the membrane
L is the thickness of the membrane

Customarily, S_i and $\boldsymbol{D}_i$ are combined into a single term, the permeability, $\boldsymbol{P}_i$, and thus, divides Fick's law into two parts, $\boldsymbol{P}_i/L$, which is membrane dependent, and Δp_i, which is process dependent. Note that $\boldsymbol{P}_i/L$ depends on the membrane and on operating conditions because S_i and $\boldsymbol{D}_i$ depend on temperature and pressure. Permeability also depends weakly on the composition of the gases present.

All mixture components have a finite permeability and the separation is based on differences in them. A term important in process design and evaluation is selectivity, α, which is the ratio of two permeabilities, $\boldsymbol{P}_1/\boldsymbol{P}_2$. An α of 20 for CO_2/CH_4 means that CO_2 moves through the membrane 20 times faster than does methane. The two components of the permeability provide two different trends with respect to molecular size and molar mass (Baker et al., 1998). For components of increasing molecular size the diffusivity decreases while the solubility tends to increase. Membrane materials are either glassy or rubbery polymers. Figure 4.23 shows the relative permeabilities for both types. Glassy membranes rely on diffusion to provide selectivity, so they are preferred for separating light gas mixtures such as CO_2/CH_4 mixtures (see Chapter 10). Rubbery membranes utilize solubility (volatility) for selectivity and are used to remove heavy components (see Chapter 12) and nitrogen (see Chapter 13) from natural gas. Note that water moves rapidly through both types of membranes.

Permeable compounds dissolve into the membrane, diffuse through it, and then travel through an inactive support material. The membranes are thin to maximize mass transfer rate and, thus, minimize required membrane surface area and cost. Membranes are either "asymmetric" or "composite." Asymmetric membranes use the same material in both the thin (0.1–0.5 μm) membrane layer and porous layer with no physical boundary between the two layers. Asymmetric membranes are attractive if the membrane polymer is inexpensive and has the required mechanical strength. Composites have the selective membrane material on top of one or two other layers, which provide the mechanical support. Expensive glassy polymers and all rubbery polymers use the composite construction. Composite membranes have membrane thicknesses up to 5 μm (Lokhandwala and Zammerilli, 2006).

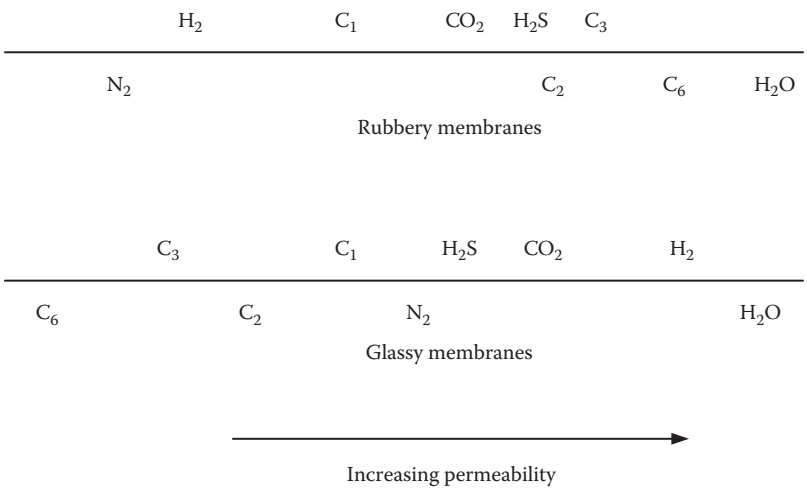


FIGURE 4.23 Relative permeabilities of gases in glassy and rubbery membranes. Positions not to scale (Baker and Lokhandwala, 2008).

The above discussion introduces the basic principles regarding membrane separation. Baker and Lokhandwala (2008) provide a good overview of membrane technology in gas processing. Readers desiring more depth should consult the engineering handbook of Kohl and Nielsen (1997) along with Baker (2004). Membrane manufacturers consider design parameters, e.g., permeabilities and selectivity, proprietary information and must provide all design information for a membrane process.

4.6.2 Membrane Process

In principle, the membrane process is simple and has no moving parts. It has three components:

1. Feed pretreatment
2. Membrane modules
3. Recompression, if required

Only the first two are discussed here. Compression is discussed in Chapter 9.

4.6.2.1 Feed Pretreatment

Because membranes are susceptible to degradation from impurities, pretreatment is usually required. The impurities possibly present in natural gas that may cause damage to the membrane (Echt et al., 2002) include:

- *Liquids*. The liquids may be entrained in the feed to the unit or formed by condensation within the unit. Liquids can cause the membrane to swell, which results in decreased flux rates and possible membrane damage. Liquids can form internally in glassy membranes by two mechanisms: (1) because of condensation of higher molar mass compounds caused by the cooling that occurs as the gas expands to a lower pressure (J–T effect) through the membrane and (2) because N_2, CO_2, and the lighter hydrocarbons diffuse more quickly than the heavier hydrocarbons, the dew point of the residue gas may increase to the point where condensation occurs. In rubbery membranes, heavier components are preferentially permeated and the dew point temperature of the residue gas decreases.

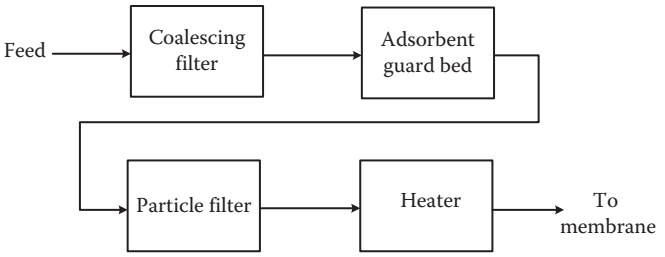


FIGURE 4.24 Schematic of membrane pretreating equipment. (Adapted from Echt et al., 2002.)

Some manufacturers (Mitariten and Mokhatab, 2019) offer membrane systems that use rubbery membrane modules as pretreatment to glassy membrane systems. The rubbery membranes dehydrate and remove heavier components that may adversely affect glassy membrane performance.

- High molar mass hydrocarbons (C_{15}^{+}) such as compressor lube oils. These compounds coat the membrane surface causing a loss of performance. The concentrations of these materials are low but the effect is cumulative.
- *Particulates*. These materials block the small flow passages in the membrane element. Erosion of the membrane could also be a problem.
- *Corrosion inhibitors and well additives*. Certain of these compounds are destructive to membrane or porous support material.

A common method for pretreating the feed gas to a glassy membrane system is shown in Figure 4.24. The coalescing filter removes any entrained liquids; the adsorbent bed takes out trace contaminants such as volatile organic compounds (VOC); the particulate filter removes any dust from the adsorbent bed; and the heater superheats the gas to prevent liquid formation in the membrane unit. The system shown has the following disadvantages (Echt et al., 2002):

- The adsorbent bed is the only unit that removes heavy hydrocarbons. Consequently, if the gas contains more heavy hydrocarbons than anticipated, or in the event of a slug of these materials, the adsorbent bed may become saturated in a relatively short time and allow heavy hydrocarbons to contact the membrane.
- Only the heater provides superheat, and consequently, if this unit fails, the entire membrane system must be shut down.

Echt et al. (2002) discuss other pretreatment methods that address the disadvantages discussed above.

Rubbery membrane systems lower the dew point temperature of the residue gas but create a low pressure stream containing heavy components with the potential for condensation if the permeate is compressed. Therefore, preheating may not be required. However, an upstream coalescing filter particulate filter may be required for removing liquid and solid particles in the feed gas.

4.6.2.2 Membrane Modules

Commercial membrane configurations are either hollow fiber elements or flat sheets wrapped into spirally wound elements; both types are used in gas processing. Figure 4.25 shows cutaway views of a hollow fiber membrane. Many of these are in hydrogen service and not in gas processing. The low-pressure, bore-feed configuration is a countercurrent flow configuration similar to a shell and tube heat exchanger with the gas entering on the tube side. It has the advantage of being more resistant to fouling because the inlet gas flows through the inside of the hollow fibers. However, the mechanical

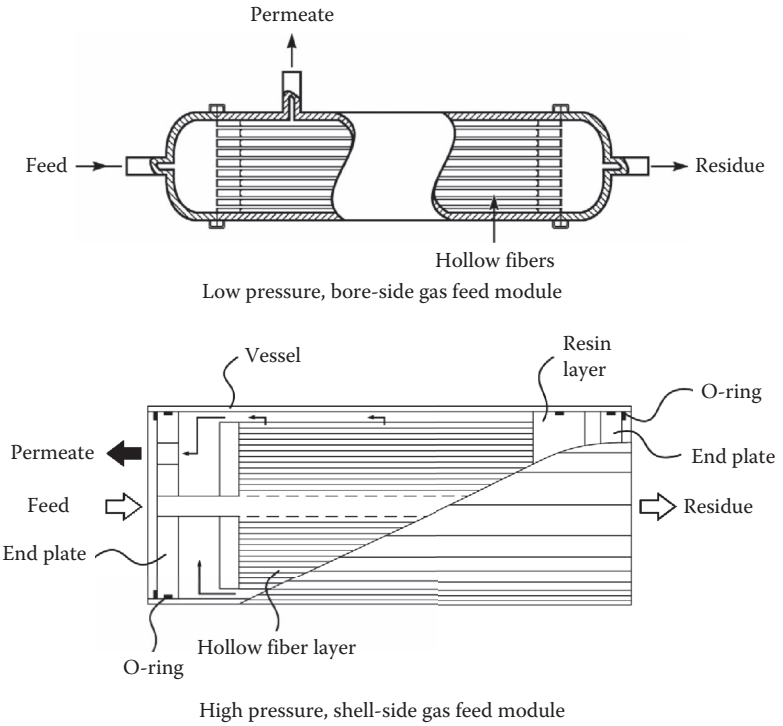


FIGURE 4.25 Cutaway view of the two module configurations used with hollow fiber membranes. (Courtesy of Membrane Technology & Research, Inc.)

strength of the membrane limits the pressure drop across the membrane. The configuration is used in low-pressure applications, such as air separation and air dehydration (Baker, 2002).

To handle high pressures, the permeate flows into the hollow fiber from the shell side. This feature makes the membrane much more susceptible to plugging, and gas pretreatment is usually required (Baker, 2002). The gas flow is crosscurrent and provides good feed distribution in the module.

In the spiral wound element shown in Figure 4.26, two membrane sheets are separated by a permeate spacer and glued shut at three ends to form an envelope or leaf. Many of these leaves, separated by feed spacers, are wrapped around the permeate tube, with the open end of the leaves facing the tube. Feed gas travels along the feed spacers, the permeating species diffuse through the membranes and down the permeate spacers into the permeate tube, and the residue gas exits at the end. The gas flow is crossflow in this configuration.

The spiral configuration is inherently more resistant than the hollow fiber membranes to trace components that would alter the polymer permeability. It also allows a wider range of membrane materials to be used.

Once the elements have been manufactured, they are grouped into modules, as shown in Figure 4.27. Echt et al. (2002) and Kohl and Nielsen (1997) provide more complete details of the construction of elements and modules.

4.6.2.3 Operating Parameters

There are a number of parameters to consider when using membranes. One of the most important is the flow configuration when multiple membrane stages are needed to produce higher purities or reduce permeate product losses. Chapter 10 gives an example showing the flow configuration for a two-stage module system. Other important parameters include:

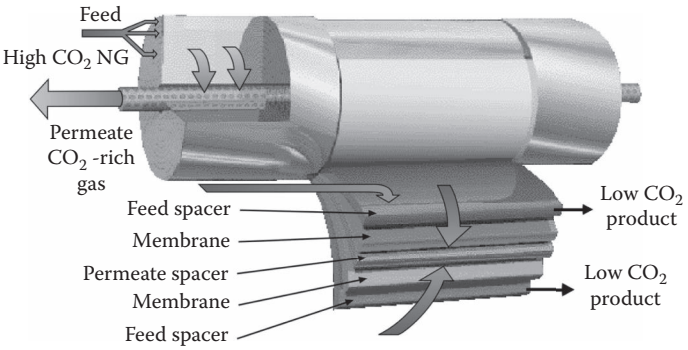


FIGURE 4.26 Cutaway view of spiral wound membrane element. (Courtesy of UOP LLC, A Honeywell Corporation.)

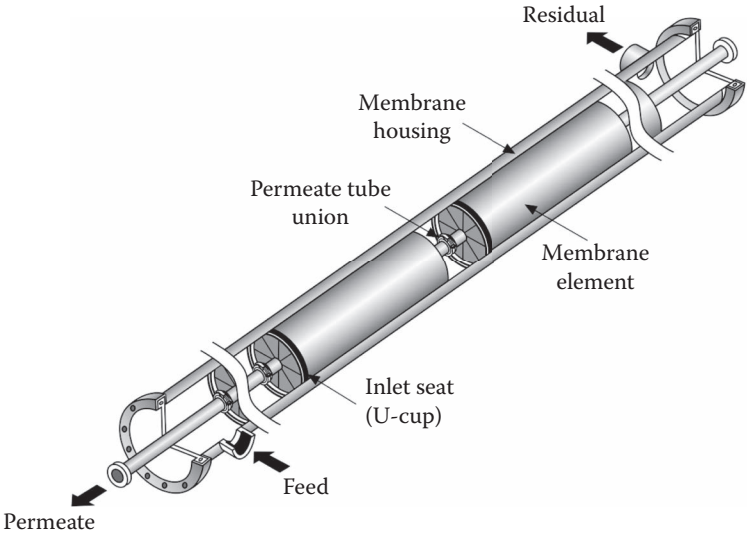


FIGURE 4.27 Cutaway view of spiral wound membrane module. (Courtesy of UOP LLC, A Honeywell Corporation.)

- *Flow rate*. Membranes work well when flow rates are reduced but lose effectiveness when flows exceed design conditions. Because of their modular design, additional membrane modules can be added in parallel if increased throughput is required.
- *Operating temperature*. Like adsorption and absorption, increasing operating temperatures reduces selectivity. However, higher temperatures increase permeability rates. The membranes used in gas processing are organic polymers and have upper temperature limits, where the material begins to degrade and shorten the useful life of the unit.
- *Feed pressure*. Increased feed pressure decreases both the permeability and selectivity. At the same time, the pressure difference across the membrane (the driving force in the membrane flux Equation 4.6) is increased, which results in a net increase in flow through the membrane. The same effect of increasing the driving force is achieved by lowering the permeate pressure. Echt et al. (2002) point out that the pressure ratio across the membrane is an important design parameter, and thus, design engineers try to maintain the lowest possible permeate pressure (see Equation 4.5).

4.7 SUMMARY

This chapter provided a brief overview of the processes commonly used in gas processing to separate gas and liquid mixtures. The following chapters discuss specific applications in various processes. This section provides a general guide to where the various separation processes are applied. Economics dictate process selection. While capital cost is a factor, often operating cost dictates the selection.

In principle, distillation can be used to separate any gas, gas–liquid, or liquid mixture. It is ideal for bulk separations, where high purity is not required. Distillation can produce high purity streams but sometimes at significant capital and energy costs. It is the last resort means of separation when requiring high purity streams or removal of trace components but often the only one available for separating mixtures containing components of similar nature.

Distillation is the only separation process requiring the processed stream to have a liquid and vapor phase. This restriction is costly in gas processing. The majority of both capital and energy costs in the typical gas plant goes into producing the refrigeration needed to liquefy the lighter hydrocarbons so that they can be separated by distillation. However, it usually remains the best option when processing large volumes and often the only option for producing some products from natural gas. The remainder of this section focuses on separation processes as alternatives to distillation.

Table 4.3 shows the types of applications where separation processes other than distillation are applied in gas processing. Bulk removal refers to separations where a portion of one or more components is removed but not to trace levels. Trace component removal involves the removal of components from a stream. Purification refers to concentrating one or more components by removing them from the mixture.

Bulk removal of components from gaseous mixtures originally had only absorption as an alternative. When effective, physical absorption is preferable to chemical absorption because the energy costs are usually lower. However, membranes can be an attractive option, especially when gas volumes are relatively small or when the low-pressure permeate gas can be used or effectively recovered at low energy cost.

Absorption is the only option to distillation for bulk separation in liquid streams. Liquid membranes are important in special applications, e.g., reverse osmosis membranes for water purification. However, liquid membranes are not used in processing natural gas.

There are a number of good alternatives to distillation for removing trace amounts of a component from either the gas or liquid. Both adsorption and absorption can be attractive options. The choice depends on the trace component being removed and the selectivity of the absorbent or adsorbent. Absorption often works well but does require a solvent. Yet, it is usually preferred

TABLE 4.3
Application of Various Separation Processes, Other than Distillation, to Common Separation Requirements in Gas Processing

	Phase of Mixture	
Separation Required	**Gas**	**Liquid**
Bulk removal	Ab(P), Ab(C), Mem	Ab(P)
Trace component removal	Ab(P), Ab(C), TSA	Ab(P), Ab(C), TSA
Purification	PSA, Mem	

Ab(P) = physical absorption, Ab(C) = chemical absorption, TSA = temperature swing adsorption, PSA = pressure swing adsorption, Mem = membrane.

to adsorption unless the required impurity level cannot be met. Adsorption has the drawback of being a batch process and being more energy intensive. If TSA is used, the whole bed, plus a regeneration gas, needs to be heated and produces a "wet" regeneration gas that usually requires recompression.

Alternatives to distillation for gas purification include both membranes and PSA. However, membranes provide relatively low selectivity and usually are used to increase purity when it is low. Although PSA can produce high purity products, it is most attractive when the light component is being purified. If the heavy component is being purified using PSA, there will be significant heavy component losses.

DISCUSSION QUESTIONS

1. What differences in physical properties are important in distillation and how does pressure and temperature affect the properties?
2. What is the major drawback to distillation when separating the various components in natural gas?
3. Considering the volatility of components in a mixture, will the components with the higher boiling point temperature tend to concentrate in the overhead or bottoms of a distillation tower? Are there exceptions and if so, why?
4. What is the major difference between a simple flash and a distillation column?
5. What are the major differences between absorption and adsorption?
6. What is the difference between physical absorption and chemical adsorption and when is one type preferred over the other?
7. What are the five different major categories of column internals and what are the relative advantages of each type?
8. What are the major differences between temperature swing adsorption and pressure swing adsorption and when is one preferred over the other?
9. Why is feed pretreatment so important in membrane processes?
10. Separation requires work (heat or pressure difference). Which of the separation processes use only heat, only pressure difference, or a combination of heat and pressure difference?
11. What are the two major physical properties that dictate the selectivity of gases in membranes?

EXERCISES

4.1 A liquid–vapor mixture of isobutane and butane is at 140°F (60°C). The vapor pressures of isobutane and butane are 126 and 92.6 psia (8.69 and 6.38 bara), respectively. If the liquid composition is 60 mol% isobutane, what is the vapor composition and partial pressure of the two components?

4.2 An adsorbent bed containing 25,000 lb_m (11,360 kg) of adsorbent removes 50 lb_m/MMscf (848 kg/10^6 Nm^3) of water from a gas stream flowing at 100 MMscfd (2.68×10^6 Nm^3/d) over an 8-h period. The bed is regenerated with a 10% slipstream of dry gas for 5 h. The regeneration furnace generates 5.0 MMBtu/h (1.47 MW). (a) Assuming all adsorbed water is removed, how much heat is required to regenerate the bed on a per lb_m (kg) of water removed? (b) Compare the heat required to remove the water with heat of vaporization at the normal boiling point on a per lb_m (kg) basis (Note that the regeneration heat is the total heat going to the bed, not the actual amount of heat absorbed by the bed, vessel walls, and moisture.)

4.3 The adsorption bed in Exercise 2 can hold an average of 10 lb_m water/100 lb_m of adsorbent before breakthrough. What fraction of the total bed capacity is used in the 8-h period?

4.4 A membrane process for removing CO_2 from a gas stream has the following design data:

	Inlet Gas	Sales Gas	Fuel Gas
Flow rate, MMscfd	100	87	13
(10^6 Nm^3/d)	(2.68)	(2.33)	(0.35)
Pressure, psig	850	840	5
	Gas Composition, mol%		
CO_2	9.6	1.9	61.0
CH_4	90.0	97.6	38.9
C_2^+	0.4	0.5	0.1

What fraction of the methane will be retained in the sales gas?

REFERENCES

Baker, R.W., Future directions of membrane gas separation technology, *Ind. Eng. Chem. Res., 41*, 1391, 2002.

Baker, R.W., *Membrane Technology and Applications*, 2nd edn. John Wiley & Sons, West Sussex, 2004.

Baker, R.W., and Lokhandwala, K., Natural gas processing with membranes: An overview, Ind. *Eng. Chem. Res.*, *47*, 2109, 2008.

Baker, R.W., Wijmans, J.G., and Kaschemekat, J.H., The design of membrane vapor-gas separation systems, *J. Membr. Sci.*, *151*, 55, 1998.

de Bruijn, J.N.H., et al., Maximizing molecular sieve performance in natural gas processing, *Eighty-First Annual Gas Processors Association Convention*, Tulsa, OK, 2002.

Echt, W.I., Dortmund, D.D., and Malino, H.M., Fundamentals of membrane technology for CO_2 removal from natural gas, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2002.

Engineering Data Book, Section 20, Dehydration, GPSA Midstream Suppliers, Tulsa, OK, 2016.

Gabelman, A., Adsorption basics: Part 1, *Chem. Eng. Progr.*, *113*(7), 48, 2017.

Geankoplis, C.J., Hersel, A.A., and Lepek, D.H., *Transport Processes and Separation Process Principles*, 5th edn. Prentice Hall International Series in the Physical and Chemical Engineering Sciences, Upper Saddle River, NJ, 2018.

Hildebrand, J.H., *An Introduction to Molecular Kinetic Theory*, Reinhold, New York, 1963.

Kohl, A., and Nielsen, R., *Gas Purification*, 5th edn. Gulf Publishing, Houston, TX, 1997.

Lemmon, E.W., McLinden, M.O., and Friend, D.G., Thermophysical properties of fluid systems, *NIST Chemistry WebBook, NIST Standard Reference Database Number 69,* Linstrom, P.J. and W.G. Mallard (eds.), National Institute of Standards and Technology, Gaithersburg, MD, 2017. http://webbook.nist.gov (Retrieved April 2019).

Lokhandwala, K., and Zammerilli, T., New nitrogen-rejection membrane technology commercialized, *Gas TIPS, 12*(4), 16, 2006.

McCabe, W., et al., *Unit Operations of Chemical Engineering*, 8th edn. McGraw-Hill, New York, 2018.

Mitariten, M., and Mokhatab, S., Integrated membrane technology for the removal of multiple components, *2019 GPA Midstream Convention*, San Antonio, TX, 2019.

Pilling, M., and Holden, B.S., Choosing trays and packing for distillation, *Chem. Eng. Progr., 105*(9), 44, 2009.

Prausnitz, J.M., Lichtenthaler, R.N., and Azevedo, E.G., *Molecular Thermodynamics of Fluid-Phase Equilibria*, Prentice-Hall Publishers, Englewood Cliffs, NJ, 1999.

Ruthven, D.M., *Principles of Adsorption and Adsorption Processes*, John Wiley & Sons, Hoboken, NJ, 1984.

Smith, J.M., et al., *Introduction to Chemical Engineering Thermodynamics*, 8th edn. McGraw-Hill Higher Education, New York, 2018.

Yang, R.T., Adsorbents: Fundamentals and Applications, John Wiley & Sons, Hoboken, NJ, 2003.

Yang, R.T., *Gas Separation by Adsorption Processes*, Imperial College Press, London, 1997

5 Phase Separation Equipment

Chapter 4 described processes for separating components of a mixture. Implicit in that description was a complete separation between phases. This chapter discusses the more common methods for obtaining the desired phase separations. Two important phase separators, slug catchers and lease separators, are discussed in Chapter 8.

Phase separators protect equipment designed to process a single phase and trap entrained phases leaving the processes. They are a critical step in ensuring problem-free operations in most processes in gas plants. Grigson et al. (2009) provide an extensive discussion on selecting and designing separators. They also supply a spreadsheet for designing separators.

The various kinds of separators can have more than one name, often depending upon geographic locale. Listed below are some common separators:

- Knockout—vessel with no internals to enhance separation.
- Scrubber—vessel designed to process high gas/liquid ratios. The liquid is entrained as a mist. The vessel may have internals but the liquid collection section is usually small. Scrubbers are commonly used to protect downstream equipment and processes.
- Flash tank—vessel designed to separate liquid and vapor. It may be a two- or three-phase separator and contain internals to separate the phases.
- Trap, line drip—small vessel installed at low spots below the gas gathering lines to remove collected liquid. Also used on pipelines to remove trace quantities of liquid, where gas/liquid ratio is extremely high. The liquid is periodically removed.
- Liquid–liquid separator—vessel designed to separate immiscible liquid phases, e.g., hydrocarbon liquids from a water-rich phase.
- Slug catcher—vessel designed to remove intermittent large volumes of liquid carried with gas stream.
- Coalescing filter separator—vessel designed to separate micron size droplets from a stream with very high gas/liquid ratios. The separator usually has two compartments with the first coalescing fine droplets and the second removing the droplets in mist extractors.
- Coalescing filter—similar to coalescing filter separator but used when entrained liquid content is lower. The unit contains only a filter.
- Dry gas filter—vessel containing filter to remove dust from gas containing no liquid.

For more details on the types of separators, see Grigson et al. (2009) and *Engineering Data Book* (2016a).

In Section 5.1, the emphasis is on the commonly used gas–liquid separators, e.g., scrubbers and flash tanks. Following sections discuss filter separators and coalescing filters, cyclone separators, and liquid–liquid separators. To help check vessel sizing, a section provides typical residence times for both gas–liquid and liquid–liquid separators in various types of service. The chapter concludes with a discussion on dry gas filters.

5.1 GAS–LIQUID SEPARATORS

Separator vessel orientation can be vertical or horizontal. Vertical separators are most commonly used when the gas/liquid ratio is high or gas flow rates are low. They are preferred offshore because they occupy less platform area. Inlet suction scrubbers at compressor stations are usually vertical because the gas/liquid ratio is high. Vertical separators are less susceptible to plugging if solids

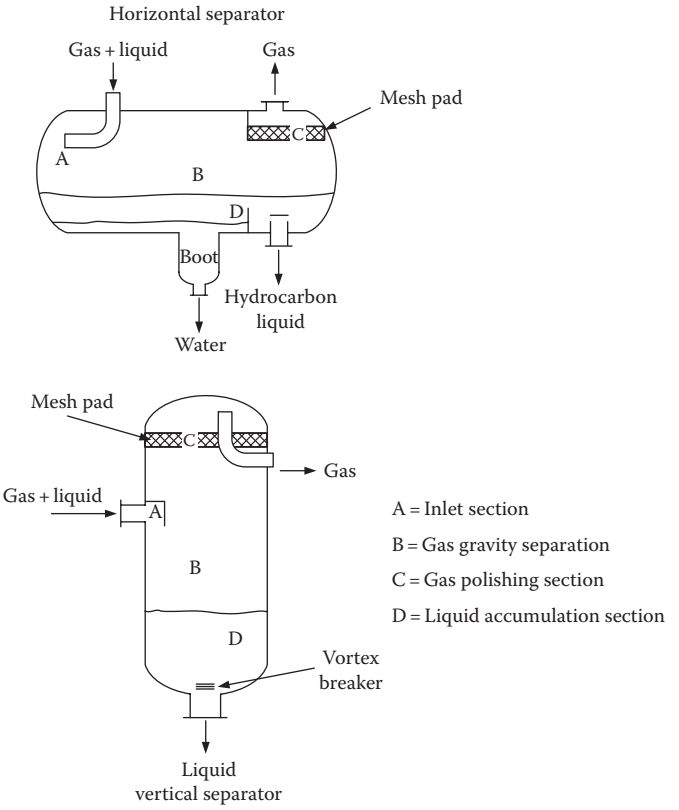


FIGURE 5.1 Gas–liquid separators.

are present. They can tolerate liquid slugs better because separation efficiency depends less on liquid levels. However, gas flow is upward, which hinders the downward flow of liquid droplets. Therefore, vertical separators can be bigger and, thus, more expensive than horizontal separators. They are not suited for liquid–liquid separation unless there are side outlets, good liquid level control and no potential for liquid slugs.

Horizontal separators are favored for large liquid volumes or if the gas/liquid ratio is low. Lower gas flow rates and increased residence times offer better liquid dropout. The larger surface area provides better degassing, and more stable liquid level as well. Liquid level is critical to separation efficiency and horizontal vessels are more susceptible to solids accumulation. Figure 5.1 shows a schematic of common gas–liquid separators and indicates the four areas or types of separation.

5.1.1 Primary Separation

Primary separation is accomplished by utilizing the difference in momentum between gas and liquid in the inlet device. Larger liquid droplets fail to make the sharp turn and impinge on the inlet wall. This action coalesces finer droplets so that they drop out quickly. Although inlet geometries vary, most separators use this approach to separate a major portion of the incoming liquid.

5.1.2 Gas Gravity Separation

Gravity settling requires low gas velocities with minimal turbulence to permit droplet fallout. The *Engineering Data Book* (2016a) provides detailed information for settling calculations. A major

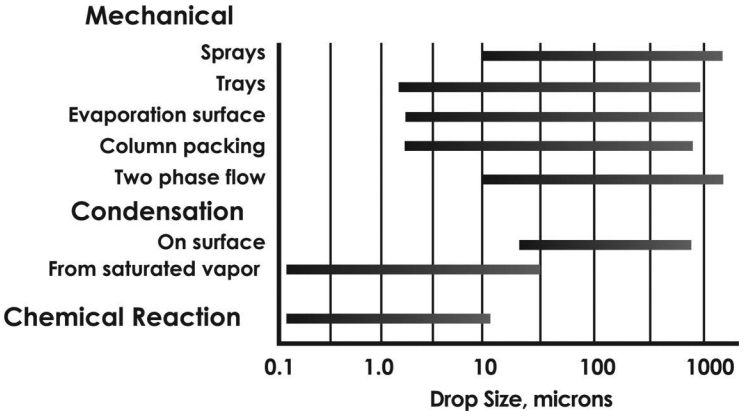


FIGURE 5.2 Typical particle sizes occurring in gas processing. (Courtesy of Koch-Glitsch LP, 2007.)

factor in settling is how quickly liquid droplets fall from the gas phase. The maximum velocity of a falling droplet is the terminal velocity. Terminal velocities increase with increasing particle size and increasing difference between liquid and vapor density. When droplet diameter is less than about 1,000 μm (1 μm = 10^{-6} m = 4×10^{-5} in.), gas viscosity becomes a factor. Increasing gas viscosity decreases terminal velocities. Particles smaller than 3 μm will not settle because they are suspended due to Brownian motion.[1] Figure 5.2 shows ranges of droplet sizes forming in various process situations.

To reduce turbulence, this section may contain vanes. They also act as droplet collectors to reduce the distance at which droplets must fall and help to prevent entrainment.

5.1.3 Gas Polishing

The gas polishing section contains an insert that forces the gas through a torturous path to coalesce small mist particles into larger droplet which will fall from the insert. These inserts can be mesh pads, vane packs, or cyclonic devices. Table 5.1 lists some of the features of the wire mesh and vane pack mist extractors. Cyclonic devices are proprietary devices and the features are manufacturer dependent.

Mesh pads are either wire or knitted mesh, usually about 6 in. (150 mm) thick. The mesh material is typically stainless steel but plastics are sometimes used. Common wire diameters are in the order of 1–10 mil (25–250 μm) to provide surface to volume ratios from about 50 to several hundred. Smaller diameter wire is needed with the smaller droplets. Coalescing occurs when impinged droplets come together on the mesh, so high surface area is important for effective mist removal. The mesh pads preferably are mounted horizontally with upward gas flow, but they can be vertical. They lose effectiveness if tilted. Mesh pads tend to be more effective in mist removal than vane packs, but are subject to plugging by solids and heavy oils.

Figure 5.3 shows several elements of a vane pack, which are corrugated plates, usually spaced 1–1.5 in. (24–38 mm) apart. The vanes force the gas and mist to follow a zigzag pattern to coalesce the mist into larger particles as they hit the plates. Coalesced drops collect and flow down the drainage traps in the plates. Systems often contain entrained solids as well, and these solids can collect on the back edge of the vane and plug the drainage channels. Liquid then collects and is re-entrained. To prevent solids accumulation and plugging, coarse filters need to be placed upstream of vane packs.

[1] Brownian motion is the random motion of very small particles caused by their collision with molecules in the continuous phase.

TABLE 5.1
Features of Mist Extracting Devices

	Wire Mesh	Vane Pack[a]
Gas capacity factor, C in Equation 5.1, ft/s (m/s)	0.22–0.39 (0.067–0.12)	Horizontal flow 0.5–1.0 (0.15–0.30) Vertical flow 0.4–0.65 (0.12–0.20)
Removal efficiency	99%–99.5% of 3–10 μm droplets	99% of 10–40 μm droplets
Operating range, % of design gas rate	30–110	Rapid decrease in efficiency with decreased gas flow
Pressure drop, inches of water (kPa)	<1 (0.25)	0.5–3.5 (0.12–0.87)

Source: *Engineering Data Book* (2016a).
[a] Vane pack sizing highly dependent on vendor sizing methods.

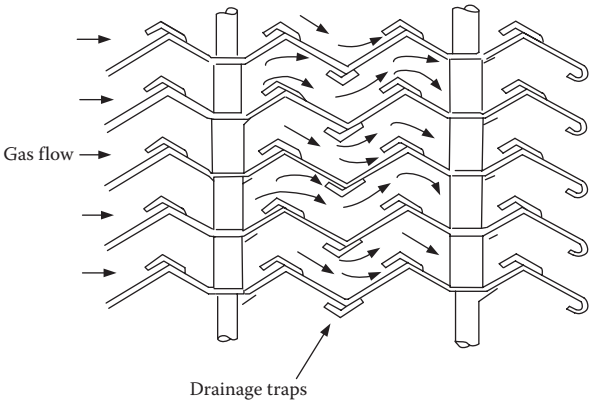


FIGURE 5.3 Sketch of the top view of a vane pack mist extractor element with liquid drainage traps. (Adapted from *Engineering Data Book*, 2016a, with permission.)

Figure 5.4 shows qualitatively the range for mist pads and vane packs. The data are based upon an air–water system and differ from natural gas data because of density and surface tension. However, Figure 5.4 indicates the regions where each demister type is effective. Note that these devices fail to coalesce droplets below around 0.5 μm, and each has both upper and lower velocity limits. The lower limit is caused by too low a velocity to force sufficient droplets impinging on the solid surface to provide coalescing. At high velocities, the coalesced droplets are stripped from the solid by the rapidly flowing gas.

The *Engineering Data Book* (2016a) and Grigson et al. (2009) provide design calculations for wire mesh and vane pack coalescing units. However, commercial designs are proprietary for vane packs and cyclonic devices. Below is a short discussion on the determination of separation performance for mesh pads and vane packs.

The two parts of separation performance are droplet removal efficiency and gas handling capacity. Manufacturers provide charts showing removal efficiency as a function of droplet size at design conditions. Gas handling capacity can be estimated by using the following equations:

$$V_t = C\sqrt{\frac{\left(\rho_l - \rho_g\right)}{\rho_g}}, \tag{5.1}$$

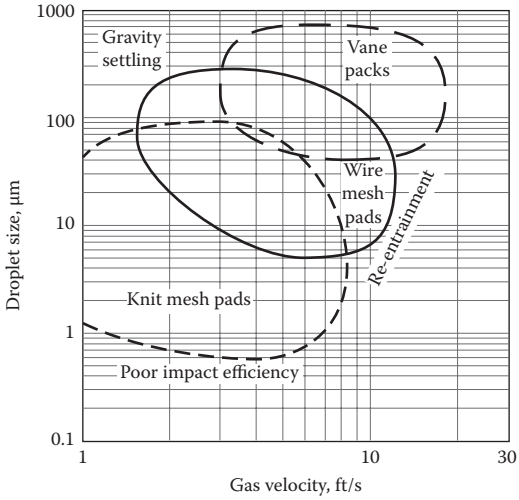


FIGURE 5.4 Approximate operating ranges for different kinds of demisters. Data are based upon water and air (multiply ft/s by 0.305 to convert to m/s). (Courtesy of ACS Industries, 2005.)

where C is the gas capacity factor given in Table 5.1, and ρ_l and ρ_g are liquid and vapor densities. The required mist extractor area, A, is given by

$$A = \frac{Q_A}{V_t}, \tag{5.2}$$

where Q_A is the actual volumetric flow rate. The *Engineering Data Book* (2016a) tabulates the percentage reduction in C as a function of pressure, but it can be estimated by

$$\Delta C(\%) = 100 - 1.35P(\text{psig})^{0.42} \tag{5.3a}$$

$$\Delta C(\%) = 100 - 4.12P(\text{barg})^{0.42} \tag{5.3b}$$

where P is in psig and barg for Equations 5.3a and 5.3b, respectively. This equation should not be used for pressures above 1,150 psig (80 barg).

Example 5.1

Estimate the mist extractor area required for a gas containing a mist with droplets primarily in the 5–10 μm size range. The inlet gas flow rate of 70 MMscfd (1.9 × 106 Nm³/d) enters the separator at 90°F (32°C) and 400 psig (27.6 barg). The compressibility factor for the gas at these conditions is 0.97. The specific gravity of the gas is 0.60 and droplet specific gravity is 0.53.

Solution

Because the particle diameter range is below 10 μm, wire mesh should be used. Use Equation 5.1 to obtain the terminal velocity for use in Equation 5.2.

First compute the gas volume and two densities. Equation 5.2 requires the actual volumetric flow, so using Equation 5.2 with the compressibility factor included, the actual volume flow of the gas is

$$Q_A = V_1 \times \frac{P_1}{P_2} \times \frac{T_2}{T_1} \times \frac{z_2}{z_1} = 70 \times 10^6 \times \frac{15}{415} \times \frac{460+90}{460+60} \times \frac{0.97}{1} = 2.6\,\text{MMcfd}\left(76 \times 10^3\,\text{m}^3/\text{d}\right).$$

Using the compressibility factor equation the gas density, ρ_g is

$$\rho_g = \frac{P \times MW}{RTz} = \frac{415 \times 0.60 \times 28.96}{10.73(460+90) \times 0.97} = 1.26\,\text{lb}_\text{m}/\text{ft}^3\,(20.2\,\text{kg/m}^3).$$

Liquid density is

$$\rho_l = 0.53 \times 62.4 = 33.1\,\text{lb}_\text{m}/\text{ft}^3\,(530\,\text{kg/m}^3).$$

Before using Equation 5.1 to compute the density difference, the capacity factor C must be corrected for pressure using Equation 5.3

$$\Delta C(\%) = 100 - 1.35P(\text{psig})^{0.42} = 100 - 1.35(400)^{0.42} = 83\%.$$

To be conservative, choose the gas capacity factor C from Table 5.1 to be 0.22 ft/s (0.067 m/s). The correction for pressure reduces it to $0.83 \times 0.22 = 0.18$ ft/s (0.055 m/s).

Then, using Equation 5.1, the terminal velocity is

$$V_t = C\sqrt{\frac{(\rho_l - \rho_g)}{\rho_g}} = 0.18\sqrt{\frac{(33.1-1.3)}{1.3}} = 0.89\,\text{ft/s}\ (0.27\,\text{m/s}).$$

Next, change actual daily flow rate to ft³/s and use Equation 5.2 to compute the area required

$$A = \frac{Q_\text{A}}{V_t} = \frac{2.6 \times 10^6}{86{,}400} \times \frac{1}{0.89} = 34\,\text{ft}^2\,(3.2\,\text{m}^2).$$

The actual geometry will depend upon the vessel design.

5.1.4 Liquid Accumulation Section

This section acts as a holder for the liquids removed from the gas in the above three separation sections. It also provides residence time for degassing of the liquid and for water and solids separation from the hydrocarbon phase. A residence time of 1–2 min should be adequate for removing light hydrocarbons from condensates (*Engineering Data Book*, 2016a). The most common solid is iron sulfide from corrosion, which can interfere with the liquid–liquid separation. If a large amount of water is present, separators often have a "boot," as shown in the horizontal separator (Figure 5.1), at the bottom of the separator for the water to collect. The *Engineering Data Book* (2016a) estimates that retention times of 3–5 min are required for light hydrocarbon–water separation by settling, if fine droplets are not present and the system contains no surface-active compounds causing emulsion formation. Section 5.4 discusses more difficult liquid–liquid separations.

5.2 FILTER SEPARATORS AND COALESCING FILTERS

As noted above, droplet sizes below 3 μm will not settle. To remove fine mist, filter separators and coalescing filters are required. They are separate units from the gas–liquid separators discussed above because they include filter elements. These filtration units are frequently used upstream of gas treating units to prevent hydrocarbon liquids and compressor oil from entering amine absorbers and causing solvent contamination and foaming problems (see Chapter 10). They are used upstream of dehydration units to protect solid adsorbents from amine solution (see Chapter 11).

Filter separators, like other gas–liquid separators, can be horizontal or vertical; the horizontal unit is most common (*Engineering Data Book*, 2016a). Figure 5.5 shows a horizontal unit that contains a filter coalescing section, followed by a final mist extraction section. The filter bundle

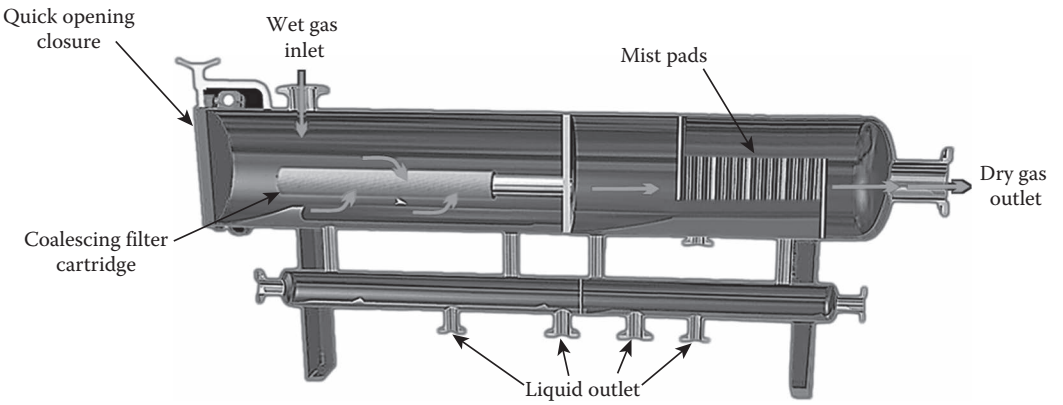


FIGURE 5.5 Horizontal filter separator. For clarity figure shows only one filter cartridge in the bundle. (Courtesy of Mahle/Nowata Filtration.)

resembles a heat exchanger bundle, with the gas entering on the shell side. The first section catches larger droplets on the outside of the filter. These droplets collect and drain through the two outlets on the left of Figure 5.5. Smaller droplets are coalesced into larger droplets as they pass through the filter. The gas, with coalesced droplets, leaves the filters and passes through a final mist extractor that contains either a mist pad or vane pack. This liquid drains through the two outlets on the right side of Figure 5.5.

Pressure drop through a clean separator is usually 1–2 psi (0.07–0.14 bar), and filters are changed when the pressure drop rises to about 10 psi (0.7 bar). The vessel generally has a quick opening closure on the filter side for filter element replacement and cleaning. Figure 5.6 shows corrosion products and hydrocarbon liquid in a filter separator on suction side of gathering line compressor.

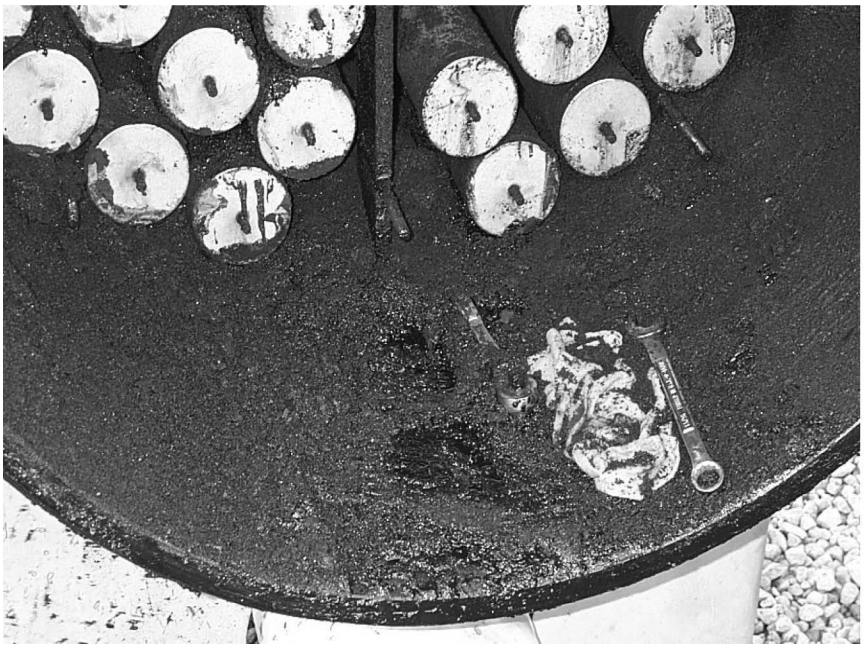


FIGURE 5.6 Filter separator on suction side of compressor in a compressor station upstream of gas plant. Solids present, excluding tools, are corrosion products. (Courtesy of Parker IPF/PECO.)

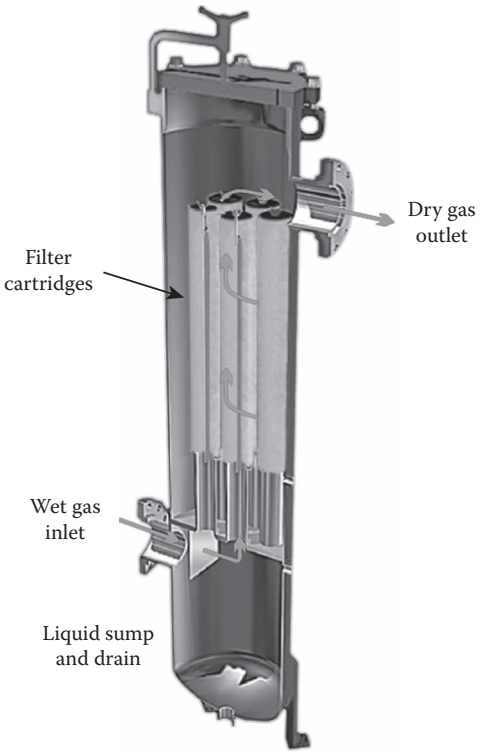


FIGURE 5.7 Coalescing filter (reverse flow coalescer). (Courtesy of Mahle/Nowata Filtration).

Coalescing filters are similar to filter separators but normally are vertical and designed for very high gas/liquid ratios, where the liquid is an aerosol. Figure 5.7 shows a typical coalescing filter, where the gas enters at the bottom of the vessel, travels up through coalescing medium, and then exits. They are often called "reverse flow coalescer" because the gas flows from the inside to the outside of the filter media. The bottom section removes droplets larger than about 300 μm (Wines and Lorentzen, 1999). The filter coalesces droplets larger than about 0.1 μm into large droplets, which run down the outside of the filter and into the liquid drain. Coalescing filters trap solids larger than about 0.3 μm, which eventually increase the pressure drop through the filter to the point that the filter medium requires replacement. Typical pressure drops through coalescing filters are comparable to those through filter separators.

Coalescing filters are used on inlet and outlets of compressors, amine treaters, and upstream of adsorption beds. Manufacturers are the best source for details of applicability and operating ranges.

5.3 CYCLONE SEPARATORS

Cyclones use centrifugal force to enhance separation of condensed phases from gas. The centrifugal force is generated by rapidly moving inlet stream forced into a circular motion, causing the liquid to collect on the inside of the vessel wall. This is done in either of two basic ways. One method is to use inlet vanes to force the liquid around the outer wall of the vessel. Other designs direct the gas into a number of smaller cylinders with each cylinder acting as a small cyclone. In either case, liquid drops out at the bottom of the cyclone. A number of different kinds of internals are used to collect the liquid. Some designs have the gas going through a settling area before exiting out the vessel top.

Cyclones are extremely efficient at high gas throughput, which means smaller vessel diameter. They are effective in removing droplets >10 μm. However, efficiency drops rapidly with decreasing inlet flow rates giving them a narrow operating range. Cyclones also have a relatively high pressure drop and have difficulties in handling liquid slugs. They are attractive in systems of relatively steady flow of gas and liquid. Cyclones are extensively used in power plants to remove condensate in steam systems, but relatively infrequently in natural gas processing because of variable flows and liquid slugging. Sterner (2001), *Engineering Data Book* (2016a), and Grigson et al. (2009) present details on various cyclone separators.

5.4 LIQUID–LIQUID SEPARATORS

Liquid–liquid separators are similar to gas–liquid separators, and the configuration depends upon whether the feed has two or three phases present. If three phases are present and the liquids separate easily by gravity, the horizontal configuration shown in Figure 5.1 is typical. Figure 5.8 shows a two-liquid phase and three-phase separator, where droplets are too small to settle by gravity. A coalescing medium is used to merge the droplets so that the phases separate by gravity.

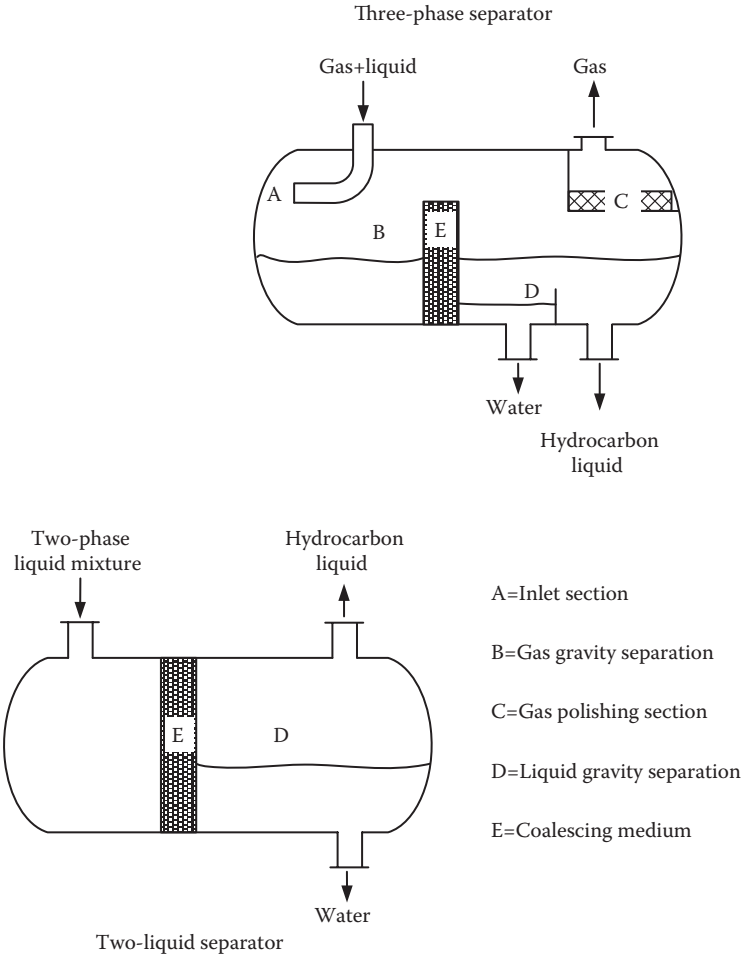


FIGURE 5.8 Horizontal two liquid and three phase separators used for breaking an emulsion.

The same equations described for gas–liquid gravity settling is applicable. The particles typically follow Stokes' law.[2] Separating liquids presents two difficulties usually not encountered with gas–liquid separations—relatively small differences in density (use of change in direction provides little or no benefit) and possible emulsions. Both factors force longer residence times. The *Engineering Data Book* (2016a) provides equations for both horizontal and vertical vessel sizing. For quick sizing the volume can be based upon residence time.

5.5 RESIDENCE TIME FOR VARIOUS SEPARATOR APPLICATIONS

This section provides typical residence times for a variety of gas–liquid and liquid–liquid separations seen in both field and plant operations. The residence time is simply the volume of the phase present in the vessel divided by the volumetric flow rate of the phase. Residence times offer a quick first sizing of simple separators.

Table 5.2 provides typical retention times for common gas–liquid separations. Note that process control and process stability may be the determining factors for residence time and require longer times than given in the table.

Table 5.3 gives residence times for liquid–liquid separations. The *Engineering Data Book* (2016a) notes some limitations in using residence times for these separations:

- Assuming equal residence times for both liquid phases may not be optimal because it is typically easier to separate oil droplets from water than vice versa.
- Using the same residence time for both vertical and horizontal separators is not valid because droplets settle more quickly in horizontal vessels if diameters are equal.
- Using residence times fails to provide an indication of how well the two phases split.

The *Engineering Data Book* (2016a) provides additional details on liquid–liquid separations, including equations for sizing both vertical and horizontal separators.

TABLE 5.2
Typical Retention Times for Gas–Liquid Separations

Type of Separation	Retention Time (min)
Natural gas-condensate separation	2–4
Fractionator feed tank	10–15
Reflux accumulator	5–10
Fractionation column sump	2[a]
Amine flash tank	5–10
Refrigeration surge tank	5
Refrigeration economizer	3
Heat medium oil surge tank	5–10[b]

Source: Grigson et al. (2009).

[a] If the fractionator column sump is feeding a downstream fractionator column, it should be sized as a feed tank.

[b] This vessel must have adequate volume to allow for expansion of the heat medium from ambient to operating temperature.

[2] Stokes law applies to settling of very small particles in laminar flow. Settling velocity increases with particle diameter but decreases with increasing viscosity. For details, see the *Engineering Data Book* (2016a).

TABLE 5.3
Typical Retention Times for Liquid–Liquid Separators

Type of Separation	Retention Time (min)
Hydrocarbon–Water	
Above 35° API hydrocarbon	3–5
Below 35° API hydrocarbon	
>100°F (38°C)	5–10
80°F (27°C)	10–20
60°F (16°C)	20–30
Ethylene glycol/hydrocarbon separators (cold separators)	20–60
Amine/hydrocarbon	20–30
Caustic/propane	30–45

Source: Grigson et al. (2009).

5.6 FILTERS

This section gives a brief overview of filtration. Winston et al. (2013) provides a detailed introduction to filtration used in gas processing.

Strictly speaking, filtration is the removal of solid particulate matter from a stream by passing the fluid through a porous medium. However, in gas processing, it frequently includes solid and liquid removal from gas streams (*Engineering Data Book*, 2016a). Filters are used to remove particles as small as 0.5–1 μm. They offer the final protection of equipment from unwanted particulate matter by trapping particles. The literature is replete with examples where adding good filtration resolved operational problems.

Filters fall into three types of service:

- Fine particulate and mist removal from a gas stream, e.g., removing solids and aerosol from gas leaving an inlet separator.
- Fine particulate removal from a dry gas stream, e.g., removing fines from a gas exiting a molecular sieve adsorbent bed.
- Fine particulate removal from a liquid stream, e.g., removing solids from rich and lean amine streams.

If a filter is in dry gas service it is important that the filter not be contacted with liquid. Liquid accumulation can cause caking and a rapid increase in pressure drop across the filter.

Figure 5.9 shows that the most commonly used filter design uses a cartridge with the unfiltered fluid contacting the outside of the cartridge. These single-stage filters have a quick opening closure so that the filter cartridge can be easily changed. Figure 5.10 shows an air filtration system that is commonly used to remove dust, or ice in cold regions. The system provides low maintenance because the unit periodically pulses air back through the filters to remove accumulated solids. The *Engineering Data Book* (2016b) provides more discussion on filtration systems for the air intake of gas turbines.

Other types of filters are used, especially for removing solids from amines and glycols. McCallum (2005) presents a case study for filtering amines using charcoal filters and after filters. Note that activated carbon and charcoal filters typically remove material from a single-phase fluid using adsorption. They are "filters" on a molecular scale and not used for phase separation, although they do trap entrained liquid droplets.

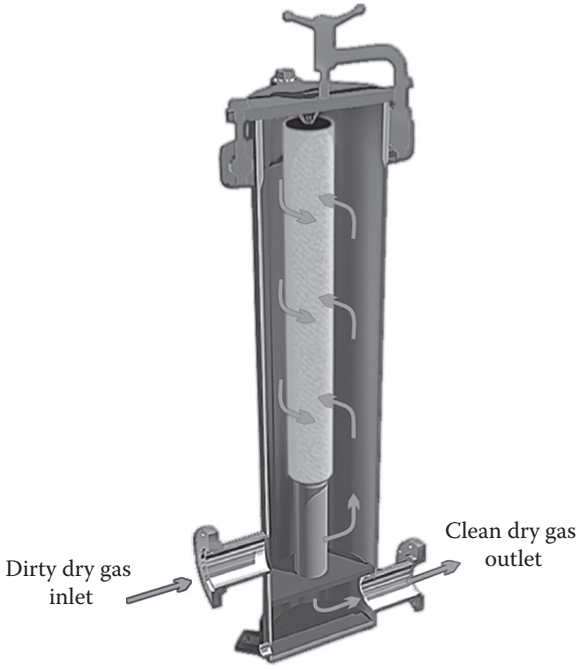


FIGURE 5.9 Dry gas cartridge filter. Only one cartridge shown for clarity. (Courtesy of Mahle/Nowata Filtration.)

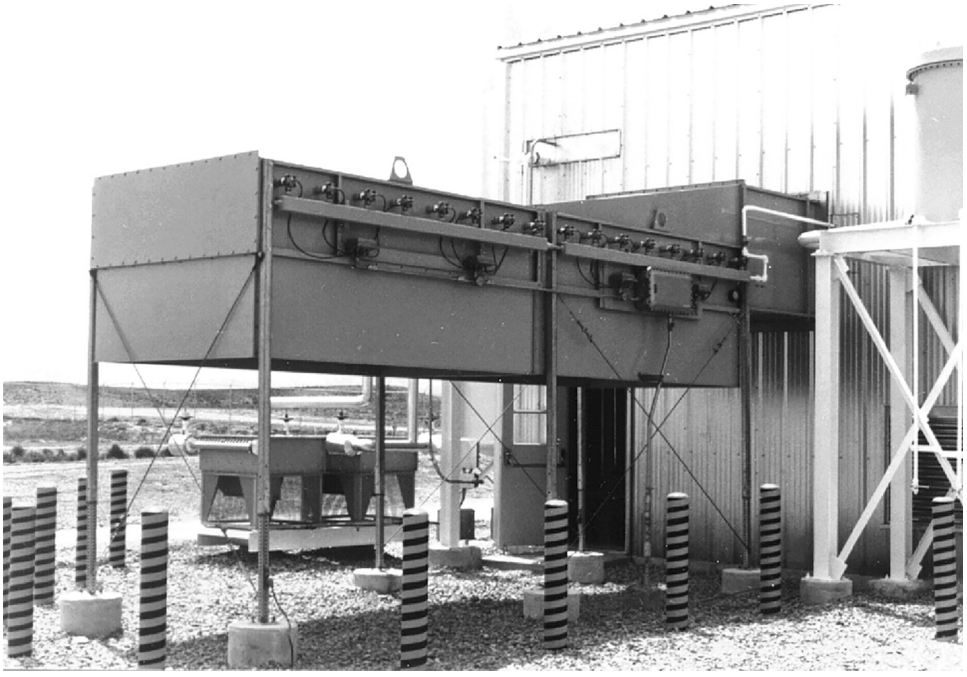


FIGURE 5.10 Self-cleaning air filtration system used on intake of gas turbine. The tubing on the side of the unit provides periodic pulses of air in the reverse direction to remove accumulated solids. (Courtesy of Donaldson Company, Inc.)

Bag filters, long used for filtering air, are also used in filtering gas and liquid streams. They replace the cartridge with a bag of filtration material. The bag, which looks like a thick wind sock, may be capped at one end. It has a porous polymer wall with the unfiltered stream flowing into or out of the annular space. Advantages of bags include their higher capacity and efficiency (Fabio et al., 1992).

DISCUSSION QUESTIONS

1. When are vertical gas–liquid separators preferred to horizontal separators?
2. What are some disadvantages of vertical gas–liquid separators compared to horizontal separators?
3. List two or three important properties of the gas and liquid phases that make it difficult to have good separation of the two phases.
4. How do wire mesh pads reduce liquid carryover?
5. What causes the upper and lower limit on gas velocity when using coalescing pads and vane packs?
6. What are some of the major differences between a filter separator and a coalescing filter, and when is one preferred over the other?
7. Cyclone separators are extremely efficient. Why are they not used widely in the gas industry?
8. What makes liquid–liquid separation usually more difficult than gas–liquid separation?
9. How do you visualize the self-cleaning air filtration systems perform the cleaning process?
10. Charcoal filters are frequently used to clean liquid and gas streams. Are they really filters? Justify your answer.

REFERENCES

Engineering Data Book, Section 7, Separation equipment, GPSA Midstream Suppliers, Tulsa, OK, 2016a.

Engineering Data Book, Section 15, Prime movers for mechanical drives, GPSA Midstream Suppliers, Tulsa, OK, 2016b.

Fabio, D.G., Ballard, D., and Perkins, J., The 3M bag filter, the cost cutting problem solver, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 1992, p. 118.

Grigson, S., LaRue, K., and Hanlon, G., Fundamentals of separation, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2009.

Koch-Glitsch LP, Mist elimination, 2007. www.koch-glitsch.com/Document%20Library/ME_ProductCatalog.pdf (Retrieved April 2019).

McCallum, V., Filtration of the Linam Ranch/Eunice treating systems, *Eighty-Fourth Annual Gas Processors Association Convention*, Tulsa, OK, 2005.

Sterner, A.J., Developments in gas-liquids separation technology, *Eightieth Annual Gas Processors Association Convention*, Tulsa, OK, 2001.

Wines, T.H., and Lorentzen, C., High performance liquid/gas coalescers for compressor protection, *Proceedings of the 1999 Compressor Workshop, Lambton College,* Sarnia, Ontario, 1999. https://chemicals-polymers.pall.com/content/dam/pall/chemicals-polymers/literature-library/non-gated/GDS116.pdf (Retrieved April 2019).

Winston, K., et al., Fundamentals of separation filtration & activated carbon, *Laurance Reid Gas Conditioning Conference*, Norman, OK, 2013.

Taylor & Francis
Taylor & Francis Group
http://taylorandfrancis.com

Part 2

Taylor & Francis
Taylor & Francis Group
http://taylorandfrancis.com

6 Overview of the Natural Gas Industry

6.1 INTRODUCTION

The Chinese are reputed to have been the first to use natural gas commercially around 500 B.C. The gas was obtained from shallow wells, transported in bamboo pipes, and used to produce salt from brine in gas-fired evaporators. Manufactured, or town gas (gas manufactured from coal) was used in both Britain and the United States in the late 17th and early 18th centuries for streetlights and house lighting. The next recorded commercial use of natural gas occurred in 1821. William Hart drilled a shallow 27-ft (9 m) gas well in Fredonia, New York, and by use of wooden pipes, transported the gas to local houses and stores (NaturalGas.org, 2013).

During the following years, a number of small, local programs involved natural gas; but large-scale activity began in the early years of the 20th century. The major boom in gas usage occurred after World War II, when engineering advances allowed the construction of safe, reliable, long-distance pipelines for gas transportation. At the end of 2016, the United States had more than 305,000 mi (4.9×10^5 km) of gas pipelines, both interstate and intrastate (Energy Information Administration, undated). These Energy Information Administration (EIA) data exclude gathering lines upstream of gas processing plants. Data (BP p.l.c., 2018) show that in 2017, the United States was the world's largest producer of natural gas (26.00 trillion cubic feet [Tcf],[1] 696×109 Nm^3) and the leading world consumer (26.16 Tcf, 701×10^9 Nm^3). These values correspond to 20% of both world production and consumption.

Although the primary use of natural gas is as a fuel, it is also a source of hydrocarbons for petrochemical feedstocks and a source of elemental sulfur, an important industrial chemical. Its importance as an energy source is expected to grow substantially in the future because natural gas presents many environmental advantages over petroleum and coal, as shown in Table 6.1. Carbon dioxide, a greenhouse gas linked to climate change, is produced from oil and coal at a rate of approximately 1.4–1.75 times higher than production from natural gas on a per unit energy generated basis.

Both atmospheric nitrogen and nitrogen in fuel are sources of nitrogen oxides (NO_X), which are greenhouse gases and a source of acid rain. Because both oil and coal contain nitrogen compounds not present in natural gas, the nitrogen oxides formed from burning natural gas are ~20% of those produced when oil or coal is burned. Particulate formation is significantly less in gas compared with coal and oil, an important environmental consideration because in addition to degrading air quality, high levels of particulates may pose significant health problems.

The values reported in Table 6.1 for sulfur dioxide can be misleading. Many natural gases contain considerable quantities of sulfur at the wellhead, but specifications for pipeline-quality gas require almost total sulfur removal before pipelining and sale. Consequently, the tabular values for natural gas represent combustion after removal of sulfur compounds, whereas the tabular values for oil and coal are reported for fuels with no sulfur recovery either before or after combustion. Note that many federal and local jurisdictions have sulfur emission limits. Nevertheless, gas produces far fewer pollutants than its competitors, and the sulfur is much easier to remove from natural gas compared to fuel oil or coal. Demand for gas, a clean fuel, is expected to rise significantly over time.

[1] Gas volumes are normally reported in terms of standard cubic feet (scf) at standard conditions of 60°F and 14.696 psia. In metric units, the volumes here are given in normal cubic meters, Nm^3, whose base conditions are 0°C, 1.01325 bar. See Section 1.2 for details of units used in this book.

TABLE 6.1
Pounds of Air Pollutants Produced per Billion Btu of Energy

Pollutant	Natural Gas[a]	Oil[b]	Coal[c]
Carbon dioxide	117,000	164,000	208,000
Carbon monoxide	40	33	208
Nitrogen oxides	92	448	457
Sulfur dioxide	0.6	1,122	2,591
Particulates	7.0	84	2,744
Formaldehyde	0.750	0.220	0.221
Mercury	0.000	0.007	0.016

Source: Energy Information Administration (1999).

[a] Natural gas burned in uncontrolled residential gas burners.

[b] Oil is #6 fuel oil at 6.287 million Btu per barrel and 1.03% sulfur with no postcombustion removal of pollutants.

[c] Bituminous coal at 12,027 Btu per pound and 1.64% sulfur with no postcombustion removal of pollutants.

6.1.1 World Natural Gas

The current status of primary energy sources for the world is summarized in Figure 6.1. Energy production from dry gas is nearly comparable to coal.

Six countries possess approximately two-thirds of the world's gas reserves (Figure 6.2), with 48% of the reserves located in Iran, Qatar, and Russia. The United States has 4.8% of the world's reserves, but is the world's largest consumer of natural gas.

Note that proven reserve estimates are truly estimates and vary among sources. Also, proven reserves depend on both gas prices and advances in exploration and production. Increased gas price causes reserve estimates to rise because economically marginal fields can be counted as proven reserves. Advances in exploration and especially drilling after about 2005 substantially increased reserves, particularly in unconventional resources, as discussed in Section 6.2.2.

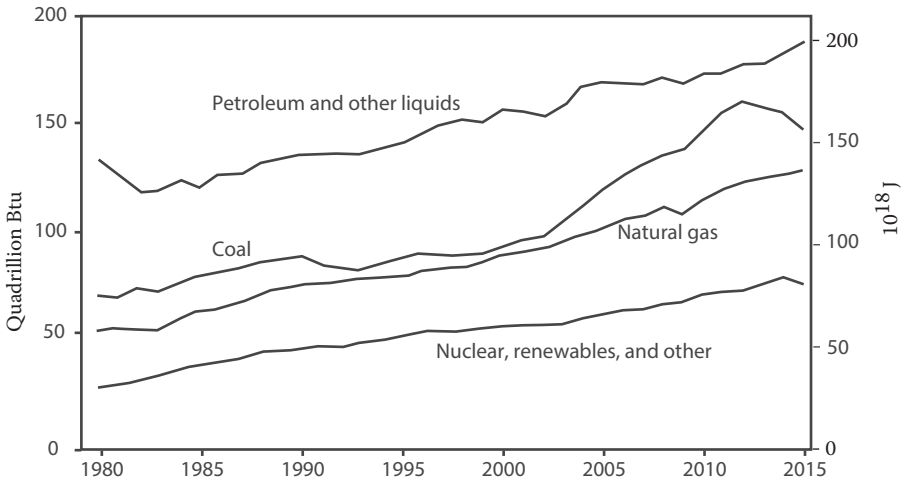


FIGURE 6.1 Total world primary energy production. The "petroleum and other liquids" includes NGLs. The "nuclear, renewables, and other" category includes hydroelectric, geothermal, wind, solar, wood and waste (Energy Information Administration, 2018a).

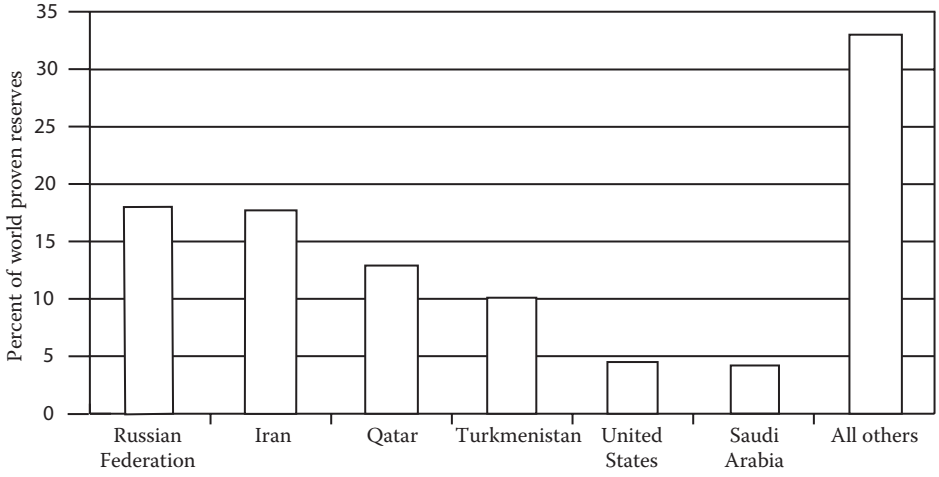


FIGURE 6.2 Major proven natural gas reserves by country. Total world proven reserves are estimated to be 6.832 Bcf (183.0×10^{12} Nm^3) (BP p.l.c., 2018).

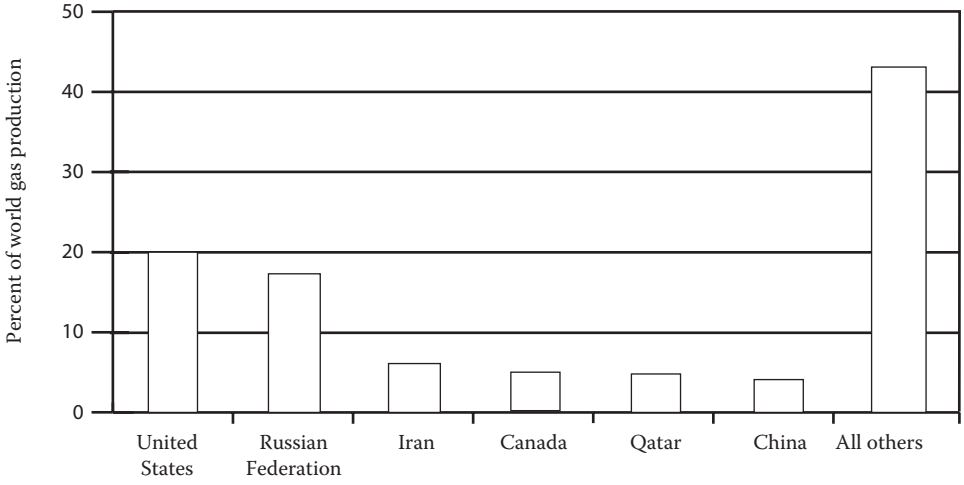


FIGURE 6.3 Major natural gas producing countries in 2017. Total world production was 130 Tcf (3.49×10^{12} Nm^3) (BP p.l.c., 2018).

Figure 6.3 shows the world production of natural gas. Figure 6.4 shows the world's natural gas consumption which was 130 Tcf (3.5×10^{12} Nm^3). Russia and the United States are responsible for 32% of world production and the United States has 20% of the world's gas consumption. The United States consumed only 0.6% more than it produced in 2017. By contrast, in 2007 the United States consumed almost 120% of production. Although the United States became an exporter in 2017, the ratio of proven reserves to 2017 production is only 11, which is lower than the other 15 countries with the highest proven reserves. The world average ratio is just over 50.

6.1.2 U.S. Natural Gas

Figure 6.5 shows the primary energy sources in the United States projected to 2050. These curves are the EIA's "Reference" case. The EIA (2018a) provides estimates based upon resource availability

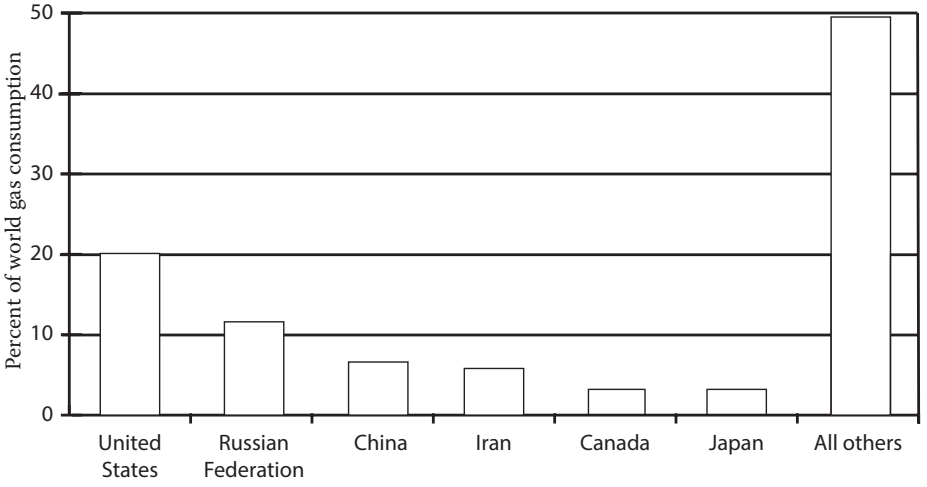


FIGURE 6.4 World natural gas consumption in 2017 (BP p.l.c., 2018).

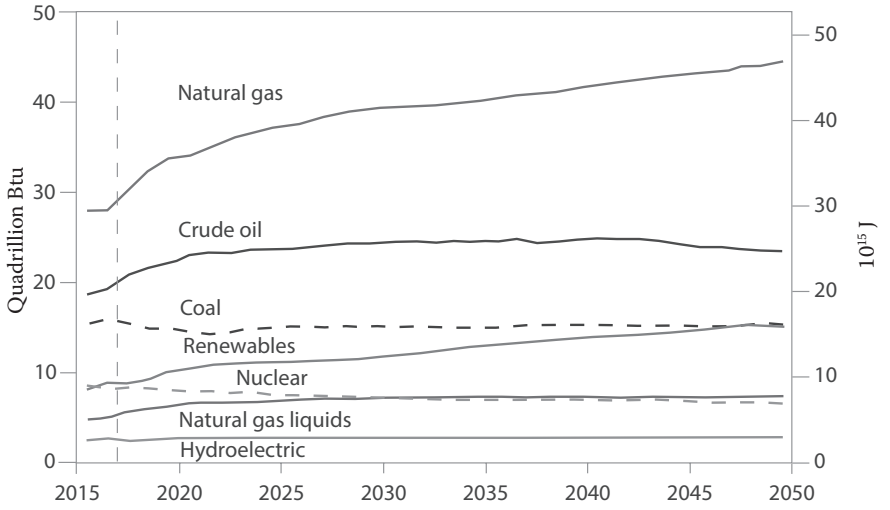


FIGURE 6.5 United States primary energy production from all significant sources, projected to 2050. (See text for details, Energy Information Administration, 2018b.)

and technology advances. They also define what is included in some of the smaller sources of energy. Natural gas plays an extremely important role in the U.S. energy, accounting for ~32% of the total energy used in 2017. It is predicted to grow to nearly 40% by 2050. Petroleum is predicted to remain about 22% of total energy production. Biomass and renewable energy, including solar, are projected to remain less than 10% of U.S. total energy production.

The flow of natural gas from wellhead to consumer is shown in Figure 6.6. The numbers reveal that:

- Substantial amounts of the gross gas produced (12%) are returned to the reservoir for field repressurization.
- Loss of gas because of venting or flaring is small, only 0.7% of the gross withdrawal.
- Nonhydrocarbon gases (principally nitrogen, carbon dioxide, hydrogen sulfide, and helium) had to be removed (1.3% of gross) to render the gas marketable.

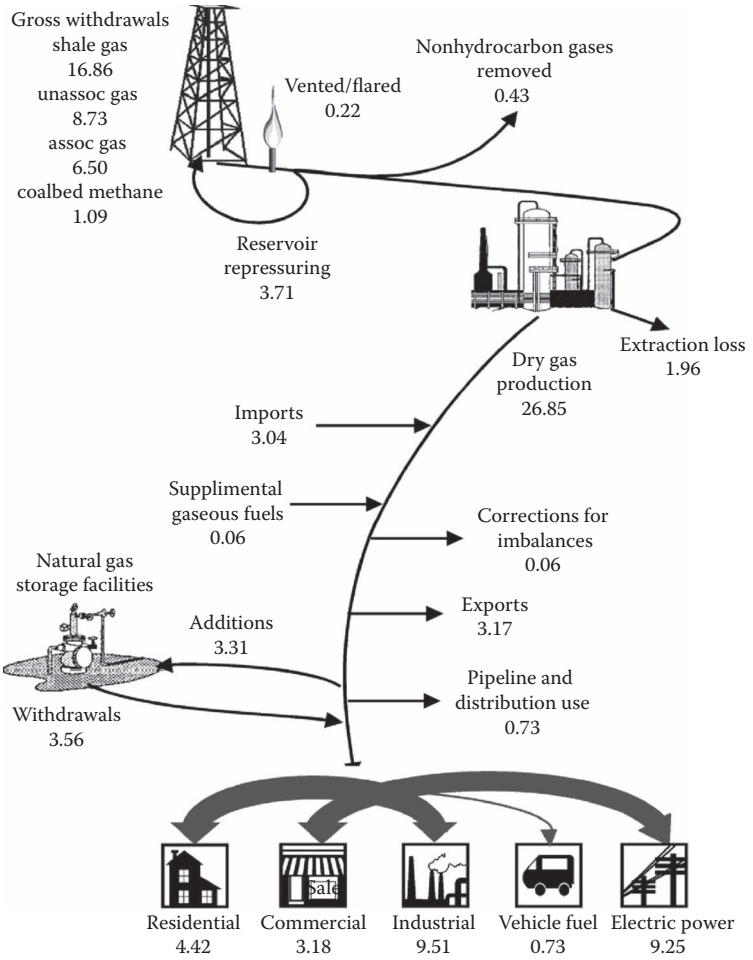


FIGURE 6.6 Flow of natural gas (Tcf) in the United States in 2017. Multiply Tcf by 2.685×10^{10} to obtain Nm^3. (Data from Energy Information Administration, 2018f.)

- Extraction losses (6.1% of gross) refer to liquids (NGL) removed from the gas (shrinkage) and sold separately as well as fuel gas, venting and flaring, and nonhydrocarbon gases removed at gas plants.
- Exports slightly exceeded imports for first time in many years. The imports come predominately from Canada via pipeline with the remainder entering as LNG.

6.2 SOURCES OF NATURAL GAS

6.2.1 Geological Background

Gas and oil are the products of the decomposition of certain types of plant and animal matter trapped in sediments of ancient lakes and oceans (Sanders, 1981). The combination of high pressure from the overburden, geothermal heat, and millions of years converted the organic matter, often initially decomposed by microbial action, into kerogen. This is the kerogen found in oil shale. Over additional millions of years, kerogens further decomposed into oil and gas. Hydrogen-rich kerogen was converted into oil while oxygen-rich kerogens became natural gas. Thermal cracking of oil also produced natural gas.

During this long time period the silt, sand, and gravel within the sediment cemented together forming voids that enclosed the decayed organic matter. Some voids become isolated while others remain interconnected.

Driven by pressure and high temperature the relatively volatile oil and gas migrated through porous rock layers toward the earth's surface. The oil and gas often were trapped when reaching an impermeable rock layer (cap or sealing rock) or by geological faults to form reservoirs.

There are many important characteristics of reservoirs but three—porosity, permeability and shape are discussed here. Porosity is the void space in the reservoir rock and typically ranges from 0% to around 20%. There is total porosity, which is all void space, and effective porosity, which considers only interconnecting void space. The latter is the most important for hydrocarbon recovery.

Permeability is a measure of the size of openings between the voids. It indicates how easily a fluid can flow between the voids of the reservoir rock. The common unit of permeability is darcy[2] (m^2). While some reservoirs have a permeability of several darcies, many producing gas fields have permeabilities in the millidarcy range. Generally, there is a roughly linear relationship between the log of effective porosity and permeability. The porosity can be artificially increased by hydraulic fracturing reservoir rock. Water, with small amounts of additives, is injected under high pressure to create cracks between the void spaces and increase production rates.

6.2.1.1 Conventional Reserves

The shape, and obviously size, plays an important role in making a gas reservoir economically viable. Ideally, the cap rock forms a dome, like the one shown on the left side of Figure 6.7. For deep, high-permeability reservoirs, simple vertical drilling is sometimes adequate. However, reservoir shapes vary widely, sometimes forming small lenses or being in a band like that shown on the right side of Figure 6.7. The combination of higher gas prices along with new horizontal and directional drilling technology made these reservoirs economically feasible to produce. Hydraulic fracturing is often used when completing a well.

As depicted in Figure 6.7 conventional natural gas generally occurs in reservoirs, either associated with crude oil (associated gas or dissolved gas) or in reservoirs that contain little or no crude oil (nonassociated gas). Associated gas is produced with the oil and separated at the wellhead or casinghead. Gas produced in this fashion is also referred to as casinghead gas, oil-well gas, or dissolved gas. Nonassociated gas is sometimes referred to as gas-well gas or dry gas. However, this "dry" gas can still contain significant amounts of NGL and water. A class of reservoirs, referred to as gas condensate reservoirs, occur at high reservoir temperatures and pressures, where the material is present not as a liquid or a gas but as a very dense, high pressure fluid (see Chapter 12 for discussion of phase behavior of high-pressure fluids).

Figure 6.7 shows a simplified flow of material from reservoir to finished product and provides an overall perspective of the steps involved in taking the gas from the wellhead to the customer. The chapters that follow provide more detail on the various steps. Note that Figure 6.7 oversimplifies the gas gathering system. These systems are typically complex and bring gas from many leases to a processing plant. Chapter 8 discusses gathering systems in more detail.

6.2.1.2 Unconventional Reserves

There are four unconventional categories having significant reserves:

- Tight gas
- Shale gas
- Coal bed methane (CBM)
- Gas hydrates

[2] A porous media having a permeability of 1 darcy will have a flow of 1 cm^3/s per cm^2 of a fluid with a viscosity of 1 cP when the pressure gradient is 1.01 bar/cm. One darcy equals 9.869233×10^{-13} $m^2 = 0.987$ μm^2.

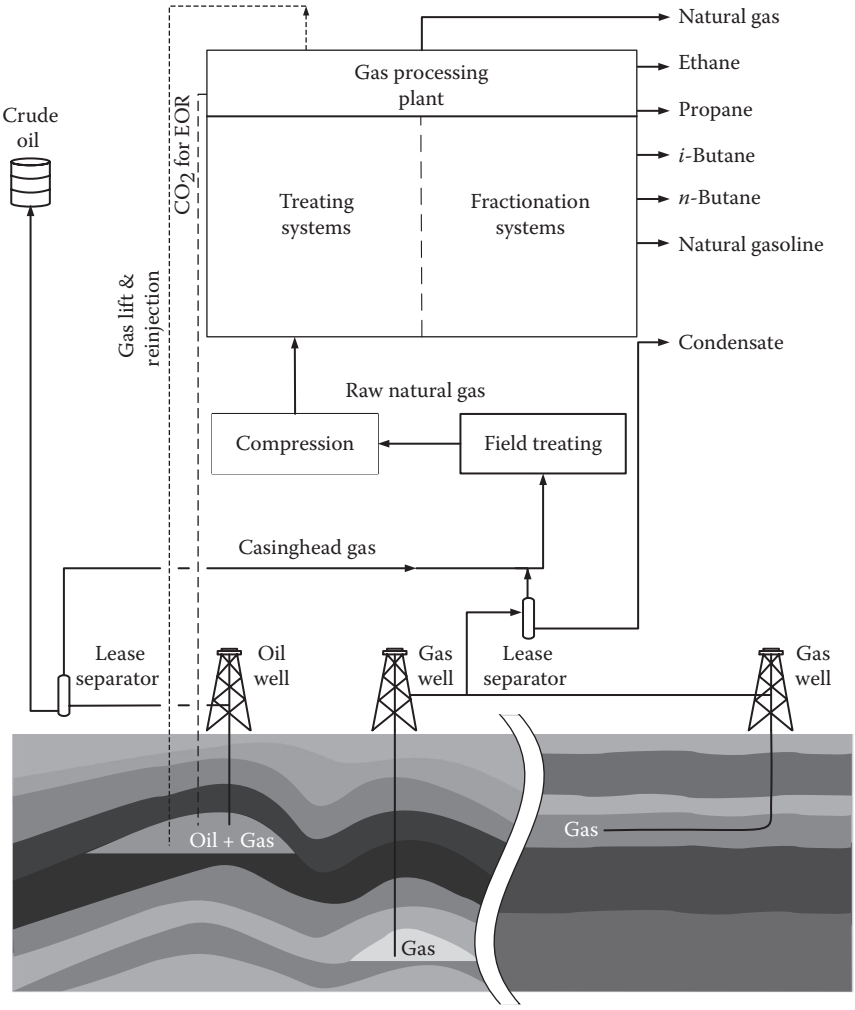


FIGURE 6.7 Schematic overview of natural gas gathering and processing. (Adapted from Cannon, 1993.)

In 2019, only the first three are economically viable resources. While these three resources may contain significant amounts of carbon dioxide, the authors found analyses reporting sulfur concentrations only in shale gas.

6.2.1.2.1 Tight Gas

A tight gas reservoir is generally considered any low-permeability gas sandstone reservoir requiring artificial stimulation to be commercially productive. In the United States, the legal definition is a reservoir of less than 0.1 millidarcy (10^{-4} μm^2) permeability and usually having a porosity of 10% or less (Coleman, 2008). See Nelson (2009) and Nelson and Batzle (2006) for more information.

The size of the pores between the voids dictates the permeability. According to Nelson (2009), a cap, or sealing, rock has median pore throat-sizes of ~0.05 μm or less, which yields very low permeability. Conventional reservoir rock has a median pore size of ~2.0 μm or higher, 40 times that of the cap rock. A 1 μm specification for pore throat-size is considered the approximate transition between low-grade conventional-reservoir rocks and tight gas sandstones.

Table 6.2 compares representative median pore throat-sizes of the different reservoir materials with the molecular diameter of methane, the most common molecule in natural gas. The ratio of

TABLE 6.2
Comparison of Reservoir Pore Throat Diameters to that of Methane

Material	Representative Median Pore Diameters for Rocks and Molecular Diameter for CH_4 (μm)	Ratio of Median Pore Diameter to CH_4 Diameter
Conventional reservoir rocks	>2	>5,000
Tight gas sandstones	0.03–1	80–5,000
Shales	0.005–1	10–3,000
Methane	3.8×10^{-4}	1

Source: Nelson (2009).

the median pore diameter to the molecular diameter of methane is shown in column 3. At the lower limit for both sandstones and shales the pore throat diameters approach molecular sizes, and consequently flow in these materials is highly restricted.

Tight gas reservoirs differ from conventional reservoirs in several ways (Tight gas sands, 2008):

- Tight gas sands are continuous stacks of low-permeability sedimentary layers charged preponderantly with gas rather than oil.
- Drilling and production costs for tight gas reservoirs can be very high, because directional drilling and hydraulic fracturing to increase permeability are required.

6.2.1.2.2 Shale Gas

Gas from the Fredonia, New York well mentioned in the introduction was shale gas (Ground Water Protection Council and ALL Consulting, 2009). However, shale gas could not compete with conventional gas sources until recently. Both horizontal drilling and hydraulic fracturing of the shale formation permit reasonable production rates and make it an attractive resource. As pointed out, shale and tight formations have comparable permeabilities. However, they differ because the shale is organic and the voids have both trapped gas and adsorbed gas which provides more gas per unit volume of void space. With horizontal drilling, 6–8 horizontal wells drilled from a single well pad reach the same reservoir volume as 16 vertical wells. This reduces both cost and environmental concerns.

Shale gas requires large water volumes to provide the fracturing. Depending upon the formation, water consumption is 2–4 million gallons (7,000–15,000 m^3) per well. While this can pose problems in arid regions, it still is less than 1% of the water consumption in the areas with shale gas plays. Fracturing is accomplished with minimal contamination of existing ground water as well. Details discussed above come from a comprehensive report on shale gas in the United States (Ground Water Protection Council and ALL Consulting, 2009).

6.2.1.2.3 Coal Bed Methane

Coal originates from carbonization of plant matter, which initially is in the form of peat (Sanders, 1981). Coal beds contain large amounts of natural gas (usually called CBM, coal seam gas (CSG), or coal bed natural gas (CBNG)). The methane, formed during the formation of the coal, is adsorbed on grains of coal, kept from desorption by the overburden pressure and often the hydrostatic pressure of water, which fills the voids between coal grains (Bryner, 2004). This gas is produced in significant quantities by drilling into the coal seam and then lowering the coal seam pressure. Water may be produced in significant amounts along with the CBM. This produced water can pose a significant problem because it typically contains large quantities of dissolved solids that make it unfit for domestic or agricultural uses. Producers work with land owners to determine the best approach for handling the produced water (Bryner, 2004).

There are several major differences between CBM and conventional gas production:

- CBM is primarily adsorbed on the coal surface as well as being dissolved in water and as a free gas.
- CBM reservoir pressure must be reduced to produce significant quantities of gas whereas conventional gas production begins at high pressure and production declines with decreasing reservoir pressure.
- CBM reservoirs may produce large quantities of water initially, but water production declines with time compared to conventional wells, where water production increases over field life.
- CBM wells are typically shallow (<4,000 ft, 1,200 m) and on land, consequently, well drilling costs are low to moderate in comparison with conventional gas wells.

6.2.1.2.4 Gas Hydrates

Naturally occurring gas hydrates (see Chapter 8 for discussion of hydrates) exist at the ocean bottom and in sediments of permafrost regions, such as northern Canada, Siberia, and Alaska. They formed from gas seeping to the earth surface, where the pressure is high and the temperatures are relatively cold. The deep ocean floor is typically 40°F–42°F (4°C–5°C) with hydrostatic pressures well above hydrate formation pressures. Seas not warmed by ocean currents can be as low as 30°F (–1°C). A U.S. Geological Survey (USGS) fact sheet provides a good overview of natural gas hydrates and where they are found (Ruppel, 2018).

6.2.1.2.5 Other Sources

There are other lower volume sources of natural gas being recovered. Two of the most common are gob gas (coalmine methane (CMM)) from existing or abandoned coal mines and landfill gas. Both gas sources are collected. The gas, which has been contaminated with air, is used for energy generation or flared to reduce methane emissions. Methane is a greenhouse gas that is 25–36 times more effective than CO_2 at trapping heat in the atmosphere over 100-year period (EPA, 2018a).

Karacan et al. (2011) review the technology involved in recovering CMM. In 2015, 38.5 Tcf ($1{,}031 \times 10^6\,Nm^3$) of CMM was recovered (EPA, 2018b). The gas was upgraded to low-Btu pipeline gas, used for local power generation/burner fuel or just flared.

In 2016, there was about 278 Bcf ($7.44 \times 10^9\,Nm^3$) of landfill gas recovered in the United States, three-quarters of the gas was used in small, local power plants and generated about 0.3% of U.S. power (EIA, 2018c). The balance was used as low-Btu fuel gas or flared. In 2018, the EPA (2018a) stated that there were 623 sites recovering landfill gas and another 470 good candidates.

6.2.2 Resource

The total proven gas reserves were 6,832 Tcf ($183.4 \times 10^{12}\,Nm^3$) for world and 308.5 Tcf ($8.2 \times 10^{12}\,Nm^3$) for the United States at the end of 2017 (BP p.l.c., 2018). At year-end 2016, the total estimated technically recoverable gas resource in the United States was 2,817 Tcf ($75.64 \times 10^{12}\,Nm^3$) (Potential Gas Committee, 2017), which excludes proven reserves. What fraction can be recovered depends upon price and drilling technology.

6.2.2.1 Conventional

Figure 6.8 shows the continual decline of conventional natural gas well production within the United States, and how important shale gas has become. Note that nonhydrocarbon gas volumes have decreased since shale gas and tight gas production increased.

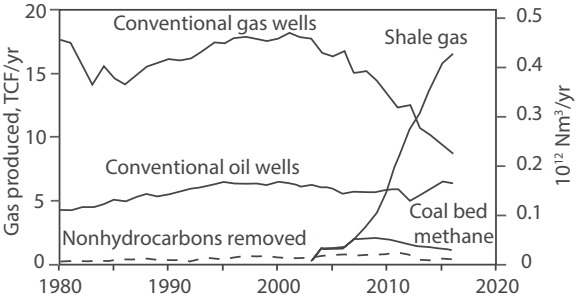


FIGURE 6.8 Sources of natural gas and nonhydrocarbon gases removed in the United States between 1968 and 2016 (Energy Information Administration, 2018d).

6.2.2.2 Shale Gas and Tight Gas

Table 6.3 shows estimated reserves of most important unconventional gas sources around the world. Although the United States has only about 15% of the reserves, it produces the majority of the shale gas and tight gas. Table 6.4 lists the major U.S. shale plays and their production and reserves at the end of 2016. The Marcellus play produced 37% of the shale gas and holds over 40% of the shale gas plus tight gas reserves. This production close to large gas-consuming areas caused a major shift in gas flows in North America. Pipeline infrastructure once used to transport gas to the Northeast United States has been modified to reverse the direction of flow or converted to alternate use.

Figure 6.9 shows both non-shale gas and shale gas production with projections to 2050. (The EIA reports shale gas as a combination of shale gas and tight gas.) During the period 1998 through 2016, production from unconventional reservoirs increased from 5.4 to 16.6 Tcf/year ($150–445 \times 10^9$ Nm^3), a 200% increase. These increases were due principally to gas prices and improved drilling with hydraulic fracturing techniques that allowed development of reserves previously uneconomical.

6.2.2.3 Coal Bed Methane

Table 6.3 shows potential 4,052 TCF (109×10^{15} Nm^3) of CBM reserves in the world and 1,629 TCF (43.6×10^{15} Nm^3) within the United States. Figure 6.8 shows U.S. production increasing in the early 2000s but then started to decline as gas prices dropped, shale gas became more competitive, and the problem of produced water was exploited by opponents. Bleizeffer (2015) discusses CBM production and its rise and fall in the Powder River Basis of Wyoming. The EPA (2010) provides a good overview of CBM production in the United States, including some economics.

TABLE 6.3
Estimated Unconventional Gas Reserves (TCF) (Divide by 37.32 to Obtain 10^{12} Nm^3)

Region	CBM	Tight Gas	Shale Gas
Australia-Asia	1,348	6,253	10,291
North America	1,629	10,784	18,318
Commonwealth of Independent States	859	28,604	45,343
Latin America	13	3,366	7,122
Middle East	9	15,447	30,872
Europe	176	3,525	5,895
Africa	18	4,000	7,901
World	4,052	71,981	125,742

Source: Dong et al. (2012).

TABLE 6.4
Major U.S. Shale Plays Production and Reserves in 2017

Basin	Shale Play	State(s)	Production TCF/ (10^6 Nm^3)	Reserves TCF/ (10^6 Nm^3)
Appalachian	Marcellus[a]	PA,WV	6.9 (185)	123.8 (3,316)
Texas-Louisiana Salt	Haynesville/Bossier	TX, LA	1.8 (48)	35.9 (961)
Permian Basin	Wolfcamp, Bone Spring	NM, TX	2.2 (59)	31.9 (854)
Western Gulf	Eagle Ford	TX	1.9 (51)	27.4 (734)
Appalachian	Utica/Pt. Pleasant	OH	1.7 (46)	26.5 (710)
Anadarko, S. OK	Woodford	OK	1.3 (35)	22.5 (603)
Fort Worth	Barnett	TX	1.2 (32)	19.2 (514)
Arkoma	Fayetteville	AR	0.6 (16)	7.1 (190)
Other shale plays			1.0 (27)	13.6 (364)
All U.S. shale			18.6 (498)	307.9 (8,248)

Source: Energy Information Administration (2018g).
[a] Marcellus shale play refers only to portions within Pennsylvania and West Virginia.

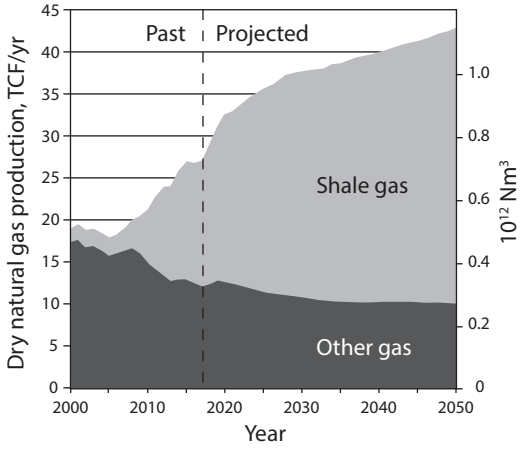


FIGURE 6.9 U.S. shale + tight gas and other gas production with estimates to 2050 (Energy Information Administration, 2018b).

6.2.2.4 Gas Hydrates

Global estimates of hydrates are 106,000–876,000 Tcf ($3–23.4 \times 10^{15}$ Nm^3) (Boswell and Collett, 2011). The USGS estimates about 51,338 Tcf (1.4×10^{15} Nm^3) of methane in hydrates in the Atlantic and Pacific oceans and Gulf of Mexico in the lower United States (Ruppel, 2018). An estimated 45 Tcf (1.2×10^{12} Nm^3) in gas hydrates is on the North Slope of Alaska, where oil is currently produced (Collett, 2001). These reserves would be the most economically attractive to produce, because the hydrates are concentrated, and much of the infrastructure for gas processing already exists. However, for the gas to reach the market, a pipeline must be built. As of 2019, there were no known commercial projects to produce naturally occurring gas hydrates. However, there are active programs assessing their potential. Descriptions of some of the U.S. programs are available from the Department of Energy (National Energy Technology Laboratory, Undated). China (Anonymous, 2018), Japan (Anonymous, 2017), and India (Collett et al., 2015) have ongoing programs to produce gas hydrates.

6.2.3 Gas Compositions

6.2.3.1 Conventional Natural Gas Compositions

Wellhead natural gas compositions vary so widely from field to field and from resource to resource that it is not possible to discuss a typical gas, but only to present examples of gases from different categories and reservoirs.

Table 6.5 shows a few conventional gas compositions. Note that water is almost always present at wellhead conditions but rarely reported. There are a few gas fields that contain no water, but unless the gas is dehydrated before reaching the gas processing plant, the common practice is to assume that the gas is water saturated entering the plant.

Water typically is not reported for several reasons. First, if liquid water is present with the gas stream, the water content will depend upon temperature and pressure of the gas being sampled, and the sample container. Second, it is extremely difficult to obtain an accurate, representative sample, and analysis of water in a gas. Water readily adsorbs on sample cylinder walls and tubing between sample cylinder and gas chromatographs, producing inaccurate analytical results.

Some gas plants receive feeds from refineries. These streams differ substantially from natural gases in that they can contain hydrogen, propylene, and butylene. They may also contain trace amounts of undesirable nitrogen compounds and fluorides. This book considers only the processing of gas and liquids coming directly from gas and oil leases.

There are a number of noteworthy features in Table 6.5:

- Gas compositions vary substantially from region to region and within the same region.
- Hydrocarbons present in natural gas are primarily alkanes (paraffins). This is typical of all conventional and unconventional natural gases. Straight chain unsaturated hydrocarbons (those possessing double or triple bonds) are never present, but aromatic compounds (e.g., benzene) are found in small amounts. Associated gases typically have higher concentrations of aromatics than nonassociated gas. When present, aromatics can pose a significant environmental problem. This is discussed in more detail in Chapter 14.
- Concentrations of ethane and heavier alkanes typically decrease with increasing carbon number.
- Normally, the only nonhydrocarbons present in significant quantities are water, helium, nitrogen, carbon dioxide, and sulfur compounds, predominantly hydrogen sulfide. Trace

TABLE 6.5
Example Gas Compositions (mol%)

	Canada (Alberta)	Western Colorado	Kansas	Wyoming	Miskar Field Tunisia	Rio Arriba County, New Mexico	Cliffside Field, Amarillo, Texas
Helium	0.0	0.0	0.45	0	0.00	0.0	1.8
Nitrogen	3.2	26.10	14.65	0	16.91	0.68	25.6
Carbon dioxide	1.7	42.66	0.0	20	13.59	0.82	0.0
Hydrogen sulfide	3.3	0.0	0.0	12	0.09	0.0	0.0
Methane	77.1	29.98	72.89	68	63.92	96.91	65.8
Ethane	6.6	0.55	6.27	—	3.35	1.33	3.8
Propane	3.1	0.28	3.74	—	0.96	0.19	1.7
Butanes	2.0	0.21	1.38	—	0.54	0.05	0.8
Pentanes and heavier	3.0	0.25	0.62	—	0.63	0.02	0.5

Source: U.S. Bureau of Mines (1972); Jones, S. et al. (1999).

amounts of mercaptans, sulfides, disulfides, and elemental sulfur may be present, especially if hydrogen sulfide concentration is more than about 2 mol%.
- Trace components, e.g., mercury, sulfur compounds other than hydrogen sulfide, are excluded from table. These are discussed more in Section 6.2.4 and in Chapter 14.

6.2.3.2 Shale Gas

Table 6.6 shows representative compositions for six of the major U.S. shale plays. Although not shown, some can contain significant amounts of C_2^+ (Because natural gas consists of alkane [paraffinic or saturated hydrocarbons], a common way to write gas components is C_1 for methane, C_2 for ethane, and so forth. Then, C_2^+ means ethane plus all higher hydrocarbons). Some gases have high nitrogen or carbon dioxide levels. Many shale plays have little or no hydrogen sulfide but up to 12% hydrogen sulfide has been found in parts of the western Canada Montney play (Giacomin, 2018).

Authors have reported that shale gas does not contain significant amounts of C_3^+ hydrocarbons but this depends upon the formation. Table 6.7 shows gas samples from five leases producing from the

TABLE 6.6
Example Shale Gas Compositions (mol%)

	Barnett[a]	Marcellus[a]	Fayetteville[b]	New Albany[a]	Antrim[a]	Haynesville[b]
N_2	2.9	0.4	0.7	—	29.0	0.1
CO_2	1.7	0.4	1.0	7.9	3.8	4.8
CH_4	86.8	85.2	97.3	89.8	62.0	95.0
C_2H_6	6.7	11.3	1.0	1.1	4.2	0.1
C_3H_8	2.0	2.9	0	1.1	1.1	0

Source: Bullin and Krouskop (2009).

[a] Values are the averages of compositions for four wells reported.

[b] Values are averages for one well.

TABLE 6.7
Representative Marcellus Shale Gas Compositions (mol%)

	Lease				
Component	**No. 1**	**No. 2**	**No. 3**	**No. 4**	**No. 5**
N_2	0.357	0.445	0.341	0.309	0.6955
CO_2	0.194	0.178	0.098	0.169	0.144
C_1	80.980	72.123	94.157	80.759	75.655
C_2	13.238	16.235	4.585	12.377	14.457
C_3	3.438	6.339	0.513	3.730	5.159
iC_4	0.431	0.775	0.070	0.681	0.744
nC_4	0.742	1.878	0.070	0.951	1.471
iC_5	0.199	0.471	0.041	0.341	0.478
nC_5	0.156	0.571	0.024	0.215	0.395
C_6^+	0.265	0.986	0.101	0.468	0.802
Total	100.000	100.000	100.000	100.000	100.000
GPM (C_2^+ m^3 liquid/1,000 Nm^3 gas)	5.22 (0.74)	7.72 (1.09)	1.47 (0.21)	5.26 (0.74)	6.64 (0.94)

TABLE 6.8
San Juan Basin Coal Bed Gas Composition

Component	mol%
Methane	88.0
Ethane	0.4
NGL	0.0
Carbon dioxide	11.6
Hydrogen sulfide	0.0
Nitrogen	0.0

Source: Anderson (1992).

Marcellus shale. Extended analysis of these samples showed hydrocarbons up to tetradecane. The high C_2^+ content of some Marcellus shale gases requires their processing before they enter the pipeline grid.

6.2.3.3 Coal Bed Methane

As is the case with conventional natural gas, the composition of the CBM produced varies widely. Table 6.8 shows a CBM gas composition from the Western United States. More compositional analyses can be found in Eble et al. (2005) and Kim (1973). In addition to methane, these gases may contain as much as 20% ethane and heavier hydrocarbons. Poorer quality gas may contain up to 20% carbon dioxide and 20% nitrogen. However, CBM gas is water saturated and predominately methane. Eble, C., Private Communication (2018) states that gases rich in higher hydrocarbons tend to be found in the beds of higher ranking coals. He also notes that no sulfur compounds have been detected in the U.S. CBM, even in high-sulfur coal beds.

6.2.4 Impurities

In addition to the major nonhydrocarbon components in natural gas (nitrogen, carbon dioxide, helium, and hydrogen sulfide) listed in Table 6.8, there are a number of minor but important impurities that may be present.

Water: Most gas produced contains water, which must be removed. Concentrations range from trace amounts to saturation.

Sulfur species: If the hydrogen sulfide (H_2S) concentration is greater than 2%–3%, carbonyl sulfide (COS), carbon disulfide (CS_2), elemental sulfur, organic sulfides, and mercaptans may be present.

Mercury: Trace quantities of mercury may be present in some gases; levels reported vary from 0.01 to 180 μg/Nm^3. Because mercury can damage the brazed aluminum heat exchangers used in cryogenic applications, conservative design requires mercury removal to a level of 0.01 μg/Nm^3 (Traconis et al., 1996).

NORM: Naturally occurring radioactive materials (NORM) may also present problems in gas processing. The radioactive gas radon can occur in wellhead gas at levels from 1 to 1,450 pCi/L (40–55,000 Bq/m^3) (Gray, 1990).

Oxygen: Some gas-gathering systems in the United States operate below atmospheric pressure. As a result of leaking pipelines, open valves, and other system compromises, oxygen is an important impurity to monitor. A significant amount of corrosion in gas processing is related to oxygen ingress. Additionally, flow back from wells hydraulically fractured are known to contain levels of oxygen.

Chapters 11 and 15 address dehydration and Chapters 10 and 15 discuss sulfur compound removal. Chapter 14 provides additional information on the last three impurities as well as methanol and arsenic.

6.3 CLASSIFICATION

Natural gases commonly are classified according to their liquids content as either lean or rich and according to the sulfur content as either sweet or sour. This section provides some quantification of these qualitative terms.

6.3.1 Liquids Content

Gas composition plays a critical role in the economics of gas processing. The more liquids, usually defined as C_2^+, in the gas, the "richer" the gas. These NGL products often have a higher sales value as a liquid than if left in natural gas. Normally NGL components must be removed to meet heating value specifications on the pipeline gas and avoid condensation in gas pipelines.

To quantify the liquids content of a natural gas mixture, the industry uses GPM, or gallons of liquid per 1,000 standard cubic feet (Mscf) of gas. (In metric units, the quantity is commonly stated as m^3 of liquid per 1,000 m^3 of gas. One GPM = 0.141 m^3 per 1,000 Nm^3). The term usually applies to ethane and heavier components (C_2^+) but sometimes applies to propane and heavier components (C_3^+). Determination of the GPM requires knowledge of the gas composition on a mole basis and the volume of liquid per mole of the components. Table B.1[3] provides the volume values commonly used in gas processing. Note that a number of components, including ethane are not liquid at 60°F (15.6°C) and 14.7 psia (1.01325 bara), so the values are hypothetical values accepted throughout the industry. Also, the actual volume of liquid obtained from a gas will be less than the GPM value because complete recovery of ethane is impractical for two reasons:

1. *Cost*: The low temperature and high compression energy required generally makes recovery of more than about 95%–99% of the ethane uneconomical. Higher ethane recovery plants also have higher recovery of propane and heavier components.
2. *Heating value specifications*: As discussed below, a specification applies to the heating value of sales gas. If the gas contains nonflammable diluents (i.e., N_2 and CO_2), hydrocarbons, in addition to methane, often must be in the gas to obtain the required heating value.

Example 6.1

Calculate the GPM (m^3 per 10^3 Nm^3) of the Alberta gas given in Table 6.5.

Solution

For clarity, this example is worked only in USES. Computation of the GPM requires summation of the product of the number of moles of each component in 1,000 scf of gas by the gallons of liquid per mole for that component.

Basis: 1,000 scf of gas.

A lb-mol of gas at standard conditions has a volume of 379.49 ft^3. This volume translates into 1,000/379.49, or 2.6351 lb-mol for 1,000 scf. This value is multiplied by the mole fraction of each component in the gas and by the gallons of liquid for each mole of a component (Table B.1). Table 6.9 summarizes the calculations.

For this example, the gal/mol for butanes was taken as the average of isobutane and *n*-butane; the value for C_5^+ was taken to be that of pure *n*-pentane. The resulting GPM for this gas is 4.34 (0.613 m^3 liquid/1,000 Nm^3 gas).

[3] See Appendix B on publisher website: www.crcpress.com/Fundamentals-of-Natural-Gas-Processing-Third-Edition/Kidnay-Parrish-McCartney/p/book/9781138612792

TABLE 6.9
Calculation of GPM of Alberta Gas

	mol%	mol	gal/mol	GPM
Helium	0	0.0000	0	0
Nitrogen	3.2	0.0843	0	0
Carbon dioxide	1.7	0.0448	0	0
Hydrogen sulfide	3.3	0.0870	0	0
Methane	77.1	2.0317	0	0
Ethane	6.6	0.1739	10.123	1.760
Propane	3.1	0.0817	10.428	0.852
Butanes	2.0	0.0527	12.160	0.641
Pentanes and heavier	3.0	0.0791	13.721	1.085
Totals	100.0	2.6351		4.338

The terms rich and lean refer to the amount of recoverable hydrocarbons present. The terms are relative, but a lean gas will usually be about 1 GPM, whereas a rich gas may contain three or more GPM. Thus, the gas described above is considered fairly rich. In regions where there is no ready ethane market, GPM is sometimes stated on a propane plus (C_3^+) basis. For this example, the C_3^+ GPM is 2.58 (0.365 m^3 liquid/1,000 Nm^3 gas).

6.3.2 Sulfur Content

Sweet and sour refer to the sulfur (generally H_2S) content. A sweet gas contains negligible amounts of H_2S, whereas a sour gas has unacceptable quantities of H_2S, which is toxic, odiferous, and corrosive. Again, the terms are relative, but generally, sweet means the gas contains less than 4 ppmv (0.25 grains/100 scf, 6 mg/Nm^3) of H_2S, the amount of H_2S allowable in pipeline-quality gas.

When present with water, H_2S is corrosive. The corrosion products are iron sulfides, FeS_x, a fine black powder, which in some situations is pyrophoric. Several papers discuss the black powder problem in pipelines and in metering (Khan et al., 2015; Sherik, 2008; Tsochatzidis, 2008).

6.4 PRINCIPAL PRODUCTS AND MARKETS

The two primary uses for natural gas are as a fuel and as a petrochemical feedstock, and consequently, the three basic reasons for processing raw natural gas are:

- *Purification*: Removal of materials, valuable or not, that inhibit the use of the gas as an industrial or residential fuel.
- *Separation*: Splitting out of components that have greater value as petrochemical feedstocks (e.g., ethane), stand-alone fuels (e.g., propane), or industrial gases (e.g., helium).
- *Liquefaction*: Increase of the energy density of the gas for storage or transportation.

Figure 6.10 provides a simplified overview of the materials present in natural gas and a slate of possible products and contaminants removed in gathering and gas processing.

The obvious use of raw natural gas is the production of pipeline-quality gas for distribution to residential and industrial consumers for fuel. Raw natural gas is also the primary source of lighter hydrocarbons used as chemical feedstocks and fuel.

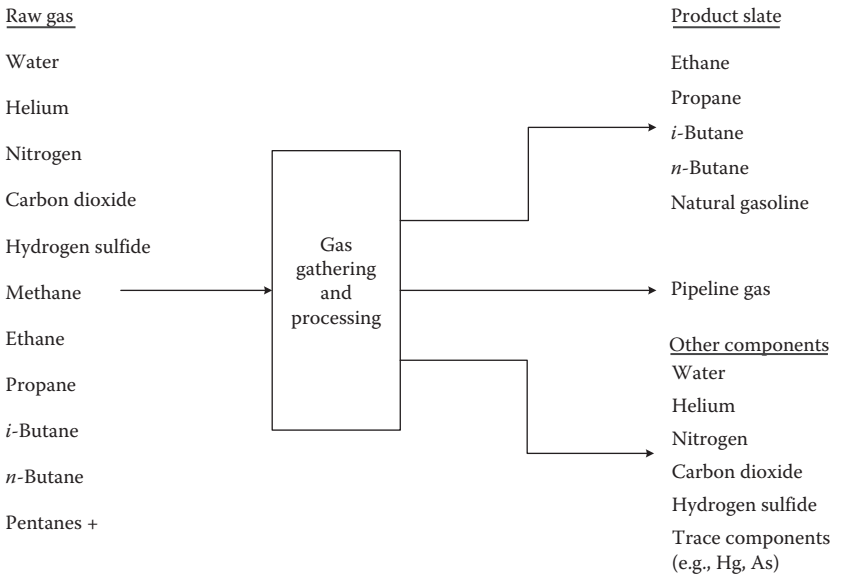


FIGURE 6.10 Generic raw gas and product slate.

6.4.1 Methane

The principal use of methane is as a fuel; it is the dominant constituent of pipeline-quality natural gas. Considerable quantities of methane are used as feedstock in the production of fertilizer and industrial chemicals, principally ammonia and methanol.

6.4.2 Ethane

The majority of the ethane used in the United States comes from natural gas plants; petroleum refineries account for the remainder. Ethane is used in the production of ethylene, the feedstock for polyethylene. Through August, 2018, 99.6% of ethane produced in the United States in 2018 came from natural gas and the balance from refineries (Energy Information Administration, 2018e). Starting in 2014 the United States began exporting ethane; through first 6 months of 2018 just over 12% of production was exported. During the same period, 98% of the remaining U.S. ethane production went to ethylene production, while 2% was blended into liquefied petroleum gas (LPG) a mixture of propane and butane with small amounts of ethane.

6.4.3 Propane

Natural gas plants provided 74% of propane in first 6 months of 2018, refineries provided 18%, and imports provided 8%. However, almost 55% of the propane generated was exported. Exports have occurred for a number of years but began increasing in 2011 and continued increasing in 2017 (Energy Information Administration, 2018e). The principal uses in the United States are petrochemical (49%), residential and commercial (40%), farm (5%), industrial (3%), and transportation (3%) (Energy Information Administration, undated).

Propane furnishes a portion of the feedstock for ethylene production. Because propane production in gas plants and refineries is directly tied to the volume processed, it is difficult to adjust the propane supply to meet changes in supply or demand.

A grade of propane, called HD-5, is sold as fuel in North America. It contains limited amounts of ethane and butanes. This product must meet GPA specifications for composition and vapor pressure. Table 6.11 provides these specifications.

6.4.4 Ethane–Propane Mix

When NGL is fractionated into various hydrocarbon streams, an ethane–propane mix (E–P mix) is sometimes produced as a chemical feedstock. This permits olefin crackers to simultaneously produce both ethylene and propylene for polymer production.

6.4.5 Isobutane

There are three sources of isobutane; natural gas plants, petroleum refineries, and isomerization plants that convert n-C_4 to i-C_4. The primary market for isobutane is as a feedstock for refinery alkylation plants. In the 2009–2018 time period, refineries have relied on non-refinery sources for the isobutane.

6.4.6 *n*-Butane

Natural gas plants and petroleum refineries account for all U.S. production of *n*-butane. Domestic usage is predominantly in motor gasoline, either as a blending component or through isomerization to isobutane, which is then used in making alkylate for motor gasoline. Specially produced mixtures of butanes and propane have replaced halocarbons as the preferred propellant in aerosols.

6.4.7 Natural Gas Liquids

NGLs include all hydrocarbons liquefied in the field or in processing plants, including ethane, propane, butanes, and natural gasoline. When such mixtures are produced in gas plants and shipped as a mixture, they are usually referred to as "Y-grade" or "raw product." EIA provides a definition of NGL (Energy Information Administration, 2012).

6.4.8 Natural Gasoline

Natural gasoline, a mixture of hydrocarbons that consist mostly of pentanes and heavier hydrocarbons and meet GPA product specifications, should not be confused with NGL, a term used to designate all hydrocarbon liquids produced in field facilities or in gas plants.

The major uses of natural gasoline are in refineries, for direct blending into gasoline and as a feedstock for C_5/C_6 isomerization. It is used in the petrochemical industry for ethylene production. Another market is as a heavy oil sands diluent.

In addition to natural gasoline, gas plants may produce "stabilized condensate." This liquid can come directly from the field or from a plant condensate stabilizer. It often contains color bodies, which make it fail natural gasoline specifications (*Engineering Data Book*, 2016; Gas Processors Association, 2014a).

6.4.9 Sulfur

In the United States, all sulfur production is the result of environmental measures to reduce the sulfur content of fuels and emissions from nonferrous metal smelters. This results in an unusual supply–demand situation. Sulfur production is due to environmental considerations and is a byproduct of the main process. Thus, production rates are independent of sulfur demand. Sulfur production in the United States has been decreasing slightly in the 2013–2017 period and is expected to remain relatively constant in near future (U.S. Geological Survey, 2018).

6.5 PRODUCT SPECIFICATIONS

6.5.1 Natural Gas

While raw natural gas compositions vary considerably from location to location, there are specifications for the sales gas in terms of both composition and performance criteria. These criteria include Wobbe Number, heating value, and combustion emission products. There also are specifications on total inerts, water, and oxygen, which are important for maintaining pipeline integrity and efficiency.

Specifications are established in contract negotiations and no firm, accepted standards exist for all gas deliveries in the United States. Consequently, values for pipeline-quality gas listed in Table 6.10 are typical but not definitive. However, many other countries have established standards. Section 6.6.2 discusses Wobbe Number specifications.

Trace condensation is a problem in some situations and leads to a hydrocarbon dew point specification (NGC+ Liquid Hydrocarbon Dropout Task Group, 2004). This occurs when it is economically attractive to keep more of the C_2^+ fraction in the sales gas or when "rich" LNG is vaporized into the pipelines (see Chapter 18). Beginning in 2008, GPA conducted a study to determine the "practical" dew point of a gas (Bullin and Fitz, 2011).

6.5.2 Liquid Products

As with gases, specifications for liquid products are based upon both composition and performance criteria and set by contracts. For liquid products, the performance specifications include Reid vapor pressure (see Section 1.7 for details of this specification), water, CO_2, H_2S, and total sulfur content.

TABLE 6.10
Typical Pipeline-Quality Gas in North America

Major Components	Minimum (mol%)	Maximum (mol%)
Methane	75	None
Ethane	None	10
Propane	None	5
Butanes	None	2
Pentanes and heavier	None	0.5
Nitrogen	None	3
Carbon dioxide	None	2–3
Total diluent gases	None	4–5
Trace Components		
Hydrogen sulfide		0.25–1.00 grains/100 scf (6–24 mg/Nm^3)
Total sulfur		5–20 grains/100 scf (120–480 mg/Nm^3)
Water vapor		4.0–7.0 lb$_m$/MMscf (68–120 mg/Nm^3)
Oxygen		1.0%
Other Characteristics		
Heating value (gross, saturated)		950–1,150 Btu/scf (37.4–45.3 MJ/Nm^3)
Liquids	Free of liquid hydrocarbons at delivery temperature and pressure	
Solids	Free of particulates in amounts deleterious to transmission and utilization equipment (3–15 μm maximum)	

Source: Adapted from *Engineering Data Book* (2016), with permission.

TABLE 6.11
Major Components[a] and Vapor Pressures of Common Liquid Products

Liquid Product	Composition Liquid Volume (%)		Reid Vapor Pressure at 100°F, psig, max (at 37.8°C, kPa, max)
Fractionation grade ethane[b]	C_1	≤3	—
	C_2	≥95	
	C_3	≤5	
Fractionation grade ethane–propane mix[b]	C_1	≤1.5	—
	C_2	75–82	
	$C_2^=$	≤4	
	$C_3^=$	≤1	
	C_3	11.5–25	
	C_4^+	≤0.8	
Fractionation grade propane[b]	$C_3^=$	≤5	208[c]
	C_3	≥90	(1,434)
	C_4^+	≤2.5	
Propane HD-5[d]	$C_3^=$	≤5	208[c]
	C_3	≥90	(1,434)
	C_4^+	≤2.5	
Commercial propane[d]	C_3 and $C_3^=$	>50	208[c]
	C_4^+	<2.5	(1,434)
Fractionation grade isobutane[b]	C_3	≤3	70[c]
	i-C_4	≥95	(483)
	n-C_4	≤4	
Fractionation grade normal butane[b]	C_3	≤0.35	50[c]
	i-C_4	≤6	(345)
	n-C_4	≥94	
	C_5	≤1.5	
Fractionation grade natural gasoline[b]	*n*-C_4	≤6	14[e]
			(97)

[a] Throughout the book C_1, C_2, etc., refer to methane, ethane, etc. The "=" denotes an olefin. The term C_4^+ denotes butane and heavier compounds.
[b] Defined by GPA Standard 2108-14 (2014a).
[c] Vapor pressure as defined by ASTM D1267-18 (2018).
[d] Defined by GPA Standard 2140-17 (2017).
[e] Vapor pressure as defined by ASTM D323-15a (2015).

Safety considerations make vapor pressure especially important for the liquid products because of regulations for shipping and storage containers.

Table 6.11 gives major component and vapor-pressure specifications for common liquid products. Table 6.12 presents upper limits of common contaminants, but actual specifications vary, depending upon contractual agreement. However, as Table 6.12 indicates, the water level in some propane products must pass a dryness test (ASTM D2713-15e1, 2015), which ensures that the water content is sufficiently low (<25 ppmw) to avoid hydrate formation when water is vaporized through an orifice (see Chapter 8). Complete specifications for LPG products, which include other minor component limitations, are available in GPA Standard 2140 (2017).

TABLE 6.12
Maximum Levels of Major Contaminants of Common Liquefied Products

	H_2S	Total Sulfur[a]	CO_2	O_2	H_2O
High ethane raw streams	#1	200	3,500		No free[b]
Ethane–propane mixes	#1	123	1,000	1,000	No free[b]
High purity ethane	#1	30	1,000	5	No free[b]
Commercial propane	#1	100	—	—	Pass test[c]
Commercial isobutane and butane	#1	140	—	—	—
Commercial butane–propane mixes	#1	140	—	—	—
Propane HD-5	#1	123	—	—	Pass test[c]

Source: *Engineering Data Book* (2016).

Note: Concentrations are in ppmw unless specified otherwise.

[a] Concentration acceptable *provided* the copper strip test, which detects all corrosive compounds, is passed. The #1 represents the passing score on the copper strip test (ASTM D1838-16, 2016). Eckersley and Kane (2004) discuss sample handling problems related to the test.

[b] Limit is no free water present in product.

[c] Moisture level must be sufficiently low to pass the ASTM D2713-151e (2015), which corresponds to roughly 25 ppmw.

6.6 COMBUSTION CHARACTERISTICS

6.6.1 Heating Value

The principal use of processed natural gas is as a fuel, and consequently, pipeline gas is normally bought and sold (custody transfer) on the basis of its heating value. Procedures for calculating the heat effect in any chemical reaction are found in standard texts on thermodynamics (e.g. Smith et al., 2018).

Determination of the heating value of a fuel involves two arbitrary but conventional standard states for the water formed in the reaction:

1. All the water formed is a liquid (gross heating value, frequently called higher heating value (HHV)).
2. All the water formed is a gas (net heating value, frequently called lower heating value (LHV)).

Lower heating value is used in calculating heat rates for gas turbines, engines, and fired equipment. The gas industry always uses the gross heating value in custody transfer. Obviously, the numerical difference between the two heating values is the heat of condensation of water at the specified conditions. Both states are hypothetical because the heating value is normally calculated at 60°F and 14.7 psia (0°C and 1.01 bara for Nm^3 basis, 15°C and 1.01 bara for Sm^3), standard conditions for the gas industry, and thus, at equilibrium, the water would be partially liquid and partially vapor. A common practice is to use GPA 2172 (Gas Processors Association, 2014b) to calculate values that corrects for nonideal behavior.

Heating values for custody transfer are determined either by direct measurement, using combustion calorimetry, or by computation of the value on the basis of gas analysis. The method is set in the sales contract. The computation method is now the most common method.

The formulas for the calculation of ideal gas gross heating values, on a volumetric basis are

$$H_v^{id}(\text{dry}) = \sum_{i=1}^{n} y_i H_{vi}^{id}, \tag{6.1}$$

$$H_v^{id}(\text{sat}) = (1 - y_w) \sum_{i=1}^{n} y_i H_{vi}^{id}. \tag{6.2}$$

The equations assume that the gas analysis is given on a dry basis, that H_{iv}^{id} is the ideal gross heating value (see Table B.1), and that the mole fraction of water is y_w when the gas is saturated at the specified conditions. The mole fraction can be calculated from

$$y_w = \frac{P_w^{\text{Sat}}}{P_b}. \tag{6.3}$$

where P_w^{sat} is the vapor pressure of water at base temperature and P_b is the base pressure selected for the calculations. The vapor pressure of water at 60°F (15.6°C), the common base temperature, is 0.25640 psia (1.76782 kPa) (GPA Standard 2172-14, Gas Processors Association, 2014b). For the United States some commonly used base pressures, P_b, which are set in sales contracts, and the values of $(1 - y_W)$ are listed below.

P_b (psia)	$1 - y_W$
14.50	0.9823
14.65	0.9825
14.696	0.9826
14.73	0.9826
15.025	0.9829

The situation with water is further complicated by the fact that gas analyses are normally given on a dry basis, even though the gas may be partially or fully saturated with water. Consequently, heating value may be calculated on a dry basis, wet (saturated) basis, or, if the water content is known, a partially saturated basis.

A complete discussion of heating value calculations, including correction of the ideal gas values to the real gas state by use of calculated compressibility factors (z), is available in GPA Standard 2172-14 (Gas Processors Association, 2014b).

Example 6.2

Calculate the heating value of the Alberta, Canada gas in Table 6.5 assuming the heating value for the butanes is that of isobutane, and the C_5^+ fraction is pure hexane.

Solution

Table 6.13 shows the calculations with heating values obtained from Table B.1. Note that Table 6.13 does not include the H_2S shown in Table 6.5 because H_2S must be removed prior to any product sales. Note also that composition values for the components have been renormalized to account for the removal of H_2S. This mixture has a gross heating value of 1221.5 Btu/scf (48.104 MJ/Nm^3).

TABLE 6.13
Calculations with Heating Values Obtained from Appendix B

	mol%	H_{vi}^{id} Btu/scf	$x_i H_{vi}^{id}$
Nitrogen	3.3	0.0	0
Carbon dioxide	1.8	0.0	0
Methane	79.7	1010.0	805.0
Ethane	6.8	1769.7	120.3
Propane	3.2	2516.1	80.5
Butanes as isobutane	2.1	3251.9	68.3
Pentanes and heavier as hexane	3.1	4755.9	147.4
Total	100.0		1221.5

6.6.2 Wobbe Number

In any gas burner, the combustion characteristics of the gas must remain constant regardless of gas composition. Several combustion factors must be considered, but one of the more important is maintaining the same heat release at the burner for a given pressure drop through a fixed orifice. This combustion characteristic is measured by the Wobbe Number or Wobbe Index, defined as the gross heating value (Btu/scf or MJ/Nm^3) of the gas divided by the square root of the specific gravity (also called relative density, the ratio of the density of the gas divided by the density of air (see section 1.3.3.1.2 for specific gravity calculation); both densities evaluated at the same pressure and temperature). The specific gravity corrects for flow through an orifice. Two gases with the same Wobbe Number are interchangeable as far as heat release at the burner is concerned.

$$W_B = \frac{\left(\text{Gross heating value}\right)}{\sqrt{\text{Specific gravity}}}. \tag{6.4}$$

The Wobbe Number is calculated from the gross heating value and specific gravity of the mixture, not from an average of the Wobbe Numbers of the constituents of the mixture. The Wobbe Number normally has a value between 1,100 and 1,400 Btu/scf (43.3–55.1 MJ/Nm^3), in the United States (NGC+ Liquid Hydrocarbon Dropout Task Group, 2004). Whereas the United States is fairly consistent in Wobbe Number specification, the value varies greatly in the rest of the world (Williams, 2007). Even within the EU, values vary between countries, and gas appliances purchased in one country may not perform properly in another country.

Some typical Wobbe Numbers are

Methane	**1,360 Btu/scf (53.56 MJ/Nm^3)**
Ethane	1,740 Btu/scf (68.53 MJ/Nm^3)
Propane	2,044 Btu/scf (80.50 MJ/Nm^3)
80% methane + 20% ethane	1,443 Btu/scf (56.83 MJ/Nm^3)
95% methane + 5% ethane	1,381 Btu/scf (54.39 MJ/Nm^3)

Wobbe Numbers are sometimes adjusted by blending natural gas with air. For example, one U.S. distribution company maintains a Wobbe Number between 1,130 and 1,280 Btu/scf (44.50–50.41 MJ/Nm^3) for gas distribution to its residential customers by blending air with the natural gas in three blending stations. A typical set of operating conditions for one of the air-blending stations is given below.

Inlet Wobbe Number	1,335 Btu/scf (52.58 MJ/Nm³)
Inlet heating value	1,080 Btu/scf (42.53 MJ/Nm³)
Inlet specific gravity	0.654
Normal outlet Wobbe Number	1,210 (47.65 MJ/Nm³)
Peak day outlet Wobbe Number	1,280 (50.41 MJ/Nm³)

Because air blending lowers the heating value of the gas, a balance must be maintained between the Wobbe Number and the gross heating value.

DISCUSSION QUESTIONS

1. What features of natural gas make it attractive as a clean fuel?
2. Considering past, present, and future, what role do you think natural gas plays in your country's energy needs and how do you think it affects the foreign polices with other nations, both rich and poor in the resource?
3. Unconventional gas resources were discovered before conventional resources. Why were they not extensively developed until recently?
4. How do the reservoirs for the three commercially viable unconventional gases differ in terms of reservoir characteristics?
5. There are number of trace components that often come with raw natural gas. Which, if any are potentially valuable? Which are potentially harmful to humans?
6. What data are needed to decide how much ethane should be left in a sales gas stream?
7. It is noted several times that water content is excluded from the gas analysis? Why do you think this is common practice?
8. Why is there a higher and lower heating value? Does it make any difference to the gas customer?
9. The text notes that air is added to natural gas to alter the Wobbe Number. Is it a safe practice to add small amounts of air to natural gas? Why? (See Table B.1[4]).

EXERCISES

6.1 A gas contains 91% methane, 5% ethane, and 4% propane and no water
   a. What is the Wobbe number of the mixture?
   b. If the gas is blended with air to obtain a gross heating value of 1,000 Btu/scf (37.3 MJ/m³) what will be the air concentration (mol %)?
   c. If the required Wobbe number for the final gas mixture is 1,130–1,280 Btu/scf (44.5–50.4 MJ/Nm³) will the Wobbe number be in the required range?

6.2 A gas plant is processing 100 MMscfd (2.7×10^6 Nm³/d) with the composition (mol %) shown below.

	Mole%	gal/lb-mol	cm³/g-mol
N_2	1.8		
CO_2	1.9		
H_2S	0.0		

(*Continued*)

[4] See Appendix B on publisher website: www.crcpress.com/Fundamentals-of-Natural-Gas-Processing-Third-Edition/Kidnay-Parrish-McCartney/p/book/9781138612792

	Mole%	gal/lb-mol	cm^3/g-mol
C_1	84.3		
C_2	6.2	10.123	84.027
C_3	2.7	10.428	86.888
i-C_4	0.6	12.386	103.25
n-C_4	1.0	11.933	99.482
i-C_5	0.5	13.843	115.42
n-C_5	1.0	13.712	114.41

Economic conditions favor removal of 90% of the C_2 and all C_3^+ from the gas. What volume of hydrocarbon liquids are produced (bbl/d, m^3/d)?

6.3 Under unusual conditions, propane may be mixed with air and used as a substitute for natural gas (propane shaving). What is the composition of a propane–air mixture to obtain a HHV equivalent to methane? Is the mixture safe? Methane and propane have HHV of 1010 and 2516.1 Btu/scf (37.706 and 93.934 MJ/Sm^3), respectively; the flammability limits of propane are 2.0–9.5 vol%.

REFERENCES

Anderson, L.E., The treatment of CSG at Val Verde plant, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 1992.

Anonymous, Second offshore methane hydrate production test finishes [Press release], 2017. Retrieved from www.meti.go.jp/english/press/2017/0629_001.html.

Anonymous, China searches for more gas hydrates in South China Sea, *The Maritime Executive,* February, 2018. www.maritime-executive.com/article/china-searches-for-more-gas-hydrates-in-south-china-sea (Retrieved April 2019).

ASTM D323-15a, *Standard Test Method for Vapor Pressure of Petroleum products (Reid Method)*, ASTM International, West Conshohocken, PA, 2015. www.astm.org/Standards/D323.htm (Retrieved April 2019).

ASTM D2713-15e1, *Standard Test Method for Dryness of Propane (Valve Freeze Method)*, ASTM International, West Conshohocken, PA, 2015. www.astm.org/Standards/D2713.htm (Retrieved April 2019).

ASTM D1838-16, *Standard Test Method for Copper Strip Corrosion by Liquefied Petroleum (LP) Gases*, ASTM International, West Conshohocken, PA, 2016. www.astm.org/Standards/D1838.htm (Retrieved April 2019).

ASTM D1267-18, *Standard Test Method for Gauge Vapor Pressure of Liquefied Petroleum (LP) Gases (LP-Gas Method)*, ASTM International, West Conshohocken, PA, 2018. www.astm.org/Standards/D1267.htm (Retrieved April 2019).

Bleizeffer, D., Coalbed methane: Boom, bust and hard lessons, Wyoming State Historical Society, 2015. www.wyohistory.org/encyclopedia/coalbed-methane-boom-bust-and-hard-lessons (Retrieved April 2019).

Boswell, R., and Collett, T.S., Current perspectives on gas hydrate resources, *Energy Environ. Sci., 4*, 1206–1215, 2011.

BP p.l.c., BP statistical review of world energy 2018 full report, 2018. www.bp.com/content/dam/bp/en/corporate/pdf/energy-economics/statistical-review/bp-stats-review-2018-full-report.pdf (Retrieved July 2018).

Bryner, C., Coalbed methane development in the intermountain west: Producing energy and protecting water, *Wyo. Law Rev., 4*(2), 541, 2004. https://repository.uwyo.edu/cgi/viewcontent.cgi?referer=https://duckduckgo.com/&httpsredir=1&article=1292&context=wlr (Retrieved April 2019).

Bullin, J.A., and Fitz, C.W., Practical hydrocarbon dewpoint specification for natural gas transmission lines, Research Report RR-213, Gas Processors Association, Tulsa, OK, 2011.

Bullin, K.A., and Krouskop, P.E., Compositional variety complicates processing plants for U.S. shale gas, *Oil Gas J., 107*(10), 50–55, 2009.

Cannon, R.E., *The Gas Processing Industry, Origins and Evolution*, Gas Processors Association, Tulsa, OK, 1993.

Coleman, J.L., Tight-gas sandstone reservoirs: 25 years of searching for "The answer", *Understanding, Exploring, and Developing Tight- Gas Sands – 2005 Vail Hedberg Conference: AAPG Hedberg,* Cumella, S.P., Shanley, K.W., and V.K. Camp (eds.), AAPG, (2), 2008, p. 221.

Collett, T., Natural gas hydrates: Vast resource, uncertain future, U.S. Geological Survey Fact Sheet FS-021-01, 2001. http://pubs.usgs.gov/fs/fs021-01/ (Retrieved April 2019).

Collett, T., et al., Indian National Gas Hydrate Program Expedition 01 report: U.S. Geological Survey Scientific Investigations Report 2012–5054, United States Geological Survey, 2015, p. 1442. https://pubs.usgs.gov/sir/2012/5054/ (Retrieved April 2019).

Dong, Z., et al., Global unconventional gas resource assessment, *SPE Econ. Manage., 4*(4), 222, 2012. www.onepetro.org/journal-paper/SPE-148365-PA (Retrieved April 2019).

Eble, C., et al., Resource assessment & production testing for coal bed methane in the Illinois Basin, Final report, Kentucky Geological Survey, Lexington, KY, 2005.

Eckersley, N., and Kane, J.A., Designing customized desulfurization systems for the treatment of NGL streams, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2004, p. 313.

Energy Information Administration, Natural gas 1998, issues and trends, U.S. Department of Energy, 1999.

Energy Information Administration, What are natural gas liquids and how are they used? U.S. Department of Energy, 2012. www.eia.gov/todayinenergy/detail.php?id=5930 (Retrieved April 2019).

Energy Information Administration, Annual energy outlook 2018, U.S. Department of Energy, 2018a. www.eia.gov/outlooks/aeo/data/browser/ (Retrieved April 2019).

Energy Information Administration, Annual energy outlook 2018 with projections to 2050, 2018b. www.eia.gov/outlooks/aeo/ (Retrieved April 2019).

Energy Information Administration, Landfill gas and biogas, 2018c. www.eia.gov/energyexplained/index.php?page=biomass_biogas (Retrieved November 2018).

Energy Information Administration, Natural gas gross withdrawals and production, U.S. Department of Energy, 2018d. www.eia.gov/dnav/ng/ng_prod_sum_dc_NUS_mmcf_a.htm (Retrieved April 2019).

Energy Information Administration, Petroleum & other liquids/petroleum supply monthly, U.S. Department of Energy, 2018e. www.eia.gov/petroleum/supply/monthly/ (Retrieved April 2019).

Energy Information Administration, U.S. natural gas flow, 2017, 2018f. www.eia.gov/totalenergy/data/monthly/pdf/flow/natural_gas.pdf (Retrieved April 2019).

Energy Information Administration, U.S. shale plays: Natural gas production and proved reserves, 2015–16, 2018g. www.eia.gov/naturalgas/crudeoilreserves/pdf/table_4.pdf (Retrieved April 2019).

Energy Information Administration, About U.S. natural gas pipelines - transporting natural gas, U.S. Department of Energy. www.eia.gov/naturalgas/archive/analysis_publications/ngpipeline/index.html (Retrieved April 2019).

Engineering Data Book, Section 2, Product specifications, GPSA Midstream Suppliers, Tulsa, OK, 2016.

Environmental Protection Agency, Coalbed methane extraction: Detailed study report, 2010. www.epa.gov/sites/production/files/2015-06/documents/cbm_report_2011.pdf (Retrieved April 2019).

Environmental Protection Agency, Basic information about landfill gas, 2018a. www.epa.gov/lmop/basic-information-about-landfill-gas (Retrieved April 2019).

Environmental Protection Agency, Coal mine methane developments in the United States, 2018b. https://nepis.epa.gov/Exe/ZyPDF.cgi/P100U0AM.PDF?Dockey=P100U0AM.PDF (Retrieved April 2019).

Gas Processors Association, GPA Standard 2108-14, GPA fractionation grade product specifications, Tulsa, OK, 2014a.

Gas Processors Association, GPA Standard 2172-14, Calculation of gross heating value, relative density, compressibility and theoretical hydrocarbon liquid content for natural gas mixtures for custody transfer, *API Manual of Petroleum Measurement Standards Chapter 14.5*, Tulsa, OK, 2014b.

Gas Processors Association, GPA Standard 2140-17, Liquefied petroleum gas specifications and test methods, Tulsa, OK, 2017.

Giacomin, S., NGL infrastructure in the western Canadian Sedimentary Basin, and Pembina's expansion from wellhead to market, GPA Midstream, Austin, TX, 2018.

Gray, P.R., Radioactive materials could pose problems for the gas industry, *Oil Gas J., 88*(26), 45, 1990.

Ground Water Protection Council, and ALL Consulting, Modern shale gas development in the United States: A primer, *Prepared for the U.S. Department of Energy Office of Fossil Energy and National Energy Technology Laboratory*, Washington, D.C., 2009. www.fossil.energy.gov/programs/oilgas/publications/naturalgas_general/Shale_Gas_Primer_2009.pdf (Retrieved April 2019).

Jones, S., et al., Simultaneous removal of water and BTEX from feed gas for a cryogenic plant, *Proceedings of the Seventy-Eighth Annual Convention Gas Processors Association*, Tulsa, OK, 1999, p. 108.Karacan, C.Ö., et al., Coal mine methane: A review of capture and utilization practices with benefits to mining safety and to greenhouse gas reduction, *Int. J. Coal Geol., 86*, 121, 2011.
Khan, T.S., et al., Characterization and preliminary root cause identification of black powder content in a gas transmission network – a case study, *J. Nat. Gas Sci. Eng., 27*, 769, 2015.
Kim, A.G., The composition of coalbed gas, Report of Investigations 7762, US Bureau of Mines, 1973. www.cdc.gov/niosh/mining/UserFiles/works/pdfs/ri7762.pdf (Retrieved April 2019).
National Energy Technology Laboratory, The National Methane Hydrates R&D Program. www.netl.doe.gov/technologies/oil-gas/FutureSupply/MethaneHydrates/maincontent.htm (Retrieved April 2019).
NaturalGas.org, History, 2013. http://naturalgas.org/overview/history/ (Retrieved April 2019).
Nelson, P.H., Pore–throat sizes in sandstones, tight sandstones, and shales, *AAPG Bull.*, *93*(3), 329, 2009.
Nelson, P.H., and Batzle, M.L., Single phase permeability, *Petroleum Engineering Handbook, General Engineering*, Fanci, J. (ed.), Society of Petroleum Engineers, Richardson, TX, 2006, p. 687.
NGC+ Liquid Hydrocarbon Dropout Task Group, White paper on liquid hydrocarbon dropout in natural gas infrastructure, Natural Gas Council for the Federal Energy Regulatory Commission, 2004, p. 36. www.naesb.org/pdf/update011905w9.pdf (Retrieved April 2019).
Potential Gas Committee, Potential Gas Committee reports record future supply of natural gas in the U.S. [Press release], July 19, 2017. Retrieved from http://potentialgas.org/press-release.
Ruppel, C., Gas hydrate in nature, US Geological Survey, 2018. https://pubs.usgs.gov/fs/2017/3080/fs20173080.pdf (Retrieved April 2019).
Sanders, J.E., *Principles of Physical Geology*, John Wiley & Sons, New York, 1981.
Sherik, A., Black powder—1: Study examines sources, makeup in dry gas systems, *Oil Gas J., 106.30*, 2008.
Smith, J.M., et al., *Introduction to Chemical Engineering Thermodynamics*, 8th edn. McGraw-Hill Higher Education, New York, 2018.
Tight gas sands, Colorado School of Mines, 2008. http://emfi.mines.edu/emfi2008/TightGasSands2008.pdf (Retrieved April 2019).
Traconis, B., et al., Mercury removal systems at Santa Barbara Extraction Plant, *Proceedings of the Seventy-Fifth Annual Convention Gas Processors Association*, Tulsa, OK, 1996, p. 123.
Tsochatzidis, N.A., Study addresses black powder's effects on metering equipment, *Oil Gas J., 106*, 12, 2008.
U.S. Bureau of Mines, Analyses of natural gas, Information Circular #8607, U.S. Bureau of Mines, 1972.
U.S. Geological Survey, Mineral commodity summaries, Sulfur, 2018. https://minerals.usgs.gov/minerals/pubs/commodity/sulfur/mcs-2018-sulfu.pdf (Retrieved April 2019).
Williams, T., European gas quality, interchangeability issues reflect regional diversity, *LNG Obs., 4*(2), 2007.

WEB SITES

Energy Information Administration, www.eia.gov/. This site provides extensive reports, tabulation of data, and statistics regarding reserves, production, transportation, storage, and consumption of energy both in the United States and worldwide.
GPA Midstream Association, https://gpamidstream.org/. This site is the home page of the major industrial organization dealing with all aspects of gas and gas liquids processing.
International Energy Agency, www.iea.org/. This site is the home page of the organization that provides a wide array of data regarding all forms of energy.
National Energy Technology Laboratory, Strategic Center for Natural Gas, www.netl.doe.gov/oil-gas/natural-gas-resources. This site is the starting point for learning about energy-related research programs of the U.S. Department of Energy.
Natural Gas Supply Association, www.ngsa.org/. Site provides a good overview of natural gas from exploration to consumption. It also gives an overview of the organization and items of importance to the natural gas industry.

Taylor & Francis
Taylor & Francis Group
http://taylorandfrancis.com

7 Overview of Gas Plant Processing

7.1 ROLES OF GAS PLANTS

The most common role of gas plants is to process raw natural gas to produce pipeline-quality natural gas and natural gas liquids (NGLs). Sale of liquids can provide a significant portion of the income from these plants. Based upon contracts with gas producers, plants may optimize profits by adjusting the fraction of liquids recovered while meeting the specifications for the sales gas.

The purpose of a gas plant is not always liquids recovery. Plants play a variety of roles in the oil and gas industry. The desired end product(s) and their market specifications dictate the processes required. Some other functions of gas plants include:

- Dehydration of gas to meet a specification, reduce corrosion, and prevent gas hydrate formation.
- Oil stabilization. One of the world's largest gas plants processes about 3.5 Bscfd of gas (9.8×10^7 Nm^3/d) on the North Slope of Alaska. The sole purpose of the facility is to stabilize liquids so that they can be put into the Alyeska pipeline. The plant helps to maximize line throughput by recovering C_4^+, which is blended into the crude oil to the pipeline. Produced gas is reinjected into the formation to enhance oil recovery. This gas will be sold if a gas pipeline is built from the North Slope.
- Carbon dioxide or nitrogen recovery for enhanced oil recovery (EOR). These plants separate natural gas from the CO_2 or N_2; the natural gas is marketed and the CO_2 or N_2 is reinjected into producing reservoirs. In N_2 projects, an air separation plant may be constructed on-site to provide additional N_2 at the beginning of the project.
- Upgrading subquality gas. To make the gas marketable, the undesired diluents N_2, H_2S, and CO_2 are removed. Of the three components, N_2 is the most difficult to remove because it requires cryogenic processing when large volumes are processed. These plants may also recover liquids to provide additional revenue and to produce pipeline-quality sales gas.
- Helium recovery. A few plants are dedicated primarily to helium recovery. Therefore, this facility is typically an addition to a gas plant. Natural gas is the primary source of helium. In the United States, the highest helium concentrations are in eastern Colorado, southwestern Wyoming, western Kansas, and the panhandles of Oklahoma and Texas.
- Liquefaction. Liquefaction can be either for producing a salable liquid (baseload plant) or for gas storage (peakshaving plant). Baseload plants are dedicated to the large-scale production of liquefied natural gas (LNG) for transportation to distant markets. These plants are in locations with large gas reserves and no pipelines to market. The first large-scale LNG production facility in the United States was in Alaska. Two other large-scale U.S. LNG export facilities began operations in July, 2018. Additionally, numerous applications for exporting LNG from North America are in the approval process with shipments of over 55 Bscfd (1.5×10^9 Nm^3/d) proposed in early 2019 (U.S. Department of Energy, 2019). In 2018, the United States had more than 90 peakshaving plants producing LNG from pipeline gas for storage purposes. Small- and mid-scale LNG production facilities similar in size to peakshaving plants now furnish fuel for truck fleets and marine applications. See Chapter 18 for more detail.

7.2 PLANT PROCESSES

Figure 7.1 is a block schematic of a gas plant that has most of the more common process elements. An overview of each element is given here, and details are provided in subsequent chapters. To show how the process elements are integrated, Chapter 20 discusses several gas plants with different configurations.

Few, if any, plants have all of the process steps shown. Which processes are in a plant is dictated by the feed gas composition and conditions required to meet the desired product specifications.

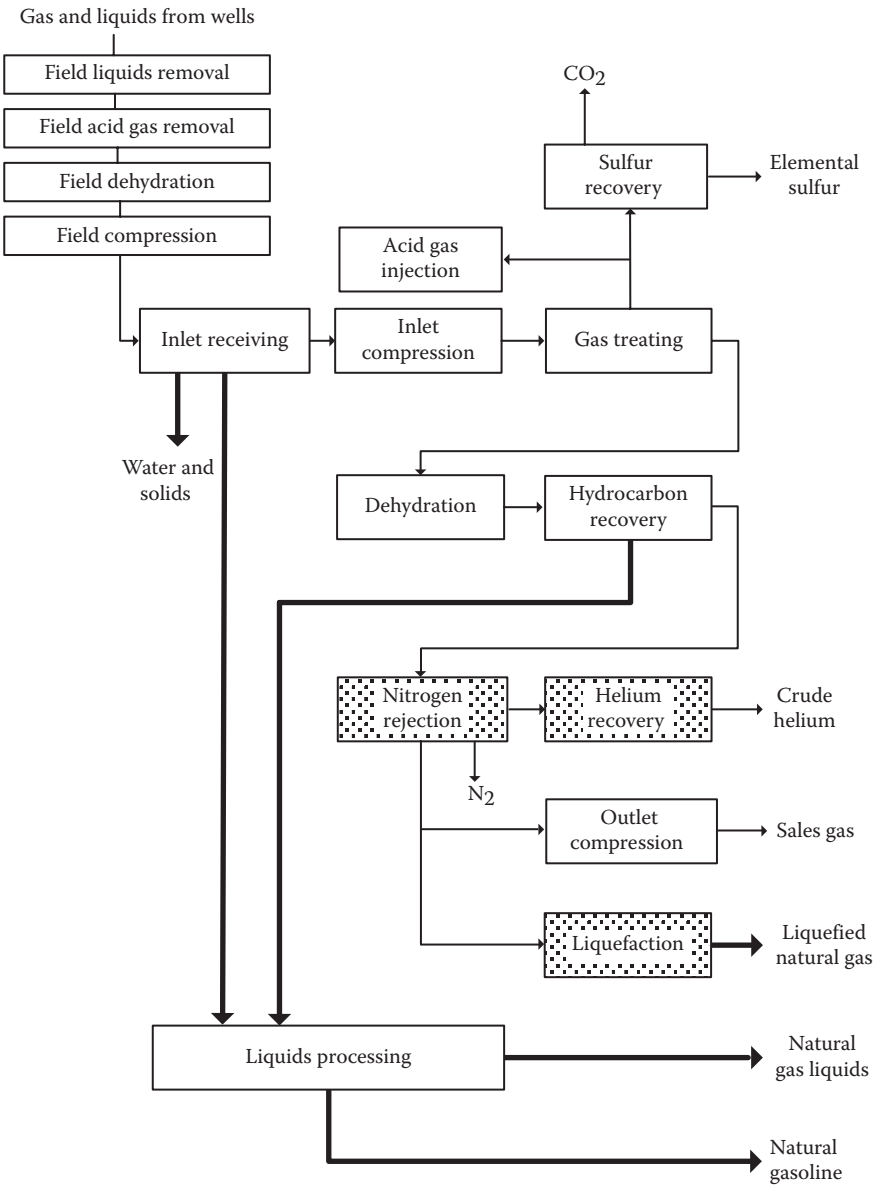


FIGURE 7.1 Block schematic of various processes of a gas plant. Processes required depend upon feed and product slate. Less common process steps for facilities in the United States are shaded. The heavier lines denote liquid streams.

7.2.1 Field Operations and Inlet Receiving

Most plants have field operations and a network of gathering lines that feed the raw natural gas and associated field liquids into the plant. The exceptions are "straddle plants," which remove ("strip") additional NGL from a gas pipeline and put residue gas back into the pipeline, and LNG peakshaving plants. Field operations may include measurement, free liquid separation, dehydration, acid gas (CO_2 and H_2S) removal, and compression. Acid gas removal is uncommon in field operations unless H_2S levels are below 100 ppmv. These processes are discussed in more detail below. Unless the gas is completely free of any liquids, once it enters the plant, the gas and liquids go into inlet receiving, where the initial gas–liquid(s) separation is made. Condensed water, free hydrocarbon liquids, and solids are removed. Water and solids are processed for disposal, and the hydrocarbon liquids go on to liquids processing, as discussed below. Chapter 8 discusses both field operations and inlet receiving. The chapter also discusses gas hydrates and how to avoid their formation.

7.2.2 Inlet Compression

Most plants have inlet compression, but compression requirements vary. High pressure is important if cryogenic liquid recovery processes are utilized. Inlet compression may be unnecessary for inlet streams with pressures of ~700 psi (50 bar) or higher. However, most onshore gas plants have some low-pressure gas streams entering the plant. Chapter 9 discusses compression. Inlet, field, and outlet compression typically use the same types of compressors. Compression is the major source of energy consumption and capital cost in most gas plants.

7.2.3 Gas Treating

Most plants have a gas treating step to remove acid gases H_2S and CO_2, along with other sulfur impurities. The majority of these plants use water-based absorbents to remove the impurities, but other solvents and processes are also used. Chapter 10 discusses various methods for the removal of these components.

7.2.4 Dehydration

Field operations sometimes dry the gas to avoid gas hydrate formation as well as to reduce corrosion. Plants that use water-based treating require the dehydration step because gas from the gas treating step typically is water saturated. Even if water-based gas treating is unnecessary, gas streams normally contain too much water to meet pipeline specifications or to enter the cryogenic section of the plant. Chapter 11 provides details on the commonly used dehydration processes.

7.2.5 Hydrocarbon Recovery

Any plant that processes natural gas to produce NGL requires a hydrocarbon recovery step. This step usually involves cryogenic separation to recover heavier hydrocarbons and to meet gas pipeline specifications. Hydrocarbon recovery can also play an important role in field operations. There it is primarily used for fuel gas conditioning and dew point control. Details of these processes are provided in Chapter 12.

7.2.6 Nitrogen Rejection

Although a less common process in the gas industry, nitrogen rejection may be needed when inlet gas contains more than about 3 vol% nitrogen. Nitrogen rejection units are typically cryogenic, although membrane and adsorbent technology are becoming more common. Chapter 13 presents details on nitrogen removal and on its use in EOR.

7.2.7 Trace Components

Raw natural gas can contain compounds in low concentrations that may require removal for environmental, product specification, or processing reasons. Helium is a valuable trace component, but recovery typically is uneconomical unless the concentration is above 0.5 vol%. A brief description of helium recovery processes is given in Chapter 14. The chapter also discusses the removal of other trace components, including BTEX (benzene, toluene, ethylbenzene, and xylenes), methanol, and mercury. BTEX is primarily an environmental concern because of possible emissions from some commonly used gas treating and dehydration units that concentrate them. Although occurring at extremely low concentrations in the gas, elemental mercury can cause mechanical failure in aluminum heat exchangers. Both BTEX and mercury are toxic.

7.2.8 Outlet Compression

The majority of plants that have cryogenic hydrocarbon recovery use turboexpanders to provide refrigeration in the cryogenic section and must recompress the gas before it goes to the pipeline. Work generated in expansion may be used to recompress the residue or sales gas. However, additional compression is usually required. Chapter 12 discusses turboexpanders coupled with compressors, and Chapter 9 covers stand-alone compressors.

7.2.9 Liquids Processing

Liquids processing occurs whenever NGL is a product. The required processing depends on the liquid content of the inlet gas and desired product slate. The hydrocarbon liquids from inlet receiving are commonly sent to a stabilizer to remove lighter hydrocarbons. Stabilizer overhead goes to a compressor so that it can be blended with inlet gas. Stabilizer bottoms are a C_5^+ condensate fraction that is sold as natural gasoline or crude oil, based upon its quality. Chapter 15 covers the common processes for treating, drying, and fractionation of liquids.

7.2.10 Sulfur Recovery

If H_2S removal is required, there are four common ways to dispose of the recovered material. The simplest is incineration if the amounts do not exceed sulfur emission limits. If low levels of sulfur are to be removed, scavengers can be used. For higher sulfur levels the H_2S is either converted to elemental sulfur or reinjected into disposal wells. Sulfur removal technologies are discussed in Chapter 16. The chapter also presents limited information on CO_2 EOR and acid gas injection.

7.2.11 Storage and Transportation

Although not shown in Figure 7.1, another "process" associated with gas plants is storage and transportation. Chapter 17 discusses the storage and transportation of natural gas and NGL products.

7.2.12 Liquefaction

A few baseload liquefaction plants are operating in the North America and more are coming on stream to export shale gas. They are important worldwide as more gas is imported to nations with limited natural gas resources. Peakshaving liquefaction plants also play an important role as a method for gas storage. Chapter 18 discusses both types of plants. Because of the unique properties of LNG, the chapter includes storage, transportation, and vaporization processes as well because they are important to LNG production and importing facilities.

7.3 IMPORTANT SUPPORT COMPONENTS

There are a number of vital support components in all gas plants. These components include utilities, process control, and safety systems. This section provides an overview of these components; the *Engineering Data Book* (2016a) provides more details.

7.3.1 Utilities

This section briefly describes some of the utilities commonly found in gas plants. Chapter 12 discusses propane refrigeration and Chapter 17 discusses storage. Section 7.3.3 covers relief systems and flares.

7.3.1.1 Electrical Power

In addition to common uses, e.g., lighting, motors, and instrumentation, gas plants use electric power for heat tracing lines and for minimizing corrosion by cathodic protection. Many gas plants constructed since around 2014 rely on electric drivers for compressors to reduce emissions. Most gas plants purchase electrical power, but some generate at least a portion of their power on-site. Cogeneration plants generate power for the plant and utilize the waste heat to generate process heat as a cost-effective means to reduce overall plant fuel consumption. Power is sometimes generated by recovering the waste heat from gas turbines in combined cycle units. The *Engineering Data Book* (2016c) provides an extensive discussion of electrical systems.

7.3.1.2 Steam Systems

Compared with refineries and most chemical complexes, steam is not extensively used in gas plants. The primary use is in reboilers on fractionation towers and amine solvent regenerators.

Steam is generated from stand-alone boilers or by recovering waste heat from gas turbine exhaust, engine exhaust, or heater flue gas. Sulfur recovery plants (see Chapter 16) use both low- and high-pressure waste heat boilers to remove heat from the highly exothermic Claus process. The high-pressure steam usually goes to steam turbines, which drive air blowers for the sulfur recovery process.

Water treating is critical for maintaining a properly operating steam system. The *Engineering Data Book* (2016c) has an excellent discussion on water treating chemistry.

7.3.1.3 Hot Oil Systems

Hot oil systems are a major source of process heat for gas plants. They have replaced the majority of steam systems because of water makeup and disposal issues. Chapter 3 briefly discusses the hot oils used and the furnaces used to heat them.

7.3.1.4 Cooling Water

Cooling water is sometimes used to cool process streams when ambient air cooling is inadequate. As noted in Chapter 3, water chemistry is a critical component of these cooling systems. Availability and cost of makeup water in many areas make the use of cooling water impractical.

7.3.1.5 Water Makeup Systems

Good quality makeup water is essential for steam, cooling water, and amine systems. Trace component accumulation will cause scaling in steam systems, fouling in cooling water heat exchangers, and foaming in amine treaters. Condensed steam can be used; however, many facilities use reverse osmosis membranes to condition makeup water. Deaeration is important because dissolved oxygen can cause solvent degradation and subsequent foaming.

7.3.1.6 Instrument Air

An uninterrupted source of clean, dry instrument air is critical to plant operations because the air drives most automated valves. Proper operation of these valves is a safety issue. Typical pressures are around 100 psig (7 barg). Plants use one or more backup compressors to ensure that compressed air is always available. Screw compressors, both oil free and oil flooded (see Chapter 9), are the most widely used because of their high availability (*Engineering Data Book*, 2016c).

Many air systems have adsorbent driers (see Chapter 11) to avoid potential air piping freezes in cold weather. Whenever high instrument flow rates are needed, air receivers (tanks) are included in the system. This permits large flow rates without lowering air pressure (*Engineering Data Book*, 2016c). These receivers also act as a short-term backup when air compressors are down.

7.3.1.7 Nitrogen Systems

Nitrogen is sometimes used as a purge gas around rotating seals, as well as a purge and blanket gas for vessels. The required purity depends on the application but is usually not high. Sometimes it is economical to store purchased liquid nitrogen and then vaporize it on-site. This is especially true when relatively large volumes are needed to purge vessels for entry. However, in many cases, the enriched nitrogen for routine operations is obtained from membrane or pressure swing adsorption (PSA) separation (see Chapters 4 and 14 for details). If large volumes are required on a continuous basis, cryogenic fractionation of air is the most economical process (*Engineering Data Book*, 2016c) but requires volumes in excess of the utilization at most gas processing plants. For peak demand, such as during maintenance, liquid nitrogen is often trucked to site and vaporized as needed.

7.3.1.8 Vapor Recovery

A number of processing steps, e.g., condensate stabilization and intermittent operations (e.g., vessel blowdowns) generate low-pressure gas, which is recovered for both economic and environmental reasons. The vapors go to vapor recovery units, which consist of a knockout drum to remove liquids, and a compressor. The discharge gas is either routed to fuel gas or to inlet gas. Any recovered liquids are sent to liquids processing.

Other common sources of low-pressure gas include vent gases from amine treating (see Chapter 10) and glycol dehydration (see Chapter 11), flash gas from the pressure letdown of liquid streams and pig receivers, distance piece vents from reciprocating compressors, seal gas for turbine operations, engine and compressor starting gas vents, and pressure control vents for product storage. Economics of recovering the gas and environmental considerations dictate whether these low-pressure vapors are recovered, flared, or vented. Most gas processing plants have some form of vapor recovery for small volumes but rely on flaring or venting for peak volumes.

7.3.1.9 Fuel Gas System

Gas plants use a portion of the gas they process to fuel the facilities. Boilers, hot oil furnaces, and internal combustion engines on compressors can use a low-pressure fuel gas, typically 50–100 psig (3.5–7 barg). The primary concern is having a clean gas of a roughly constant heating value. The dew point of the gas must be sufficiently low to avoid liquid condensation. Fuel gas is sometimes used to blanket solvent storage tanks to prevent air diffusing into and degrading the solvent.

Gas turbines (discussed in Chapter 9) require higher fuel gas pressures and have tighter specifications (*Engineering Data Book*, 2016c). Fuel pressure depends on turbine type. Most industrial gas turbines require 300–400 psig (20–30 barg) gas. Higher efficiency turbines can require fuel gas pressures as high as 600 psig (40 barg).

To avoid possible condensation, turbine manufacturers typically require fuel gas inlet temperatures to be 30°F–50°F (15°C–30°C) above the gas dew point. Several methods can be used to meet specifications:

1. Heat the fuel gas.
2. Use plant residue sales gas.
3. Use low temperature separators for fuel conditioning (see Chapter 12).
4. Use membranes for fuel conditioning (see Chapter 12).

7.3.2 Process Control

Process control has always played a role in gas plants but has become more important over the years as plants are operated with less on-site staff. Most plants use distributed control systems (DCS) for both process control and capturing and storing operating history. Programmable logic controllers (PLC) are used to control individual systems or pieces of equipment in a process. The control system holds process variables, such as flows, levels, temperatures, and pressures to a set point selected by plant operators. Both DCS and PLC systems monitor process conditions to provide alarms. In the 1990s, advanced process control (APC) systems became available. These supervisory systems "sit" on top of existing DCS and PLC systems, providing sophisticated plant control. APC uses multivariable algorithms that are trained in the plant to optimize operations by automatically adjusting set points based on current operating conditions using economic constraints.

Another type of process control commonly used is supervisory control and data acquisition (SCADA). One important use of SCADA is the monitoring of field instrumentation and operations. These systems provide the capability of controlling field dehydration equipment, flow valves, and compressor stations from the gas plant.

Automation requires accurate input data to make the proper control decisions. Plants usually have a full-time instrument technician to maintain and calibrate the many temperature, pressure, and flow sensors, as well as instruments required for compositional and trace component analysis. The technicians take advantage of plant shutdowns because, often, that is the only time they can service many of the instruments without disrupting plant operations.

7.3.3 Safety Systems

Safety systems are critical to all gas plants. These systems include the plant emergency shutdown system, fire and gas detection systems, burner management systems, pressure safety relief valves, and the plant vent and flare system.

Modern plants may include a safety instrumented system (SIS) which is designed to comply with IEC 16511 (International Electrotechnical Commission, 2018). Since 2004 these standards have been largely harmonized and many operating companies adopted them as an important part of their operating approach to safety in gas processing. A properly designed safety system will fail into a safe mode upon loss of energy.

The *Engineering Data Book* (2016b) provides criteria for sizing relief systems and flares. Proper sizing of relief valves, rupture disks, and piping is critical to ensure that the operating systems can be vented safely to prevent overpressure of piping and equipment. The design often is complicated by the need to consider potential two-phase flows through valves and piping. Design specifications commonly follow API 520 (2014a) and API 521 (2014b).

In addition to the flare itself, flare systems typically include one, and sometimes two (high pressure and low pressure), knockout drums to catch liquids. Pipe flares are probably the most common flare in gas plants. In normal operations, the flare flame is barely detectable. If the plant is flaring mostly methane, the flame is bright but smokeless. If methane plus heavier hydrocarbons are flared, the flame will be a darker yellow and may smoke. To make the flare smokeless, air, steam, or water spray may be added. Techniques for ensuring complete mixing of air with fuel are also used. If the fuel has a low-Btu content (e.g., tail gas from a sulfur recovery unit), fuel gas is added to ensure stable combustion. Since flares and incinerators are considered control devices for

environmental purposes, many agencies including the U.S. EPA (undated) require a minimum heat content (heating value) for gases sent to these devices.

7.4 CONTRACTUAL AGREEMENTS AND ECONOMICS

When plant modifications are under consideration, the customary analysis for optimization of the balance between capital expenditures and operating costs applies. However, contractual agreements complicate a gas plant economic study whenever the producer and processor are not the same company. There are very few places in North America where the producer and processor are the same company. The specific terms of the producer and processor contracts must be incorporated into the analysis because often there is a disproportionate distribution of the benefits derived from any given capital improvement project. Outside of North America the producer and processor are the same company and formal contracts are unnecessary.

The basic kinds of gas supply contracts commonly used between producers and processors in North America (Drinkwine, P.M., Private Communication, 2018) are:

- Fee-based
- Percentage of proceeds
- Keep whole or Wellhead purchase

In addition to these basic types there are numerous alternative provisions which can be used with the basic contract.

7.4.1 Fee-Based Contracts

In fee-based contracts, the producer pays the gas processor a set fee based on gas volumes processed. The processor may obtain additional income by charging fees for additional services, such as gathering, treating, compression, pipeline transmission, and marketing. In these contracts, the processor's income is independent of gas and NGL prices. These contracts are the most conservative for the processor because processor's profit is not affected by gas and NGL commodity prices. This type of contract is often preferred by investors backing midstream processors because they carry no commodity risk for the processor. All commodity price risk remains with the producer.

7.4.2 Percentage of Proceeds Contracts

In percentage of proceeds (POP) contracts, the two parties agree to what percentage of the proceeds from the sale of the gas and liquids is to be retained by the producer. Typically, the producer retains more than 80% of the proceeds from the sale of all products. The percentage may differ for the various products but are often the same. (Other products can include sulfur, nitrogen, carbon dioxide, and helium.)

In the case of multiple producers, each producer has a percentage share of the proceeds, allocated based on each producer's contribution to the proceeds. Allocations are prorated based on the composition of the gas delivered from each lease. Producers and processors share the risk of fluctuating commodity prices of gas and NGL. Note that this type of contract is based on residue gas and liquid products "saved and sold" and therefore "losses" and fuel consumed in the operation are provided by the producer. With this contract structure the commodity price risk is shared between the producer and processor. It should be noted that the term "losses" is often used for what is termed "lost and unaccounted for" in accounting. There may or may not be any physical losses as these volumes could just be measurement differences.

7.4.3 Keep Whole or Wellhead Purchase Contracts

In keep whole contracts, the processor agrees to return to the producer 100% of the Btu content of the raw gas (keep the producer whole on Btu's) in exchange for retaining ownership of all products derived from the gas. The processor retains all liability for fuel, processing costs, and the purchase of replacement Btu's for those extracted as a liquid product.

These contracts are speculative from the processor's point of view. The potential profit is directly related to the market price of residue sales gas and NGL versus the agreed price at the wellhead. The producer is exposed to fluctuating gas market prices, usually based on some published index such as Henry Hub price. The producer, in essence, sells the whole hydrocarbon stream on a Btu basis to the processor. The processor makes or loses money, depending on the price difference (price margin) between plant products and the agreed gas value. This is the riskiest for the processor but can be the most profitable contract when ethane and propane are more valuable as a liquid product than as a component of sales gas.

If the processor has keep whole contracts with the producer, operational changes can force the processor to purchase gas at a higher price to meet the energy delivery requirement of the contract. For this type of contract, fuel used for processing and other losses can be a significant factor in processor profit or loss.

Wellhead purchase contracts are financially much the same as keep whole contracts, where the processor executes a contract to purchase total Btu's from the producer at a negotiated price usually based against a published index. This purchase is a straightforward purchase, and the processor's profits depend on the cost of gathering and production, and the selling price of the gas and liquids. For this type of contract, the commodity risk is solely borne by the processor.

7.4.4 Alternate Contract Provisions

It is common to blend elements of several different contract types into the overall contract. This allows the contract to accommodate changing market conditions. Also, it allows for new capital investment and operational changes. For example:

- Adding fees for services like compression and treating to a basic POP contract.
- Fixed efficiency contract provisions where the processor agrees to provide a certain percentage recovery (efficiency) of NGL components from the gas and to pay the producer based on the market value of the liquid production and resultant residue gas. The processor makes money by processing at a higher efficiency. Efficiency can be stated in the contract (theoretical) or on measured efficiency (actual). For fixed efficiency agreements items like fuel, "lost and unaccounted for" and product recovery can all be part of the settlement calculation.
- Contracts may contain a sliding scale of fees or proceeds percentage penalties for variations from contracted gas volume, liquid content, impurities, and delivery pressure.
- Contracts may allow the producer to take their proceeds in kind (actual NGL or sales gas) or to opt for a cash settlement. Depending on the ability of the producer to get favorable terms for marketing, transportation, and fractionation costs, the producer may sell their products to a third party at the tailgate of the plant.

Gas processing contracts can be quite complex and settlement calculations tedious.

7.4.5 Capital Expenditures

How costs are shared between producer and processor for capital projects depend on the nature of the project and the contract. New capital items that benefit both parties may be cost shared. However, maintenance, replacements, and costs of environmentally driven projects are borne by

the processor as a cost of staying in business. Situations arise in which capital costs are too high for the processor to absorb alone. Then producers must decide to share the costs, choose a different processor, or cease production.

The combination of the varied and complex contractual agreements, the proprietary nature of economic data, and the sometimes-biased data in the literature limits the discussion of economics in this book. Chapter 19 provides some capital cost data, but otherwise, only qualitative economic comparisons are provided in the other chapters.

7.5 OPERATIONAL MEASURES

Each gas processing company uses its own analytical methods to evaluate their plant and field assets and to make and guide economic decisions. This section discusses three of the more commonly used methods in the United States (Kuchinski, J., Private Communication, 2009):

- Shrinkage
- Btu efficiency
- Frac spread

Shrinkage typically is used to monitor plant performance. However, Btu efficiency normally includes both field and plant performance. Note that only basic concepts are given because exact details vary among companies.

7.5.1 Shrinkage

Simply stated, shrinkage is the difference in volumes of inlet gas entering and the residue gas exiting the gas plant. Shrinkage, when expressed as a fraction or a percentage, is a convenient factor used in modeling and forecasting. Most operations people use actual volumes; however, because gas is bought and sold on an energy basis, shrinkage is sometimes based on the difference in energy content between inlet and outlet.

Sources of shrinkage within the plant include

1. Removal of the C_2^+ fraction, which is sold as a liquid, e.g., NGL and LPG, commonly on a volumetric basis. This shrinkage is solely due to the C_2^+ fraction entering the plant as a gas and leaving as a liquid.
2. Fuel consumed to run compressor engines; to fire steam boilers, hot oil, and molecular sieve regeneration heaters; and to fire any directly fired reboilers.
3. Gas lost to flaring from venting and upsets.
4. Removal of acid gases (CO_2 and H_2S), nitrogen, and water vapor.

Unless the feed gas is extremely lean in liquids (low GPM) conversion to liquids is the most important factor. Also, factors like acid gas and nitrogen content need to be considered. Shrinkage on a volume basis can be as high as 30% for plants with low inlet pressure gas, acid gas concentrations of several percent, "rich" inlet streams (>5 GPM [0.7 m^3 liquid/1,000 Nm^3 gas] on C_2^+ basis), and recovering greater than 80% of available ethane combined with close to 100% of C_3^+. Some data sources use only the conversion to liquids in calculating shrinkage (West, 2006) and include the other terms in extraction losses.

7.5.2 Energy Efficiency

Energy efficiency, or Btu efficiency, is analogous to shrinkage on an energy basis but considers both field and plant operations. It often is considered a direct indicator of operating efficiency on an

"asset wide basis," i.e., all gathering systems, field operations, and the gas plant. It is a direct measure of the energy consumed and system losses required to take the gas from the receipt point to the point of product sales, generally at the plant tail gate. This performance measure attempts to give credit for the energy content of all products available for sale, including residue, NGLs, stabilized condensate, and elemental sulfur.

Factors such as field pressure, gathering system integrity, acid gas content, liquid content, and plant efficiency dictate energy efficiency. An asset that contains low pressure fields, high acid gas content, an aging gathering system, and an older gas plant could have an energy efficiency as low as 85%. By contrast, an asset with a high-pressure gas field, little acid gas content, and a modern gas plant can have efficiencies as high as 95%–99%. Field pressure is a major reason for the difference in this comparison. When providing service for low-pressure gas, it can take up to six or seven stages of compression to gather and process raw gas and deliver the resultant residue sales gas to a transmission pipeline. By contrast, it may only take two stages of compression when gathering high-pressure raw gas.

7.5.3 Processing Margin (Frac Spread)

Shrinkage and energy efficiency provide a measure of asset performance, but they are not commonly used to make plant operating decisions. Several of the contracts discussed in Section 7.4 provide the gas processor the ability to profit from differences in commodity price for ethane and propane, sold on an energy basis as a gas versus as liquid. When the value of ethane and propane are more valuable as a chemical feedstock than as a fuel, natural gas plants operate to recover as much C_2^+ as possible while still meeting sales gas specifications. (Note that butanes are not considered because of residue gas energy content and hydrocarbon dew point specifications.) Gas processors use frac spread to determine how much ethane and propane to keep in the sales gas.

Frac spreads use current market prices for natural gas (usually market centers, e.g., Henry Hub, see Chapter 17) and ethane, propane, or NGL prices at a major fractionating facility, such as Mont Belvieu, TX (Schimmoller, 2003) and Conway, KS. Using the data from Table B.1,[1] to convert from $/gal to $/MMscf for ethane and propane multiply by 15.18 and 11.00, respectively. Processors look at the frac spread of each component individually to determine optimum operating conditions.

Figure 7.2 shows historical frac spreads based on ethane and propane liquid prices at Mont Belvieu, TX. There are a few periods where propane has been less valuable as a liquid product, but it is almost always attractive to recover propane. Figure 7.2 shows that the economics of ethane recovery is highly variable over time. Historical price data are publicly available for chemical feedstocks.

To effectively use frac spread to make processing decisions requires taking into account how other costs change when altering plant operations. Such factors as the change in compressor loading, and therefore, fuel cost, must be considered. Most gas plants send their NGL to fractionation facilities and contractual fees for the liquids processing must be considered. Because the processor typically has fixed-fee contracts for transportation and fractionation (T&F fee) of the liquid, changes in ethane and propane rejection are made only when there are major shifts in the simple frac spread. T&F fees range from around 10¢ per gallon (cpg) to over 30 cpg in the United States (Keller, 2012) which corresponds to 1.10–3.30 $/MMscf for propane and 1.60–4.75 $/MMscf for ethane. These charges reduce the net profit or "netback" to the processor.

In summary, the frac spread is a useful tool for making processing elections to either reject or recover liquids from the raw gas. However, making the correct decision requires more analysis than just simple consideration of the frac spread.

[1] See Appendix B on publisher website: www.crcpress.com/Fundamentals-of-Natural-Gas-Processing-Third-Edition/Kidnay-Parrish-McCartney/p/book/9781138612792

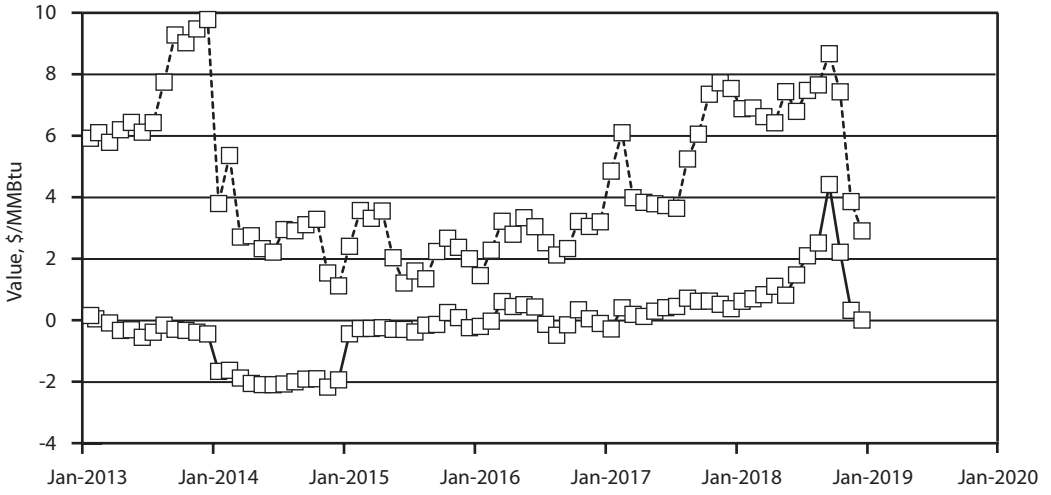


FIGURE 7.2 Historical frac spreads for propane (- -) and ethane (—) based upon EIA futures price data. Chart gives difference in value between commodities as liquid at Mont Belvieu, TX and as gas, on energy basis (Energy Information Administration, 2019a–c).

DISCUSSION QUESTIONS

1. Which of the processing steps in Figure 7.1 will always be present in gas plants that recover high fractions of ethane?
2. Which processing steps in Figure 7.1 are selected based on inlet feed compositions?
3. Which processing steps in Figure 7.1 are selected based on inlet feed conditions?
4. What are the key safety systems within a gas plant and how do they protect both plant personnel and plant facilities?
5. Chapter 3 states that condensing heat transfer coefficients are higher than those with no phase change. Why would gas processors want to use hot oil instead of steam as a heat source?
6. Why would gas processors prefer POP contracts?
7. Assuming a POP contract, which is more important, maximizing liquids production or minimizing fuel consumption?
8. Any large capital expenditure in a gas plant must be justified on an economic basis. What factors are important in making the economic analysis?
9. What is the difference between shrinkage and energy efficiency? List factors that affect each of them.
10. What operational factors need to be considered when accurately calculating the frac spread?

REFERENCES

API Standard 520-1, *Sizing, Selection, and Installation of Pressure-Relieving Devices, Part I - Sizing and Selection,* 9th edn. American Petroleum Institute, Washington, DC, 2014a.

API Standard 521, *Pressure-Relieving and Depressuring Systems,* 6th edn. American Petroleum Institute, Washington, DC, 2014b.

Energy Information Administration, Natural gas data, 2019a. www.eia.gov/dnav/ng/hist/rngc1M.htm (Retrieved April 2019).

Energy Information Administration, Natural gas liquids spot prices, 2019b. www.eia.gov/naturalgas/weekly/#tabs-prices-4 (Retrieved April 2019).

Energy Information Administration, Petroleum & other liquids, U.S. Department of Energy, 2019c. www.eia.gov/dnav/pet/hist/LeafHandler.ashx?n=PET&s=EER_EPLLPA_PF4_Y44MB_DPG&f=M (Retrieved April 2019).

Engineering Data Book, 14th edn. GPSA Midstream Suppliers, Tulsa, OK, 2016a.

Engineering Data Book, Section 5, Relief systems, GPSA Midstream Suppliers, Tulsa, OK, 2016b.

Engineering Data Book, Section 18, Utility systems and maintenance, GPSA Midstream Suppliers, Tulsa, OK, 2016c.

Environmental Protection Agency, Air pollution control technology fact sheet, Flare, EPA-452/F-03-019, undated. www3.epa.gov/ttn/catc/dir1/fflare.pdf (Retrieved April 2019).

International Electrotechnical Commission, IEC TR 61511-0:2018, Functional safety - safety instrumented systems for the process industry sector, 2018. https://webstore.iec.ch/publication/60766 (Retrieved April 2019).

Keller, A.B., NGL 101- the basics, U.S. Department of Energy, 2012. www.eia.gov/conference/ngl_virtual/eia-ngl_workshop-anne-keller.pdf (Retrieved April 2019).

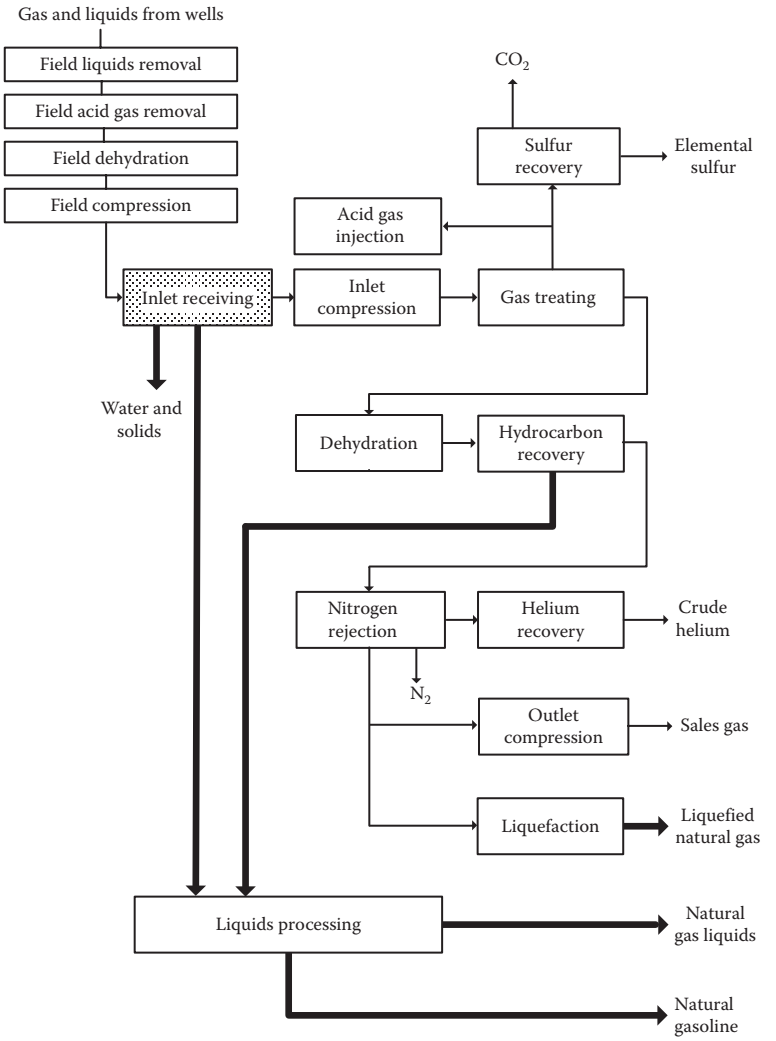
Schimmoller, B., Gas processing margins are in structural decline, *Oil Gas J., 101.35*, 2003.

U.S. Department of Energy, Summary of LNG export applications of the Lower 48 States, 2019. www.energy.gov/fe/downloads/summary-lng-export-applications-lower-48-states (Retrieved April 2019).

West, J., Improving EIA's natural gas shrinkage estimates, *Eighty-Seventh Annual Gas Processors Association Convention*, Tulsa, OK, 2006.

Taylor & Francis
Taylor & Francis Group
http://taylorandfrancis.com

8 Field Operations and Inlet Receiving



8.1 INTRODUCTION

Gas processors usually take custody of the metered gas leaving the gas–liquid separator at the wellhead because well operations are normally not under their direct supervision. This chapter touches on wellhead operations and then discusses the field operations and equipment for moving the gas into the gas plant and then through inlet receiving, the first of many gas–liquid separations

in the typical gas plant. The chapter includes a discussion of gas hydrates because their control and prevention are critical to field operations.

Onshore field operations collect gas from many wells. This requires numerous gathering lines, compressor stations, and sometimes routine pigging. Offshore operations may have fewer wells and little or no compression. However, both onshore and offshore operations are subject to disruptions, which change feed rates and compositions to the gas plant. Field disruptions are the most common cause of plant upsets and reduced revenue. Typical operating costs for full service, midstream assets (gathering, compression, gas conditioning, and processing) in the lower 48 of the United States in 2018 ranged from \$0.20 to \$0.75/Mscf (\$7.50–\$28/10^3 Nm^3). Operating and maintenance for field operations can consume one-half to two-thirds of this cost (Drinkwine, P.M., Private Communication, 2018).

8.2 FIELD OPERATIONS

8.2.1 Wellhead Operations

Many factors affect what operations occur at the wellhead. Probably, the most important is whether the well produces oil and gas or just gas. Figure 8.1 shows a high-pressure gas–oil separation process (GOSP), where associated gas is recovered from oil by putting the produced liquids through three separators at successively decreasing pressures. The number of separators depends upon the wellhead pressure but the final stage is as low as 3 psig (0.2 barg) to maximize gas recovery and to "stabilize" the crude oil for storage and transport. The final stage pressure is dictated by downstream operations on the crude line. Frequently liquids from several wells are fed to the same high-pressure separator to minimize the number of separators, compressors, and meters. This is especially true for offshore operations.

Associated gas is almost always saturated with water. Either dehydration (usually glycol dehydration, see Chapter 11) or hydrate inhibitors (see Section 8.3) are used to prevent hydrate formation.

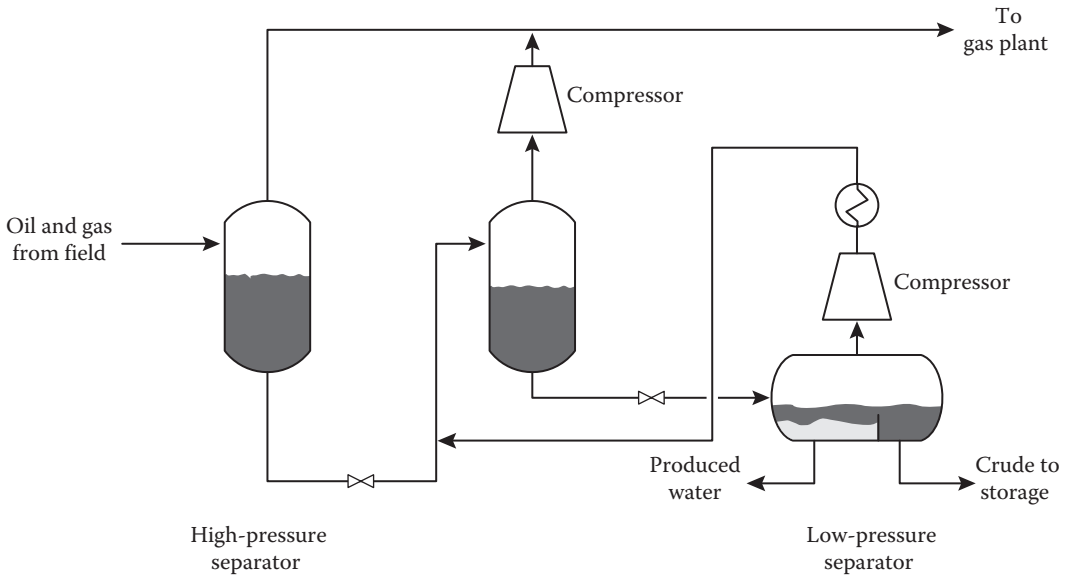


FIGURE 8.1 Gas-Oil Separation Process (GOSP) for removing gas from high-pressure oil well.

For unassociated gas wells producing gas and condensate, many factors dictate what operations are needed at the wellhead. These include:

- Water content
- Hydrocarbon liquids content in produced gas
- Range of ambient temperature
- Pressure
- Well age

These factors determine what, if any, separation is required. A few gas wells produce a dry gas, in terms of both condensate and water. This gas requires no separator at the wellhead and is sent directly to either a gas plant or pipeline. Most wells produce some water and condensate and a single-stage, three-phase separator is adequate. The produced liquids may be stored and trucked from the site.

For cases where wet gas goes through a choke (pressure letdown) before entering a separator or where winter temperatures are cold, the separator may have firetube heaters (see Section 3.4.2) to prevent hydrate formation. There are many fired separator configurations. A simple direct fired separator, as shown in Figure 3.7, has the produced liquids in direct contact with the fire tube. A common configuration is indirect heating with glycol as the bath liquid. Wellhead gas and liquids are heated in the tube shown in Figure 3.7 and then flashed into a small horizontal separator on top of the fired unit. Designs incorporate weirs for water–condensate separation and demisters to prevent entrained liquids leaving with the gas.

Reservoir pressures decline with production, often with increased water make. (The one exception is coal bed methane production where large quantities of water must be removed before significant gas production begins.) If the well produces no liquids, production slows and vacuum blowers are used to produce the gas at an economical rate. In these situations, the reservoir pressure may be less than 100 psig (7 barg) with wellhead pressures of 2.5 psia (0.2 bara). (Unconventional gas sources such as coal bed methane and gas from landfills operate at low pressures and usually require vacuum blowers.)

If the gas well produces liquids and fails to have sufficient pressure to continuously push the liquids out, artificial "lift" methods, e.g., plunger lift, are needed. Lift methods are beyond the scope of this book. Langston (2003) provides descriptions of various lift methods and provides a good source of many other wellhead operations.

Figure 8.2 shows a wellhead site in Colorado, where two wells use a common liquids storage tank. Both use fired separators (vent stacks are visible on the right side). Note that there is a wind indicator on a pole in the center of picture, which indicates the direction that the site can be approached safely. The lines from the tops of the separators go to the meter sheds. Solar panels provide the power to electronically transmit meter readings. Gas processors take custody of the gas leaving the meter. Metering is a critical part of wellhead operations and is discussed below.

8.2.2 Gathering Systems

For offshore production, many wells are tied back to a platform, and then the gas from multiple platforms are tied together into large pipelines that go to the gas plant, which usually is onshore. For onshore wells, especially if operated by independent producers, an extensive network of small lines from individual wells tie into increasingly larger lines. The smaller gathering lines may be aboveground or buried. Aboveground gathering lines are much cheaper and easier to maintain but are exposed to the environment. Surface coating for corrosion prevention and possibly insulation may be required. Plastic pipe is often used on low pressure ($\lesssim$50 psig [3.5 barg]) lines to reduce costs and eliminate corrosion problems.

For low-pressure gathering systems, the processor commonly uses a "drip system." This system involves having a vessel, often simply a larger diameter pipe, below low points in the gathering line. Liquids drain from the gathering line into the vessel. The vessel is periodically emptied and the

FIGURE 8.2 Gas wells with condensate tank and fired separators.

liquid is trucked to the gas plant for processing. Drip systems reduce the liquid load on the line and help reduce liquid slugging into the plant and pigging frequency (Section 8.2.5 discusses pigging).

As conventional gas fields are depleted, low wellhead and line pressures are becoming more common. Subambient (vacuum) lines are a major concern for gas processors because of potential air ingress from leaks. As noted in Chapter 6, oxygen is an unwelcome component because it enhances corrosion, adversely affects several plant processes, and can cause the sales gas to be subquality if the concentration exceeds pipeline specifications, which can be as low as 10 ppmv (Jordan et al., 2006). Cooper et al. (2011) discuss problems caused by oxygen. Chapter 14 discusses oxygen removal. The oxygen problem is severe enough in some areas that personnel are dedicated to "chasing air" to find the leaks. They analyze pipeline contents for oxygen and work back into the field to find the source. Once found, the line or well is shut down for repairs. Some sour gas gathering systems have on-line oxygen analyzers. Jordan et al. (2006) discuss field monitoring of oxygen in gathering systems, including situations when acid gases are present.

Since the 1990s, gas processors have installed SCADA (supervisory control and data acquisition) systems to monitor both plant and field operations. These systems provide gas plant operators with the capability to remotely shut down lines, which may be in a desolate country, far from the plant.

8.2.3 Compressor Stations

Figure 8.3 shows an onshore compression station, commonly called a booster station. This is a large station with the compressors inside a building. The fans provide interstage and final cooling of the gas. Many booster stations are small with the compressors exposed to ambient conditions which may decrease their availability.

Figure 8.4 is a schematic of common operations at a booster station. (Booster stations are rarely used in offshore production unless the line is roughly 100 mi or more offshore.) In addition to compressing the gas to move it into the gas plant, the stations usually have inlet suction separators (scrubbers) to remove condensed liquids. The condensate is either reinjected downstream of the compressor discharge or stored before being trucked to the gas plant. Some booster stations include treating (Chapter 10) or dehydration facilities (see Chapter 11) to reduce corrosion and to mitigate hydrate formation. When required, chemical inhibitors for corrosion and gas hydrate prevention are injected into the discharge gas using metering pumps to control injection rates. Cathodic protection is also widely used for corrosion inhibition.

FIGURE 8.3 Booster station on gathering system.

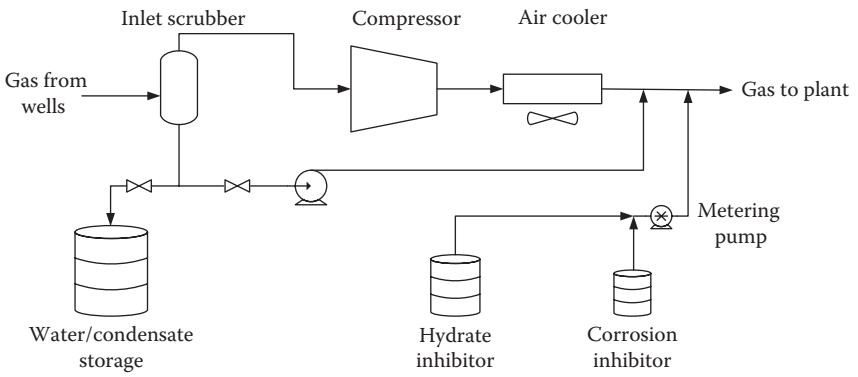


FIGURE 8.4 Schematic of common operations at a compression station on a gathering system. Condensed liquids may be stored or returned to the line. Some locations may have dehydration or sweetening facilities.

How to handle condensed liquids at booster stations is an economic and contractual decision. Liquids collection requires tankage and trucking to move the liquids to the plant. The benefits are higher line capacity, reduced corrosion rates, and reduced chemical hydrate and corrosion inhibitor injection rates. Also, pigging requirements (see Section 8.2.5) as well as the potential for large liquid slugs entering the plant are reduced. Putting liquids back into the pipeline eliminates the need for tanks and trucking, but increases chemical costs, puts more importance on good pigging practices, and probably increases pipeline maintenance costs.

The gathering and processing contract with the producer may require field separation to facilitate determination of ownership and properly account for condensed liquids. The large quantity of liquids in rich gas systems is often sufficient to drive the economics to include field separation and handling of these liquids.

Calculation of the pressure drop in these two-phase lines is complex and not covered here. The *Engineering Data Book* (2016b) discusses two-phase flow and gives some calculation methods. However, the best results are obtained from computer models.

Compressor power requirements depend upon gas flow and compression ratio (see Chapter 9). Booster station power requirements range from the teens to the thousands of horsepower (tens of kilowatts to megawatts). Compressors are driven by electric motors, internal combustion engines, and gas turbines. Power requirements and availability of fuel dictate the best choice. Some compressor

drivers are internal combustion engines that have been in service for 50 or more years and have been rebuilt many times. Compressor engines are usually fueled with natural gas. The best fuel is sales gas from the plant or nearby transmission pipeline because it is clean and has a stable heating value. However, this type of fueling requires piping between the source and booster station. If the raw gas has sufficiently low sulfur levels to meet emission standards it can be used. However, the fuel may be too rich for the engines. Fuel-gas conditioners employ low temperature separators (LTS) or membranes to remove heavier hydrocarbons from the gas and lower the heating value (see Chapter 12). If rich gas is used with internal combustion engines, the timing of the engine must be retarded to prevent detonation problems (Kuchinski, J., Private Communication, 2005). Electric motors are often used in remote sites when the pipeline gas is unavailable or where emissions from a gas engine are an environmental concern. Also, the high availability and the relative ease of running wire instead of fuel lines make them attractive when electrical power is available.

8.2.4 Pipeline Fieldwork

Gas wells may be far away from the plant and gathering lines may pass through both remote and populated areas. Pipeline codes depend upon population density.

Although they vary slightly, these laws and codes generally follow the principle of exposure to the public. An area that is heavily populated or contains buildings where the public congregates (e.g., a school) requires a higher standard of design than in a remote, sparsely populated area. In addition to population, factors such as operating pressure, service (gas gathering versus transmission), and composition (sweet versus sour gas) are factored into the regulations and codes. Pipelines falling under these regulations are categorized according to public risk and proximity to structures and roadways. The category dictates such things as pipe wall thickness, frequency, and method of inspections.

This section briefly discusses two important aspects involving pipelines—location notification and design, and ongoing maintenance. Regarding pipeline location notification, in many areas there is a government-run system for notification of work near utilities and pipelines. This usually consists of a well-advertised, toll-free phone number, which must be called before anyone initiates digging or construction. Gas pipeline operators are then notified and they must mark their pipelines in a prescribed manner. Although upkeep of notification maps and data represent an added burden to pipeline operators, the extra effort results in fewer accidents involving pipelines. Participation in the notification program is mandatory in most jurisdictions.

The design and ongoing maintenance of gas pipelines is regulated in many areas around the globe. In the United States, there are both federal and state requirements. For example, the U.S. Department of Transportation has regulatory authority under Title 49 CFR192 and CFR195 (U.S. Department of Transportation, 2018). There are codes such as ASME B31.4-2016 Pipeline Transportation Systems for Liquid Hydrocarbons and Other Liquids and ASME B31.8-2016 Gas Transmission and Distribution Piping Systems, which cover the design of pipelines. In some areas, these ASME codes are incorporated by reference into regulations.

8.2.5 Pigging

Pigging is the process of forcing a solid object (a pig) through a pipeline. Two papers by Webb (1978a,b) provide an extensive discussion of pigging for both liquid and gas pipelines. The process involves inserting the pig, via a pig launcher, into the pipeline, moving it through the line using pressure drop, and removing it by using a pig receiver. Pigging is used to perform any of the following functions:

1. Provide a barrier between different liquid products that use the same pipeline.
2. Check wall thickness and find damaged sections of lines (“Smart Pigs”).

3. Remove debris such as dirt and wax from lines.
4. Provide a known volume for calibrating flow meters.
5. Coat inner pipe walls with inhibitors.
6. Control the buildup of condensed hydrocarbon liquids and water in multiphase pipelines.

For field operations, the sixth function is the most important when bringing in wet gas from the field. The need for pigging can be minimized if gas flow rates are high enough to carry the liquid at the same velocity. However, this results in high compression costs because the pressure drops will be large. Therefore, gathering systems typically operate in the two-phase stratified flow region, where the pressure drop is lower, and the liquid flow rate is much slower than the gas flow rate. (See the *Engineering Data Book* (2016b) for more details about two-phase flow.) Thus, liquid accumulates in low spots in the line. Field operations follow a rigorous pigging schedule to prevent large slugs of liquid entering the plant that would flood inlet receiving and carry liquids into the gas processing plant. If the normal pigging schedule is interrupted for any reason, the next pig run through the pipeline will displace a much larger volume of liquid. Fortunately, plant operators usually know when a "killer pig" is coming, and plan operations accordingly. Common techniques to deal with extraordinarily large liquid slugs include drawing down liquid levels in inlet receiving, to the extent possible, shutting in gas and shutting down field compressors. Since restarting field booster compressors after maintenance can produce large liquid slugs, care is usually taken to slowly increase flows when a compressor is placed in operation. Varnell and Godby (2003) discuss procedures to minimize the potential for slugging problems.

Figure 8.5 shows examples of pigs and spheres used in two-phase service. Pigs are usually made of polyurethane foam. The smaller, projectile-shaped pigs in the front of the picture and the larger ones with similar shape are used for cleaning out soft deposits, gauging lines, and removing water after a line is hydrotested. The pig in the center of the back row has metal brushes for taking out solids such as scale. The back two pigs on the left are designed for bidirectional flow. Larger pigs have a metal mandrel holding the cups and disks, which can be replaced after wear (Girard Industries, 2019).

Figure 8.6 shows a simplified schematic of a pig launcher and a receiver ("pig catcher") used in gas service. A bypass line ("kicker") is used to bring the chamber, holding the pig, to line pressure. A grate must be placed at the branch of the two major lines to prevent the pig from getting stuck at the intersection. The pig receiver in Figure 8.6 shows vent gas going to a vapor recovery unit.

FIGURE 8.5 Different shapes of foam spheres and pigs used to clean gathering lines. (Courtesy of Girard Industries.)

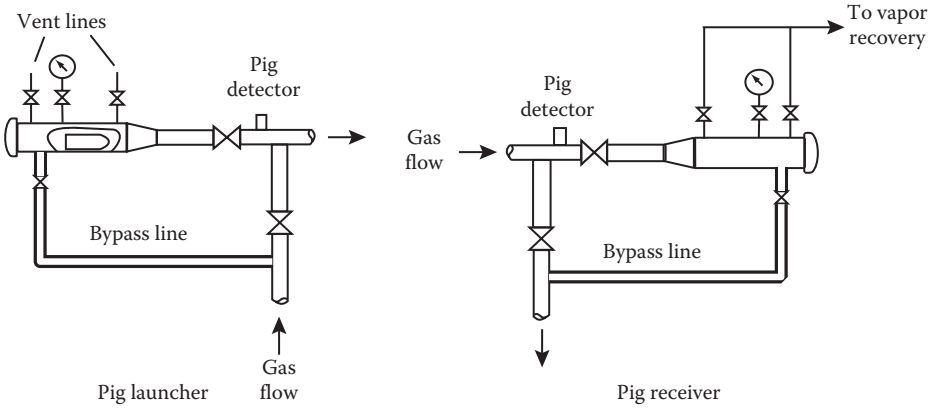


FIGURE 8.6 Simple schematics of pig launcher and receiver for gas service.

However, it may go to flare or possibly low-pressure fuel gas. If the receiver is located far from processing facilities, vent gas may be vented to atmosphere. Webb (1978b) provides general procedures for launching and receiving pigs.

Both pigs and spheres can be launched remotely. Spheres, like those shown in the left front of Figure 8.5, are more commonly used in gathering lines because the launching tends to be more reliable. Spheres for nominal 2–4 in. (50–100 mm) diameter lines are solid, whereas larger ones are inflated, usually with water or ethylene glycol–water mixtures.

Pigs and spheres are launched from a pipe branch that can be isolated and purged for loading.

Figure 8.7 shows a remote sphere launcher. The launchers typically hold three to five spheres and are inclined so that spheres can be inserted remotely by gravity feed.

Figure 8.8 shows a remote pig launcher. These function by having a pig drop inside a large ball valve from the vertical pipe section shown. The ball valve is normally open. Flow is momentarily interrupted when the valve is shut to allow a pig to drop into the valve. The valve is then reopened to resume flow and launch the pig. If the pig enters the ball valve at an angle, it is possible that it will

FIGURE 8.7 Remote automated sphere launcher. (Courtesy of Epic Integrated Services, Odessa, Texas.)

FIGURE 8.8 Remote automated pig launcher. A pig is on ground, left of launcher. (Courtesy of Beeline Gas Systems.)

not drop in completely and not be launched. A weight sits on top of the pigs to help ensure that they slide down the barrel properly.

Remote pig launchers have three distinct advantages. The first is the obvious convenience of launching pigs remotely, which can be important when the launcher can become inaccessible in bad weather. The second advantage is that it reduces pigging labor costs because multiple pigs are loaded at one time. The third is that the automated pig launchers significantly reduce the volume of gas vented in pigging operations because the launcher needs to be opened one time to load multiple pigs.

Pressure differential drives the pig through the line. However, pigs usually stop intermittently when they come to low points, where pools of liquid accumulate. Field and plant operators learn the typical run times for pigs in a line, and in-line detectors signal a pig's location.

Figure 8.9 shows a smart pig, typical of those used on larger metal gas gathering lines and transmission lines. Although not used on a frequent basis, smart pigs are an integral component in maintaining pipeline integrity. These pigs use one of three methods for detecting flaws and damage to pipelines (PHMSA Pipeline Safety Program, 2014):

1. Magnetic flux
2. Ultrasonics
3. Geometry

Magnetic flux tools impose a magnetic field on the pipe wall and detect changes in the field caused by changes in wall thickness or cracks. Ultrasonic tools measure differences in wall thicknesses by monitoring changes in the velocity of sound in the wall. They are sensitive to wall deposits, such as wax, so the lines need to be cleaned first. The geometry tools use mechanical means to detect changes in wall thickness. Smart pigs have onboard data recording and an odometer to track position.

8.2.6 Gas Metering

One of the most important functions of field operations is gas flow measurement. For most gas processing plants field measurement drives settlement accounting back to each delivery point (the point

FIGURE 8.9 Smart pig being removed from pig receiver. The pig uses magnetic flux to detect corrosion and mechanical damage in pipeline wall. (Courtesy of ROSEN Group.)

where the processor takes custody of the gas) into the gathering system. Not only must metering equipment be properly installed and maintained, it must be of the proper quality to ensure a correct settlement with the producers. Most gas gathering and processing facilities have electronic metering like that shown in Figure 8.2. However, a few still use paper chart recorders, often as backup.

It is important that field personnel understand the type of measurement required for each metering point under the contract and make certain that appropriate metering is in place. For example, for a plant with percent of proceeds contracts (see Chapter 7), it is important that all meters used for these contracts be of equal precision and accuracy. This assures the accurate allocation of liquid products and residue sales gas back to the delivery point and to each producer. If a facility has different types of contracts, additional metering must be installed in specific locations to allow proper settlement accounting.

A clear understanding of the metering requirements for each delivery point into the gathering system is required to properly communicate changes in the gathering system flows to accounting personnel. Also, whenever there is field venting or flaring of gas, which has been metered into the system, it is important to properly account for the lost gas.

Measurement of liquids formed through condensation and entering the gathering system through carryover from lease separation equipment complicates the proper accounting for both the gas and liquids. Dealing with products allocation is beyond the scope of this book but proper operation of the field gathering metering system is critical to achieve a fair and correct settlement.

8.3 GAS HYDRATES

A field of technology, called flow assurance, exists for ensuring that hydrocarbons flow unimpeded by line blockage from wells to the point of processing. The three areas of concern are:

1. Wax and asphaltene solids deposition
2. Scale (inorganic salt) deposition
3. Gas hydrate solids formation

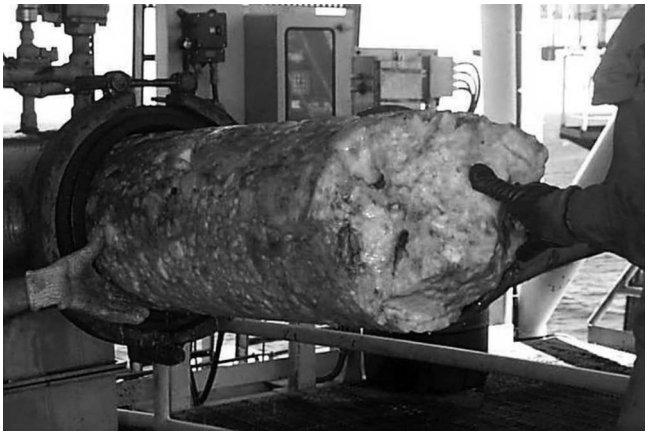


FIGURE 8.10 Hydrate plug formed in condensate line offshore Brazil. (Courtesy of Petrobras SA.)

For gas gathering systems, wax and asphaltene deposition is normally not a serious problem and can be remediated by pigging. Scale is a common problem at the wellhead but should not be one in the pipeline. However, gas hydrates strike fear into the hearts of flow assurance people for two reasons. First, hydrate plugs like that shown in Figure 8.10 can form within minutes without prior warning. The other solids take weeks, months, or years of accumulation to cause plugging and are usually detected by increased pressure drop. Second, although hydrate formation can be inhibited, inhibitor injection pump failure, separator failure, and process upsets can suddenly make pipeline contents vulnerable to hydrate formation. Sloan (2000) provides a good overview of hydrate problems and how to address them, especially for offshore situations where hydrate plugging can be a major problem.

8.3.1 Properties

Gas hydrates are a class of solid, nonstoichiometric compounds called clathrates. Gas hydrates should not be confused with salt hydrates, which form stoichiometric compounds of salts and water. Gas hydrates form when the host material, water, through hydrogen bonding, forms a caged structure that contains a single guest molecule, such as methane. Figure 8.11 illustrates conceptually one cell in a hydrate lattice containing a methane molecule. Both host and guest must be present for the solid to form.

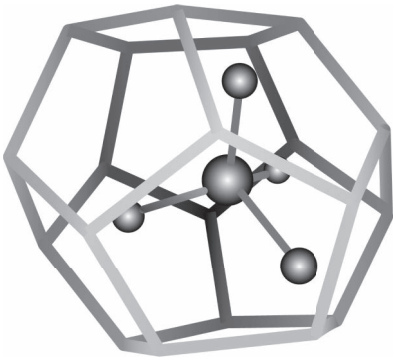


FIGURE 8.11 Conceptual image of one hydrate cage with a methane molecule inside. Hydrogen atoms are not shown but oxygen atoms are located at each intersection point of outer cage.

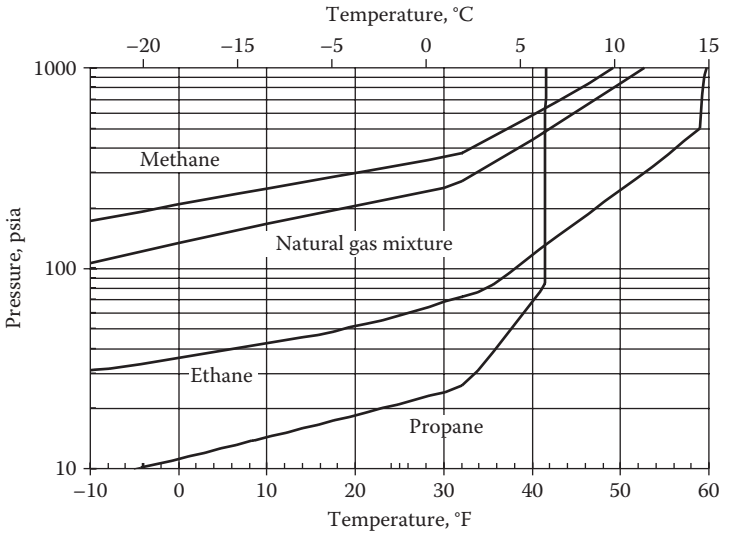


FIGURE 8.12 Hydrate formation conditions for pure methane, ethane, and propane (Data from Sloan and Koh, 2008.) and a natural gas mixture from Rio Arriba County, New Mexico. Mixture composition given in Table 6.3; line computed using CSMHYD. Hydrates form at temperatures below the lines shown above. See text for details.

Gas hydrates were a laboratory curiosity until Hammerschmidt (1939) determined that they caused pipeline plugging. As Figure 8.12 shows, hydrates form at temperatures well above the freezing point of water. Figure 8.12 has a break in all curves at 32°F (0°C) because the hydrates are in equilibrium with gas and ice at the lower temperatures, and with gas and liquid water at the higher temperatures. For the ethane hydrate line, an abrupt change occurs at 57°F (14°C). At this point, the hydrate is in equilibrium with gaseous ethane, liquid ethane, and liquid water (i.e., the hydrate formation line intersects the vapor pressure line, which is not shown). At higher temperatures, the ethane hydrate is in equilibrium with liquid ethane and liquid water. The same explanation applies to the break in the propane curve. For gas processing applications, the intersection with the vapor pressure line puts an upper temperature limit on hydrate formation because the line is essentially vertical at temperatures above the intersection and at pressures commonly seen in gas processing. No similar point exists for methane, because methane has a critical temperature of about −117°F (−82°C) (see Table B.1[1]).

While there are many different hydrate structures, natural gas forms in either of two structures, called Structure I and Structure II. Both structures contain large and small cavities. The small cavity, which is depicted in Figure 8.11, will hold methane, nitrogen, oxygen, and hydrogen sulfide. The larger cavities of Structure I can accommodate carbon dioxide or ethane as well. The smaller cavities of Structure II are almost the same size as those of Structure I but the larger cavities are sufficiently large to hold ethane, propane and the butanes. Because Structure II forms when propane is present at more than trace amounts, Structure II is the most common hydrate structure formed in natural gas mixtures. For details of hydrate structure, composition, and phase behavior, see e.g., Sloan and Koh (2008) and Carroll (2003).

Figure 8.12 also illustrates the compositional dependence on hydrate formation with the predicted hydrate formation conditions for a Rio Arriba County, New Mexico, gas mixture (see Table 6.3). The hydrate formation curve for the natural gas mixture was calculated using the

[1] See Appendix B on publisher website: www.crcpress.com/Fundamentals-of-Natural-Gas-Processing-Third-Edition/Kidnay-Parrish-McCartney/p/book/9781138612792

program CSMHYD available from Center for Hydrate Research (Colorado School of Mines, 2018). This mixture contains only 1.33 mol% ethane and 0.19 mol% propane, but the hydrate formation temperature at a given pressure is more than 10°F higher than pure methane. This large effect is because pure methane forms a Structure I hydrate while Structure II hydrates form when ethane and especially propane are present.

At a given pressure, pure methane forms hydrates at the lowest temperature. Adding ethane, hydrogen sulfide, or carbon dioxide raises the formation temperature if no propane is present. However, as noted above, having low concentrations of propane raises the formation temperature significantly. Also, in mixtures containing propane, adding carbon dioxide or hydrogen sulfide may lower formation temperatures. The *Engineering Data Book* (2016c) discusses this effect. Nitrogen and oxygen will lower the hydrate formation temperature of the mixture. Heavier compounds (e.g., C_5^+) are too large to fit into the cages formed by natural gas and have an insignificant effect as a diluent in natural gas because their concentration is so low. Helium also acts as a diluent.

8.3.2 Hydrate Formation Prediction

Thermodynamics provides a powerful tool for predicting the temperature and pressure for hydrate formation of a gas of known composition. However, even when hydrates are thermodynamically possible, they may never form. Hydrate formation kinetics are complex and poorly understood, partly because the crystal growth process depends upon so many variables. Because of this uncertainty, operating conditions should be outside the hydrate region.

Since the 1970s, a method based upon statistical thermodynamics has been used to predict formation temperatures to within a few degrees Fahrenheit. It is the most successful and widely used application of statistical thermodynamics in industry. The model is complex and requires a computer program to be used. However, commercial simulators and stand-alone programs are available that use improved models. They incorporate the effect of thermodynamic inhibitors, and accurately predict phase behavior for all phases present. The book by Sloan and Koh (2008) includes a sophisticated and highly accurate program that uses the statistical thermodynamic model.

Before the statistical mechanical model, two empirical methods were widely used. One employs *K*-values similar to those used for vapor–liquid equilibrium calculations, and the other is based upon gas gravity. The *K*-value method gives slightly better results for sweet natural gas with specific gravities between 0.6 and 0.8, and it is better for sour gases. We discuss only the gas gravity correlation, which is adequate for quick calculations. (The *Engineering Data Book* (2016c) provides details of both empirical methods.) When more accurate values are needed, computer programs that employ the statistical mechanical model should be used.

Figure 8.13 shows hydrate formation prediction curves for natural gases as a function of gas specific gravity. For below 1,000 psi (70 bar), the gas gravity curves can be approximated by

$$t(°\mathrm{F}) = -16.5 - \frac{6.83}{(\mathrm{SpGr})^2} + 13.8 \ln\left[P(\mathrm{psia})\right] \tag{8.1a}$$

$$t(°\mathrm{C}) = -6.44 - \frac{3.79}{(\mathrm{SpGr})^2} + 7.68 \ln\left[P(\mathrm{bar})\right] \tag{8.1b}$$

Specific gravity is defined in Section 1.3.3.1.2. For natural gas calculations, the specific gravity is defined as the molar mass of the gas divided by 28.9625.

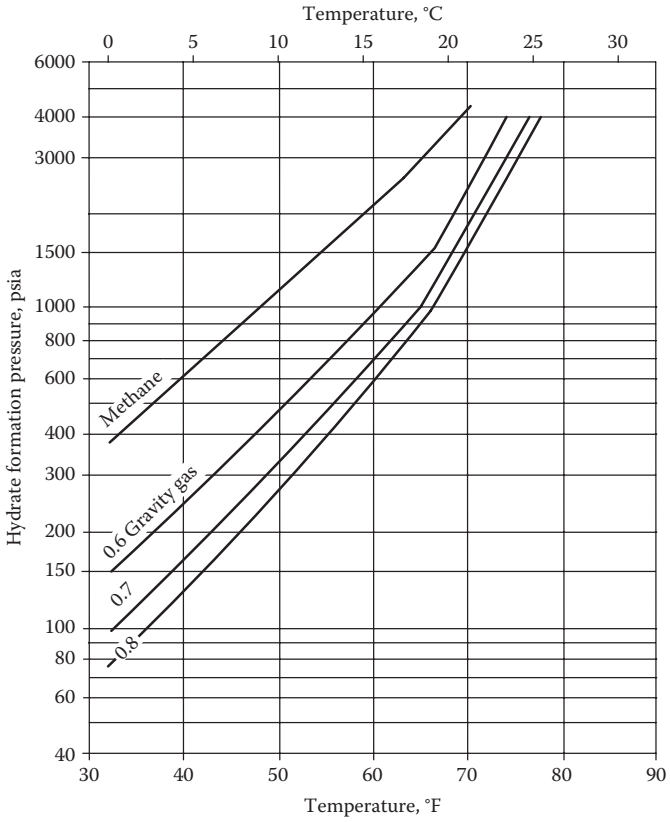


FIGURE 8.13 Pressure-temperature curves for estimation of hydrate formation conditions as a function of gas gravity. These curves should be used for approximation purposes only. Divide pressure by 14.5 to obtain bars. (Adapted from *Engineering Data Book*, 2016c, with permission.)

TABLE 8.1
Gas Composition for Example 8.1

Component	Mole Fraction	Molar Mass	lb_m/lb-mol Mixture (kg/kg mol Mixture)
CO_2	0.002	44.01	0.09
N_2	0.094	28.01	2.63
C_1	0.784	16.04	12.58
C_2	0.060	30.07	1.80
C_3	0.036	44.10	1.59
iC_4	0.005	58.124	0.29
nC_4	0.019	58.124	1.10
Totals	1.000		20.08

Example 8.1

Estimate the hydrate formation temperature at 325 psia (22.4 bar) for the gas with the composition in Table 8.1. Compare the results from Figure 8.13 or Equation 8.1 with the experimentally reported value for the gas of 50°F (10.0°C) (*Engineering Data Book*, 2016c).

Solution

Use of either Figure 8.13 or Equation 8.1 requires knowledge of the specific gravity of the gas, so the molar mass must be calculated first, as shown in Table 8.1. The specific gravity = molar $mass_{gas}/28.96 = 20.08/28.96 = 0.693$.

Using Equation 8.1, the hydrate formation temperature is $-16.5 - 6.83/(0.693)^2 + 13.8 \times \ln(325) = 49°F$ (9.5°C). Figure 8.13 gives 50°F (10.0°C). The computer program CSMHYD predicts that hydrates form at 49°F (9.4°C). The agreement is exceptionally good between the methods and experimental data for this example.

Gas hydrates can form anywhere in a pipeline or process stream, but they are particularly likely to form downstream of orifices or valves because of cooling from Joule–Thomson (J–T) expansion effects. The *Engineering Data Book* (2016c) provides charts for estimation of how much pressure drop is allowed to avoid hydrate formation during expansion. However, the charts are only estimates, and calculations by a computer program should be used to determine the possibility of hydrate formation.

8.3.3 Hydrate Inhibition

Three ways are used to avoid hydrate plugging in natural gas streams:

1. Operate outside the hydrate formation region
2. Dehydrate the gas
3. Add hydrate inhibitors

The first option is ideal but often impractical. If practical and economically feasible, dehydration is the next best option. Because of the high gas volumes and high pressures, offshore operations frequently use dehydration (see Chapter 11), but it is less common in onshore field operations. The third best, but most commonly used option, is addition of inhibitors. Whenever operating conditions are prone to hydrate formation and liquid water may be present in the lines, field operators control hydrate formation by use of chemical inhibitors. They are added at the wellhead and at booster stations through positive displacement pumps so that the addition rate can be accurately controlled.

Regarding dehydration, how dry a gas should be to prevent hydrate formation is uncertain. The gas obviously should have a water dew point below the lowest operating temperature to avoid water condensation. Thermodynamics predicts that hydrates can form even when the gas phase is unsaturated with water. Hydrates have been reported several times in gas pipelines with no free water and unusually long gas residence times but the phenomenon is extremely rare (Sloan, E.D., Private Communication, 2005). The difficulty in forming hydrates with no liquid water present is explainable through mechanistic arguments. Nominally, six water molecules are required for each guest molecule. However, 20 or more water molecules are needed to form a cage around a gas molecule, and many cages must combine to form the hydrate lattice (see Figure 8.11). Therefore, the likelihood of sufficient number of water molecules at the extremely low concentrations coming together in the gas phase to form the lattice is low. However, Nicholas et al. (2009) observed hydrate formation in unsaturated condensate. Plugging occurred only when liquid water was present.

Use of chemical inhibitors is the least attractive hydrate inhibition method for several reasons:

- The proper inhibitor dosage must be known to avoid plugging or needless chemical costs, but oftentimes it is determined empirically. Sometimes excessive amounts of inhibitor are used to ensure hydrate prevention which is expensive and can cause downstream problems.
- The chemical cost, although it is usually a small fraction of overall operating costs.
- The reliability of inhibitor injection can be a problem because of malfunctioning injection pumps and depleted inhibitor reservoirs, especially at remote sites.

- The transportation of inhibitors to the injection site often requires handling of hazardous materials.
- The potential for inhibitors to cause problems in downstream operations.
- The interaction between hydrate inhibitors and other additives may reduce the effectiveness of some of the additives—an effect that is usually determined empirically.
- The inhibitor may carry into product streams and exceed product specifications, causing a cost penalty on product or require removal of the inhibitor in the plant. Chapter 14 discusses removing inhibitors.

Despite these problems, millions of dollars are spent each year on hydrate inhibitors because they require minimal capital cost and because injection rates are readily altered according to flow and operating conditions.

There are three classes of chemical hydrate inhibitors:

1. Thermodynamic
2. Kinetic (KHI)
3. Antiagglomerate (AA)

Thermodynamic inhibitors have been in use since around 1940. They are essentially antifreeze. The latter two types are technologies developed in the late 1990s. They are low-dosage inhibitors that inhibit crystal growth or prevent agglomeration of hydrate crystals to prevent blockage. Most onshore operations use thermodynamic inhibitors. Offshore producers use thermodynamic inhibitors but increasingly use the newer inhibitors, sometimes in combination with thermodynamic inhibitors, to reduce or eliminate thermodynamic inhibitor usage.

8.3.3.1 Thermodynamic Inhibitors

Thermodynamic inhibitors (TIs), mainly methanol and ethylene glycol, are widely used. Inorganic salts are effective but rarely used, and further discussion focuses only to methanol and ethylene glycol.

The required dosage of TIs is predictable, but the concentrations can be high, over 50 wt% of the water phase. A number of empirical correlations, based upon the thermodynamic properties of solutions, predict the amount of any hydrate inhibitor required to depress hydrate formation temperatures. The two most commonly used are discussed here (more rigorous methods are used with the computer models mentioned above). Hammerschmidt (1939) proposed the following equation:

$$\Delta t(^\circ\mathrm{F}) = \frac{2{,}335 X_i}{MW_i(1 - X_i)} \tag{8.2a}$$

$$\Delta t(^\circ\mathrm{C}) = \frac{1{,}297 X_i}{MW_i(1 - X_i)} \tag{8.2b}$$

or

$$X_i = \frac{\Delta t(^\circ\mathrm{F}) MW_i}{\Delta t(^\circ\mathrm{F}) MW_i + 2{,}335} \tag{8.3a}$$

$$X_i = \frac{\Delta t(^\circ\mathrm{C}) MW_i}{\Delta t(^\circ\mathrm{C}) MW_i + 1297}, \tag{8.3b}$$

where

Δt is the hydrate depression temperature difference, °F (°C)
X_i is the mass fraction of inhibitor in the free water phase
MW_i is the molar mass of the inhibitor

The *Engineering Data Book* (2016c) recommends use of this equation for methanol concentrations of 20–25 wt% of the water phase; it recommends the equation for glycol concentrations up to 50 wt%. However, it notes that the constant 2,335 may be too low in field situations and a constant as high as 4,000 may be appropriate. The smaller value is best used first, and then lower concentration levels can be tried based on operating experience. There sometimes is a tendency to overtreat just to ensure that hydrates do not form.

Nielsen and Bucklin (1983) proposed

$$\Delta t(^{\circ}\mathrm{F}) = -129.6 \ln x_{\mathrm{W}}, \tag{8.4a}$$

$$\Delta t(^{\circ}\mathrm{C}) = -72.0 \ln x_{\mathrm{W}}, \tag{8.4b}$$

where x_{W} is the mole fraction of water in the aqueous phase. The paper provides details on the equation's derivation and gives example calculations. It also discusses methanol injection systems. The *Engineering Data Book* (2016c) recommends use of this equation for methanol concentrations up to 50 wt%.

The following three sections discuss methanol, ethylene glycol, and compare relative advantages of the two.

8.3.3.1.1 Methanol

Methanol is volatile and boils at 148°F (65°C). Because the gas volume greatly exceeds the water volume in most gas gathering systems, methanol vaporization losses must be considered. While it prefers the aqueous phase, it is slightly soluble in condensate. Figure 8.14 provides a means for estimation of vaporization losses. To estimate the methanol losses in a paraffinic condensate phase use

$$\ln(K_{\mathrm{MeOH}}) = 5.44 - 0.0184\, t(^{\circ}\mathrm{F}) \tag{8.5a}$$

$$\ln(K_{\mathrm{MeOH}}) = 4.85 - 0.0332\, t(^{\circ}\mathrm{C}) \tag{8.5b}$$

where K_{MeOH} is mole fraction of methanol in the aqueous phase divided by mole fraction of methanol in the hydrocarbon phase. The equation is a fit of line for zero toluene content line found in Figure 20–51 of the *Engineering Data Book* (2016c). If the hydrocarbon phase has an aromatic content of more than about 20 mol% (expressed as toluene), The *Engineering Data Book* figure should be used to adjust for the increased methanol solubility.

Separation of methanol from water requires distillation. Some gas plants have recovery facilities, but most ship the water–methanol mixtures elsewhere for recovery or disposal. If the sales gas or NGL products will be chemical feedstocks, methanol may have to be removed because it can be a catalyst poison. Most pipeline companies have a methanol specification on NGL products and charge a fee if it exceeds the specification. A fee for high concentrations of methanol in hydrocarbon liquids from offshore Gulf of Mexico is imposed to cover methanol removal costs. This motivated producers to consider ethylene glycol[2] and low-dosage inhibitors. Chapter 14 discusses gas processing problems associated with methanol and methods of removal.

The high vapor pressure and flammability of methanol also presents a safety hazard. This problem is a concern for offshore operations, where large quantities of methanol must be stored.

8.3.3.1.2 Ethylene Glycol

For ethylene glycol, both vaporization losses and solubility loss in NGL are negligible. Ethylene glycol is viscous and must be either diluted, usually with water, or kept in a warm storage vessel

[2] Ethylene glycol is commonly called monoethylene glycol (MEG) when used as hydrate inhibitor.

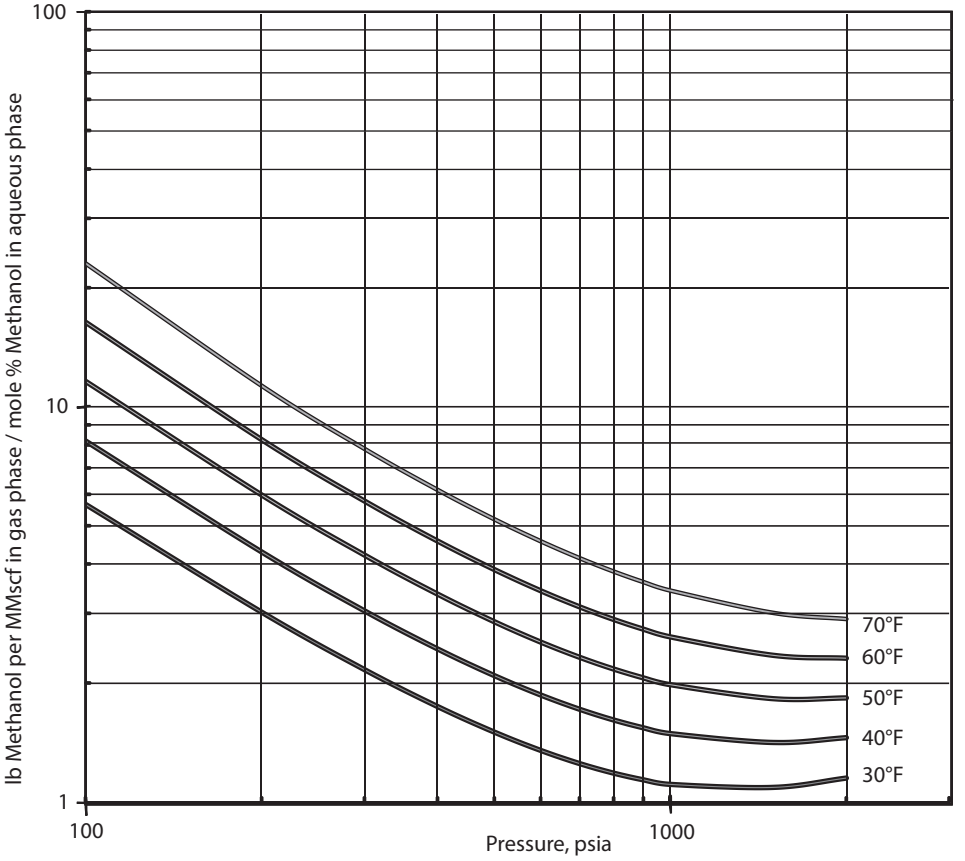


FIGURE 8.14 Distribution of methanol between gas phase and aqueous phase as function of pressure and temperature. Data based upon both vapor–liquid and liquid–liquid equilibria data (Author calculation using ProMax® (Bryan Research & Engineering LLC, 2019).)

in cold weather (Figure B.14 shows the viscosity as a function of temperature and concentration). Ethylene glycol is relatively easy to recover, as it remains with the aqueous phase and can be concentrated by evaporation of the water. The reclamation can take place at the gas plant and lean glycol trucked back to the field. For offshore operations the glycol is pipelined back to the offshore platform. Produced salts will accumulate in recycled glycol. Several companies offer glycol reclamation processes that remove salt accumulations.

8.3.3.1.3 Methanol versus Ethylene Glycol

Methanol is more widely used than ethylene glycol, and both have advantages and disadvantages, primarily on the basis of their physical properties. Both inhibitors are hydrophilic and remain predominantly with a condensed water phase, even if a condensed hydrocarbon phase is present.

Both inhibitors are toxic and restrictions apply to their disposal, both on land and at sea. One quirk of ethylene glycol is that it interferes with the oil and grease test performed on water to be discharged from offshore platforms, giving false high values.

Viscosity is not a factor with methanol. As a general rule, the *Engineering Data Book* (2016c) recommends ethylene glycol for continuous hydrate inhibition and methanol for intermittent use. The volatility and low viscosity of methanol makes it valuable for hydrate plug remediation.

Example 8.2

A sweet gas with a specific gravity of 0.73 leaves a gas–liquid separator at 100°F (37.8°C) and 600 psia (41.4 bara) saturated with water. The gas drops to 35°F (1.7°C) before reaching the next booster station at 500 psia (34.5 bara). Assume that no hydrocarbon condensate has formed in the line. Calculate how much methanol must be added per MMscf (10^3 Nm^3) to prevent hydrate formation between the separator and the booster station. Repeat the calculation for ethylene glycol, which is added in an 80 wt% mixture with water.

Solution

Use of Equation 8.1 or Figure 8.13 shows that the hydrate formation temperature at 600 psia (41.4 bara) is 59°F (15°C). This value means a 59°F − 35°F = 24°F (13.3°C) subcooling into the hydrate region, and hydrate formation is probable without inhibition. Determination of the inhibitor rate requires:

1. Determination of the amount of liquid water formed
2. Calculation of the required amount of inhibitor in the water phase
3. Calculation of the required amount of inhibitor in the gas phase

1. The water content of the gas leaving the separator is 95 lb_m/MMscf and 13 lb_m/MMscf at 35°F and 600 psia (see Figure 11.1 to obtain these data). Therefore, 95 lb_m − 13 lb_m = 82 lb_m of water per MMscf (1,390 kg/10^6 Nm^3) drops out in the line, assuming maximum water condensation.

METHANOL REQUIREMENT

2. To estimate the aqueous phase concentration of methanol, rearrange Equation 8.4 to give

$$\ln x_W = \frac{-\Delta t(°F)}{129.6} = \frac{-24}{129.6} = -0.185$$

$$x_W = 0.831 \quad \text{or} \quad x_{MeOH} = 1.0 - 0.831 = 0.169 \text{ mole fraction.}$$

Because the molar mass of MeOH is 32, the weight fraction is (0.169 × 32)/(0.831 × 18 + 0.169 × 32) = 0.266 or 0.362 lb_m methanol/lb_m water. Thus, the methanol needed in the water phase is 0.362 × 82 = 29.7 lb_m/MMscf (500 g/10^3 Nm^3).

3. To estimate the methanol in the vapor phase use Figure 8.14, which, at 35°F and 500 psia, gives a distribution coefficient of approximately 1.7. Then the vapor content is 1.7 × 16.9 mol % MeOH in aqueous phase = 29 lb_m/MMscf (470 g/10^3 Nm^3). Thus, the vapor phase holds as much methanol as the aqueous phase. The total amount of methanol required is (30 + 29) = 59 lb_m/MMscf (990 g/10^3 Nm^3). If a condensate phase was present as well, the losses would have to be added for that phase. The condensate amount of methanol will be much less than what goes into the aqueous and vapor phases.

ETHYLENE GLYCOL REQUIREMENT

4. Use Equation 8.3 with the constant 2,335 (1,297) and a molar mass of ethylene glycol of 62 to obtain the mass fraction of pure glycol required

$$X_i = \frac{24 \times 62}{24 \times 62 + 2{,}335} = 0.39.$$

However, the glycol is diluted to 80 wt%. To obtain the mass of inhibitor solution added per unit mass of free water present to obtain the desired concentration, use $X_0/(X_i - X_0)$, where X_0 is the weight fraction of inhibitor in the solution to be added. The amount of inhibitor solution added per pound of free water initially present is then 0.8/(0.8 − 0.39) = 1.95, and the total amount of ethylene glycol solution added is 1.95 × 82 = 160 lb_m/MMscf (2.70 g/10^3 Nm^3).

At these conditions, glycol loss into the vapor phase is negligible, so the total amount of solution required is 160 lb_m/MMscf (2.78 g/10^3 Nm^3).

8.3.3.2 Kinetic Inhibitors

Antiagglomerates prevent small hydrate particles from agglomerating into larger sizes to produce a plug. They reside in the liquid hydrocarbon phase and are most often used in oil or condensate pipelines. They require testing to determine the best additive and to ensure proper concentrations. While used in the United States, their use is prohibited in some countries because of environmental concerns.

KHI inhibitors slow crystal formation by interfering with the construction of the cages. Their advantage is that they can be used at concentrations in the 1 wt% range in the aqueous phase, and they are nonvolatile. Their disadvantage is that the proper dosage must be determined empirically, as too much inhibitor may enhance hydrate formation rates. These inhibitors are limited to a subcooling (difference between desired operating temperature and hydrate formation temperature at constant pressure) of 28°F (15.5°C). However, Mehta and Klomp (2005) recommend a maximum subcooling of 20°F (11°C) for these kinds of inhibitors. KHI inhibitors are being used in many offshore operations and will become more widely applied as experience with their use increases. They are used in combination with methanol to reduce the total methanol being sent to the plant.

Both AA and KHI inhibitors are nonvolatile and stay with the condensed phase. Because of this plus their use at low concentrations, there currently is little incentive to recover the chemicals. The AA compounds are emulsifying agents which could cause foaming problems if not treated. Sloan (2000) gives more details on the use of these inhibitors with an emphasis on offshore operations.

8.4 INLET RECEIVING

Gas and liquids entering the gas plant typically pass through emergency shutdown valves, which isolate the plant from incoming streams, pig receivers, and then inlet receiving, where condensed phases drop out. Gas from inlet receiving goes to inlet compression (if necessary), and the liquids go to storage for processing (see Chapter 15). The initial gas–liquid separation occurs in a slug catcher. Slug catchers are critical because downstream gas processing units rely on a continuous gas stream free of liquids, even when surges of liquid enter the plant. A slug catcher is a gas–liquid separator sized to hold the biggest slug a plant will experience. Depending upon slug catcher design, inlet receiving handles just slugs or combines slug catching with liquid storage. Kimmitt et al. (2001) detail the process to properly size and design a slug catcher, and the *Engineering Data Book* (2016a) provides details on separator design. Chapter 5 provides an overview of separator principles.

This section briefly describes two kinds of slug catchers, manifolded piping and inlet vessels. The most difficult part of a slug catcher design is the proper sizing. Sizing requires knowledge of the largest expected liquid slug, as downstream capacity to handle liquids from the slug catcher could be small compared with the liquid influx.

8.4.1 Manifolded Piping

One reason piping is used instead of separators is to minimize vessel wall thickness. This feature makes manifolded piping attractive at pressures above 500 psig (35 barg). The simplest slug catcher design is a single-pipe design that is an increased diameter on the inlet piping. However, this design requires special pigs to accommodate the change in line size. Figure 8.15 shows a schematic of typical multipipe harp design for a slug catcher. Figure 8.16 shows a view from the end of a multipipe slug catcher. The number of pipes varies, depending upon the required volume and operating pressure. Also, some designs include a loop line, where some of the incoming gas bypasses the slug catcher. Primary separation occurs when the gas makes the turn at the inlet and liquid goes down the pipes. Liquid distribution between pipes can be a problem, and additional lines between the tubes are often used to balance the liquid levels. In harp designs, the pipes are sloped so that the liquid drains toward the outlet.

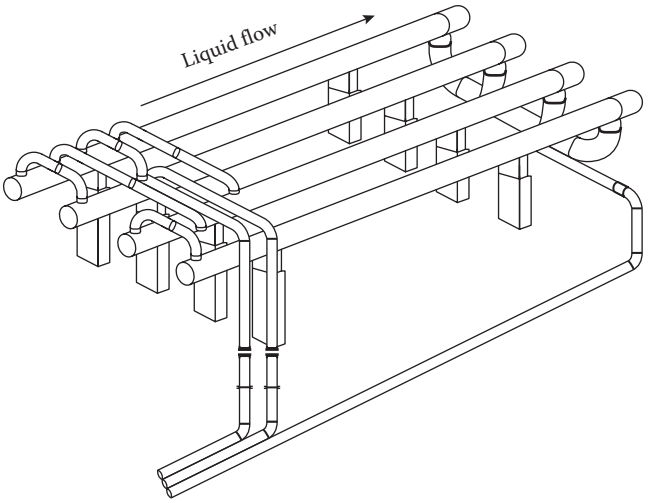


FIGURE 8.15 Schematic of multiple-pipe slug catcher. (Courtesy of Epic Integrated Services, Houston, Texas.)

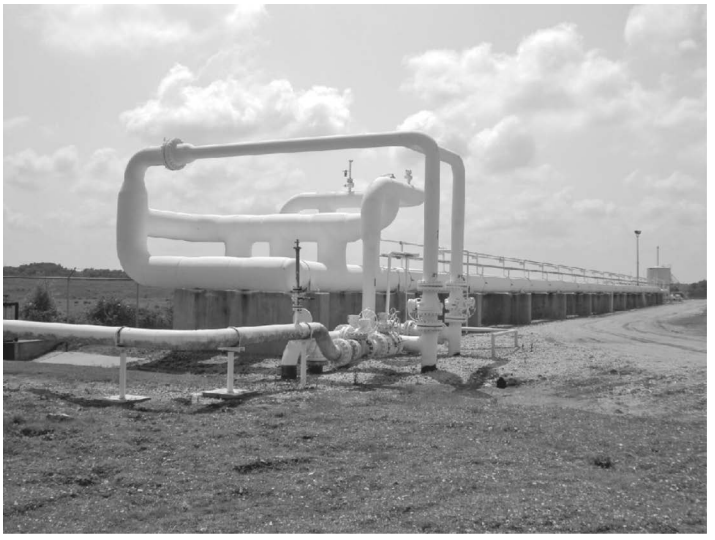


FIGURE 8.16 Multipipe slug catcher with liquid volume of 500 Bbls (80 m^3). Nominal inlet gas rate is 206 MMscfd (5.1×10^6 Nm^3/d). (Courtesy of DCP Midstream.)

Gravity settling occurs as the gas flows to the vapor outlet on the top while the liquid flows out the bottom outlet. Pipe diameters are usually relatively small (usually <48 in. [1,200 mm]), so settling times for the gas phase are short.

Because manifolded piping is strictly for catching liquid slugs, demisters are usually installed downstream in scrubbers. Likewise, liquid goes to other vessels, where degassing and hydrocarbon–water separation occurs.

Kimmitt et al. (2001) note several advantages to the pipe design, including the fact that design specifications are based upon pipe codes instead of vessel codes. Also, the slug catcher can be underground, which reduces maintenance costs and insulation costs if the slug catcher would otherwise need to be heated.

FIGURE 8.17 Inlet receivers at a gas plant.

8.4.2 Inlet Vessels

Figure 8.17 shows inlet vessels, commonly called inlet receivers, which are slug catchers. They are simply gas–liquid separators that combine slug catching with some liquid storage. This type is usually employed where inlet pressures are relatively low or where space prohibits using manifold piping designs. Horizontal vessels are preferred, unless area is limited (as on offshore platforms), because they provide the highest liquid surface area. Usually two or three vessels are manifolded together to permit larger volumes and to allow servicing of one vessel without plant disruption. Length-to-diameter ratios are typically 3:1 to 5:1 to maintain a low gas velocity through the gravity settling section. See Chapter 5 for more details on gas–liquid separators.

With their large volume, inlet vessels usually act as primary storage for inlet liquids as well. The vessels typically contain demisters, so additional separation may not be necessary before the gas goes to compression.

8.4.3 Comparison of Slug Catcher Configurations

The following is a comparison of piping, vertical vessels, and horizontal vessels for slug catching:

- *Land or surface requirements*: If no land constraints apply, piping is attractive. If constraints are severe, as on offshore platforms, vertical vessels are preferred. Otherwise horizontal vessels are the best choice.
- *Operating pressure*: If inlet pressures are greater than about 500 psig (35 barg), significant savings in material costs can be achieved by use of the smaller diameter piping slug catcher.
- *Gas–liquid separation capability*: Horizontal vessels provide the best separation, whereas piping provides the least because its main function is to catch liquid slugs. The large liquid surface area of horizontal vessels provides the best degassing. Piping has the shortest gas residence time when liquid levels are properly maintained in the vessels. However, with piping, small diameter gas scrubbers can be used for demisting.
- *Liquid storage*: Horizontal vessels can act as primary liquid storage, whereas liquids from vertical vessels and piping must be sent to another vessel. Regardless of slug catcher used, liquids will go to low-pressure flash drums and stabilizers to recover light ends (see Chapter 15).

Gas plants routinely receive gas from more than one inlet line. In many cases, the inlet line pressures differ. To minimize required compression on the gas that leaves inlet receiving, slug catchers may operate at each of the inlet line pressures.

8.5 SAFETY AND ENVIRONMENTAL CONSIDERATIONS

Some common safety issues involved with field operations include the following:

- *Leaking pipelines*: Leaks present a danger of fire if an ignition source is available and of poisoning if the gas contains high hydrogen sulfide concentrations. Respirators may be required for work in a sour gas field.
- *Plugged pipelines*: Plugs can be caused by solids blockage, such as hydrates or, occasionally, a stuck pig. Clearing a hydrate plug can be done by depressurization of both sides of the plug to prevent it from dislodging and becoming a projectile that potentially damages the line. Hydrate plugs have ruptured lines resulting in fatalities. Dislodging a hydrate plug in subsea lines can be complex. See Sloan (2000) for more details. Hydrate plugs can also be decomposed by pressurizing the line with nitrogen gas (Panter et al., 2011). Decomposition occurs at operating temperature and pressure, breaking down the plug into small particles. It has been used in the field (Sloan E.D., Private Communication, 2019).

Spheres rarely stick in well-maintained pipelines. The two most common reasons for sticking are gas bypass and line obstruction. A sphere manufacturer should be consulted if common company practice fails.

Other than the liquid slugging problem already mentioned few safety considerations apply to inlet receiving. One hazardous operation in this area is retrieval of pigs from the pig receiver.

The impact of liquid slugs must be considered in the piping design. Often, inlet slug catching equipment is designed to field codes, which allow thinner piping than would be used in a gas processing plant. If liquid slugs are anticipated, the required pipe anchors and wall thickness should be checked to ensure that the unit can handle the increased pipe stresses potentially induced by the momentum of large slugs of liquid.

From an environmental perspective, the most obvious problem is leaking pipelines. However, if hydrate inhibitors are used, berms are required around inhibitor storage tanks to prevent soil contamination; in the case of methanol, the potential for fire exists as well.

Pig receivers are vented into low-pressure fuel lines. Following a venting from inlet receivers, the valves must be checked for proper reclosure.

A major environmental concern in field operations is the control of exhausts from compressors. Carbon monoxide and NO_X are the major pollutants from engines driving compressors. If raw gas is burned, sulfur removal for reducing sulfur oxide emissions may be required.

In situations in which the plant is required to shut-in, gas may have to be vented or flared at remote booster stations. Rich gas in gathering systems may be heavier than air at lower temperatures, which can make venting hazardous. If the gas is sour, configurations that permit the gas to go to flares may be required.

DISCUSSION QUESTIONS

1. Based upon your knowledge contrast the differences between onshore and off-shore field operations.
2. What are the major functions that may take place at booster stations?
3. What are the advantages and disadvantages of reinjecting condensed liquids downstream of compressors at booster stations?
4. Why are liquid slugs coming into the plant a problem? What are ways to avoid the problems?

5. Referring to Figure 8.6, what would be the procedure for loading and launching a pig?
6. What are the advantages and disadvantages of using remote pig launchers?
7. Why is field metering so important?
8. Why are gas hydrates such a potential problem and how are the problems minimized?
9. What are the relative merits of using methanol and ethylene glycol for hydrate prevention?
10. What are the relative advantages and disadvantages of the two major types of slug catchers?

EXERCISES

8.1 A 6 in. pipe (cross-sectional area = 0.2006 ft^2 (0.01864 m^2)) gas line transports 20 MMscfd (0.536×10^6 Nm^3/d). An 8 mi (12.9 km) segment of the line is pigged. Assuming that the average pipeline temperature is 80°F (27°C) and average operating pressure is 250 psig (17.2 barg), what would be the average pig speed (mph, km/h) in the line and the minimum time it would take to traverse the pigged segment? Assume ideal gas behavior and that there is minimal gas slippage around the pig.

8.2 Assume that the gas in the line in Exercise 8.1 condenses 0.01 GPM (1.41 m^3 liquid/10^6 Nm^3 gas) over the 8 mi (12.9 km) distance and the line is pigged once a day. How many gallons (m^3) of condensate would the pig remove from the line?

8.3 Chapter 6 noted that gas hydrates are found on the ocean floor. Assuming the seafloor temperature to be 4°C (39°F) and an average seawater density of 1.04, what is the minimum depth that pure methane hydrate could form on the seafloor using methane curve in Figure 8.13?

8.4 Use Equation 8.1 to compute the hydrate formation pressure for pure methane at 40°F (4.4°C) and compare with value shown in Figure 8.13. If values don't agree, why not?

8.5 Compute the concentration of methanol needed to provide 18°F (10°C) of subcooling into the hydrate region using the Hanmmerschmidt and Nielsen and Bucklin equations. Assume specific gravity of methanol is 0.79.

8.6 In Example 8.2, it was assumed that no condensate is produced in the line. Using the same operating conditions, and the dosages given in the example, if 0.02 GPM (2.83 m^3 liquid/10^6 Nm^3 gas) of condensate (molar mass = 80, SpGr = 0.65) forms in the line, estimate the additional amount (lb_m per MMscf, g per 10^3 Nm^3) of methanol required to account for loss in condensate.

REFERENCES

Bryan Research & Engineering LLC, ProMax® 5.0, 2019.

Carroll, J.J., *Natural Gas Hydrates: A Guide for Engineers*, Gulf Professional Publishing, Houston, TX, 2003.

Colorado School of Mines, Center for Hydrate Research, 2018. http://hydrates.mines.edu/CHR/Home.html (Retrieved April 2019).

Cooper, M.W., et al., Amine system performance: Mitigating amine unit challenges from oxygen, bicine, and heat stable salts, a follow-up to "Handling trace oxygen at the Saunders gas processing facility", *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2011, p. 151.

Engineering Data Book, Section 7, Separation equipment, GPSA Midstream Suppliers, Tulsa, OK, 2016a.

Engineering Data Book, Section 17, Fluid flow and piping, GPSA Midstream Suppliers, Tulsa, OK, 2016b.

Engineering Data Book, Section 20, Dehydration, GPSA Midstream Suppliers, Tulsa, OK, 2016c.

Girard Industries, 2019. www.girardind.com/ (Retrieved April 2019).

Hammerschmidt, E.G., Preventing and removing gas hydrates formations in natural gas pipelines, *Oil Gas J.*, *37*(52), 66, 1939.

Jordan, T.J., et al., Handling trace oxygen at the Saunders gas processing facility, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2006.

Kimmitt, R.P., et al., Proven methods for design and operation of gas plant liquid slug catching equipment, *Eightieth Annual Convention Gas Processors Association*, Tulsa, OK, 2001.

Langston, L.V., *The Lease Pumper's Handbook*, The Commission on Marginally Producing Oil and Gas Wells of Oklahoma, 2003. http://digitalprairie.ok.gov/cdm/ref/collection/stgovpub/id/298909 (Retrieved April 2019).

Mehta, A.P., and Klomp, U.C., An industry perspective on the state of the art of hydrates management, *Proceedings of the Fifth International Conference on Gas Hydrates*, Trondheim, 2005, p. 1089.

Nicholas, J.W., et al., Measuring hydrate/ice deposition in a flow loop from dissolved water in live liquid condensate, *AIChE J., 55*(7), 1882, 2009.

Nielsen, R.B., and Bucklin, R.W., Why not use methanol for hydrate control? *Hydroc. Proc., 62*(4), 71, 1983.

Panter, J.L., et al., Hydrate plug dissociation via nitrogen purge: Experiments and modeling, *Energ. Fuel, 25*, 2572, 2011.

Sloan, E.D., *Hydrate Engineering*, Society of Petroleum Engineers, Richardson, TX, 2000.

Sloan, E.D., and Koh, C.A., *Clathrate Hydrates of Natural Gases*, 3rd edn. CRC Press, Boca Raton, FL, 2008.

U.S. Department of Transportation, Fact sheet: In-line inspections (smart pig), 2014. https://primis.phmsa.dot.gov/comm/FactSheets/FSSmartPig.htm (Retrieved April 2019).

U.S. Department of Transportation, TITLE 49--Transportation Subtitle B--Other regulations relating to transportation Chapter I--Pipeline and hazardous materials safety Administration, Department of Transportation Subchapter D--Pipeline safety, 2018. www.ecfr.gov/cgi-bin/text-idx?SID=faabf128b537556517c1aa5e001a4d44&mc=true&tpl=/ecfrbrowse/Title49/49CIsubchapD.tpl (Retrieved April 2019).

Varnell, B., and Godby, S., Managing plant inlet liquid slugs, *Eighty-Second Annual Gas Processors Association Convention*, Tulsa, OK, 2003.

Webb, B.C., Guidelines set out for pipeline pigging, *Oil Gas J., 76*(46), 196, 1978a.

Webb, B.C., More guidelines given for gas liquid pipeline pigging, *Oil Gas J., 76*(48), 74, 1978b.

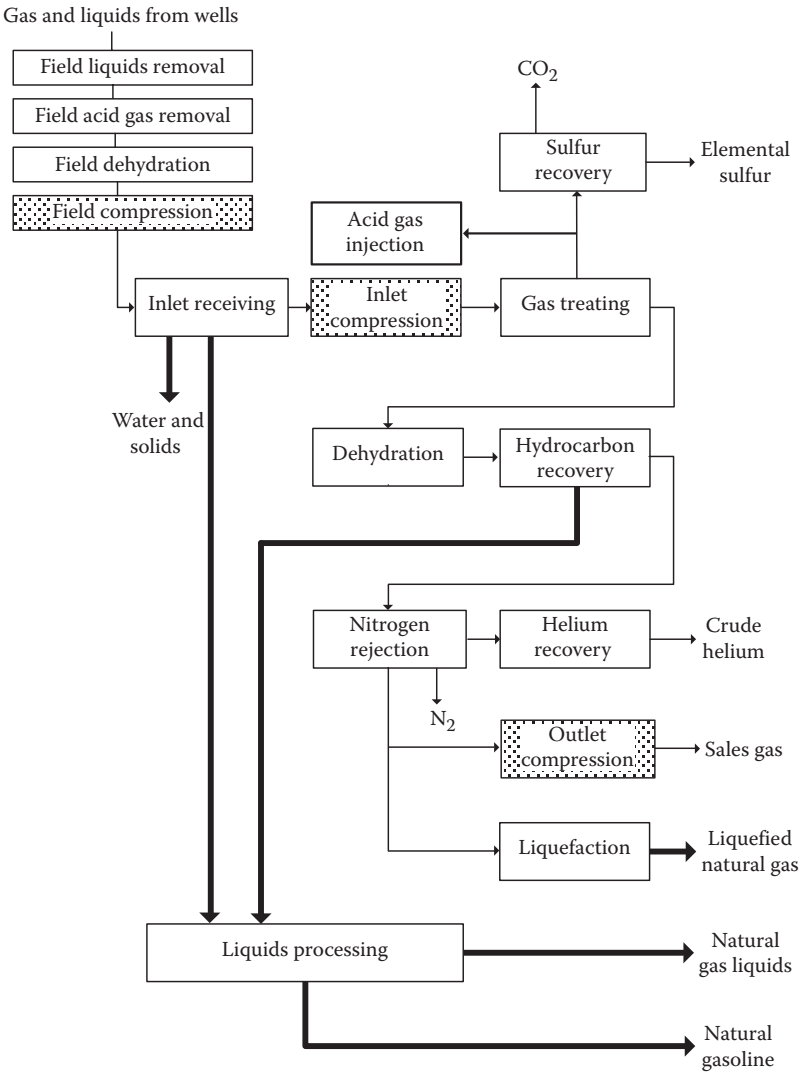
WEB SITES

Occupational Safety and Health Administration (OSHA), www.osha.gov/SLTC/etools/oilandgas/illustrated_glossary.html. Site provides excellent glossary of terms used at drilling sites. Not directly related to gas processing.

Colorado School of Mines Hydrate Research Program, hydrates.mines.edu/CHR/Home.html. Site gives details of current research activities and provides the free downloading of the hydrate prediction program CSMHYD to compute hydrate formation conditions.

Taylor & Francis
Taylor & Francis Group
http://taylorandfrancis.com

9 Compression



9.1 INTRODUCTION

Pressure plays a major role in gas processing, as it moves gas from the field, through the gas plant, and into the sales gas line. Pressure provides the source for cooling the gas to low temperatures. Plant process streams that undergo compression include:

- Gas leaving inlet receiving (Chapter 8). To maximize liquids recovery, the inlet gas is typically at 700–1,000 psi (50–70 bar) when it enters the hydrocarbon recovery section (see Chapter 12).
- Gas coming from stabilizing the liquids in liquids processing (see Chapter 15).

- Gas from vapor recovery facilities that collect low-pressure gas (see Chapter 7). Low-pressure gas not used as fuel gas is compressed for hydrocarbon recovery.
- Gas exiting hydrocarbon recovery and entering a pipeline (see Chapter 12). For gas plants using turboexpanders, mechanical energy generated by the turboexpander provides part of plant compression. However, additional outlet compression is required to bring the residue sales gas to pipeline pressure.

Typically, the only other demands for hydrocarbon gas compression are recompressing adsorption bed regeneration gas and propane refrigeration. Some plants avoid propane refrigeration by using higher inlet gas pressures. This option is attractive when the inlet gas contains relatively small amounts of C_2^+ hydrocarbons or when high ethane recoveries are not required.

Gas and refrigeration compressors typically are the largest capital expense in the construction of a new gas processing plant. They account for up to 50%–60% of the total installed cost of the facility. They also tend to have the largest maintenance expense in a gas plant.

As in the case of pumps, the two broad categories of compressors are positive displacement and dynamic. Positive displacement compressors increase pressure by decreasing volume. Their performance is relatively insensitive to the molar mass of the gas being compressed.

Dynamic compressors convert gas velocity (kinetic energy) to pressure. Their discharge pressure is sensitive to molar mass. For a constant discharge pressure, the head (i.e., compression work) is inversely proportional to the molar mass of the gas.

After reviewing some fundamentals regarding compression, this chapter presents a short discussion of compressor drivers and then an overview of the various types of compressors typically found in gas plants and lists their strengths and weaknesses. This discussion is followed by ways to estimate power requirements for a given set of flow conditions or to estimate flow conditions for a given compressor design. Jandjel (2000) provides a good overview of compressors for gas and air service, and the *Engineering Data Book* (2016a) gives details on power requirements.

9.2 FUNDAMENTALS

This section reviews some basic thermodynamic relations in compression and then defines some of the common efficiencies used to rate compressors.

9.2.1 Thermodynamics of Compression

To compute the reversible[1] shaft work, w_s, of a continuous open process that increases the absolute pressure from P_1 to P_2 requires evaluation of the integral (see a standard thermodynamics textbook (e.g., Smith et al., 2018))

$$w_s = -\Delta h = -\int_{P_1}^{P_2} v\, dP, \tag{9.1}$$

where all variables are based upon energy per unit mass. Because the gas is compressible, the integral depends upon the *PV* path. To minimize the work requires minimizing the volume during compression, which implies that the process must be isothermal. For an ideal gas, where $v = RT/P$, the reversible isothermal shaft work is given by

$$w_s = \frac{-RT \ln\left(P_2/P_1\right)}{MW} \tag{9.2}$$

[1] Reversibility is used here in the thermodynamic sense. A reversible process occurs with an infinitesimal driving force so that there is no change in entropy (see Chapter 1). Such processes are impossible because it would take infinite time to complete the process. Reversible processes are a hypothetical, ideal process but valuable because they are often useful for estimating energy requirements and provide a basis for calculating efficiency.

where

R is the gas constant
MW is the molar mass
T is the absolute temperature

Reversible isothermal work is the minimum work requirement for a compression process. The negative sign indicates that work is being done on the system, i.e., gas. Note that all pressures are in absolute units.

Achieving isothermal compression requires infinitely good heat transfer to remove all heat of compression. This case is unrealistic and isothermal work calculations are rarely used in practice.

The other extreme is no heat transfer (adiabatic). All heat generated in compression goes into the gas phase, which maximizes the volume and, thus, requires the maximum ideal work for compression. Compressors, although operating irreversibly, more closely follow this path because compression takes place rapidly, with little time allowed for heat transfer to the surroundings. For reversible adiabatic (isentropic) compression of an ideal gas, the PV path follows

$$Pv^{\gamma} = \text{constant} \tag{9.3}$$

and the work is calculated by

$$w_s = \frac{\gamma RT_1}{MW(\gamma - 1)}\left[1 - \left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma}\right] \tag{9.4}$$

where

T_1 is the absolute inlet temperature
γ is the ratio of the molar heat capacities:

$$\gamma = \left(\frac{C_P}{C_V}\right) = \left[\frac{C_P}{(C_P - R)}\right] \tag{9.5}$$

The value of γ is both temperature and composition dependent. Mixture molar gas heat capacities at constant pressure are computed by

$$C_{PM} = \sum y_i C_{P_i} \tag{9.6}$$

and the heat capacity at constant volume, C_{VM}, is computed the same way. Appendix B[2] gives ideal gas heat capacity values at constant pressure for natural gas components as a function of temperature. The common practice is to determine the heat capacity ratio at the average of suction and discharge temperatures.

Equations 9.2 and 9.4 show that the work required is a function of the ratio of absolute pressures, often referred to as the "compression ratio." The operating pressures have a significant effect on compressor design and cost. They have only a secondary effect on the work in that they change the heat capacities and γ. This effect is commonly ignored because the calculations provide only estimates. Equations of state, which use Equation 9.1, are needed to obtain more accurate work and power requirements.

[2] See Appendix B on publisher website: www.crcpress.com/Fundamentals-of-Natural-Gas-Processing-Third-Edition/Kidnay-Parrish-McCartney/p/book/9781138612792

TABLE 9.1
Data for Example 9.1

	mol%	C_P at 100°F Btu/lb-mol-°R	yC_P
Helium	0.45	4.97	0.022
Nitrogen	14.65	6.96	1.020
Methane	72.89	8.65	6.305
Ethane	6.27	12.92	0.810
Propane	3.74	18.20	0.680
Butanes	1.38	24.32	0.336
Pentanes and heavier	0.62	40.81	0.253
C_{PM}			9.426

Example 9.1

Compute the ideal gas heat capacity ratio, γ, for the southwest Kansas gas in Table 6.5 (Chapter 6) at 100°F (38°C). Assume all butanes to be *n*-butane and C_5^+ fraction to be hexane (Table 9.1).

Solution

Tables B.2 and B.3 list ideal gas, molar capacities at constant pressure, C_P, of the commonly found components in natural gas processing. Table 9.1 shows the calculations to obtain the mixture heat capacity of 9.43 Btu/lb-mol-°F (39.5 J/mol-K).

Using Equation 9.5 the C_{VM} for the mixture is $C_{PM} - R = 9.43 - 1.99 = 7.44$ Btu/lb-mol-°R (31.1 J/mol-K) and $\gamma = 9.43/7.44 = 1.33$.

The outlet temperature, T_2, for a reversible, adiabatic compression of an ideal gas can be calculated by

$$T_2 = T_1\left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma} \tag{9.7}$$

However, the *Engineering Data Book* (2016a) recommends use of the following empirical equation to obtain a more representative discharge temperature

$$T_2 = T_1\left[1+\left\{\frac{\left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma}-1}{\eta_{IS}}\right\}\right] \tag{9.8}$$

where η_{IS} is the isentropic efficiency discussed below. Compressors have some heat loss and are irreversible. The *PV* path followed in this case is

$$Pv^{\kappa} = \text{constant} \tag{9.9}$$

where κ is the empirically determined polytropic constant. This constant replaces γ in the above equations and thus the reversible polytropic work is

$$w_s = \frac{\kappa RT_1}{MW(\kappa-1)}\left[1-\left(\frac{P_2}{P_1}\right)^{(\kappa-1)/\kappa}\right] \tag{9.10}$$

Unless the value of κ is known, γ is used for the typical quick calculations on compressors.

All the major components in natural gas behave like ideal gases at near-ambient pressure and ambient and above temperatures. However, they become increasingly nonideal with increasing pressure. To estimate the work of compression, ideal gas behavior can be assumed. However, to accurately determine the reversible w_s requires use of either an equation of state or thermodynamic charts, such as a temperature–entropy or pressure–enthalpy diagram to accurately calculate h. (See Chapter 1 for discussion of pressure–enthalpy, PH, diagrams.)

Example 9.2

Assume ideal gas behavior, and compute the reversible work required to compress a natural gas mixture from 10 to 60 psig (0.69–4.1 barg), both isothermally and adiabatically, with an initial temperature of 80°F (26.7°C). Also, calculate the exit temperature for adiabatic compression. The molar mass of the gas is 18, and the ratio of heat capacities is 1.15. Assume the compressor is 100% efficient for this calculation.

Solution

REVERSIBLE ISOTHERMAL COMPRESSION

From Equation 9.2, the work is

$$w_s = \frac{-RT\ln\left(P_2/P_1\right)}{MW} = -\frac{1.986(80+460)}{18}\ln\left[(60+14.7)/(10+14.7)\right]$$

$$= -65.9\,\text{Btu/lb}_m\left(-153\,\text{kJ/kg}\right)$$

REVERSIBLE ADIABATIC COMPRESSION

Using Equation 9.4 to compute the work gives

$$w_s = \frac{1.15\times1.986\times(80+460)}{18(1.15-1)}\left[1-\left(\frac{60+14.7}{10+14.7}\right)^{(1.15-1)/1.15}\right]$$

$$= -70.9\,\text{Btu/lb}_m\,(-165\,\text{kJ/kg})$$

The outlet temperature is given by Equation 9.7:

$$T_2 = (80+460)\left[\frac{(60+14.7)}{(10+14.7)}\right]^{(1.15-1)/1.15} = 624°\text{R}$$

$$t_2 = 624-460 = 164°\text{F}\,(73°\text{C})$$

Thus, the reversible adiabatic work of compression is about 8% higher than the isothermal work.

Example 9.3

Pure methane is compressed in a reversible, adiabatic process from 20 to 100 psig (1.4–6.9 barg). The initial temperature is 50°F (10°C). Determine the work assuming an ideal gas and by using a methane PH diagram (Figure B.16 or B.17). Also find the discharge temperatures using both methods.

Solution

First compute the work assuming methane is an ideal gas. The molar mass of methane is 16 and the ideal gas heat capacity is 8.40 Btu/lb-mol-°F (Table B.2). Then γ is computed using Equation 9.5:

$$\gamma = \left(\frac{C_P}{C_V}\right) = \left[\frac{C_P}{(C_P - R)}\right] = \frac{8.40}{(8.40 - 1.99)} = 1.31$$

Apply Equation 9.4 to compute the reversible adiabatic work

$$w_s = \frac{1.31 \times 1.986 \times (50 + 460)}{16(1.31 - 1)}\left[1 - \left(\frac{100 + 14.7}{20 + 14.7}\right)^{(1.31-1)/1.31}\right] = -87.5\,\text{Btu/lb}_m\,(-203\,\text{kJ/kg})$$

Using Equation 9.7 to calculate the exit temperature

$$T_2 = (50 + 460)\left[\frac{(100 + 14.7)^{(1.31-1)/1.31}}{(20 + 14.7)}\right] = 677°\text{R}\,(376\,\text{K})$$

$$t_2 = 677 - 460 = 217°\text{F}(103°\text{C})$$

To calculate the work using the PH diagram (Figures B.16 or B.17) locate the point at 50°F and 35 psia and read the enthalpy value, h_1, of ~405 Btu/lb_m. The calculations assume that the entropy remains constant (reversible, adiabatic process). The entropy at these conditions is ~1.63 Btu/lb_m-°F. Exit conditions are at 115 psia and an entropy of 1.63 Btu/lb_m-°F. At this point, the enthalpy, h_2, is ~495 Btu/lb_m. The exit temperature is ~210°F (98°C). The work of compression is

$$w_s = -\Delta h = h_2 - h_1 = 405 - 495 = -90\,\text{Btu/lb}_m\,(-200\,\text{kJ/kg})$$

The agreement between the two methods for both the work and the exit temperature is good considering the possible error in reading the PH diagram and assumption of ideal gas behavior.

9.2.2 Multistaging

Multistaging of compressors is done for any of several reasons. An obvious reason is that cooling the gas between stages reduces the gas volume, and thus the work required. Although this reason is important, the major reason for multistaging is materials limitations. Assuming γ remained constant in Example 9.2 and the outlet gas pressure was 625 psig (43.1 barg), the outlet temperature would be 365°F (185°C). Considering materials of construction, seals, and lubricants, the *Engineering Data Book* (2016a) recommends about 300°F (150°C) as a "good average" for outlet temperatures for reciprocating compressors. If high pressure is involved, 250°F–275°F (120°C–140°C) is recommended. Assuming the initial temperature is near ambient, these maximum temperatures suggest pressure ratios of 3:1 to 5:1.

The minimum work is obtained when each stage of a multistage unit does the same amount of work, and thus most compressors will have approximately the same pressure ratio for each stage. In this case, the compression or pressure ratio, PR, for m stages is computed by

$$\text{PR} = \left(\frac{P_2}{P_1}\right)^{1/m} \tag{9.11}$$

(Note that these compression ratios are always the ratio of absolute pressures.) Then the total work of compression will be the sum of the work in each stage, as computed by Equation 9.4.

Example 9.4

Determine the number of stages required to compress the gas in Example 9.2 from 10 to 625 psig (0.68–43.1 barg) using a compression ratio of 3:1. Also, calculate the exit temperature for each stage if the gas enters each stage at 80°F (26.7°C).

Solution

To determine the value of *m*, Equation 9.11 is rearranged to give

$$m = \frac{\ln(P_2/P_1)}{\ln(\mathrm{PR})} = \frac{\ln\left[(625+14.7)/(10+14.7)\right]}{\ln(3)} = 2.96 \text{ or } 3 \text{ stages}$$

The actual pressure ratio will be $[(625+14.7)/(10+14.7)]^{1/3} = 2.96$. Equation 9.7 gives a discharge temperature of 162°F (72°C).

9.2.3 Compressor Efficiencies

Several efficiencies are used to define compressor performance. The most common is the reversible adiabatic efficiency, commonly referred to as the isentropic efficiency and defined as

$$\eta_{\mathrm{IS}} = \frac{w_{\mathrm{s}}}{w_{\mathrm{s,ACTUAL}}} \tag{9.12}$$

with w_s computed by Equation 9.4 and $w_{s,ACTUAL}$ is the actual energy input required.

The other commonly used efficiency, especially with centrifugal compressors, is the polytropic efficiency, η_P, defined as

$$\eta_{\mathrm{P}} = \frac{\left[(\gamma-1)/\gamma\right]}{\left[(\kappa-1)/\kappa\right]} \tag{9.13}$$

This value approximates the ratio of isentropic work to the polytropic work (i.e., Equation 9.4 divided by Equation 9.10), if the pressure-ratio term is ignored. The polytropic efficiency will always be higher than the isentropic efficiency. It can be used to calculate work when applied to Equation 9.10 and is useful for estimating discharge conditions, as in Equation 9.14.

$$T_2 = T_1\left(\frac{P_2}{P_1}\right)^{(1/\eta_{\mathrm{P}})(\gamma-1)/\gamma} \tag{9.14}$$

Example 9.5

Using adiabatic compression calculations from Example 9.2, calculate actual work required assuming the isentropic efficiency is 75%. Calculate revised exit temperature using Equation 9.8.

Solution

The reversible adiabatic work required for compression was –70.9 Btu/lb_m (–165 kJ/kg). Rearranging Equation 9.12 to calculate $w_{s,ACTUAL}$ gives

$$w_{\mathrm{s,ACTUAL}} = \frac{w_{\mathrm{s}}}{\eta_{\mathrm{IS}}} = \frac{-70.9}{0.75} = -94.5\frac{\mathrm{Btu}}{\mathrm{lb_m}}\left(-219.7\frac{\mathrm{kJ}}{\mathrm{kg}}\right)$$

Using Equation 9.8 to calculate the exit temperature gives

$$T_2 = (80+460)\left[1+\left\{\frac{\left(\frac{60+14.7}{10+14.7}\right)^{\frac{1.15-1}{1.15}}-1}{0.75}\right\}\right] = 652°\text{R}\,(362\,\text{K})$$

$$t_2 = 652-460 = 192°\text{F}\,(89°\text{C})$$

Correcting for efficiency increases discharge temperature by 28°F (16°C).

Example 9.6

Determine the isentropic efficiency of a compressor if the polytropic efficiency is 77% and the gas has $\gamma = 1.15$. Assume the molar mass of the gas is 18, the inlet temperature is 80°F (26.7°C), and the compression ratio is 3.0.

Solution

Conversion from polytropic to adiabatic efficiency requires the following steps:

1. Calculate ideal polytropic work.
2. Calculate the actual work by dividing polytropic work by polytropic efficiency.
3. Calculate isentropic work.
4. Calculate isentropic efficiency from ratio of isentropic work to polytropic work.

Step 1. Both γ and η_P are given so Equation 9.13 can be used to determine κ for use in Equation 9.10. However, η_P can be used in combination with γ in Equation 9.10 to give

$$w_s = \frac{\gamma R T_1 \eta_P}{MW(\gamma-1)}\left[1-\left(\frac{P_2}{P_1}\right)^{(1/\eta_P)(\gamma-1)/\gamma}\right]$$

$$= \frac{1.15\times1.986(80+460)0.77}{18(1.15-1)}\left[1-(3.0)^{(1/0.77)(1.15-1)/1.15}\right] = -72.1\,\text{Btu/lb}_m\,(-168\,\text{kJ/kg})$$

Step 2. The actual work required is

$$w_s = \frac{-72.1}{0.77} = -93.6\,\text{Btu/lb}_m\,(-218\,\text{kJ/kg})$$

Step 3. The isentropic work required is

$$w_s = \frac{1.15\times1.986\times(80+460)}{18(1.15-1)}\left[1-(3)^{(1.15-1)/1.15}\right] = -70.3\,\text{Btu/lb}_m\,(-164.4\,\text{kJ/kg})$$

Step 4. The isentropic efficiency is then –70.3/–93.6 = 0.75 or 75%, two percentage points below the polytropic efficiency.

The efficiencies above provide the work requirements on a per unit mass or volume basis. Section 9.5 discusses general calculations for compressor capacities and power requirements.

Reciprocating compressors also have a volumetric efficiency. This efficiency is the actual volume of gas in the piston cylinder divided by the piston displacement (PD) volume and includes the "dead" volumes associated with the valves and other mechanical clearances, such as those

between the piston and heads. Considering only piston displacement, the volumetric efficiency, η_V, is computed by

$$\eta_V = 100 - \left(\frac{P_2}{P_1}\right) - C\left[\left(\frac{z_2}{z_1}\right)\left(\frac{P_2}{P_1}\right)^{1/\gamma} - 1\right] \tag{9.15}$$

where

z is the compressibility factor ($z = Pv/RT$)

C is the percent clearance given by

$$C = \frac{100\left(\text{clearance volume}\right)}{\left(\text{piston displacement volume}\right)} \tag{9.16}$$

Note that the volumetric efficiency decreases with increasing compression ratio.

Ideally, vendor information on a compressor's volumetric efficiency is available. However, once a compressor is overhauled, the data probably are inaccurate. Even if the compressor is several years old and has not been overhauled, the data for that particular unit is important to have as manufacturers modify efficiency data for newer models. The preferred way to obtain the current volumetric efficiency on older units is to obtain a *PV* curve from a compressor analyzer and back calculate the efficiency.

If valid volumetric efficiency information on the compressor is unavailable, several corrections to the volumetric efficiency must be made (*Engineering Data Book*, 2016a):

1. Subtract 4% for volumes around suction and discharge valving.
2. Subtract 5% for nonlubricated compressors to account for slippage losses.
3. Subtract 4% for compressing propane or heavier gas.

The first correction always applies, and if the last two apply, they are cumulative. Therefore, the volumetric efficiency could be as much as 13% lower than calculated by Equation 9.15. Note that these corrections apply to capacity calculations but not to calculating power requirements.

The volumetric efficiency is required to estimate compressor capacity and equivalent capacity. Section 9.5.1 discusses these calculations.

9.3 DRIVERS

There are four commonly used prime movers for compressors:

- Electric motors
- Internal combustion engines
- Gas turbines
- Steam turbines

This section provides a brief overview of these various types in gas processing. Later sections provide additional details.

Electric motors are widely used on small compressors and sometimes on larger units as well. They are low maintenance and have availability[3] rates of 99%. They can be variable speed drives (VSD), which change speed by varying the frequency to the motor. This permits compressor speeds to be adjusted easily. Compressor speed can also be adjusted using fluid couplings but these are uncommon. Fluid couplings can be less expensive to purchase than VSDs but they also are less efficient (*Engineering Data Book*, 2016b).

[3] It is common to confuse availability and reliability. In quality control, availability is the percentage of time a given piece of equipment is available for service; reliability represents the probability that the equipment will not fail over a specified time period. Mean time between failures is indicative of reliability.

Contrary to intuition, electric motors are often used in remote locations. This is because of their high availability and because it is often easier to run wiring than to lay fuel gas piping from the plant or nearby transmission line to a remote compressor site. This assumes that power lines are economically available.

Internal combustion engines have been the major compressor driver since compressors started being used in the gas industry. It is common to find 50-year old engines in the United States still in service. These engines have been rebuilt many times. A major disadvantage to internal combustion engines is their relatively poor availability of roughly 95%–97% although higher availabilities are attainable with a rigorous maintenance program. Additional drawbacks are noted below.

Gas turbines are used to drive large compressors and are commonly used with centrifugal compressors. They have a high availability and are well suited for gas plants and transmission pipelines. Section 9.4.2 discusses them in more detail.

Steam turbines have limited use in most gas plants because there tends to be few high-pressure steam systems. They are most commonly found on sulfur recovery plants for energy recovery. The turbines drive air blowers in the process. However, steam turbines are important in cogeneration and combined cycle units.

9.4 COMPRESSOR TYPES

Reciprocating compressors were the only choice when the natural gas industry began. Although still widely used, many new units are other compressor types. In the 1980s, centrifugal compressors came into common use in gas processing plants. Rotary screw compressors started being used in the 1990s. However, reciprocating compressors will remain dominant in gas processing for many years to come. Table 9.2 (compiled from numerous sources) lists the cost-effective ranges for various compressor types used in gas plants, along with isentropic efficiency ranges. Both reciprocating and screw compressors are positive displacement while the centrifugal compressors are the dynamic type.

Figure 9.1 shows the range of discharge pressures as a function of actual inlet gas flow rates at suction temperature and pressure (acfm or am^3/h) for the compressor types discussed here. The figure provides only a guideline, as the values vary among different sources. Other factors besides those listed in Table 9.2 must be considered when the various compressor types are evaluated. These considerations are noted when discussing each compressor type.

TABLE 9.2
Typical Cost-Effective Ranges of Compressors Used in Gas Processing

		Maximum Pressure, psig (barg)		
	Inlet Flow Rate,[a] acfm (am^3/h)	Inlet	Discharge	Isentropic Efficiency (%)
		Reciprocating		
Single stage	1–2,000 (2–3,500)	No limit	<3,000 (200)	75–85
Multistage	1–3,000 (2–5,000)	No limit	<60,000 (4,000)	75–85
		Centrifugal		
Single stage	80–150,000 (140–250,000)	No limit	1,500 (100)	70–75
Multistage	700–300,000 (1,200–500,000)	No limit	10,000 (700)	70–75
		Rotary Screw		
Oil-free	<40,000 (70,000)	<150 (10)	<350 (25)	70–80
Oil-injected	<10,000 (20,000)	<400 (30)	<800 (60)	70–80

[a] Compressor gas volumes are based upon actual gas flow rates at suction temperature and pressure.

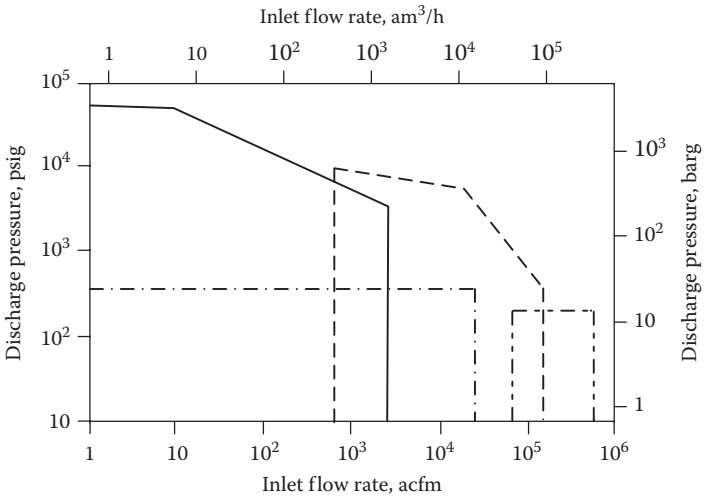


FIGURE 9.1 Ranges of discharge pressure as a function of actual flow rates for various compressor types. Ranges for reciprocating (—), centrifugal (- - -) and axial (— - - —) are for multistaged units. The rotary screw compressor (- · –) is single stage. (Adapted from *Engineering Data Book*, Section 13, 2016a, with permission.)

9.4.1 Positive Displacement Compressors

A variety of positive displacement compressors are used. This section discusses those that have a flow capacity of at least 10 acfm (actual cubic feet per minute) (20 am^3/h) and discharge pressures greater than 100 psig (7 barg). This excludes diaphragm compressors, which have lower flow rates, and various rotary-vane compressors, which are limited to lower discharge pressures.

9.4.1.1 Reciprocating Compressors

Reciprocating compressors are common in both field and plant facilities. Figure 9.2 shows an engine-driven reciprocating compressor. In addition to being an established and known technology, they offer the highest efficiency, and their performance is relatively unaffected by gas composition. With well-maintained ring seals, they produce an oil-free output. Also, they can handle smaller gas volumes and higher discharge pressures than other types of compressors. They have the advantage of being able to quickly startup and shutdown. Only reciprocating and centrifugal compressors have sufficiently high discharge pressures to meet high-pressure gas processing and gas transmission

FIGURE 9.2 Reciprocating compressor at a gas wellhead. The large box on the left contains the fans for cooling the gas. (Courtesy of GE Oil & Gas.)

requirements. Many reciprocating units have been replaced by centrifugal compressors for high-volume service, but reciprocating units often remain as backups.

Reciprocating compressors are frequently multistage and will have either single-acting or double-acting pistons (*Engineering Data Book*, 2016a). Double-acting piston is the most common. Single-acting compressors are usually smaller capacity units. Single-acting cylinders are seldom specified for new units and frequently are the result of refurbishing a compressor unit for a new service. Both single-acting and double-acting cylinders may be on a single frame.

Unfortunately, reciprocating compressors have a number of drawbacks; the major one is availability, which is 95%–97% compared with 98%–99% for some other compressor types. However, units can have availabilities as high as 99%. These high values tend to be found where operators closely monitor the units and they are on electrically driven. Gas engine drivers are typically more prone to failure than a compressor.

Their efficiency advantage decreases when the throughput is reduced. Remedies for reduced volumes include:

- Use of variable speed drives
- Adjustment of suction pressure
- Use of inlet-valve unloaders (which prevent the valves from seating)
- Recirculation of gas to compensate for lower input rates

Also, the compression ratio typically is limited to about 3:1 to 4:1 per stage. A combination of high temperature limitations, as noted previously, and rod load are the constraining factors for the compression ratio.

Reciprocating compressors tend to be noisy. They are the only ones requiring pulsation dampeners (snubbers). These compressors are susceptible to condensed phases, which erode cylinder walls, destroy lubricating fluids, and damage the rings. Finally, for the same volume of throughput, they occupy much more space than the other types. In spite of the drawbacks, the versatility of reciprocating compressors will keep them in the gas industry for a long time.

Because of their widespread use, the (*Engineering Data Book*, 2016a) gives extensive details on reciprocating compressors, including details on controls and pulsation dampeners. The book also includes a troubleshooting guide listing common problems and likely sources of the problems.

9.4.1.2 Oil-Free Rotary Screw Compressors

Rotary screw compressors use two screws, or lobes (see Figure 9.3), to compress the gas. Gas enters as the threads at the suction side are separated, and it moves down the threads as the screws rotate. Clearance between the threads decreases and compresses the gas. The gas exits in an axial port at the end of the screws. A timing drive keeps the two screws synchronized. The screws run at ≈3,600 rpm. Unlike reciprocating compressors, essentially all gas is displaced (i.e., the volumetric efficiency is near 100%).

These compressors were first used in the steel industry to compress air that contained up to 200-μm sized particulates. Thus, they can easily process streams containing condensate droplets. They have availabilities of over 99%.

The primary limitation of oil-free screw compressors is the relatively higher capital cost when compared to oil-injected screw compressors. For gas processing, this limitation prevents more frequent use. Also, because they have low clearances to achieve high efficiency, they are subject to wear and have somewhat higher maintenance when compared to oil-injected units. However, they are used for vapor recovery and compression of low-pressure gases up to the suction pressure of high-pressure compressors. The ability to inject liquid to increase the pressure ratio makes them attractive for propane refrigeration units, although the oil-injected compressors discussed next are widely used as well.

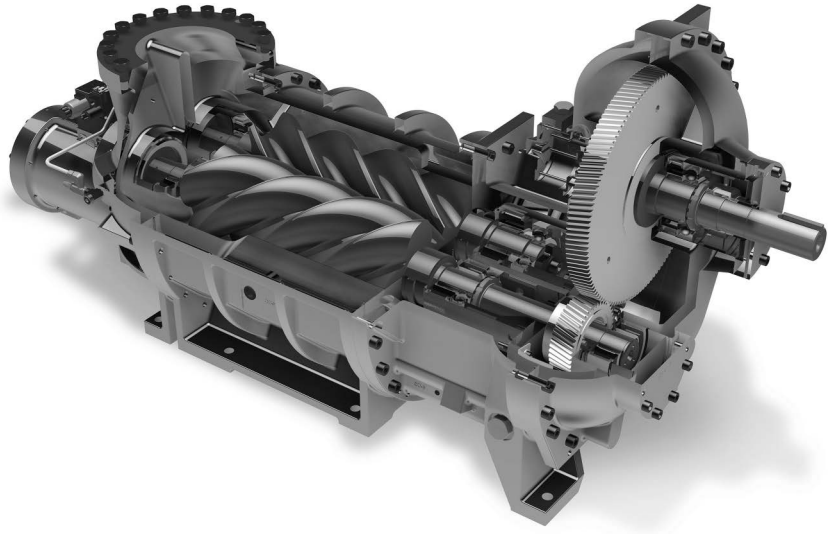


FIGURE 9.3 Cutaway view of an oil-injected rotary screw compressor. (Courtesy of Frick Industrial Refrigeration.)

9.4.1.3 Oil-Injected Rotary Screw Compressors

Unlike the oil-free rotary screw compressor, the oil-injected screw compressor needs no timing drive. The injected oil provides the seal between each screw and the casing and between the screws. It also provides lubrication and a heat-sink to absorb some of the heat of compression. Oil floods the unit at various points along the screws. The oil-injected rotary screw compressor is similar to the oil-free version but has two ports (Bruce, 2000; Ohama et al., 2004). Like the oil-free compressor, the oil-injected rotary screw compressor has an axial port, which in this case, removes gas and remnants of oil. This compressor type also has a slide valve located on the bottom of the compressor that removes the fluids through a radial port.

The slide valve provides a major advantage for these compressors because its position determines the volumetric throughput. The slide valve may be "fixed" and thus require manual repositioning to adjust volumetric flows or may be adjusted automatically. If the pressure ratio remains constant, some loss in efficiency occurs when the volumetric throughput is adjusted because the optimum volume ratio is a function of pressure ratio (Bruce, 2000). Bruce (2000) provides details on turndown strategies for oil-injected screw compressors. Volumetric turndown of up to 90% is possible without significant drop of compressor efficiency.

The oil system is a closed-loop system in these compressors and is a critical component, as the oil provides both sealing and cooling. Discharged gas and oil go to a scrubber that contains a demister to reduce oil concentration to less than 10 ppm (Bruce, 2000). The discharged oil is cooled from 170°F–220°F (75°C–105°C) to 140°F–160°F (60°C–70°C) before being reinjected.

Oil injection permits pressure ratios up to 23:1, but maximum discharge pressures are still below the highest pressures required for gas processing. These compressors are well suited for and frequently used in propane refrigeration systems. These compressors have become the preferred compressors for vapor recovery and fuel gas compression because of the following reasons:

- Improved lubricants that are both stable and inert
- Improved filtration systems that remove oil droplets down to less than 1 μm in size and to concentrations less than 1 ppm to meet oil-free specifications
- Improved pressure and flow limits

These improvements address past concerns regarding these compressors. However, oil compatibility with the process components can still be a problem and selection of the proper oil is important.

Some units have extremely tight clearances between the lobes to increase discharge pressure. A drawback to close tolerances is that if shut down, the compressor must cool before being restarted to avoid seizure of the screws.

For offshore applications, the oil-injected screw compressor has several advantages over reciprocating compressors in low-pressure service, including:

- Small size, about one quarter of that required by reciprocating compressor for comparable capacity
- Low maintenance
- Less vibration and noise
- Ease of adjusting to variable inlet flows
- High availability

In addition to relatively low discharge pressure, the other disadvantages involve the oil system. The lubricating oil must be compatible with the hydrocarbons present at the operating conditions. Hydrocarbon solubility in the oil must be minimal to prevent foaming problems on the suction side and to avoid loss of the oil lubricating properties. Whereas oil-free screw compressors handle "dirty gas" extremely well, oil-injected systems are more susceptible to solids. If solids are present the oil filtration systems must be maintained properly. Energy is spent to compress the oil, but this work is comparable to pumping liquid and is trivial compared with the work of gas compression.

9.4.2 Dynamic Compressors

The two dynamic compressor types are centrifugal and axial. Axial compressors handle large gas volumes and have higher efficiencies than do centrifugals. However, they generally have discharge pressures below 200 psig (14 barg) and are restricted to clean gases. Although not used for processing the natural gas, axial compressors will be discussed briefly in the context of their use in the gas turbines that drive centrifugal compressors. Axial compressors are also used in very large refrigeration systems like those in LNG plants in combination with centrifugal compressors.

To illustrate how axial and centrifugal compressors work in tandem, Figure 9.4 shows a schematic of a typical gas turbine-driven centrifugal compressor. Figure 9.5 shows a gas turbine compressor system. The centrifugal compressor is the large cylindrical unit in the center of the picture, with the two large attached pipes. The large ductwork to the left of the compressor is for the turbine exhaust gas, and the one further to the left is intake air to the axial turbine.

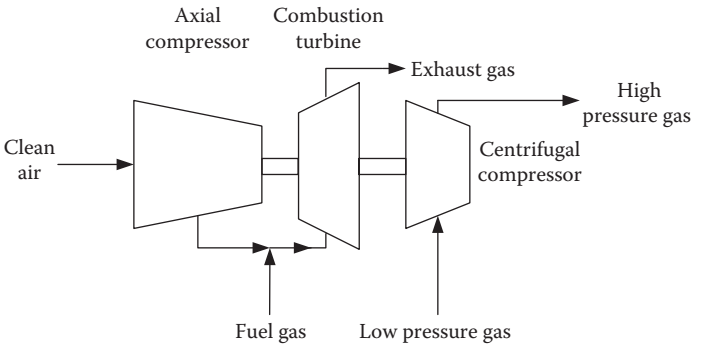


FIGURE 9.4 Schematic of a gas turbine-driven centrifugal compressor.

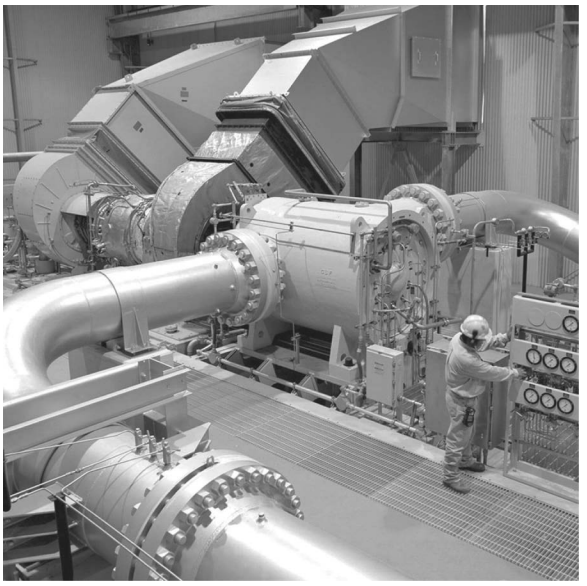


FIGURE 9.5 Large gas turbine-driven centrifugal compressor. See text for details of the figure. (Courtesy of Solar Turbines.)

9.4.2.1 Centrifugal Compressors

Since the 1980s, centrifugal compressors have been replacing reciprocating compressors and are widely used throughout the industry. With their high flow rates and relatively high discharge pressures, they commonly provide both inlet and outlet compression. They are also used extensively for gas pipeline transmission. In gas processing, they are usually powered by either a gas turbine or a turboexpander but can be steam or electrically driven.

Figure 9.6 shows a cutaway view of a multistage centrifugal compressor. Basically, the compressor consists of a rapidly rotating (1,000–20,000 rpm for natural gas applications) impeller (rotor), surrounded by a stationary diaphragm. (For more details on these compressors, see the *Engineering*

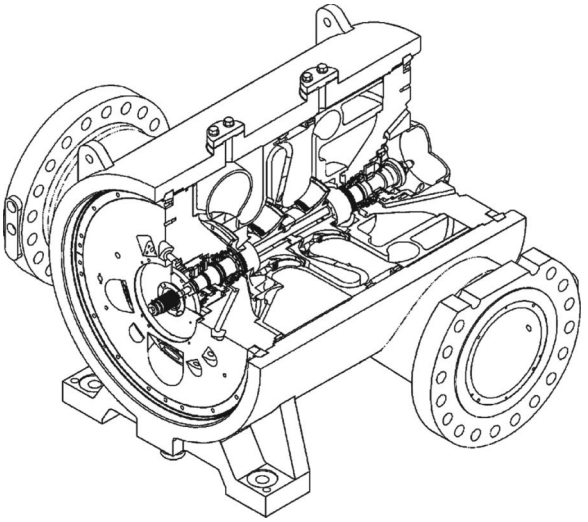


FIGURE 9.6 Cutaway of a centrifugal compressor. (Courtesy of Solar Turbines.)

Data Book, 2016a.) Centrifugal compressors work by having gas enter the rotor of each stage near the rotor shaft. The gas is spun outward at a high velocity into the channels of the stationary diaphragm, which are called diffusers or diffuser passages, where the velocity converts to pressure (kinetic energy into pressure head). The diffuser contains vanes to maximize conversion of velocity to pressure and to direct gas into the next stage. Vendors estimate that about one-third of the pressure increase occurs in the diffuser, and the rest comes from the rotors.

The rotor can be open or shielded on one or both sides. A survey of literature from compressor manufacturers indicates that most compressors for natural gas service are shielded on both sides (i.e., closed), as shown in Figure 9.6. The blades in the rotor are swept back to improve aerodynamics and mechanical stability. A nice feature of these compressors is that multiple stages are on the same drive shaft. The one exception is the centrifugal compressor driven by a turboexpander. These are single-stage and rotor is unshielded.

Like other compressors, exit temperature limits the stage pressure ratio in centrifugal compressors. A single stage may consist of more than one impeller. The *Engineering Data Book* (2016a) recommends a maximum discharge temperature of 400°F (200°C) for mechanical reasons.

A major difference between positive displacement and centrifugal compressors is how discharge pressure affects gas flow. Figure 9.7 shows the interaction between pressure head (i.e., discharge pressure) and actual flow rate for reciprocating, axial, and centrifugal compressors. For reciprocating compressors, the gas flow rate is nearly constant and independent of the downstream pressure (constant volume–variable head), which is why relief valves or other devices are necessary to protect the compressor and downstream equipment from excessive discharge pressures.

For centrifugal compressors, like centrifugal pumps, the downstream pressure greatly affects the throughput (constant head–variable volume). The range over which the compressor functions properly is limited. If downstream pressure becomes too high (or inlet pressure becomes too low), the compressor cannot push the gas out and backflow occurs, which results in a drop in the discharge pressure. Then the compressor raises the discharge pressure only to go into backflow again. This cyclic process is called "surge" and must be avoided because the pressure oscillations cause overheating and vibration that can damage internal bearings. Most compressors, including those driven by turboexpanders, come with surge control systems that protect the compressor by gas recirculation. The *Engineering Data Book* (2016a) discusses surge control methods.

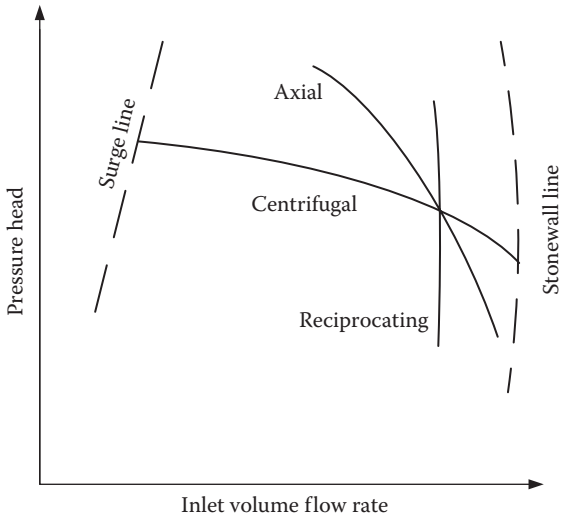


FIGURE 9.7 Relationship between compressor and inlet-volume flow rate for centrifugal, axial, and reciprocating compressors.

The other limit occurs when the gas flow through the compressor reaches sonic velocity and flow cannot be increased. This limit is choked flow or "stonewall." To increase the flow requires internal modifications.

Centrifugal compressors have other disadvantages. Perhaps the most important is the effect of gas density on discharge pressure. This effect is not a factor where the gas composition remains nearly constant, such as in pipeline transmission boosters or refrigeration. However, if used in applications where gas composition changes over time, the compressors must be restaged periodically to obtain maximum efficiency while maintaining a constant flow rate and discharge pressure. Restaging is expensive in terms of both capital outlay and downtime.

Gases that flow into centrifugal and axial compressors must be free of condensed phases because the particles damage the vanes. Their off-design operation is poor compared with the other compressors, and they are not good for intermittent operations. However, where they can be used, their high on-stream time readily offsets their drawbacks.

9.4.2.2 Axial Flow Compressors

Axial compressors routinely compress large volumes of gas (50,000–500,000 acfm [$0.08–0.8 \times 10^3$ am^3/h]) at pressures up to about 200 psig (14 barg). They are smaller and more efficient than centrifugals. As the name implies, axial compressors use stationary and rotating vanes to push the gas in an axial direction instead of in a radial direction like centrifugal compressors.

Figure 9.7 shows that axial compressors have a similar behavior to centrifugal compressors, but in combination with a gas turbine and centrifugal compressor they operate in a range where neither surge nor stonewalling occurs. They are ideal for moving large volumes of air, such as that needed to feed the gas turbines used to drive compressors and generators. The remainder of this section focuses on axial compressors used in gas turbines.

A gas-fired turbine works on the same principle as a jet engine. Figure 9.8 shows a cutaway view of an axial compressor in a gas turbine. Clean air enters the axial compressor at the lower left side of the drawing. It is compressed in the 11 stages of the axial compressor, exiting at 650°F–950°F (350°C–500°C). Fuel is burned with this hot air in the combustion zone and increases the gas temperature to 1,800°F–2,300°F (1,000°C–1,250°C). The high-temperature, high-pressure gas then

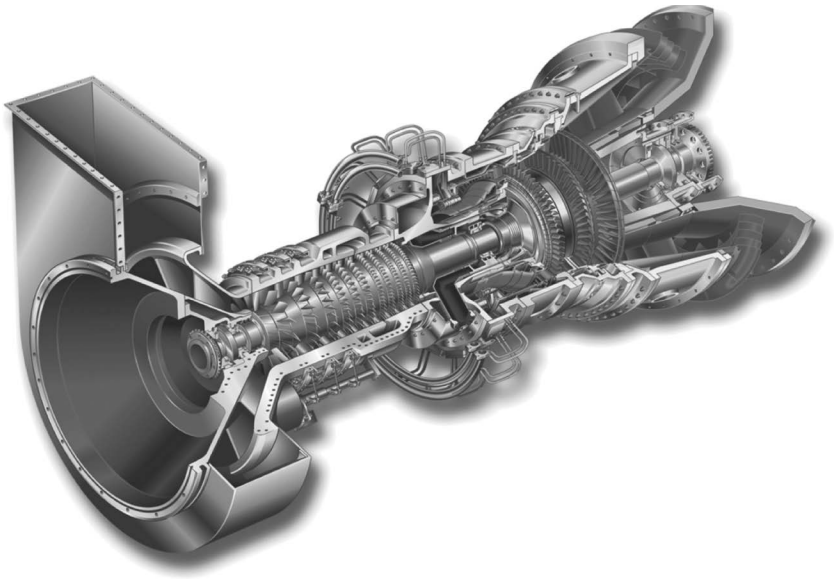


FIGURE 9.8 Cutaway view of a gas-fired turbine. (Courtesy of GE Oil & Gas.)

passes over the three turbine blades to generate the mechanical energy and exits at approximately 950°F (500°C).

Like all heat engines, the turbine thermal efficiency is driven by temperature differences. Gas turbines follow the Brayton cycle (Smith et al., 2018), and ideal efficiencies (defined as the ratio of net work generated divided by heat input) can be up to 40%. However, vendor literature indicates actual overall efficiencies in the 28%–35% range. Turbine ratings are often expressed in terms of heat rate, which is the heat required to generate the power required (Btu/hp-h or kJ/kW-h). Note that the lower heating value is used in this calculation. The *Engineering Data Book* (2016a) provides additional details on the calculation of heat rates and power on the basis of operating conditions. The book also describes combined cycle units that use the high-temperature waste heat to generate steam for additional power generation.

Example 9.7

Compute the overall thermal efficiency of a gas turbine that has a heat rate of 8,500 Btu/hp-h (12,000 kJ/kWh).

Solution

The thermal efficiency is the reciprocal of the heat rate. Including the conversion between energy and power (2,544 Btu/hp-h or 3,600 kJ/kW-h), the thermal efficiency is

$$\begin{aligned}\text{Thermal efficiency} &= 2{,}544/\text{heat rate}\left(3{,}600/\text{heat rate}\right)\\ &= 2{,}544/8{,}500\left(3{,}600/12{,}000\right)\\ &= 0.30\,\text{or}\,30\%\end{aligned}$$

(If the heat rate is stated in Btu/kW-h, the conversion is 3,414 Btu/kW-h.)

For applications in which the speed is nearly constant, a single-shaft machine with all rotating components can be on the same shaft. However, if a variable-speed centrifugal compressor is needed, a second shaft will be coupled to the turbine shaft to permit the compressor and turbine to run at different speeds.

The axial compressor–gas turbine unit is known for high availability. However, the greater number of moving parts and seals, along with high-temperature operation, makes the turbine the least reliable of the turbine–centrifugal compressor combination. Air filtration systems are mandatory to protect the axial compressor from particulate matter. In offshore applications, demisters replace the filters. Self-cleaning filters (see Figure 5.10) that use pulses of clean air from one filter bank to blowout another filter bank are used in many environments. They have the advantage of being able to de-ice a filter bank at the same time when in cold-weather service. The *Engineering Data Book* (2016b) provides additional recommendations on filtration systems.

Plant operators watch the combustion zone exhaust temperature closely because it indicates how close the internal gas turbine temperature is to materials limits. High ambient temperatures sometimes raise the exhaust temperature to a point where gas throughput and developed power must be curtailed.

9.5 CAPACITY AND POWER CALCULATIONS

This section provides some methods for estimating the capacity and power requirements of compressors when ideal gases or nearly ideal gases are used. The *Engineering Data Book* (2016a) provides more detailed calculations. Most of the calculations are independent of compressor type.

Screw compressors with liquids present require either polytropic or more rigorous thermodynamic methods to be used. Reciprocating compressors require knowledge of displacement volumes to compute flow rates, as will be discussed below. If accurate calculations are needed, equation of state methods should be used, along with information about the compressor performance provided by the vendor.

9.5.1 Capacity

9.5.1.1 General Calculations

In this section, we assume that the gas can be described by

$$PV = nzRT \tag{9.17}$$

where z is the compressibility factor. (Appendix B.4 provides charts to estimate z.)

Example 9.8

Estimate the compressibility factor, z, for the gas composition given in Table 9.3 at 120°F and 600 psig.

Solution

One commonly used method for estimating the compressibility factor for a gas or gas mixture is to use a general compressibility factor chart (see Appendix B.4), which assumes that the compressibility factor for any gas with a molar mass less than 40 is a function of the reduced pressure, P_R, and temperature, T_R, of the gas. (For more details on this "corresponding states" method, see a book on physical properties (e.g., Poling et al., 2000.) For a pure gas, the reduced pressure and temperature are obtained by division of the absolute temperature by the critical temperature and the absolute pressure by the critical pressure. For mixtures, the critical properties are obtained by use of pseudocritical pressure and temperature for the mixture defined by (*Engineering Data Book*, 2016c)

$$P_{CM} = \sum y_i P_{C_i} \quad \text{and} \quad T_{CM} = \sum y_i T_{C_i}$$

The reduced temperature for the mixture is (120+460)/377.5 = 1.54, and the reduced pressure is (600+14.7)/663.3 = 0.93. From the compressibility chart in Appendix B.4, the compressibility factor is 0.91.

TABLE 9.3
Data for Example 9.8

Component	Mole Fraction, y	P_c, psia	yP_c	T_c, °R	yT_c
Methane	0.88	667	586.1	343	301.8
Ethane	0.06	707	42.4	550	33.0
Propane	0.03	616	18.5	666	20.0
i-Butane	0.01	528	5.3	734	7.3
Butane	0.02	551	11.0	765	15.3
Mixture properties			663.3		377.5

For capacity calculations, the actual volumetric flow rate, Q (acfm, am^3/h), is based upon inlet conditions to each stage. To compute the actual flow rate from gas flows given as standard flow rates (scfm or Nm^3/h) use

$$Q = \text{scfm}\left(\frac{14.7}{P_1\,(\text{psia})}\right)\left(\frac{T_1\,(°\text{R})}{520}\right)\left(\frac{z_1}{z_R}\right) \tag{9.18a}$$

$$Q = \text{Nm}^3/\text{h}\left(\frac{1.01}{P_1\,(\text{bara})}\right)\left(\frac{T_1\,(\text{K})}{273}\right)\left(\frac{z_1}{z_R}\right) \tag{9.18b}$$

where the subscript "1" denotes inlet conditions. The subscript R refers to the conditions used to define the reference state, in this case, 14.7 psia (1.01 bara) and 60°F (0°C). In these equations, the units must be consistent and the temperatures are absolute (°R or K). If mass flow rates are used, the molar mass (MW), of the gas as well as the mass flow rate, $\dot{m}$ must be known:

$$Q = \frac{10.73\,\dot{m}\left(\text{lb}_\text{m}/\text{min}\right)T_1\,(°\text{R})}{MW\,P_1(\text{psia})}\left(\frac{z_1}{z_R}\right) \tag{9.19a}$$

$$Q = \frac{8.314\,\dot{m}\left(\text{kg/h}\right)T_1\,(\text{K})}{MW\,P_1\,(\text{bara})}\left(\frac{z_1}{z_R}\right) \tag{9.19b}$$

If the molar flow rate $\dot{n}$ is given, the actual gas flow rate is computed by

$$Q = 379.5\dot{n}\,(\text{lb-mol/h})\left(\frac{T_1\,(°\text{R})}{520}\right)\left(\frac{14.7}{P_1\,(\text{psia})}\right)\left(\frac{z_1}{z_R}\right) \tag{9.20a}$$

$$Q = 0.08314\dot{n}\,(\text{mol/h})\left(\frac{T_1\,(\text{K})}{P_1\,(\text{bara})}\right)\left(\frac{z_1}{z_R}\right) \tag{9.20b}$$

9.5.1.2 Reciprocating Compressors

Calculating the throughput of a reciprocating compressor requires knowledge of the volume displaced during each stroke. Normally, the PD is in ft^3/min (m^3/h), which is the product of cross-sectional area, stroke travel, and RPM. The equations for computing PD depend upon compressor type and are given below, in dimensioned form (*Engineering Data Book*, 2016a).

For a single-acting piston compressing only on the outer end (most common configuration)

$$\begin{aligned}\text{PD}\left(\text{ft}^3/\text{min}\right) &= \frac{\pi D^2\left(\text{in}^2\right)}{4}\times\text{RPM}\left(\frac{\text{rev}}{\text{min}}\right)\times\text{Stroke}\,(\text{in})\times\frac{\text{ft}^3}{1{,}728\,\text{in}^3}\\ &= 4.55\left(10^{-4}\right)\times D^2\times\text{RPM}\times\text{Stroke}\end{aligned} \tag{9.21a}$$

$$\begin{aligned}\text{PD}\left(\text{m}^3/\text{h}\right) &= \frac{\pi D^2\left(\text{mm}^2\right)}{4}\times\text{RPM}\left(\frac{\text{rev}}{\text{min}}\right)\times\text{Stroke}\,(\text{mm})\times\frac{\text{m}^3}{10^9\,\text{mm}^3}\times\frac{60\,\text{min}}{\text{h}}\\ &= 4.7\left(10^{-8}\right)\times D^2\times\text{RPM}\times\text{Stroke}\end{aligned} \tag{9.21b}$$

For a single-acting piston compressing only on the crank end (D is piston diameter and d is the rod diameter)

$$\begin{aligned}\mathrm{PD}\left(\mathrm{ft^3/min}\right) &= \frac{\pi\left(D^2-d^2\right)\left(\mathrm{in^2}\right)}{4}\times\mathrm{RPM}\left(\frac{\mathrm{rev}}{\mathrm{min}}\right)\times\mathrm{Stroke\,(in)}\times\frac{\mathrm{ft^3}}{1{,}728\,\mathrm{in^3}}\\ &= 4.55\left(10^{-4}\right)\times\left(D^2-d^2\right)\times\mathrm{RPM}\times\mathrm{Stroke}\end{aligned} \tag{9.22a}$$

$$\begin{aligned}\mathrm{PD}\left(\mathrm{m^3/h}\right) &= \frac{\pi\left(D^2-d^2\right)\left(\mathrm{mm^2}\right)}{4}\times\mathrm{RPM}\left(\frac{\mathrm{rev}}{\mathrm{min}}\right)\times\mathrm{Stroke\,(mm)}\times\frac{\mathrm{m^3}}{10^9\,\mathrm{mm^3}}\times\frac{60\,\mathrm{min}}{\mathrm{h}}\\ &= 4.7\left(10^{-8}\right)\times\left(D^2-d^2\right)\times\mathrm{RPM}\times\mathrm{Stroke}\end{aligned} \tag{9.22b}$$

For double-acting piston compressing on both the crank and the piston end (excluding the tail rod type, which has rods on both side of the piston)

$$\begin{aligned}\mathrm{PD}\left(\mathrm{ft^3/min}\right) &= \frac{\pi\left(2D^2-d^2\right)\left(\mathrm{in^2}\right)}{4}\times\mathrm{RPM}\left(\frac{\mathrm{rev}}{\mathrm{min}}\right)\times\mathrm{Stroke\,(in)}\times\frac{\mathrm{ft^3}}{1{,}728\,\mathrm{in^3}}\\ &= 4.55\left(10^{-4}\right)\times\left(2D^2-d^2\right)\times\mathrm{RPM}\times\mathrm{Stroke}\end{aligned} \tag{9.23a}$$

$$\begin{aligned}\mathrm{PD}\left(\mathrm{m^3/h}\right) &= \frac{\pi\left(2D^2-d^2\right)\left(\mathrm{mm^2}\right)}{4}\times\mathrm{RPM}\left(\frac{\mathrm{rev}}{\mathrm{min}}\right)\times\mathrm{Stroke\,(mm)}\times\frac{\mathrm{m^3}}{10^9\,\mathrm{mm^3}}\times\frac{60\,\mathrm{min}}{\mathrm{h}}\\ &= 4.7\left(10^{-8}\right)\times\left(2D^2-d^2\right)\times\mathrm{RPM}\times\mathrm{Stroke}\end{aligned} \tag{9.23b}$$

With the displacement volume, suction pressure and volumetric efficiency (Equation 9.15), the net capacity can be computed. Note that compressor vendors usually use a standard pressure of 14.4 psia[4] (0.99 bara), instead of 14.7 psia when working in USES. In dimensioned form, the equivalent volume is

$$\begin{aligned}\mathrm{MMcfd} &= \frac{z_{14.4}}{z_1}\frac{\eta_V}{100}\times\mathrm{PD}\left(\frac{\mathrm{ft^3}}{\mathrm{min}}\right)\times\frac{P_1}{14.4}\times\frac{1{,}440\,\mathrm{min}}{d}\times\frac{10^{-6}\,\mathrm{MMft^3}}{\mathrm{ft^3}}\\ &= \frac{\eta_V}{z_1}\times\mathrm{PD}\times P_1\times10^{-6},\ \text{assuming}\ z_{14.4}=1\end{aligned} \tag{9.24a}$$

$$\begin{aligned}m^3/d &= \frac{z_{1\,\mathrm{bar}}}{z_1}\frac{\eta_V}{100}\times\mathrm{PD}\left(\frac{\mathrm{m^3}}{\mathrm{h}}\right)\times\frac{P_1}{1}\times\frac{24\,\mathrm{h}}{d}\\ &= 0.24\times\frac{\eta_V}{z_1}\times\mathrm{PD}\times P_1,\ \text{assuming}\ z\,\text{at}\,1\,\mathrm{bar}=1\end{aligned} \tag{9.24b}$$

Note that Equation 9.24 gives the flow rate at inlet temperature and 14.4 psia (1 bara). Example 9.9 shows the use of these equations.

[4] The 14.4 psia value was selected long ago as a matter of convenience to make calculations simpler because a day contains 1,440 min; see, for example, Equation 9.24a.

Example 9.9

A reciprocating compressor is used to compress a gas from 50 to 185 psig (3.4–12.8 barg). The gas has a specific heat ratio of 1.25 at the average cylinder wall temperature and the suction temperature of 90°F (32°C). The gas can be assumed to be ideal at these conditions.

The compressor is double acting with a 7 in. (178 mm) inner wall diameter and a 2 in. (50 mm) diameter push rod. The compressor has a 6 in. (150 mm) stroke, 12% average clearance and runs at 950 rpm. What is the volumetric flow rate (MMscfd, Nm^3/d) of the compressor?

Solution

Determining the throughput requires computing the displacement, PD, using Equation 9.23 in this case and then Equation 9.24.

$$\begin{aligned}\text{PD} &= 4.55\left(10^{-4}\right)\times\left(2D^2 - d^2\right)\times\text{RPM}\times\text{Stroke}\\ &= 4.55\left(10^{-4}\right)\times\left(2\times 7^2 - 2^2\right)\times 950\times 6 = 244\,\text{ft}^3/\text{min}\left(415\,\text{m}^3/\text{h}\right)\end{aligned}$$

To compute volumetric flow rate in Equation 9.24, use Equation 9.15 to obtain volumetric efficiency, η_V, with $C = 12\%$ and compressibility factors of one.

$$\begin{aligned}\eta_V &= 100 - \left(\frac{P_2}{P_1}\right) - C\left[\left(\frac{z_2}{z_1}\right)\left(\frac{P_2}{P_1}\right)^{1/\gamma} - 1\right]\\ &= 100 - \left(\frac{200}{65}\right) - 12\left[\left(\frac{200}{65}\right)^{1/1.25} - 1\right]\\ &= 100 - 3.1 - 17.5 = 79.4\%\end{aligned}$$

$$\begin{aligned}\text{MMcfd} &= \frac{\eta_V}{z_1}\times\text{PD}\times P_1\times 10^{-6}\\ &= 79.4\times 244\times 65\times 10^{-6}\\ &= 1.2\,\text{MMcfd}\left(34\times 10^3\,\text{m}^3/\text{d}\right)\end{aligned}$$

$$\text{Then}\quad \text{MMscfd} = 1.2\,\text{MMcfd}\times\left(\frac{460+60}{460+90}\right)\times\left(\frac{65}{14.4}\right) = 5.1\,\text{MMscfd}\left(140\times 10^3\,\text{Nm}^3/\text{d}\right)$$

9.5.2 Power Requirements

The ideal power requirements for isentropic compression make use of the shaft work calculated in Equation 9.4 and the isentropic efficiency to give

$$\text{Power} = \dot{m} z_{\text{avg}} w_S \tag{9.25}$$

where

$\dot{m}$ is the mass flow rate

z_{avg} is the average of the inlet and outlet compressibility factors.

Because they are the more common compressor types, the *Engineering Data Book* (2016a) gives some useful methods for estimating power requirements for reciprocating and centrifugal compressors. The following paragraphs give these relationships.

9.5.2.1 Reciprocating Compressors

An empirical equation (*Engineering Data Book,* 2016a) for estimating the power required for reciprocating compressors is

$$\text{Brake hp} = 22\,\text{PR}\,m\,\text{MMcfd} \tag{9.26a}$$

$$\text{Brake kW} = 0.014\,\text{PR}\,m\,\text{m}^3/\text{h} \tag{9.26b}$$

where brake hp (brake kW) is the actual work delivered to the compressor.

One should be aware of several items when using these equations. First, when using USES, volume should be on the basis of 14.4 psia and suction temperature. Also, Equation 9.26a was originally developed for large low-speed (300–400 rpm) compressors that process gas with a specific gravity of 0.65 and for *PR* values greater than 2.5. However, the equation provides a quick estimate of power requirements, which should be within 10% of correct value. The *Engineering Data Book* (2016a) provides correction factors to Equation 9.26 for multistage units but they do not exceed 10%. For more accurate values, the specific compressor vendor should be consulted. When using Equation 9.26b, the volume should be based on 1 bara and suction temperature.

Example 9.10

Use Equation 9.26 to estimate the brake horsepower needed to compress 30 MMscfd (33.5×10^3 Nm^3/h) of the gas in Example 9.1 from 10 to 625 psig (0.69–43.1 barg). Assume the intake temperature to be 80°F (26.7°C).

Solution

Example 9.4 showed that three stages are necessary to go from 10 to 625 psig. Use Equation 9.18, and assume the compressibility factors to be unity, to correct the volumetric flow rate to 14.4 psia and 80°F:

$$\text{MMcfd} = \text{MMscfd}\left(\frac{14.7}{P_1\,(\text{psia})}\right)\left(\frac{T_1\,(^\circ\text{R})}{520}\right) = 30\left(\frac{14.7}{14.4}\right)\left(\frac{460+80}{520}\right) = 31.8\,\text{MMcfd}\left(33.5\times10^3\ \text{Nm}^3/\text{h}\right)$$

Using Equation 9.26a, the estimated horsepower requirement is

$$\text{Brake hp} = 22\,\text{PR}\,m\,\text{MMcfd} = 22\times2.96\times3\times31.8 = 6{,}200\,\text{hp}\left(4.6\,\text{MW}\right)$$

9.5.2.2 Centrifugal Compressors

As in the case of centrifugal pumps, head, h_d ([ft-lb_f/lb_m, kJ/kg]) is commonly used in with centrifugal compressor calculations, instead of pressure. (See Chapter 2 for discussion of head.) The isentropic head, h_{dIS}, is given by

$$h_{dIS} = -z_{avg}w_S = \frac{z_{avg}}{MW}\frac{\gamma RT_1}{\gamma-1}\left[\left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma} - 1\right] \tag{9.27}$$

where z_{avg} is the average compressibility factor between inlet and discharge temperature and pressure. If polytropic head, h_{dP}, is needed, replace γ with κ. The relationship between isentropic and polytropic head is

$$\frac{h_{dP}}{h_{dIS}} = \frac{\eta_p}{\eta_{IS}} \tag{9.28}$$

The actual power in compressing the gas is

$$\text{Power} = \dot{m}\frac{h_{\text{dIS}}}{\eta_{\text{IS}}} \tag{9.29}$$

for isentropic compression. The isentropic power can be calculated by use of the isentropic head and efficiency. For an estimation of the mechanical losses, the *Engineering Data Book* (2016a) suggests

$$\text{Mechanical losses} = (\text{Power})^{0.4} \tag{9.30}$$

so that the brake hp requirement will be the sum of Equations 9.29 and 9.30.

To provide variable flow rates, centrifugal compressors vary the speed of the compressor. The effect of RPM on compressor performance follows the affinity, or fan laws, which are valid for single-stage compressor or multistage compressor with low compression ratios or very low Mach numbers. The fan laws give

$$\frac{Q_1}{Q_2} = \frac{\text{RPM}_1}{\text{RPM}_2} \tag{9.31}$$

$$\frac{h_1}{h_2} = \left(\frac{\text{RPM}_1}{\text{RPM}_2}\right)^2 \tag{9.32}$$

$$\frac{\text{Brake hp}_1}{\text{Brake hp}_2} = \left(\frac{\text{RPM}_1}{\text{RPM}_2}\right)^3 \tag{9.33}$$

Although these relations are useful, they become less accurate with deviations of more than about 10% from design conditions. For most accurate values, the vendor should be consulted.

Example 9.11

A centrifugal compressor increases sales gas pressure from 400 to 950 psig (27.6–65.5 barg). The gas volume is 700 MMsfd (217 Nm^3/s). The sales gas has a molar mass of 16.8, average compressibility of 0.86 and a heat capacity ratio of 1.33. If η_{IS} is 75%, what is the estimated hydraulic power of the compressor if the suction temperature is 80°F?

Solution

To compute the power requires first computing the discharge head using Equation 9.27:

$$h_{\text{dIS}} = \frac{z_{\text{avg}}}{MW}\frac{\gamma RT_1}{\gamma - 1}\left[\left(\frac{P_2}{P_1}\right)^{(\gamma-1)/\gamma} - 1\right] = \frac{0.86}{16.8}\frac{1.33\times 1{,}545\times(460+80)}{1.33-1}\left[\left(\frac{965}{415}\right)^{(1.33-1)/1.33} - 1\right]$$

$$= 40{,}100\ \text{ft-lb}_\text{f}/\text{lb}_\text{m}\ (120\ \text{kJ/kg})$$

The mass flow rate is

$$\dot{m}\left(\text{lb}_\text{m}/\text{s}\right) = 700\times 10^6\ \frac{\text{ft}^3}{\text{d}}\times\frac{d}{86{,}400s}\times\frac{\text{lb-mol}}{379\ \text{ft}^3}\times 16.8\frac{\text{lb}_\text{m}}{\text{lb-mol}} = 360\ \text{lb}_\text{m}/\text{s}\left(164\ \text{kg/s}\right)$$

and the power is found using Equation 9.29:

$$\text{Power} = \dot{m}\frac{h_{\text{dIS}}}{\eta_{\text{IS}}} = 360\frac{\text{lb}_\text{m}}{\text{s}}\times 40{,}100\frac{\text{ft-lb}_\text{f}}{\text{lb}_\text{m}}\times\frac{\text{hp-s}}{550\ \text{ft-lb}_\text{f}}\Big/0.75 = 35{,}000\ \text{hp}\left(26.1\ \text{MW}\right)$$

9.6 COMPARISON OF RECIPROCATING AND CENTRIFUGAL COMPRESSORS

Only reciprocating and centrifugal compressors can meet the demand for discharge pressures in the 1,000 psi (70 bar) range. When gas volumes are large enough for centrifugal compressors to be considered, they usually have many advantages over reciprocating compressors, including (*Engineering Data Book*, 2016a):

- Lower initial and maintenance costs
- Higher reliability (longer time between failures)
- Less operating attention
- Greater throughput per unit of platform area
- Adaptability to high-speed, low-maintenance drivers

Both efficiency and maintenance must be considered when reciprocating and centrifugal compressors are compared. Reciprocating compressors are far more efficient than centrifugal compressors (see Table 9.2). Heat rates of gas turbines and internal combustion engines vary widely with power output and vendor, but generally internal combustion engines have lower heat rates than gas turbines. The *Engineering Data Book* (2016a) lists these data for major vendors. If the gas processor shares the fuel costs with the producer (e.g., with POP contracts (see Chapter 7)), the difference in efficiencies is not a major factor for the gas processor, because most of the fuel cost is borne by the producer. For fixed fee contracts, the increased efficiency is important to the processor. The primary drawback of centrifugal compressors is that they cannot be readily adapted to changes in volumetric flow and gas molar mass. This limits their use in some gas processing applications.

However, the processor typically pays all maintenance costs. These costs for reciprocating compressors run approximately four times higher. If a 100 MMscfd (2.7×10^6 Nm^3/d) plant has 70,000 hp (50 MW) devoted to inlet and outlet compression, the savings by use of centrifugal compressors can be several million dollars per year.

9.7 SAFETY AND ENVIRONMENTAL CONSIDERATIONS

Apart from the dangers inherent in high-pressure, high-temperature equipment, noise is the main safety concern related to compression. Normally, ear protection is worn in the plant, but it is a must around compressors, which produce noise levels in the 85–95 dbA range.

Exhaust emissions from compressor prime movers are a major environmental concern. Newer internal combustion engines that drive reciprocating compressors were designed to meet an emission level of less than 2 g NO_X per horsepower-hour by use of "clean burn or lean burn" units. However, tighter controls are sometimes imposed and catalytic converters, which reduce NO_X to N_2 and oxidize CO to CO_2, are installed. Standards vary by jurisdiction. This requirement applies to smaller booster station compressors as well as large plant units. Emission standards are one of the reasons that smaller booster stations use electric motor-driven compressors where reliable power is available.

High air-to-fuel ratios combined with good combustor designs minimize CO emission from gas turbines. Nitrogen oxides are the most significant exhaust pollutant and high-efficiency systems increase NO_X production. Water is often added to reduce NO_X production. This addition helps reduce the NO_X formed from N_2 in the combustion air. Water may actually enhance NO_X production from the organic nitrogen, as well as increase CO production (*Engineering Data Book*, 2016b). Modification of the air–fuel ratio and combustor design help keep the NO_X exit concentration level in the 10–15 ppm range. If lower NO_X emissions are required, selective catalytic reduction can be added to reduce NO_X to N_2. These devices use NH_3 to reduce the NO_X.

Fugitive emissions from seals and vents can be a difficult source to control because they are often at slightly above atmospheric pressure and too low to be routed to the plant flare. Some plants have installed small incinerators just for these emission sources.

DISCUSSION QUESTIONS

1. Comparing pumps and compressors, list some significant similarities and differences between the two.
2. For rough calculations does it take more work to compress a gas from 100 to 1,000 psia than to compress from 10 to 100 psia? Does this differ from pumping a liquid from 100 to 1,000 psia, and if so, why is there a difference?
3. Why does it take more work to compress a gas isentropically than isothermally?
4. What limits the pressure ratio in the different kinds of compressors discussed in this chapter?
5. What are the different kinds of efficiencies for compressors and which are specific to a certain type?
6. Which types of compressors are best suited for essentially constant inlet flow? For variable inlet flow?
7. What is the difference between isentropic and polytropic efficiency? Which will always be higher than the other?
8. When and why is multistaging necessary?
9. For a given pressure ratio, does the head in a centrifugal compressor increase or decrease with increasing molar mass?
10. What is surge and why is it important?

EXERCISES

9.1 A gas mixture has the following composition:
C_1 89 vol%
C_2 6 vol%
C_3 5 vol%
Using Appendix Table B.2 (B.3)[5] what is the value of the heat capacity ratio, γ, at 150°F (65°C)?

9.2 A field compressor boosts a raw gas stream from 8 psig (0.55 barg) to 450 psig (31.0 barg). The maximum acceptable pressure ratio is 3.
a. How many stages will be required assuming the compression ratio is constant for all stages?
b. What is the compression ratio based upon the number of stages required?

9.3 A two-stage reciprocating compressor compresses propane from 1 to 235 psig (7 kPa to 16.2 barg) in a refrigeration system. The compression ratio is the same in both stages. Suction temperatures to the first and second stages are –20°F (–28.9°C) and 80°F (26.7°C). The adiabatic compressor efficiency is 80%.
a. Compute the isentropic work required (Btu/lb_m, kJ/kg) in each stage of the propane compressor and the discharge temperature assuming ideal gas behavior.
b. Compute the isentropic work required (Btu/lb_m, kJ/kg) in each stage of the propane compressor and the discharge temperature using the PH diagrams in Appendix B.

9.4 A centrifugal compressor has a polytropic efficiency of 78% for a gas with a molar mass of 17.5 and a heat capacity ratio of 1.17. The gas is compressed from 640 to 1,050 psig (44.1–72.4 barg); suction temperature is 86°F (30°C) and the gas volume is 690 MMscfd (18.5×10^6 Nm^3). What is the hp (MW) of the compressor? Assume the compressibility factor is one in the calculations.

[5] See Appendix B on publisher website: www.crcpress.com/Fundamentals-of-Natural-Gas-Processing-Third-Edition/Kidnay-Parrish-McCartney/p/book/9781138612792

9.5 The sales gas from a gas plant is compressed from 330 to 1,000 psig (22.7–69.0 barg) to meet pipeline requirements using a centrifugal compressor. The compressor has an isentropic efficiency of 75% and the gas turbine has a heat rate of 8,200 Btu/hp-h (11,600 kJ/kWh). Low-pressure sales gas is the fuel to the gas turbine. The gas is 99 vol% methane and 1 vol% ethane. Assuming the suction temperature is 60°F (15.6°C) and the heat capacity ratio is constant at that temperature, what fraction of low-pressure sales gas is consumed in compressing the gas to pipeline specifications?

REFERENCES

Bruce, J.T., Screw compressors: A comparison of applications and features to conventional types of machines, *Proceedings of the Seventy-Ninth Annual Convention Gas Processors Association*, Tulsa, OK, 2000, p. 229.

Engineering Data Book, Section 13, Compressors and expanders, GPSA Midstream Suppliers, Tulsa, OK, 2016a.

Engineering Data Book, Section 15, Prime movers for mechanical drives, GPSA Midstream Suppliers, Tulsa, OK, 2016b.

Engineering Data Book, Section 23, Physical properties, GPSA Midstream Suppliers, Tulsa, OK, 2016c.

Jandjel, D.G., Select the right compressor, *Chem. Eng. Progr.*, *96*(7), 15, 2000.

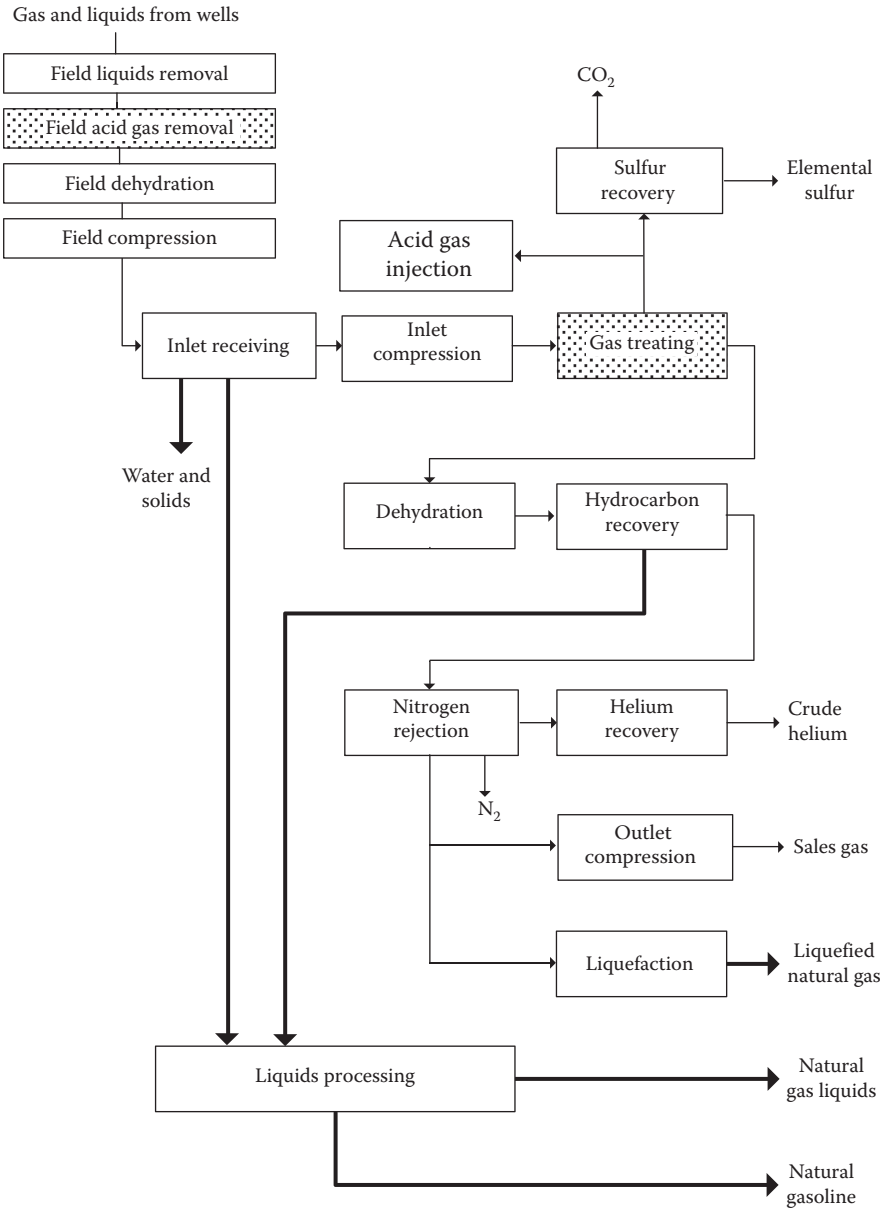
Ohama, T., et al., High pressure oil-injected screw gas compressors (API 619 design) for heavy duty process gas applications, *Proceedings of the Thirty-Third Turbomachinery Symposium*, Houston, TX, 2004. https://lms.i-know.com/pluginfile.php/28882/mod_resource/content/123/Oil%20Injected%20Screw%20Compressors.pdf (Retrieved April 2019).

Poling, B.E., et al., *The Properties of Gases and Liquids,* 5th edn. McGraw Hill, New York, 2000.

Smith, J.M., et al., *Introduction to Chemical Engineering Thermodynamics,* 8th edn. McGraw-Hill Higher Education, New York, 2018.

Taylor & Francis
Taylor & Francis Group
http://taylorandfrancis.com

10 Gas Treating



10.1 INTRODUCTION

Gas treating involves removal of the "acid gases" carbon dioxide (CO_2) and hydrogen sulfide (H_2S) along with other sulfur species to sufficiently low levels to meet contractual specifications, to minimize pipeline corrosion, or to permit additional processing in the plant without corrosion or plugging problems. This chapter focuses on acid gas removal because they are the most prevalent; when applicable, other sulfur compounds are discussed. Processes for removal of H_2S by direct conversion to elemental sulfur are discussed in Chapter 16.

Many good references on gas treating can be found in the proceedings of the Laurance Reid Gas Conditioning Conference and Gas Processors Association. In addition, Kohl and Nielsen (1997) is a good general-purpose reference. For a brief introduction to many of the processes used in gas treating, refer to Goar (1971). Although dated, this paper provides a good, broad overview. Additionally, Johnson et al. (2006, 2007a–c) provide a good review of trace sulfur and other trace component removal.

In this introduction, the following questions are addressed briefly to set the stage for the remainder of the chapter:

1. Why are the acid gases a problem?
2. What are typical acid gas concentrations in natural gas?
3. How much purification is needed?
4. What is done with acid gases after separation from the natural gas?
5. What processes are available for acid gas removal?

10.1.1 The Problem

Hydrogen sulfide is highly toxic, and in the presence of water it forms a weak, corrosive acid. The threshold limit value (TLV) for prolonged exposure is 10 ppmv and at concentrations greater than 1,000 ppmv, death occurs in minutes (*Engineering Data Book*, 2016b). It is readily detectable at low concentrations by its "rotten egg" odor. Unfortunately, at toxic levels, it is odorless because it deadens nerve endings in the nose in a matter of seconds.

Carbon dioxide is nonflammable and, consequently, large quantities are undesirable in a fuel. Like H_2S, it forms a weak, corrosive acid in the presence of water. Although not toxic to humans like H_2S, it is heavier than air and can cause burning sensation in lungs and asphyxiation resulting in death if adequate ventilation is not provided.

When natural gas H_2S concentrations are well above the ppmv level, other sulfur species can be present. These compounds include carbon disulfide (CS_2), mercaptans (RSH), and sulfides (RSR), in addition to elemental sulfur. If CO_2 is present as well, the gas may contain trace amounts of carbonyl sulfide (COS). Although it can occur naturally, a major source of COS is formation during the regeneration of molecular sieve beds used in dehydration (see Chapter 11). One common method of determining ppmv levels of H_2S in gases is to use stain tubes, which involves sampling gas into a glass tube that changes color based on H_2S concentration. This method is good for spot and field testing. A continuous method measures reflectance from a lead acetate-coated tape that darkens in the presence of H_2S. This test, ASTM D4084-07 (2017), detects H_2S down to 0.1 ppmv. It is specific to H_2S but can be used to detect total sulfur by hydrogenating the gas to convert other sulfur species to H_2S before going to the detector.

The presence of H_2S in liquids is usually detected by the copper strip test (ASTM D1838-16, 2016). This is the standard test to detect the presence of materials that could corrode copper fittings.

10.1.2 Acid Gas Concentrations in Natural Gas

Although many natural gases are free of objectionable amounts of H_2S and CO_2, substantial quantities of these impurities are found in both gas reserves in the United States and production in the

United States. In a survey of U.S. gas resources, which did not include any unconventional gas resources, Meyer (2000) defined subquality gas as that containing $CO_2 \geq 2\%$, $N_2 \geq 4\%$, or $H_2S \geq 4$ ppmv. These criteria were selected because gases that contain these amounts of impurities generally require upgrading or blending for delivery to a pipeline. Using these criteria, Meyer (2000) estimated that 41% of proven nonassociated gas reserves are subquality and 34% of 1996 gas production in the lower 48 states was subquality. For associated gas reserves, he estimated that 13% was subquality. It is obvious that removal of H_2S and CO_2 is a major concern in gas processing.

The CO_2 levels can be over 5 mol% in some U.S. shale plays (see Table 6.5). However, the H_2S levels tend to be below 100 ppmv for most unconventional gases. In the United States, the Haynesville shale gas H_2S can be several 100 ppmv (Compton et al., 2012). The Montney gas in western Canada ranges from ppmv to 12 mol% (Giacomin, 2018).

10.1.3 Purification Levels

The inlet conditions to the treating section of a gas processing plant are generally temperatures near ambient and pressures in the range of 300–1,000 psig (20–70 barg), so the partial pressures of the entering acid gases can be quite high. If the gas is to be purified to a level suitable for pipeline transportation and used as a residential or industrial fuel, then the H_2S concentration must be reduced to 0.25 grains/100 scf (4 ppmv, 6 mg/Nm^3) (*Engineering Data Book*, 2016a), and the CO_2 concentration must be reduced to a maximum of 2–3 mol%. However, if the gas is to be processed for NGL recovery or nitrogen rejection in a cryogenic process, CO_2 may have to be removed to prevent it freezing out and plugging equipment. If the gas is being fed to an LNG liquefaction or nitrogen rejection facility, then the maximum CO_2 level should be about 50 ppmv (Klinkenbijl et al., 1999) because of potential solids formation.

10.1.4 Acid Gas Disposal

What becomes of the CO_2 and H_2S after their separation from the natural gas? The answer depends on the quantity of the acid gases and H_2S concentration.

For CO_2, if the quantities are large, it is sometimes used as an injection fluid in enhanced oil recovery (EOR) projects. See Chapter 16 for more details. If EOR is unfeasible, then the gas can be vented, provided it satisfies environmental regulations for impurities and greenhouse gas limits. Moritis (2008) gives a general discussion on the state of EOR in the United States. Jurisdictions around the world may have limits on CO_2 and H_2S emissions to the atmosphere.

In the case of H_2S, four disposal options are available:

1. Incineration and venting of the flue gas, if environmental regulations regarding sulfur dioxide emissions can be satisfied
2. Reaction with H_2S scavengers, such as iron sponge
3. Conversion to elemental sulfur by use of the Claus or a direct process (see Chapter 16)
4. Disposal by injection into a suitable underground formation (see Chapter 16)

The first two options are applicable to smaller quantities of H_2S, and the last two are required if the amount is too high to make the first two options feasible.

10.1.5 Purification Processes

Four scenarios are possible for acid gas removal from natural gas:

1. CO_2 removal from a gas that contains no H_2S
2. H_2S removal from a gas that contains no CO_2

3. Simultaneous removal of both CO_2 and H_2S
4. Selective removal of H_2S from a gas that contains both CO_2 and H_2S

Because the concentrations of CO_2 and H_2S in the raw gas to be processed and the allowable acid gas levels in the final product vary substantially, no single process is markedly superior in all circumstances and, consequently, many processes are presently used. Figure 10.1 summarizes some commercially available methods and groups them into the generally accepted categories. Amine and alkali salt processes involve solvent components reacting with the acid gas while physical processes only absorb the acid gas. More discussion of the differences between chemical and physical solvents can be found in Chapter 4. Hybrids are a mix of physical and chemical solvents. Details of processes not discussed in this chapter may be found in the handbook by Kohl and Nielsen (1997) or the proceedings of the Laurence Reid Gas Conditioning Conference.

A summary of some of the more important items that must be considered before selecting a process include (*Engineering Data Book*, 2016b):

- Type and concentration of impurities and hydrocarbon composition of the sour gas. For example, COS, CS_2, and mercaptans can affect the design of both gas and liquid treating facilities. Compared to chemical solvents, physical solvents absorb more C_3^+ hydrocarbons, which often make physical solvent processes less attractive.
- Temperature and pressure at which the sour gas is processed. High acid gas partial pressures (50 psia [3.5 bara] or higher) in the feed favor physical solvents, whereas low partial pressures favor chemical solvents.
- Specifications for the outlet gas, the acid gas, and liquid products. The impact of gas treating on liquid products is addressed in Chapter 12. Chemical processes remove acid gases to lower concentrations than do physical processes.
- Volume of gas to be processed and amount of H_2S to be removed
- Desired selectivity for acid gas removal.
- Capital, operating, and royalty costs for the process.
- Environmental constraints, including air emission regulations and disposal of byproducts considered hazardous chemicals.

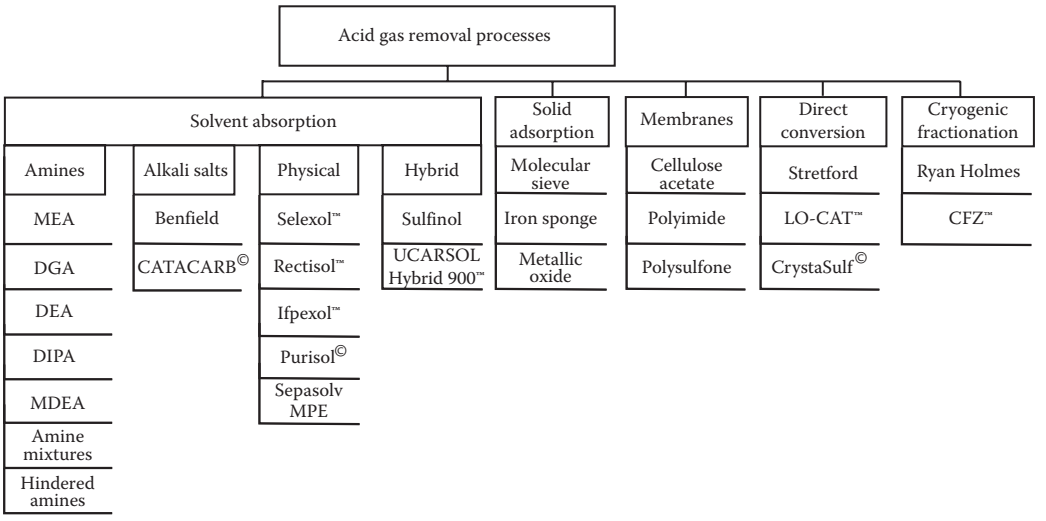


FIGURE 10.1 Acid gas removal methods.

If gas sweetening is required offshore, both size and weight are additional factors that must be considered. Whereas CO_2 removal is sometimes performed offshore, H_2S removal is rarely done unless absolutely necessary because of the problems of handling the reaction byproducts, acid gas stream, or elemental sulfur. The same is true for onshore field operations unless spent reaction products and sulfur stream can be readily and safely removed from the site.

Selection criteria for the solvent-based processes are discussed by Tennyson and Schaaf (1977). Figure 10.2 shows updated guidelines for process selection. The guidelines in the figure are approximate because process selection must include current economic considerations.

Table 10.1, adapted from Echterhoff (1991) and updated, presents a summary of the more widely used acid gas processes, including degree of purification attainable, selectivity for H_2S removal, and removal of the sulfur compounds COS, CS_2, and mercaptans. As a rule, these sulfur compounds exist at much lower concentrations than H_2S, but their removal is important if product specifications have an upper limit on total sulfur. Note that in cases of high propane recovery, most of the COS, CS_2, and mercaptans present in the feed will stay with the liquid product (NGL). The distribution and removal of these sulfur compounds from liquids is discussed in Chapter 15. All of the amines are susceptible to degradation by O_2, forming undesirable and corrosive compounds.

This discussion considers only the more commonly used amine processes, the Selexol® physical absorption process, molecular sieve adsorption, membranes, H_2S scavengers, and biological processes. Not discussed are processes like ExxonMobil's CFZ™ for CO_2 removal. Many newer amine process installations have employed a proprietary blend of amines, usually methyldiethanolamine (MDEA) based. The use of these formulations was introduced by BASF as a product called aMDEA. This solvent was a proprietary mixture of MDEA with piperazine. Once the BASF patents expired, most solvent suppliers began offering a similar product and formulations with other amines. For a more comprehensive discussion of acid gas purification, the reader should refer to Kohl and Nielsen (1997), the *Engineering Data Book* (2016b), and the proceedings of the Laurance Reid Gas Conditioning Conference.

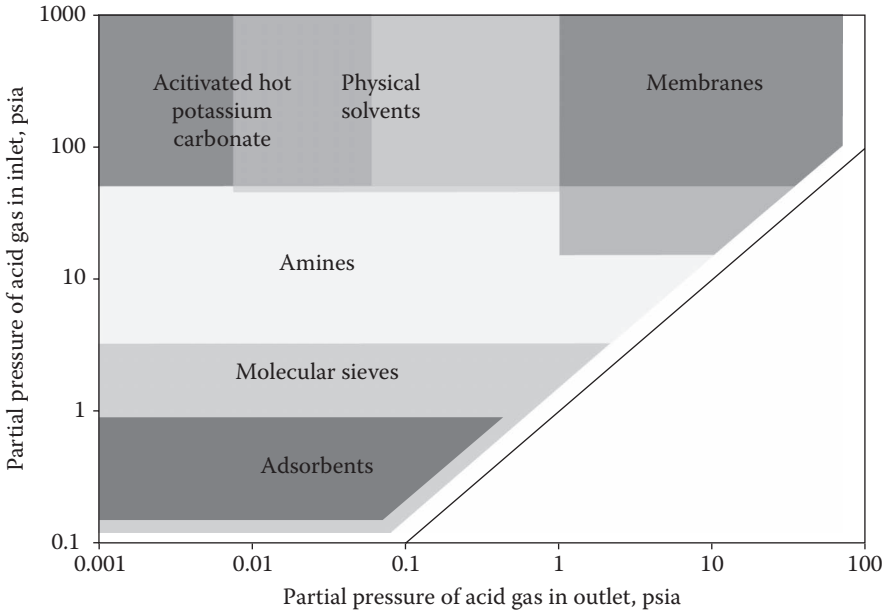


FIGURE 10.2 Process selection chart for acid gas removal.

TABLE 10.1
CO_2 and H_2S Removal Processes for Gas Streams

Process	Normally Capable of Meeting H_2S Specification[a]	Removes COS, CS_2, and Mercaptans	Selective H_2S Removal	Minimum CO_2 Level Obtainable	Solution Subject to Degradation? (Degrading Species)
MEA	Yes	Partial	No	10 ppmv at low pressure	Yes (COS, O_2, CS_2, and mercaptans)
DGA®	Yes	Partial	No	10 ppmv at low pressure	Yes (CO_2, COS, O_2, CS_2)
DEA	Yes	Partial	No	50 ppmv	Some (O_2 CS_2, HCN, and mercaptans)
DIPA	Yes	COS only	Yes	Not applicable	Some (O_2 CS_2, HCN, SO_2, SO_3, and mercaptans)
MDEA	Yes	Slight	Yes	Bulk removal	Some (O_2, SO_2, SO_3)
MDEA blends	Yes	Partial	No	50 ppmv	Some (O_2 CS_2, HCN, and mercaptans)
Sulfinol®	Yes	Partial	Yes	50 ppmv, 50% slippage while meeting H_2S product specification	Some (CO_2, CS_2, O_2, SO_2 and SO_3)
Hot potassium carbonate	Yes, with special design features	Partial	No	Not reported	Not reported
Stretford, LO-CAT™, CrystaSulf©	Yes	No	Yes	CO_2 is not removed	Not reported
Selexol®	Yes	Yes	Some	Can be slipped or absorbed	No
Rectisol®	Yes	Yes	No	1 ppmv	Not reported
Molecular sieves	Yes	Yes (except CS_2)	Yes	Can remove CO_2 to less than 10 ppmv	Not applicable
Membranes	No	Slight	No	Feed concentration dependent	Not applicable

Source: Adapted and updated from Echterhoff (1991).
[a] H_2S specification is 0.25 grain H_2S per 100 scf (4 ppmv, 6 mg/Nm^3).

10.2 CHEMICAL ABSORPTION PROCESSES

In solvent absorption, the two major cost factors are the solvent circulation rate, which affects both equipment size and operating costs, and the energy requirement for regenerating the solvent per quantity of acid gas removed. Table 10.2 summarizes some advantages and disadvantages of removal processes. This section focuses on chemical absorption processes.

10.2.1 Amines

Amines are compounds formed from ammonia (NH_3) by replacing one or more of the hydrogen atoms with another hydrocarbon group. The replacement of a single hydrogen atom produces a primary amine, replacement of two hydrogen atoms produces a secondary amine, and replacement of all three of the hydrogen atoms produces a tertiary amine. Primary amines are the most reactive, followed by the secondary and tertiary amines. Sterically hindered amines are compounds in which the reactive nitrogen is partially shielded by neighboring groups so that larger molecules cannot

TABLE 10.2
Comparison of Chemical and Physical Solvents

Advantages	Disadvantages
Chemical Solvents	
Relatively insensitive to H_2S and CO_2 partial pressure	High regeneration energy requirement
Can reduce H_2S and CO_2 to ppm levels	Amines are in a water solution, and thus the treated gas leaves saturated with water
Physical Solvents	
Low regeneration energy requirements	May be difficult to meet H_2S specification
Can be selective between H_2S and CO_2	Very sensitive to acid gas partial pressure
	C_3^+ hydrocarbons are partially absorbed

easily approach and react with the nitrogen. The amines are used in water solutions in concentrations ranging from approximately 15–50 wt% amine. Appendix B[1] provides some of the physical properties of amines and of amine–water mixtures. Commonly used amines are alkanolamines, amines with OH groups attached to the hydrocarbon groups to reduce amine volatility.

Figure 10.3 shows the formulas for the common amines used in gas processing.

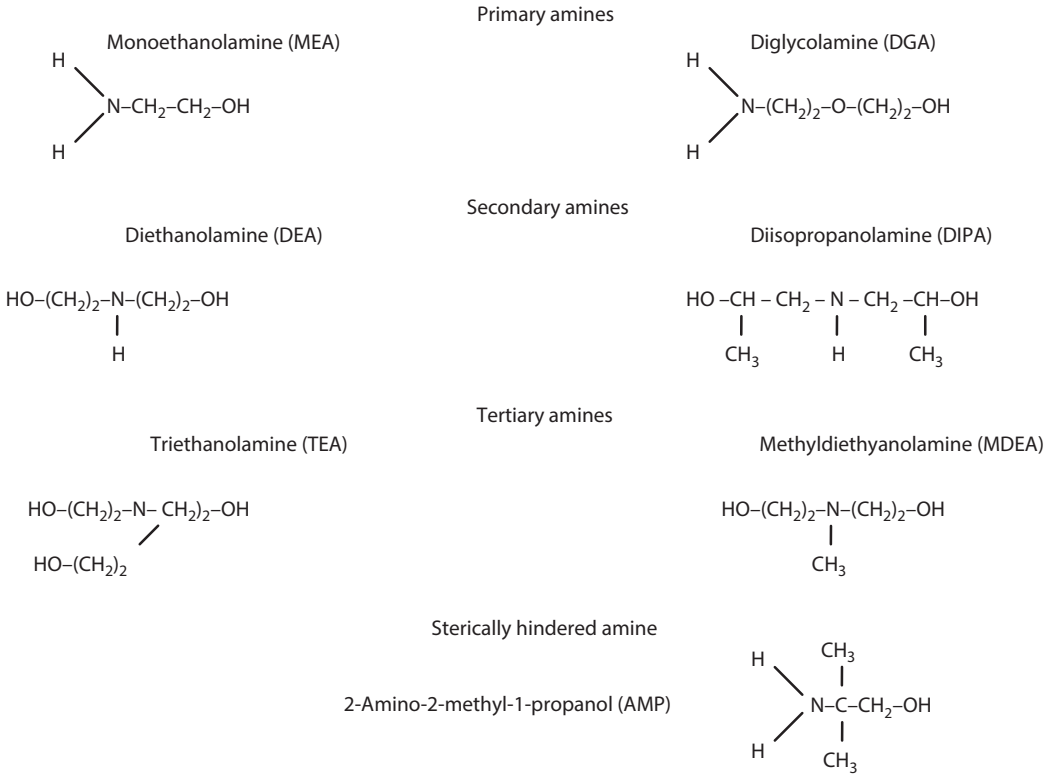


FIGURE 10.3 Molecular structures of commonly used amines.

[1] See Appendix B on publisher website: www.crcpress.com/Fundamentals-of-Natural-Gas-Processing-Third-Edition/Kidnay-Parrish-McCartney/p/book/9781138612792

Amines remove H_2S and CO_2 in a two-step process:

1. The gas dissolves in the liquid (physical absorption).
2. The dissolved gas dissociates into a weak ionic acid, reacts with the weakly basic amines.

Absorption from the gas phase is governed by the partial pressure of the H_2S and CO_2 in the gas, whereas the reactions in the liquid phase are controlled by the reactivity of the dissolved species. The principal reactions (see, e.g., *Engineering Data Book*, 2016b) are given in the next section. It should be noted that the absorption rate of the acid gas into the liquid is enhanced over that with no liquid phase reaction because the concentration of H_2S and CO_2 near the vapor–liquid interface is lower than if there were no reaction.

10.2.1.1 Basic Amine Chemistry

Amines are bases, and the important reaction in gas processing is the ability of the amine to form salts with the weak acids formed by H_2S and CO_2 in an aqueous solution. When a gas stream that contains the H_2S, CO_2, or both, is contacted by an amine solution, the acid gases react to form a soluble acid–base complex, a salt, in the treating solution. The reactions of an amine with both H_2S and CO_2 are highly exothermic. Regardless of the structure of the amine, H_2S reacts rapidly with primary, secondary, or tertiary amines via a direct proton transfer reaction, as shown in Equation 10.1, to form the amine hydrosulfide:

$$R_1R_2R_3N + H_2S \leftrightarrow R_1R_2R_3NH^+HS^- \tag{10.1}$$

The reaction is shown for a tertiary amine but applies to primary and secondary amines as well. The reaction between the amine and the CO_2 is more complex because CO_2 reacts via two different mechanisms. When dissolved in water, CO_2 hydrolyzes to form carbonic acid (Equation 10.2), which in turn slowly dissociates to bicarbonate (Equation 10.3). The bicarbonate then undergoes an acid–base reaction with the amine as shown by Equation 10.4. Equation 10.5 shows the overall reaction.

$$CO_2 + H_2O \leftrightarrow H_2CO_3\left(\text{carbonic acid}\right) \tag{10.2}$$

$$H_2CO_3 \leftrightarrow H^+ + HCO_3^-\left(\text{bicarbonate}\right) \tag{10.3}$$

$$H^+ + R_1R_2R_3N \leftrightarrow R_1R_2R_3NH^+ \tag{10.4}$$

$$CO_2 + H_2O + R_1R_2R_3N \leftrightarrow R_1R_2R_3NH^+HCO_3^-\left(\text{overall reaction}\right) \tag{10.5}$$

This acid–base reaction occurs with any of the alkanolamines, regardless of the amine structure, but the reaction is not as rapid as that of H_2S, because the carbonic acid dissociation step to the bicarbonate is relatively slow.

A second CO_2 reaction mechanism, shown by Equations 10.6–10.8, requires the presence of a labile (reactive) hydrogen in the molecular structure of the amine.

$$CO_2 + 2R_1R_2NH \leftrightarrow R_1R_2NH_2^+R_1R_2NCOO^- \tag{10.6}$$

$$R_1R_2N^+HCOO^- + R_1R_2NH \leftrightarrow R_1R_2NCOO^- + R_1R_2NH_2^+ \tag{10.7}$$

$$CO_2 + 2R_1R_2NH \leftrightarrow R_1R_2NH_2^+R_1R_2NCOO^- \tag{10.8}$$

This second reaction mechanism for CO_2, which forms the amine salt of a substituted carbamic acid, is called the carbamate formation reaction and occurs only with primary and secondary

amines. The CO_2 reacts with one primary or secondary amine molecule to form the carbamate intermediate (Equation 10.6), which in turn reacts with a second amine molecule to form amine salt (Equation 10.7). The rate of CO_2 reaction via carbamate formation is much faster than the CO_2 hydrolysis reaction, but slower than the H_2S acid–base reaction. The stoichiometry of the carbamate reaction indicates that the capacity of the amine solution for CO_2 is limited to a loading of 0.5 mol of CO_2 per mol of amine if the only reaction product is the amine carbamate. However, the carbamate undergoes partial hydrolysis to form bicarbonate, which regenerates free amine. Hence, CO_2 loadings greater than 0.5, as seen in some plants that employ diethanolamine (DEA), are possible through the hydrolysis of the carbamate intermediate to bicarbonate.

The fact that CO_2 reacts by two mechanisms with different reaction (kinetic) rates, significantly affects the relative absorption rates of H_2S and CO_2 among the different alkanolamines. For primary and secondary amines, little difference exists between the H_2S and CO_2 reaction rates because of the rapid carbamate formation for CO_2 absorption. However, because the tertiary amines have no labile hydrogen, they cannot form the carbamate. Tertiary amines must react with CO_2 via the slower hydrolysis mechanism in Equation 10.5. With only the slow acid–base reaction available for CO_2 absorption, MDEA and some formulated MDEA products yield significant selectivity toward H_2S relative to CO_2, and, consequently, most of the H_2S is removed while some of the CO_2 "slips" through with the gas. Because the CO_2 reaction with water to form bicarbonate is slow and the H_2S reaction is fast for MDEA, the H_2S reaction is considered gas phase limited and the CO_2 reaction is considered liquid phase limited.

Some MDEA-based formulations, especially those using piperazine, react more rapidly with CO_2 and can be considered as more like secondary amines. The principle advantages of these formulations are lower regeneration energy and lower circulation rates when compared to primary and secondary amines.

For the reactions discussed above, high pressure and low temperature drive the reactions to the right. High temperatures and low pressures favor the reverse reaction, which provides a mechanism for the regeneration of the amine solution.

Accurate modeling of the vapor–liquid phase behavior of CO_2 and H_2S in amine solutions for process design requires incorporation of ionic chemistry into the above equations. In addition, absorption and reaction rate must be modeled accurately. As the demand for lower sulfur contents increased, modeling became more important. The GPA Midstream Association (GPA) conducts a multiyear research program to provide the data needed to improve amine modeling, including the widely used models of Kent and Eisenberg (1976). Details of the work are available by downloading the latest Cooperative Research brochure from the GPA Midstream website (2019 Cooperative Research, 2018).

Brief descriptions of some commonly used amines follow; more detailed discussions are available in the handbook of Kohl and Nielsen (1997) and the *Engineering Data Book* (2016b). Table 10.3 provides an abbreviated list of the more important operating parameters for the commonly used amines. Values are typical, but they depend upon specific design and operating conditions.

10.2.1.2 Monoethanolamine

Monoethanolamine (MEA) is a primary amine. It is the strongest base of the amines used in gas treating and thus the most reactive for acid gas removal. It has the advantage of a high solution capacity at moderate concentrations and is generally used for gas streams with moderate levels of CO_2 and H_2S when complete removal of both impurities is desired.

Monoethanolamine has a number of disadvantages, including:

- A relatively high vapor pressure that can result in vaporization losses
- The formation of irreversible reaction products with COS and CS_2
- A high heat of reaction with the acid gases that results in high energy requirements for regeneration (see Tables 10.3 and 10.4)

TABLE 10.3
Some Representative Operating Parameters for Amine Systems[a]

	MEA	DGA®	DEA	MDEA
Maximum wt% amine concentration	25	60	40	65
Rich amine acid gas loading mole acid gas/mole amine	0.45–0.52	0.31–0.38	0.21–0.81	0.21–0.61
Acid gas pickup mole acid gas/ mole amine	0.33–0.40	0.31–0.38	0.20–0.80	0.20–0.60
Lean solution residual acid gas mole acid gas/mole amine	0.12±	0.06±	0.01±	0.005–0.01
Approximate reboiler heat duty, MBtu/gal (kJ/L) lean solution	1.0–1.2 (280–335)	1.1–1.3 (300–360)	0. 84–1.0 (235–280)	0. 8–0.9(220–250)
Normal reboiler temperature range, °F (°C)	225–260 (107–127)	250–270 (121–132)	230–260 (110–127)	230–270 (110–132)

Source: Adapted from *Engineering Data Book* (2016b), with permission.
[a] Numbers given are representative only. All values depend upon specific design and operating conditions.

TABLE 10.4
Average Heats of Reaction[a] of the Acid Gases in Amine Solutions

Amine	H_2S, Btu/lb_m (kJ/kg)	CO_2, Btu/lb_m (kJ/kg)
MEA	610 (1,420)	825 (1,920)
DGA®	674 (1,570)	850 (2,000)
DEA	555 (1,290)	730 (1,700)
MDEA	530 (1,230)	610 (1,425)

Source: *Engineering Data Book* (2016b), with permission.
[a] The heats of reaction vary with both acid gas loading and solution concentration. Values shown are typical.

- The inability to selectively remove H_2S in the presence of CO_2
- Higher corrosion rates than most other amines if the MEA concentration exceeds 20% at high levels of acid gas loading (Kohl and Nielsen, 1997)
- The formation of corrosive thiosulfates when reacted with oxygen

Heat stable salts are slowly formed in all alkanolamine solutions, primarily from reaction with CO_2. Oxygen also contributes to the formation of these salts. In addition to fouling regenerator reboilers, high concentrations of salts in the solution can cause foaming (often called "stacking" by operators), which degrades contactor efficiency. One advantage of primary amines such as MEA and DGA® over other amines is that thermal reclaimers can be installed in-line for intermittently removing these salts, along with the irreversible products formed by reaction with COS, CS_2, and O_2 (see Section 10.2.1.10).

10.2.1.3 Diglycolamine

Compared with MEA, the lower vapor pressure and lower corrosiveness, of diglycolamine [2-(2-aminoethoxy) ethanol] (DGA®) allows its use in relatively high concentrations (50–70 wt%),

resulting in lower circulation rates. Because of its lower vapor pressure, DGA® is frequently used in higher temperature gas treating applications. Like MEA, it can be thermally reclaimed to remove heat stable salts and reaction products.

10.2.1.4 Diethanolamine

DEA, a secondary amine, is a weaker base and less reactive than MEA. Compared with MEA, it has a lower vapor pressure and thus, lower evaporation losses. It can operate at higher acid gas loadings, typically 0.35–0.7 mol acid gas/mol of amine versus 0.4–0.5 mol acid-gas/mol for MEA. It also has a lower energy requirement for regeneration. Concentration ranges for DEA are 30–40 wt% and are primarily limited by corrosion. DEA forms regenerable compounds with COS and CS_2 and can be used for their partial removal without significant solution loss. DEA has the disadvantage of undergoing irreversible side reactions with CO_2 and forming corrosive degradation products; thus, it may not be the best choice for high CO_2 gases. DEA also undergoes irreversible side reactions with O_2. Because DEA thermally decomposes below its normal boiling point, removal of these degradation products and heat stable salts must be done by use of either vacuum distillation or ion exchange. The reclaiming may be done offsite or in portable equipment brought onsite.

10.2.1.5 Methyldiethanolamine

MDEA, a tertiary amine, can be used to selectively remove H_2S to pipeline specifications while "slipping" some of the CO_2. As noted previously, the CO_2 slippage occurs because H_2S hydrolysis is much faster than that for CO_2, and the carbamate formation reaction does not occur with a tertiary amine. Consequently, short contact times in the absorber are used to obtain the selectivity. MDEA has a low vapor pressure and can be used at concentrations up to 50 wt% without appreciable corrosion or vaporization losses. Even with its relatively slow kinetics with CO_2, MDEA is used for bulk removal of CO_2 from CO_2-rich gases because the regeneration energy requirement is lower than those for the other amines. Like DEA, it is not reclaimable by conventional thermal methods.

10.2.1.6 Sterically Hindered Amines

In acid gas removal, steric hindrance involves alteration of the reactivity of a primary or secondary amine by a change in the alkanol structure of the amine. A large hydrocarbon group (see Figure 10.3) attached to the nitrogen shields the nitrogen atom and hinders the carbamate reaction. The H_2S reaction is not significantly affected by amine structure because the proton is small and can reach the nitrogen. However, CO_2 removal can be significantly slowed if the amine structure hinders the fast carbamate formation reaction and allows only the much slower bicarbonate formation (see Equations 10.3 and 10.4).

10.2.1.7 Mixed Amines

The selectivity of MDEA can be reduced by addition of MEA, DGA®, DEA, or other amines (Sterner, 2001). Thus, it can be tailored to meet the desired amount of CO_2 slippage and still have lower energy requirements than primary and secondary amines. Because of lower energy requirements, most new amine systems use MDEA or a proprietary MDEA-based blend. The following section looks at the difference in heats of reaction.

10.2.1.8 Heats of Reaction

The magnitude of the exothermic heats of reaction, which includes the heat of solution, of the amines with the acid gases is important because the heat liberated in the reaction must be added back in the regeneration step. Thus, a low heat of reaction translates into smaller regeneration energy requirements. Table 10.4 summarizes values for some common amines. The values in Table 10.4 are approximate because heats of reaction vary with acid gas loading and solution concentration. Jou et al. (1994) and Carson et al. (2000) report measured heats of reaction for CO_2 in MEA, DEA, and MDEA.

It should be noted that the heat of reaction is not the only component of regeneration energy. Because MDEA and MDEA based blends can be tailored to the treating objective, these solutions can take advantage of the higher solution amine concentrations typical of MDEA based solvents. This, in turn, leads to higher solution loading and lower circulation rates. As regeneration energy requirements are proportional to circulation rate, these formulated solvents often provide optimum cost for a given treating requirement.

10.2.1.9 Process Flow Diagram

A typical, simplified, diagram for the removal of acid gases from natural gas with a primary amine is shown in Figure 10.4. Table 10.5 presents typical operating conditions for MEA amine treating. The sour gas feed enters the bottom of the contactor at pressures up to 1,000 psi (70 bar) and temperatures in the range of 90°F (30°C). The sour gas flows upward, countercurrent to the lean amine solution, which flows down from the top. The lean amine inlet temperature is maintained 5°F (3°C) or more above the inlet gas temperature to prevent condensation of heavier hydrocarbon liquids. Intimate contact between the gas and amine solution is achieved by use of either trays or packing in the contactor.

The contactor operates above ambient temperature because of the combined exothermic heat of absorption and reaction. The maximum temperature is generally in the lower portion of the tower because the majority of the absorption and reaction occurs near the bottom. The "bulge" temperature in the tower can be up to about 180°F (80°C). A typical temperature profile for the contactor is shown in Figure 10.5. The treated gas leaves the top of the tower water saturated and at a temperature controlled by the temperature of the lean amine that enters, usually around 100°F (38°C). The maximum temperature reached in the contactor and the shape of the temperature profile are functions of several parameters, including feed gas temperature, amine type, relative amount of CO_2 and

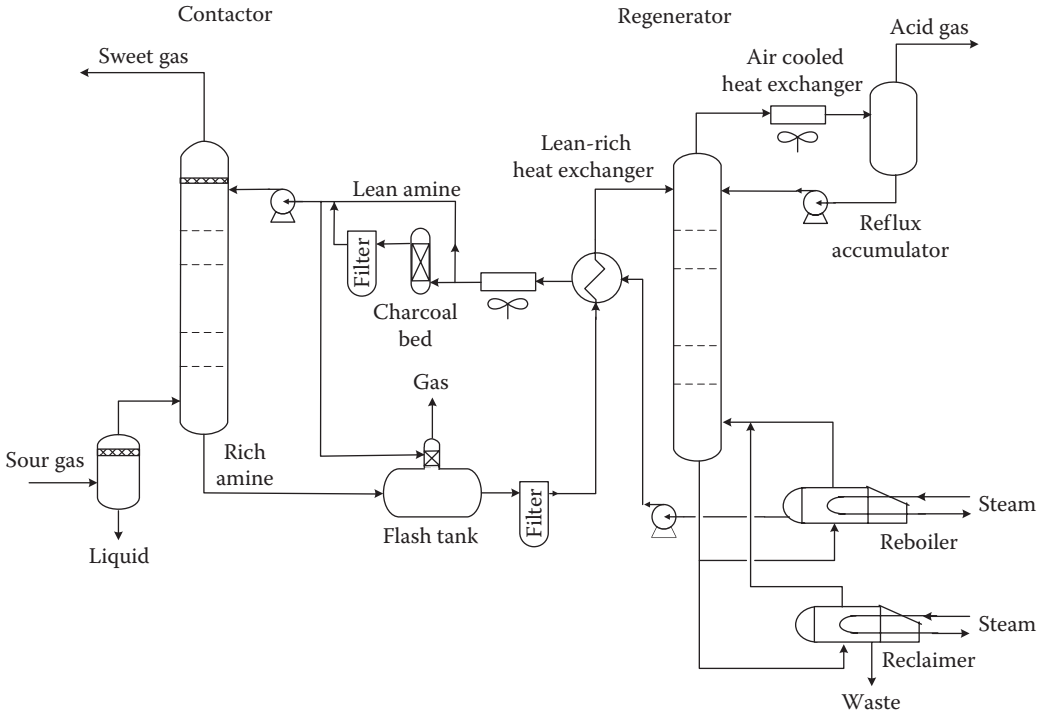


FIGURE 10.4 Process flow diagram for amine treating. For primary amines, 1%–3% of amine circulation is fed to a reclaimer. (Adapted from Smith, 1996.)

TABLE 10.5
Typical Operating Conditions for MEA Treating

	Contactor
Inlet pressures	<1,500 psig (100 barg)
Inlet temperatures	60°F–110°F (15°C–45°C) (lower temperatures enhance absorption equilibrium)
Pressure drop	5–10 psi (35–70 kPa)
Amine circulation rate	Based on a net amine loading of ~0.35 to 0.45 mol of acid gas/mol amine
Tray efficiencies	25%–30%
Outlet H_2S concentration	Typically H_2S <0.25 grains/100 scf (6 mg/Nm^3)
	Amine Losses
Total	25% of system inventory per year
	Regenerator (Reboiler and Still)
Column internals	Packed equivalent to 20 trays
Reboiler temperature	~260°F (130°C)
	Flash Tank
Pressure	50–75 psig (3.5–5 barg)
Temperature	150°F (65°C)

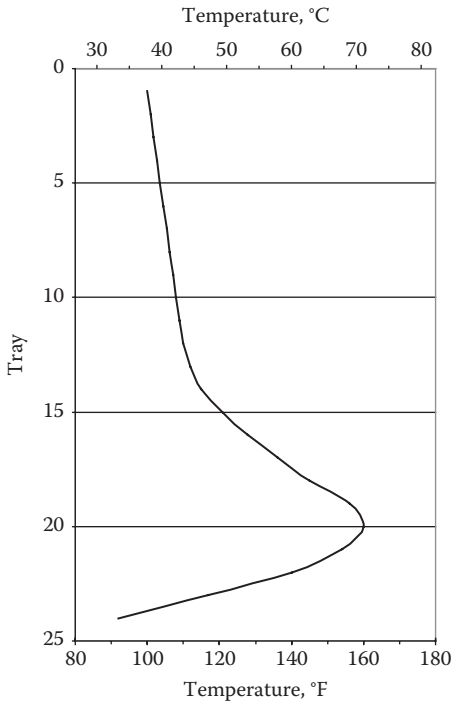


FIGURE 10.5 Typical 24-tray contactor temperature profile.

H_2S in the feed gas, relative feed gas and amine rates, reaction kinetics, and contactor mass transfer. To reduce amine losses and compensate for water loss in the treated gas, the gas is sometimes water washed. This may be done by having additional trays with water entering at the top or a separate vessel downstream of the contactor. The water should be deaerated makeup water.

The rich amine leaves the absorber bottom at temperatures near 140°F (60°C). The rich amine pressure is reduced to 75–100 psig (5–7 barg) to remove dissolved hydrocarbons and acid gases in a flash tank. The flashed dissolved hydrocarbons are often washed with lean amine to remove acid gases and then used as fuel gas. The rich amine then passes through a heat exchanger and enters the solvent regenerator (stripper) at temperatures in the range of 180°F–200°F (80°C–100°C). The regenerator reboiler commonly uses hot oil as the heating medium to prevent high skin temperatures or hot spots, which can degrade the amine. Sometimes low-pressure steam generated by hot oil is used. The vapor generated at the bottom flows upward through either trays or packing, where it contacts the rich amine and strips the acid gases from the liquid that flows down. A stream of lean amine is removed from the regenerator bottoms, cooled to about 100°F (40°C), and enters the contactor at the top to cool and condense water and amine in the upward-flowing vapor stream. The regenerator overhead vapor, which consists mostly of acid gases and water vapor, passes through a condenser to recover water and amine and is often processed for sulfur recovery (see Chapter 16).

The lean amine exits the bottom of the regenerator at about 260°F (130°C) and is pumped to the contactor operating pressure. The lean amine exchanges heat with the rich amine stream and is further cooled before it enters the top of the contactor. Both the treated gas leaving the gas contactor and the acid gas from the regenerator are water saturated.

Smith (1996) states the major pieces of equipment and the operating conditions are also representative of DEA and DGA® units, with the exception of the reclaimer. DEA and MDEA units do not have online thermal reclaimers, and DGA® reclaimers operate at slightly higher temperatures of 375°F–385°F (190°C–195°C).

Lyddon and Nguyen (1999) evaluated several modifications to the basic flow scheme for amine units that can increase gas throughput. When additional capacity exists in the regenerator but not in the absorber, and additional pressure drop is acceptable, static mixers may help. Blending sour gas and lean amine before the absorber essentially provides one additional absorber stage. Two configurations were considered. In one case, a side stream of sour gas passes through a static mixer. Following separation from the amine, the gas is blended with the sweet gas from the absorber. In the other case, the whole stream goes through the static mixer upstream of the inlet separator before it enters the absorber. In both cases, the rich amine from the static mixer goes to the regenerator. Lyddon and Nguyen (1999) report one case in which use of the bypass static mixers provided a 17% increase in plant capacity. The same approach has also been used on MEA without a static mixer if the absorber inlet piping promotes sufficient mixing of inlet gas and amine. This arrangement is not as effective as a static mixer but generally has less pressure drop.

10.2.1.10 Amine Reclaiming

Amines react with CO_2 and contaminants, including oxygen, to form organic acids. These acids then react with the basic amine to form heat stable salts (HSS). As their name implies, these salts are heat stable, accumulate in the amine solution, and must be removed. For MEA and DGA® solutions, the salts are removed through the use of a reclaimer (see Figure 10.4), which utilizes a semicontinuous distillation process, as described by Smith (1996). The reclaimer is filled with lean amine, and a strong base such as sodium carbonate or sodium hydroxide is added to the solution to neutralize the heat stable salts. A slipstream of 1%–3% of the circulating amine is then continuously added to the reclaimer while the mixture is heated. Water and amine vapor are taken off the top, leaving the contaminants in the liquid bottoms. Heating is continued until the temperature is approximately 300°F (150°C) for MEA or 360°F–380°F (180°C–195°C) for DGA®. The cycle is then stopped and the bottoms that contain the contaminants (dissolved salts, suspended solids) are removed. DEA does not form a significant amount of nonregenerable degradation products, and it requires more difficult reclaiming through vacuum distillation or ion exchange. Further details on reclaimers can be found in the *Engineering Data Book* (2016b), Smith (1996), Simmons (1991), and Holub and Sheilan (2000).

10.2.1.11 Operating Considerations

A comprehensive discussion of operating issues is given by Holub and Sheilan (2000) and is beyond the scope of this book. The brief discussion here of their work highlights a few of the most important considerations.

10.2.1.11.1 Corrosion

Some of the major factors that affect corrosion are:

- Amine concentration (higher concentrations can increase corrosion)
- Rich amine acid gas loading (higher gas loadings in the amine can increase corrosion)
- Oxygen in the gas to be treated
- HSS (higher concentrations of some salts promote corrosion)

Severe corrosion could destroy vessels and piping. Even minor corrosion can cause foaming. To prevent corrosion, a number of measures are often taken but using stainless steel for wetted parts is often the most cost effective. Carbon steel piping and equipment in amine systems often form a thin oxide or sulfide layer, which helps protect the steel from further corrosion. Lowering the rich amine fluid velocity is often effective in helping to maintain this protective layer. The type of layer formed is thought to be a function of the relative amount of H_2S and CO_2 in the system. In general, higher amounts of CO_2 promote the formation of an oxide layer and above a certain H_2S level, a stable sulfide layer is formed. There are documented cases where, as gas fields aged, increasing H_2S levels destroyed the once stable oxide layer but the H_2S level was insufficient to form a sulfide layer. The result was greatly accelerated corrosion in the absorber bottoms and rich amine system.

10.2.1.11.2 Solution Foaming

Foaming of the liquid amine solution is a major problem because it causes poor solution distribution and increased solution holdup with resulting carryover and off spec gas. Causes of foaming include:

- Suspended solids
- Liquid hydrocarbons
- Surface-active agents, such as those contained in inhibitors and compressor oils
- Amine degradation products, including heat stable salts

The best remedy to foaming is to have properly designed and operating inlet separators and filters to remove the offending materials. Figure 10.4 shows filtration of the rich amine to remove suspended solids and a charcoal adsorption bed to remove dissolved impurities from the lean amine. This combination is considered best practice to minimize foaming. Another approach is to add antifoaming agents. However, the wrong type or concentration of antifoaming agents can cause foaming and they must be used with care.

10.2.1.11.3 Heat Stable Salts

As mentioned above, amine degradation products, including heat stable salts, can cause both corrosion and foaming. They are normally eliminated by using amine reclaimers (see Section 10.2.1.10). Sometimes reclaiming is accomplished through the use of outside contractors who specialize in periodic reclaiming using ion exchange or vacuum distillation techniques. For very small units, a "bleed and feed" approach, where a small portion of the solution is continuously bled from the system and replaced with fresh solution, can be cost effective.

10.2.1.11.4 Filtration

Historically, amine filtration was performed on the lean solution to prevent operator exposure to H_2S during filter element change out. More recent designs, however, favor filtration of the rich amine.

This has the advantage of removing particles before they enter the amine flash tank or regenerator. If rich amine filtration is practiced, extreme care must be taken in the maintenance procedure to prevent exposure to H_2S. Some operating companies require extensive personnel protective equipment including breathing apparatus for this work.

A number of operating companies with relatively high solids in the gas to an amine plant have installed a bag filter upstream of their existing filters to save cost and reduce downtime. These filters have proven extremely cost effective in this service, especially on rich amine. Filters are discussed in Chapter 5.

Additional information on proper filtration can be found in James and Arshad (2017) and Engel and Northrop (2018a,b).

10.2.1.11.5 Housekeeping

Keeping the amine solvent and equipment clean is essential for good operating results. In addition to adequate filtration, makeup water and fresh solvent are important. The water must be high quality and usually comes from a reverse osmosis unit or steam condensate. For the initial solvent charge, many facilities procure their amine delivered to the site premixed to insure good quality water is used. If an amine sump is used to collect amine from drains, it is important that this sump be blanketed, usually with low-pressure fuel gas or nitrogen, to prevent oxygen contact with any amine being returned to the system. The sump must be kept clean to avoid system contamination. Many plants use a small filter on the amine returned from the sump to insure amine quality.

Finally, routinely monitoring the amine concentration is critical. Water can be lost with the exiting treated gas and acid gas. Oxygen-free, makeup water should be added as needed.

10.2.2 Alkali Salts

The hot potassium carbonate process for removing CO_2 and H_2S was developed by the United States Bureau of Mines and is described by Benson and coworkers in two papers (Benson et al., 1954, 1956). Although the process was developed for the removal of CO_2, it can also remove H_2S in the presence of CO_2. Special designs are required for removing H_2S to pipeline specifications or to reduce CO_2 to low levels.

The process flow diagram is very similar to the amine process shown in Figure 10.4 except that it contains no flash tank. Like the amine process, after physical absorption into the liquid the CO_2 and H_2S react chemically with the solution. The chemistry is relatively complex, but the overall reactions are represented by

$$K_2CO_3 + CO_2 + H_2O \leftrightarrow 2KHCO_3 \tag{10.9}$$

$$K_2CO_3 + H_2S \leftrightarrow KHS + KHCO_3 \tag{10.10}$$

In a typical application, the contactor will operate with the lean carbonate solution entering near 225°F (110°C) and leaving at 240°F (115°C). The rich carbonate pressure is reduced to approximately 5 psig (0.3 barg) as it enters the stripper. One third to two thirds of the absorbed CO_2 is released by the pressure reduction, reducing the amount of steam required for stripping (Kohl and Nielsen, 1997). The lean carbonate solution leaves the stripper at the same temperature as it enters the contactor and eliminates the need for heat exchange between the rich and lean streams. The heat of solution for absorption of CO_2 in potassium carbonate is small, approximately 32 Btu/ft^3 (1.2 MJ/m^3) of CO_2 (Benson et al., 1954). Consequently, the temperature rise in the contactor is small and less energy is required for regeneration compared to amine systems. Kohl and Nielsen (1997) give a thorough discussion of the process and its many modifications.

To enhance the basic process, a number of additives have been proposed, including amines (Seagraves et al., 2010). In addition, various corrosion inhibition systems have been devised for the

process but many of them depend on toxic heavy metals. There are still a few units in operation in gas processing. For new applications, this process is often replaced with amine or membrane systems or membrane/amine hybrid systems.

10.3 PHYSICAL ABSORPTION

In the amine and alkali salt processes, the acid gases are removed in two steps: physical absorption followed by chemical reaction. In processes such as Selexol® or Rectisol®, no chemical reaction occurs and acid gas removal depends entirely on physical absorption. Some of the inherent advantages and disadvantages of physical absorption processes are summarized below:

- Physical absorption processes are generally most efficient when the partial pressures of the acid gases are relatively high because partial pressure is the driving force for the absorption.
- Heavy hydrocarbons are strongly absorbed by the solvents used and, consequently, acid gas removal is most efficient in natural gases with less than 1 mol% heavier hydrocarbons unless dew point control is desired.
- Solvents can be chosen for selective removal of sulfur compounds (e.g., H_2S, COS, and mercaptans), which allows CO_2 to be slipped into the residue gas stream and reduce separation costs.
- By proper selection of the flow scheme, separate H_2S and CO_2 streams can be produced (see, e.g., Hegarty and Goar, 2010).
- Energy requirements for the regeneration of the solvent are lower than in systems that involve chemical reactions.
- Separation can be carried out at near-ambient temperature, but most often is at below-ambient temperatures.
- Partial dehydration occurs along with acid gas removal, whereas amine processes produce a water-saturated product stream that must be dried in most applications.

Burr and Lyddon (2008) compare several physical absorption processes in terms of acid gas removal ability, equipment required, and power requirements. Also, Kohl and Nielsen (1997) provide information on various absorption processes. Selexol® is a typical application of physical absorption and a number of open literature articles describe the process. McJannett (2012) provides guidelines on when Selexol® is a viable option and discusses a variety of applications. Consequently, it was selected as an example to describe the absorption process.

10.3.1 Solvent Properties

Selexol® is a polyethylene glycol and has the general formula:

$$CH_3 - O - CH_2 - (CH_2 - O - CH_2)_n - CH_2 - O - CH_3$$

Because Selexol® is a mixture of homologues (the value of n in the general formula for Selexol® varies), the physical properties discussed below are approximate. The Selexol® process is licensed from UOP.

Table 10.6 presents R_K, the ratio of the K-value[2] for methane, K_{CH4} (arbitrarily assigned a value of 1), to the K-values of the other component, $R_K = K_{CH4}/K_{component}$. Table 10.7 lists some physical properties of Selexol®. An R_K value greater than unity indicates that the solubility of the component

[2] The K-value is the ratio of the mole fraction of the component in the vapor phase (y) to its mole fraction in the liquid phase (x), $K = y/x$. High K-values indicate the material is predominately in the vapor phase, whereas low K-values indicate a higher concentration in the liquid phase (x).

TABLE 10.6
Typical Relative Ratio of *K*-Values

Component	R_K	Component	R_K
CH_4	1	H_2S	134
C_2H_6	6.4	C_6H_{14}	165
CO_2	15	CH_3SH	340
C_3H_8	15.3	C_7H_{16}	360
Isobutane	28	CS_2	360
n-Butane	35	SO_2	1,400
COS	35	C_6H_6	3,800
Isopentane	67	C_4H_4S	8,100
n-Pentane	83	H_2O	11,000

Source: Sweny (1980).
$R_K = (K_{CH4}/K_{Component})$ in Selexol® solvent for various solutes, where $K_{CH4} = 1$.

TABLE 10.7
Representative Property Data for Selexol®

Molar mass (approximate) = 280
Flash point (Cleveland open cup) = 304°F (151°C)
Freezing point[a] = −8 to −20°F (−22 to −28°C)
Vapor pressure at 25°C = <0.01 mm Hg
Specific heat at 77°F (25°C) = 0.49 Btu/lb_m-°F (2.0 kJ/kg-K)
Density at 77°F (25°C) = 1,030 kg/m^3 (8.60 lb_m/gal)
Viscosity at 77°F (25°C) = 5.8 cP (5.8×10^{-3} N-s/m^2)
Thermal conductivity at 77°F (25°C) = 0.11 Btu/h-ft °F (0.19 W/m-K)
Surface tension at 77°F (25°C) = 34.3 dynes/cm (0.0343 N/m)
Heat of solution at 77°F (25°C), Btu/lb_m of solute (kJ/kg)
CO_2 = 160 (372)
H_2S = 190 (442)
CH_4 = 75 (174)
Odor = very mild
Toxicity = nil

Source: Sweny and Valentine (1970) and Clare and Valentine (1975).
[a] Slush appears at −8°F (−22°C) complete solidification at −20°F (−29°C).

in Selexol® is greater than that of methane. The values should be regarded as only representative because pressure and temperature are not specified and, as previously noted, the composition of Selexol® is variable.

Because R_K for CO_2 and H_2S are 15 and 134, respectively, these gases are preferentially absorbed (relative to CH_4), and, consequently, physical absorption is an effective technique for acid gas removal. The process can reduce H_2S to 4 ppmv, reduce CO_2 to levels below 50 ppmv, and essentially remove all mercaptans, CS_2, and COS. However, McJannett (2012) notes that Selexol® usually is not a good choice for H_2S removal unless there is a very high partial pressure of H_2S or other special circumstances in natural gas treating. He suggests that it can be attractive in some gasifier applications. It is used to reduce CO_2 levels to around 2% but rarely used to obtain levels in the thousands of ppm in natural gas (McJannett, 2012).

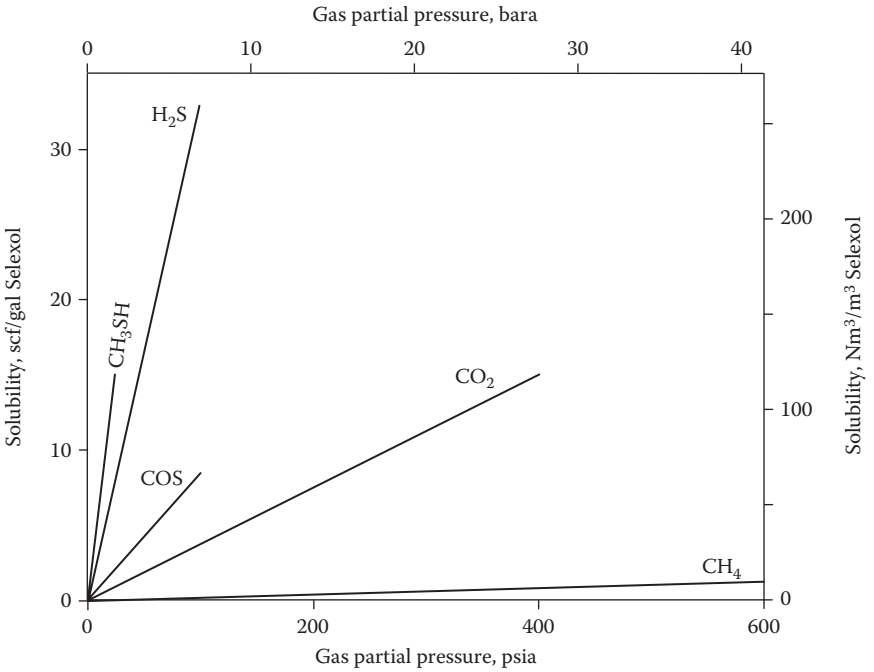


FIGURE 10.6 Solubility of various gases in Selexol® solvent at 70°F (21°C) as a function of partial pressure. (Based on data by Sweny and Valentine, 1970.)

Two additional features of Table 10.6 are worth mentioning. Because the R_K values for hydrocarbons heavier than CH_4 are fairly high (6.4 for C_2H_6, 15.3 for C_3H_8, and 35 for n-C_4H_{10}), Selexol® will remove substantial quantities of these hydrocarbons, a feature that can be either positive or negative, depending on the composition of the gas being processed and the desired products. The R_K value of H_2O is extremely high and consequently, Selexol® provides some dehydration.

Bucklin and Schendel (1985) reported gas solubility data in the form of absorption coefficients (volume of gas absorbed per volume of liquid). These values were converted for some of the compounds into volume of gas absorbed/volume of Selexol® solvent and plotted in Figure 10.6. The figure assumes a Henry's law relationship,[3] which provides approximate solubility at higher pressures. The lines also ignore probable interaction between solutes. Epps (1994) discusses the limited solubility of hydrocarbons in the solvent (when the solvent is saturated, a second liquid hydrocarbon phase forms above the Selexol® phase) and the effect of absorbed water on the solubility of hydrocarbons.

10.3.2 Representative Process Conditions

Applications of Selexol® are varied and, consequently no typical process flow diagram is available. Sweny (1980) presents flow diagrams for nine different applications, and Epps (1994) discusses plants for the dehydration of natural gas and hydrocarbon dew point control.

One application discussed by Epps (1994) that treats gas going to LNG peakshaving plants is shown in Figure 10.7. This configuration was selected for discussion because it is a modern application and both inlet and outlet gas compositions were reported (Table 10.8). The plant pretreats the gas to reduce CO_2, ethane, and heavier hydrocarbon levels before final purification in molecular

[3] For an ideal system, Henry's law assumes a linear relation between the solubility of gas component i and its partial pressure, $y_iP = k_ix_i$ where k_i is the Henry's constant.

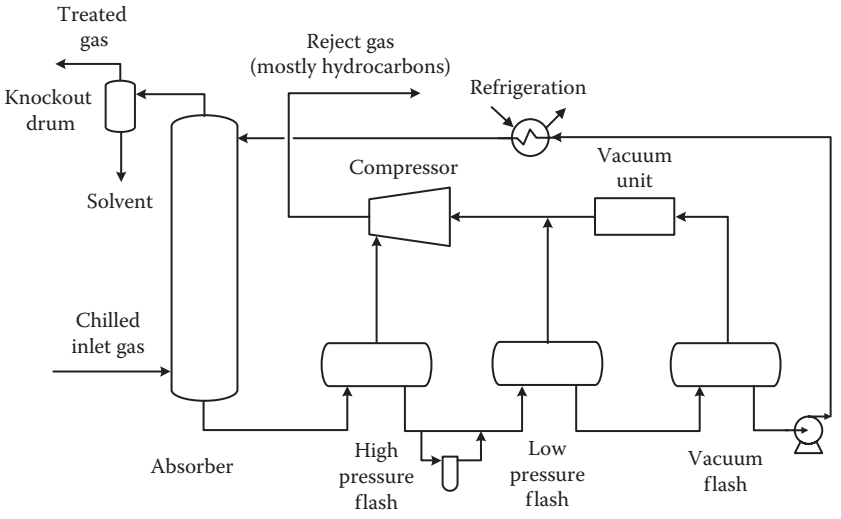


FIGURE 10.7 Process schematic for a Selexol® gas treating facility. (Adapted from Epps, 1994.)

TABLE 10.8
Composition of Inlet and Outlet Gas in a Selexol® Unit

	Gas Composition (mol%)	
Component	**Inlet**	**Outlet**
Hydrogen sulfide	0.0002	—
Methyl mercaptan	0.00050	0.00012
Carbon Dioxide	2.44	0.29
Nitrogen	0.785	0.88
Methane	86.317	93.02
Ethane	7.539	5.33
Propane	2.403	0.35
Heavier hydrocarbons	0.515	0.130

Source: Epps (1994).

sieve units and subsequent liquefaction. The plant is designed to process 26 MMscfd (0.70×10^6 Nm^3/d) entering the Selexol® unit at 603 psia (41.6 bara) and 32°F (0°C). The lean solvent, cooled to 25°F (–3.9°C) with propane refrigerant, enters the absorber where it absorbs CO_2 and some of the ethane and heavier hydrocarbons. The rich solvent from the absorber is regenerated by reduction of the pressure in three flash drums, from 603 to 106 psia (41.6–7.3 bara) in the high-pressure drum, from 106 to 16 psia (7.3–1.1 bara) in the medium-pressure drum, and from 16 to 3 psia (1.1–0.21 bara) in the vacuum drum. Lean Selexol® from the vacuum drum is sent to the propane chiller. The treated gas that leaves the absorber passes through a knockout drum and filter separator to remove entrained Selexol® and condensed hydrocarbons.

Table 10.8 shows that the treated gas meets the specifications of a maximum of 0.50% CO_2 and 6.5% ethane and heavier hydrocarbons. In addition, the water content of the gas is reduced from 75 to 12 ppmv, H_2S is reduced from 2 ppmv to below detectable limits, and methyl mercaptan is reduced from 5 to 1 ppmv. Unlike the amine systems, no irreversible products are generated in the process, thus eliminating the need for reclaiming.

Other detailed descriptions of acid gas removal with Selexol® are given by Echt et al. (2017), Hegwar and Harris (1970), Johnson (1984), Judd (1978), Mortko (1984), Oberding et al. (2004), Raney (1976), and Shah (1989).

10.3.3 Hybrid Processes

Table 10.2 shows the strengths and weaknesses of chemical and physical solvent systems. To take advantage of the strengths of each type, a number of hybrid processes, commercially used and under development, combine physical solvents with amines (*Engineering Data Book*, 2016b). Depending upon the solvent–amine combination, nearly complete removal of H_2S, CO_2, and COS is possible. Other hybrid systems provide high H_2S and COS removal while slipping CO_2. Sulfinol® currently is one of the more commonly used processes. This process uses a combination of physical solvent sulfolane with diisopropanol amine (DIPA), MDEA or MDEA/piperazine, and water. The amine(s) selected depends upon the acid gases in the feed and whether CO_2 removal selectivity is desired. Like the physical solvent processes, the hybrid systems may absorb more hydrocarbons, including BTEX (benzene, toluene, ethylbenzene, and xylene), but that is controlled by adjusting solution water content.

10.4 ADSORPTION

Acid gases, as well as water, can be effectively removed by physical adsorption on synthetic zeolites. Applications are limited because water displaces acid gases from the adsorbent bed. Chapter 4 provides the basic concepts and Chapter 11 provides more details on adsorption for dehydration. Figure 10.8, which shows typical isotherms for CO_2 and H_2S on molecular sieve, indicates that at ambient temperatures substantial quantities of both gases are adsorbed even at low partial pressures.

Molecular sieve can reduce H_2S levels to the 0.25 grains/100 scf (6 mg/Nm^3) specification and CO_2 to well below 50 ppmv. However, this reduction requires relatively large beds and is generally reserved for low inlet acid gas concentrations or for final cleanup downstream of other acid gas removal systems.

Chi and Lee (1973) studied the coadsorption of H_2S, CO_2, and H_2O on a 5 Å molecular sieve from a natural gas mixture under a variety of conditions. Figure 10.9, adapted from their paper, shows a typical concentration versus time curve. In the figure, y is the concentration in the exit stream and y_o is the concentration in the inlet to the bed. The gas that entered the bed was saturated

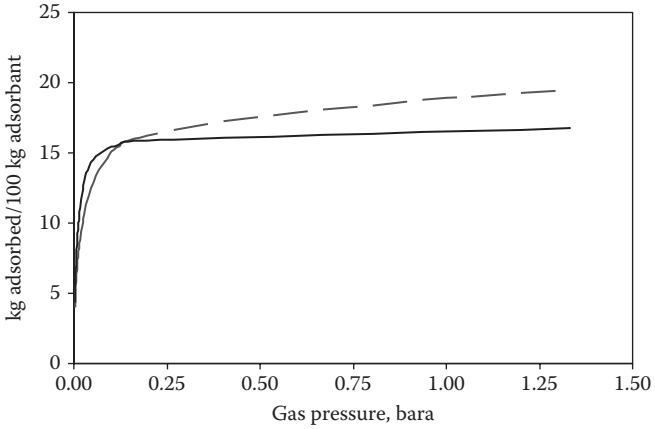


FIGURE 10.8 Adsorption of H_2S (—) and CO_2 (- -) on type 5 A molecular sieve at 77°F (25°C). (Adapted from Linde, undated.)

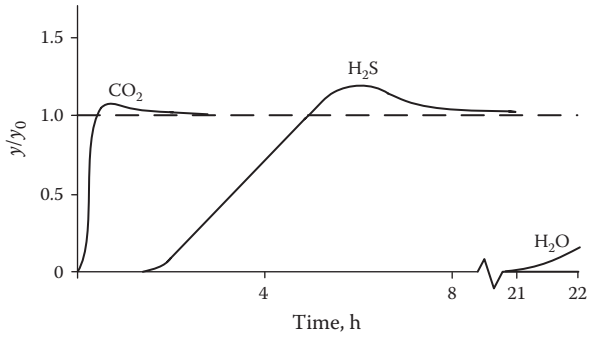


FIGURE 10.9 Effluent H_2S and CO_2 concentration from adsorption bed as a function of time. (Adapted from Chi and Lee, 1973.) See text for details.

with H_2O and contained both CO_2 (1.14 mol%) and H_2S (0.073 mol%). Because the CO_2 content of the gas was 15.6 times that of the H_2S, the bed quickly saturated with CO_2, and its breakthrough was almost instantaneous. As the H_2S was adsorbed and moved down the column, it displaced the CO_2 and, consequently, after approximately 30 min, the CO_2 exit concentration peaked at a value greater than its inlet concentration.

The same phenomenon occurs when the H_2S is displaced by water. Because the H_2S must be removed to extremely low levels, the bed is effectively exhausted from the perspective of H_2S purification shortly after H_2S breakthrough occurs and, thus, well before the bed is totally saturated with H_2O. This example illustrates the principle of a bed mass transfer zone, as shown in Figure 4.21. Chi and Lee (1973) present empirical correlations for the prediction of dynamic saturation capacity and breakthrough times for H_2S under a variety of operating conditions.

Detailed information on adsorber design calculations is available in the paper by Cummings and Chi (1977) and the handbook by Kohl and Nielsen (1997). The *Engineering Data Book* (2016b) notes that a key point in design is to treat the regeneration gas because the peak H_2S concentration may be 30 times the H_2S concentration in the feed.

Figure 10.10 shows a typical flow diagram for removal of H_2S from natural gas. The configuration is similar to that for dehydration but with the significant difference that the regeneration gas contains quantities of H_2S as well as water as it leaves the adsorbent bed and must be treated.

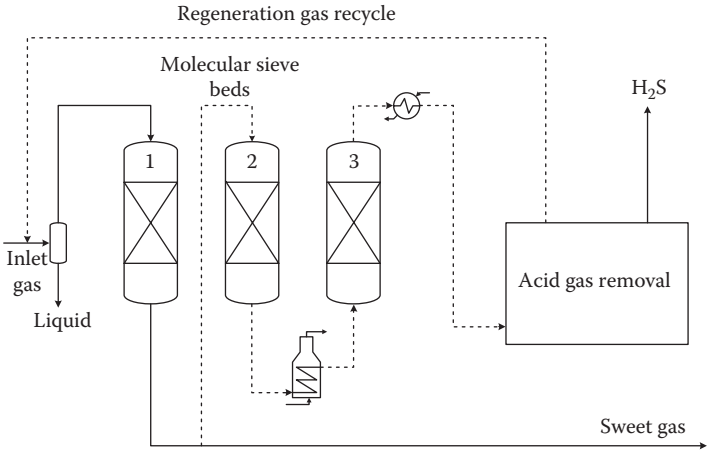


FIGURE 10.10 Schematic of integrated natural gas desulfurization plant. Dashed line denotes regeneration gas stream. (Adapted from *Engineering Data Book*, 2016b, with permission.)

The flow configuration shows the first bed in the adsorption cycle, the second bed cooling down after regeneration, and the third bed undergoing regeneration with hot gas.

A similar flow scheme is often used for CO_2 from natural gas before liquefaction. Note that bed capacity for CO_2 adsorption is low compared to that for water. Thus, for practical bed sizes in CO_2 removal service, the adsorption cycles must be short, often 2 h or less. Note too that for short adsorption cycles the beds must be insulated on the inside. This eliminates the time required to heat and cool the vessel wall. Most adsorption systems having adsorption cycles of 8 h or more have the insulation on the outside.

10.5 CRYOGENIC FRACTIONATION

Distillation is the most widely used process to separate liquid mixtures. At first glance, it seems a good prospect for removing CO_2 and H_2S from natural gas because the vapor pressures of the principal components are considerably different (Figure 10.11). However, problems are associated with the separation of CO_2 from methane, CO_2 from ethane, and CO_2 from H_2S. These difficulties are summarized below (*Engineering Data Book*, 2016c) and discussed in Sterner (2001).

Carbon dioxide from methane: Relative volatilities (K_{C1}/K_{CO2}) at typical distillation conditions are about 5 to 1. Therefore, one would expect simple fractionation to work. However, because the liquid CO_2 phase freezes when it becomes concentrated, the practical maximum vapor concentration of methane is only 85–90 mol%. ExxonMobil uses this phenomenon to advantage in their Controlled Freeze Zone (CFZ™) CO_2 removal process (Northrop and Bialek, 2004).

Carbon dioxide from ethane: In addition to solidification problems, CO_2 and ethane form an azeotrope[4] and consequently, a complete separation of these two by simple distillation is impossible. Figure 10.12 shows an isotherm at −64°F (−53°C) for the system, and the azeotrope appears at approximately 0.6 mol fraction of CO_2.

Carbon dioxide from hydrogen sulfide: This distillation is difficult because, as Figure 10.13 shows, the mixture forms a pinch at high CO_2 concentrations. This separation by conventional distillation is complicated by the need to have an overhead product that has roughly 100 ppmv or less H_2S if the stream is vented. The bottoms product should contain less than ~60 vol% CO_2, if the stream is fed to a Claus unit. (See Chapter 16 for details on Claus unit feed concentrations.)

A number of techniques are available for solving these problems, but the Ryan/Holmes process (Holmes et al., 1982) is probably the most widely used. This process is an extractive

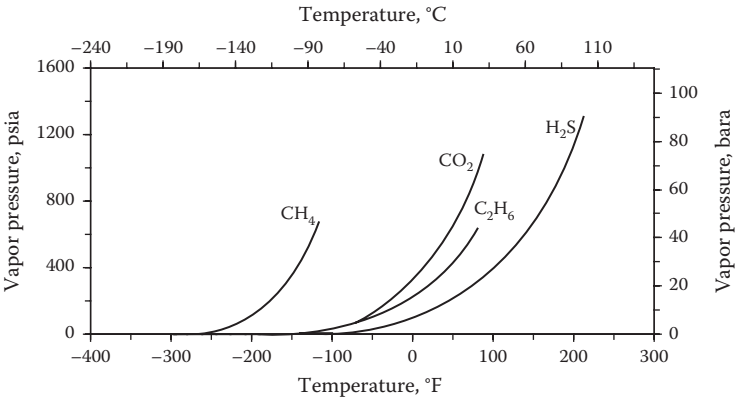


FIGURE 10.11 Vapor pressure of light natural gas components (Lemmon et al., 2017).

[4] An azeotrope is when the liquid and vapor phases are equal. A binary azeotropic mixture cannot be distilled to produce a pure overheads and bottoms product.

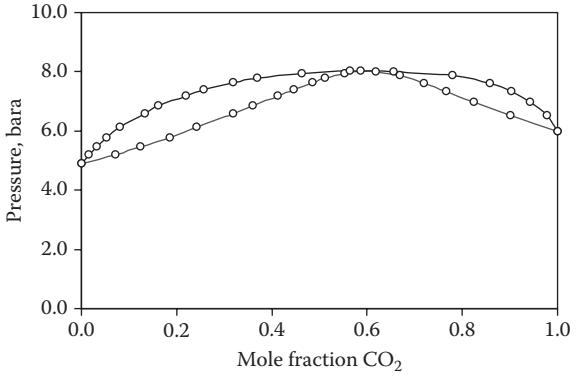


FIGURE 10.12 Vapor–liquid equilibrium curve for CO_2 and C_2H_6 at −64°F (−53°C). Azeotropic composition is 0.60 mol fraction CO_2 (Brown et al., 1988).

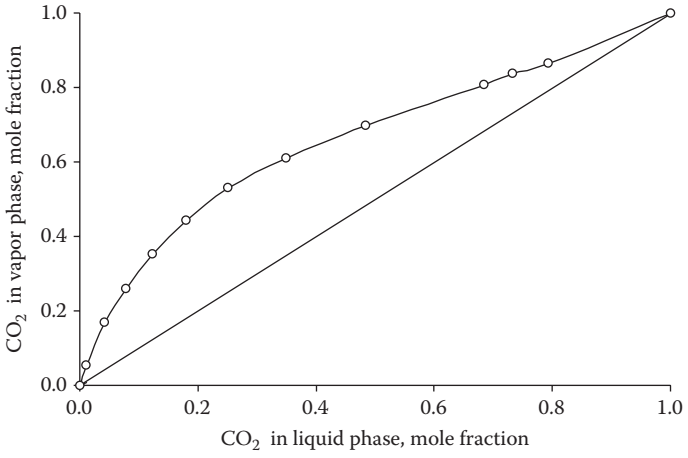


FIGURE 10.13 Vapor–liquid equilibrium curve for CO_2 and H_2S at 20 atm (Bierlein and Kay, 1953).

distillation process[5] that uses hydrocarbons to significantly alter the behavior of the system and thus, effectively eliminate the distillation problems. The hydrocarbons are normally mixtures of propane and heavier hydrocarbons obtained from the feed mixture. As a result, no additional separations are required. Readers are referred to the original paper for details.

10.6 MEMBRANES

Membranes are used in natural gas processing for dehydration, fuel gas conditioning, and bulk acid gas removal, but presently CO_2 removal is by far the most important application. The fundamentals of membrane separations are presented in Chapter 4.

[5] Extractive distillation makes distillation of close boiling components possible by addition of a solvent to the mixture to alter the relative volatility of the two key components. The products from the distillation include one of the keys at high purity and a mix of the other key plus the solvent. This mixture is fractionated in another column for recovery of the solvent and production of the pure second key.

10.6.1 Carbon Dioxide Removal from Natural Gas

Many different types of membranes have been developed or are under development for industrial separations (Baker, 2002; Echt et al., 2002), but for CO_2 removal, the industry workhorse is cellulose acetate. These membranes are of the solution-diffusion type, in which a thin layer (0.1–0.5 μm) of cellulose acetate is on top of a thicker layer of a porous support material. To protect the membrane from chemical attack and mechanical abrasion a highly permeable 1–2 μm layer is often added on top of the membrane (Baker, 2002). Permeable compounds dissolve into the membrane, diffuse across it, and then travel through the inactive support material. The membranes are thin to maximize mass transfer and, thus, minimize surface area and cost, so the support layer is necessary to provide the needed mechanical strength.

Figure 10.14 shows a single-staged unit designed to process 50 MMscfd (1.3×10^6 Nm^3/d) of gas containing 3.2 vol% CO_2 and reduce concentration to 3 mol% to meet pipeline specifications. The permeate is blended back into fuel gas. The unit, installed in 2004, is still operational in 2019 with no problems.

10.6.2 Operating Considerations

Each pass through a membrane represents a single stage of separation. The degree of separation is a function of relative permeabilities and pressure difference across the membrane (see Section 4.6). Increasing the pressure difference enhances separation but increases potential recompression cost and loss of desired product. To address this issue a number of different flow arrangements can be used with membranes. Figures 10.15 and 10.16 show simplified examples for the CH_4/CO_2 separation. In the single-stage unit, the overall methane recovery is only 90.2%, but the process requires flow through only one membrane stage and no recompression is needed. To increase methane recovery to 98.7%, a two-stage unit requires recompression of the first-stage permeate. Lower levels of methane loss are obviously possible by application of three or more stages, but additional elements can quickly become uneconomical because of both membrane cost and recompression cost.

FIGURE 10.14 Carbon dioxide membrane skid installed in gas plant.

	A	B	C
Composition (mol%)			
Methane	93.0	98.0	63.4
Carbon dioxide	7.0	2.0	36.6
Flow rate, MMscfd (Nm^3/h)	20.00 (22.33×10^3)	17.11 (19.10×10^3)	2.89 (3.23×10^3)
Pressure, psig (barg)	850 (59)	835 (57)	10 (0.7)
Methane recovery = 90.2%			

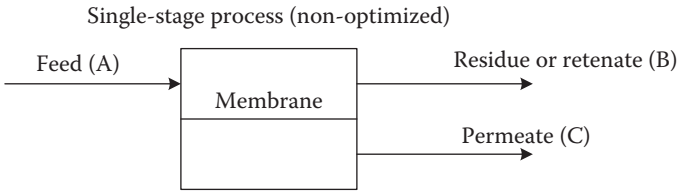


FIGURE 10.15 A non-optimized single-stage CO_2/CH_4 membrane separation process (Spillman and Cooley, 1989).

	A	B	C	D	E
Composition (mol%)					
Methane	93.0	98.0	18.9	63.4	93.0
Carbon dioxide	7.0	2.0	81.1	36.6	7.0
Flow rate, MMscfd	20.00	18.74	1.26	3.16	1.90
(Nm^3/h)	(22.34×10^3)	(20.92×10^3)	(1.41×10^3)	(3.53×10^3)	(2.12×10^3)
Pressure, psig (barg)	850 (59)	835 (57)	10 (0.7)	10 (0.7)	850 (59)
Methane recovery = 98.7%					

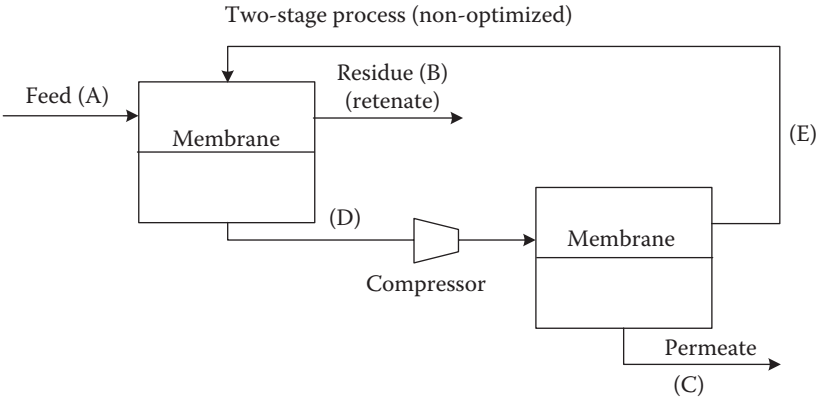


FIGURE 10.16 A non-optimized two-stage CO_2/CH_4 membrane separation process (Spillman and Cooley, 1989).

The second law of thermodynamics dictates that energy is required for a separation. For membrane processes, the energy penalty is loss of pressure. However, in many processes, the cost of recompression, if needed, still makes membranes an attractive separation process. The decision to apply separation membranes is a classic economic analysis. With membranes, the gas lost to

the permeate stream must be weighed against the fuel to remove acid gas with other systems, such as amines. In the case of membranes, a major portion of the operating cost is the cost of replacing membranes when they have reached the end of their operating life. Generally, if membrane life is more than 3 years, they are economically competitive with other removal systems. When choosing treating options, membranes are often a good choice for bulk CO_2 removal but are often a more expensive choice if low concentrations are required in the product gas.

10.6.3 Advantages and Disadvantages of Membrane Systems

The pros and cons of commercial membrane systems are discussed by Kohl and Nielsen (1997) and Echt et al. (2002). The following summarizes their conclusions:

10.6.3.1 Advantages

- Low capital investment when compared with solvent systems
- Ease of operation: Process can run unattended
- Ease of installation: Units are normally skid mounted
- Simplicity: No moving parts for single-stage units
- High turndown: The modular nature of the system means very high turndown ratios can be achieved
- High reliability and on-stream time
- No chemicals needed
- Good weight and space efficiency

10.6.3.2 Disadvantages

- No economy of scale: Because of their modular nature, they offer very little economy of scale
- Clean feed: Pretreatment of the feed to the membrane to remove particulates and liquids is generally required (see Section 4.6.2.1 for general description of pretreatment)
- Gas compression: Because pressure difference is the driving force for membrane separation, considerable recompression may be required for either or both the residue and permeate streams

For natural gas systems, the following disadvantages also apply:

- Generally higher hydrocarbon losses than solvent systems
- H_2S removal: H_2S and CO_2 permeation rates are roughly the same, so H_2S specifications may be difficult to meet
- Bulk removal: Best for bulk removal of acid gases; membranes alone cannot be used to meet ppmv specifications

For offshore applications, membranes are attractive because of unattended operation, no chemicals needed or generated, and good weight and space efficiency.

10.7 NONREGENERABLE HYDROGEN SULFIDE SCAVENGERS

When the quantity of sulfur to be removed is small, approximately 400 lb_m/d (180 kg/d) or less, the processes discussed previously are expensive relative to small-scale batch processes for H_2S removal. These processes generally use a nonregenerable scavenger and can remove H_2S to 4 ppmv or less and remove propyl and lighter mercaptans. Many technologies are in general use, and a summary is shown in Table 10.9.

TABLE 10.9
H_2S Scavenger Processes

Solid-based processes:	Iron oxides
	Zinc oxides
Liquid-based processes:	Nitrites
	Polyamines (triazines)
	Caustic
	Alkali
	Aldehydes
	Ethanedial
	Amine sulfide
	Metal-oxide slurries

Source: Echt et al. (2017) and Holub and Sheilan (2000).

According to Houghton and Bucklin (1994), the most widely used of the solid scavengers are those that utilize iron oxides, especially iron sponge. Current literature indicates that blends containing triazine are the most common liquid scavengers. Alkali and caustic scavengers remove both CO_2 and H_2S but the other scavenger compounds remove only H_2S. However, some of the other scavengers may not perform as well if CO_2 concentrations are very high. Houghton and Bucklin (1994) provides detailed economic comparisons of some popular scavenger processes. Leppin et al. (2009) discuss a computer model for direct injection of liquid scavengers. Additional detailed discussions of all the above processes may be found in Veroba and Stewart (2003), Echt et al. (2017), and the *Engineering Data Book* (2016b). The practical limits for sulfur loading in liquid scavengers are described in Warren and Bertrand (2015) and Schulz (2018). Echt et al. (2017) give economics on some of the current technologies.

10.8 BIOLOGICAL PROCESSES

Cline et al. (2003) describe a biological process for removing H_2S from natural gas. Echt et al. (2017) provide an overview of process and a brief economic analysis. In this process, the gas stream that contains the H_2S is first absorbed into a mild alkaline solution and the absorbed sulfide is oxidized to elemental sulfur by naturally occurring microorganisms. This process is known as the Thiopaq® process and is marketed as the Shell/Pacques process. The process has been utilized for biogas sweetening since 1993, and in traditional oil and gas treating since 2002 (Rollenhagen et al., 2010).

Cline et al. (2003) reported the successful startup and operation of a commercial plant in Canada. The plant is designed to treat a high-pressure natural gas and produce a product that meets H_2S specifications (4 ppmv or lower). The plant sulfur capacity is approximately 1 ton/d, with a sulfur removal efficiency of 99.5% or higher. The authors offer the following claims regarding the process:

- Cost effective up to 50 ton/d (50 ton/d) of sulfur
- H_2S concentrations in the sour gas from 50 ppmv to 100 vol%
- Sour gas pressures to 1,100 psig (75 barg)
- H_2S concentrations in the sweet gas as low as 1 ppmv
- Formation of hydrophilic sulfur that prevents equipment fouling or blocking

Additional information on processes making direct conversion of H_2S to elemental sulfur can be found in Chapter 16.

10.9 SAFETY AND ENVIRONMENTAL CONSIDERATIONS

10.9.1 Amines

The obvious safety concern with amine treating is the potential for H_2S leaks in the plant, even from spilled rich amine. Additionally, some equipment operates at high temperatures. Filtration is a critical component of amine processes. Changing rich amine filters requires special equipment and care. Caustic handling is another hazard if reclaiming is performed on-site. Reclaimer waste products may be toxic and must be handled with care (*Engineering Data Book*, 2016b). If the gas to be treated contains methyl mercaptan, work procedures must consider that this material is more toxic to humans than H_2S.

From an environmental perspective, in addition to the remote chance of hydrogen sulfide release, amines have an affinity for BTEX, which may be vented during amine regeneration if sulfur is not recovered. Chapter 14 provides more details. If MEA or DGA® is used with reclaimers, the reclaimer solids present a disposal problem because caustic or soda ash is required.

10.9.2 Adsorbents and Scavengers

Safety and environmental problems associated with adsorbents such as molecular sieve are relatively minor. Thorough regeneration and purging must be done before the adsorbent can be replaced. However, it should be nonhazardous and disposable in a land fill.

Most scavengers are respiratory and eye irritants. Spent iron sponge is pyrophoric, and great care must be taken in the removal and disposal of reacted iron sponge material (Veroba and Stewart, 2003). The manufacturer's recommendations for this material must be carefully followed to prevent a serious incident. Echt et al. (2017) discuss safety and environmental concerns on many low-tonnage sulfur removal processes,

10.9.3 Membranes

Membranes are probably the safest and most environmentally friendly of the processes for gas treating. No chemicals are used, no waste disposal byproducts are generated, and membranes operate at near ambient temperatures.

DISCUSSION QUESTIONS

1. What makes H_2S an undesirable compound in natural gas?
2. What makes CO_2 an undesirable compound in natural gas?
3. Most acids contain a reactive hydrogen. What makes CO_2 acidic?
4. Compare the merits of physical and chemical absorption for acid gas removal. In what applications will physical absorption be preferred to chemical absorption?
5. What are the advantages of using tertiary amines instead of primary or secondary amines for acid gas removal?
6. What are heat stable salts? How do they form and how are they removed?
7. What are the common causes of foaming in amine contactors and what are the ways to mitigate or eliminate the problem?
8. How important is contactor temperature and pressure for physical absorption compared to chemical absorption?
9. What makes acid gas removal by cryogenic distillation difficult?
10. What are the strengths and weaknesses of removing acid gases using membranes?
11. Which of the H_2S removal processes are attractive options when small amounts of H_2S are removed?

EXERCISES

10.1 Feed gas enters an amine treating unit at a rate of 100 MMscfd (2.68×10^6 Nm^3/d). The gas contains 5% CO_2 and no H_2S. The treater uses 18 wt% MEA solution. Assume the lean amine contains 0.12 mol CO_2/mol of amine and the rich amine contains 0.45 mol CO_2/mol amine. To meet the pipeline specification of 2% CO_2, what minimum lean amine flow rate in gpm (m^3/h) (based on density at 60°F (15°C)) is required? Amine properties are given in Appendix B[6].

10.2 The unit described in Exercise 10.1 experiences corrosion. Upon checking, the operator determines that the rich amine loading is much higher than 0.45 mol/mol and is causing corrosion. The high loading is due to complete removal of CO_2 from the gas by the MEA. Without changing solvent, how might the treating requirement be accomplished using 18 wt% MEA and meeting the 2% outlet specification? (*Hint*: Consider changing contactor gas flow.)

10.3 The 18 wt% MEA used in the treating unit in Exercise 10.1 is replaced with 31 wt% DEA solution. If the lean amine contains 0.05 mol CO_2/mol of amine and the rich DEA solution contains 0.38 mol of CO_2/mol of amine, how much will the required lean amine solution flow rate change (based on density at 60°F (15°C))?

10.4 Using the heat of reaction given in Table 10.4, what amount of heat (Btu/h, GJ/h) is generated by the reaction of amine and acid gas in Exercises 10.1 and 10.3?

10.5 The gas entering an MDEA treating unit contains 0.5 mol% H_2S and 8 mol% CO_2. Inlet flow rate is 120 MMscfd (3.22×10^6 Nm^3/d). The treater uses 50 wt% MDEA solution and has an inlet pressure of 1,000 psig (70 barg). The plant dehydrates the gas and then sells it as pipeline-quality gas. The pipeline specification requires that the gas contain no more than 0.25 grains/100 scf (6 mg/Nm^3) of H_2S and a maximum of 2% mol CO_2.

   a. Assuming that the rich MDEA holds 0.4 mol of acid gas/mol of MDEA and the lean amine contains essentially no H_2S and 0.005 mol of CO_2/mol amine, what is the minimum amine circulation required (gpm [m^3/h] at 60°F (15°C)) to obtain pipeline-quality gas?

   b. How much sulfur (LTD (tonnes/d)) would be produced from the acid gas leaving the treater, assuming 99.95% sulfur recovery? (See Chapter 16 for a discussion of sulfur recovery.)

10.6 If the MEA unit in Exercise 10.1 is converted to 50 wt% MDEA, what is the annual savings in operating expense? Assume an MEA flow rate of 686 gpm (156 m^3/h). Rich MDEA can hold 0.45 mol of acid gas per mole of amine and the lean amine has essentially zero acid gas. Use properties from Table 10.3 and Appendix B. Ignore amine losses and pumping cost. Fuel gas costs $3.00/MMBtu and the furnace is 80% efficient.

REFERENCES

GPA Midstream Association, 2019 cooperative research, 2018. www.gpamidstream.org/assets/gpa/pdf/2019-GPA-Midstream-Research-Brochure.pdf (Retrieved April 2019).

ASTM D1838-16, *Standard Test Method for Copper Strip Corrosion by Liquefied Petroleum (LP) Gases*, ASTM International, West Conshohocken, PA, 2016. www.astm.org/Standards/D1838.htm (Retrieved April 2019).

ASTM D4084-07, *Standard Test Method for Analysis of Hydrogen Sulfide in Gaseous Fuels (Lead Acetate Reaction Rate Method)*, ASTM International, West Conshohocken, PA, 2017. www.astm.org/Standards/D4084.htm (Retrieved April 2019).

Baker, R.W., Future directions of membrane gas separation technology, *Ind. Eng. Chem. Res., 41*, 1391, 2002.

[6] See Appendix B on publisher website: www.crcpress.com/Fundamentals-of-Natural-Gas-Processing-Third-Edition/Kidnay-Parrish-McCartney/p/book/9781138612792

Benson, H.E., Field, J.H., and Haynes, W.P., Improved process for CO_2 absorption uses hot carbonate solutions, *Chem. Eng. Progr., 52*, 433, 1956.

Benson, H.E., Field, J.H., and Jimeson, R.M., CO_2 absorption employing hot potassium carbonate solutions, *Chem. Eng. Progr., 50*, 356, 1954.

Bierlein, J.A., and Kay, W.B., Phase equilibrium properties of system carbon dioxide-hydrogen sulfide, *Ind. Eng. Chem., 45*(3), 618, 1953.

Brown, T.S., Kidnay, A.J., and Sloan, E.D., Vapor-liquid equilibria in the carbon dioxide + ethane system, *Fluid Phase Equil., 40*, 169, 1988.

Bucklin, R.W., and Schendel, R.L., Comparison of physical solvents used for gas processing, *Acid and Sour Gas Treating Processes*, Newman, S.A. (ed.), Gulf Publishing Company, Houston, TX, 1985. p. 1197.

Burr, B., and Lyddon, L., A comparison of physical solvents for acid gas removal, for sweetening, *Eighty-Seventh Annual Gas Processors Association Convention*, Tulsa, OK, 2008.

Carson, J.K., Marsh, K.N., and Mather, A.E., Enthalpy of solution of carbon dioxide in (water + monoethanolamine, or diethanolamine, or N-methyldiethanolamine) and (water + monoethanolamine + N-methyldiethanolamine) at T = 298.15K, *J. Chem. Thermo., 32*, 1285, 2000.

Chi, C.W., and Lee, H., Natural gas purification by 5A molecular sieves and its design method, *AIChE Sym. Ser., 69*(134), 95, 1973.

Clare, R.T., and Valentine, J.P., Acid gas removal using the Selexol® process, *Second Quarterly Meeting of the Canadian Natural Gas Processors Association*, Tulsa, OK, 1975.

Cline, C., et al., Biological process for removal from gas streams, the Shell-Paques/THIOPAQ gas desulfurization process, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2003.

Compton, A., Bincaz, I., and Bermel, C., Comparative H_2S economics for shale gas, *Ninety-First Annual Gas Processors Association Convention*, Tulsa, OK, 2012.

Cummings, W., and Chi, C.W., Natural gas purification with molecular sieves, *Canadian Chemical Engineering Conference,* Calgary, Alberta, Canada, 1977.

Echt, B., et al., Fundamentals of low-tonnage sulfur removal and recovery, *Laurance Reid Gas Conditioning Conference*, Norman, OK, 2017.

Echt, W.I., Dortmund, D.D., and Malino, H.M., Fundamentals of membrane technology for CO_2 removal from natural gas, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2002.

Echterhoff, L.W., State of the art of natural gas processing technologies, GRI -91/0094, Gas Research Institute, 1991.

Engel, D.B., and Northrop, P.S., Manage contaminants in amine treating units: Part 2: Rich amine filtration, inlet separation and amine foaming, *Hydroc. Proc., 97*(7), 41, 2018a.

Engel, D.B., and Northrop, P.S., Managing process contaminants in amine treating units: Part 1: Lean amine filtration, *Hydroc. Proc., 97*(6), 57, 2018b.

Engineering Data Book, Section 2, Product specifications, GPSA Midstream Suppliers, Tulsa, OK, 2016a.

Engineering Data Book, Section 21, Hydrocarbon treating, GPSA Midstream Suppliers, Tulsa, OK, 2016b.

Engineering Data Book, Section 25, Phase equilbria, GPSA Midstream Suppliers, Tulsa, OK, 2016c.

Epps, R., Use of Selexol® solvent for hydrocarbon dewpoint control and dehydration of natural gas, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 1994, p. 26.

Giacomin, S., NGL infrastructure in the Western Canadian Sedimentary Basin, and Pembina's expansion from wellhead to market, *Ninety-Seventh GPA Midstream Convention*, Tulsa, OK, 2018.

Goar, B.G., Todays gas treating processes, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 1971, p. D1.

Hegarty, W.P., and Goar, B.G., Insights into physical solvent acid gas removal processes, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2010, p. 64.

Hegwar, A.M., and Harris, R.A., Selexol® solves high H_2S/CO_2 problem, *Hydroc. Proc., 49*(4), 103, 1970.

Holmes, A.S., et al., Pilot tests prove Ryan/Holmes cryogenic acid gas/hydrocarbon separations, *Proceedings of the Sixty-First Annual Gas Processors Association Convention*, Tulsa, OK, 1982, p. 75.

Holub, P.E., and Sheilan, M., Fundamentals of gas sweetening, *Laurance Reid Gas Conditioning Conference*, Norman, OK, 2000.

Houghton, J.E., and Bucklin, R.W., Nonregenerable H_2S scavenger update, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 1994, p. 110.

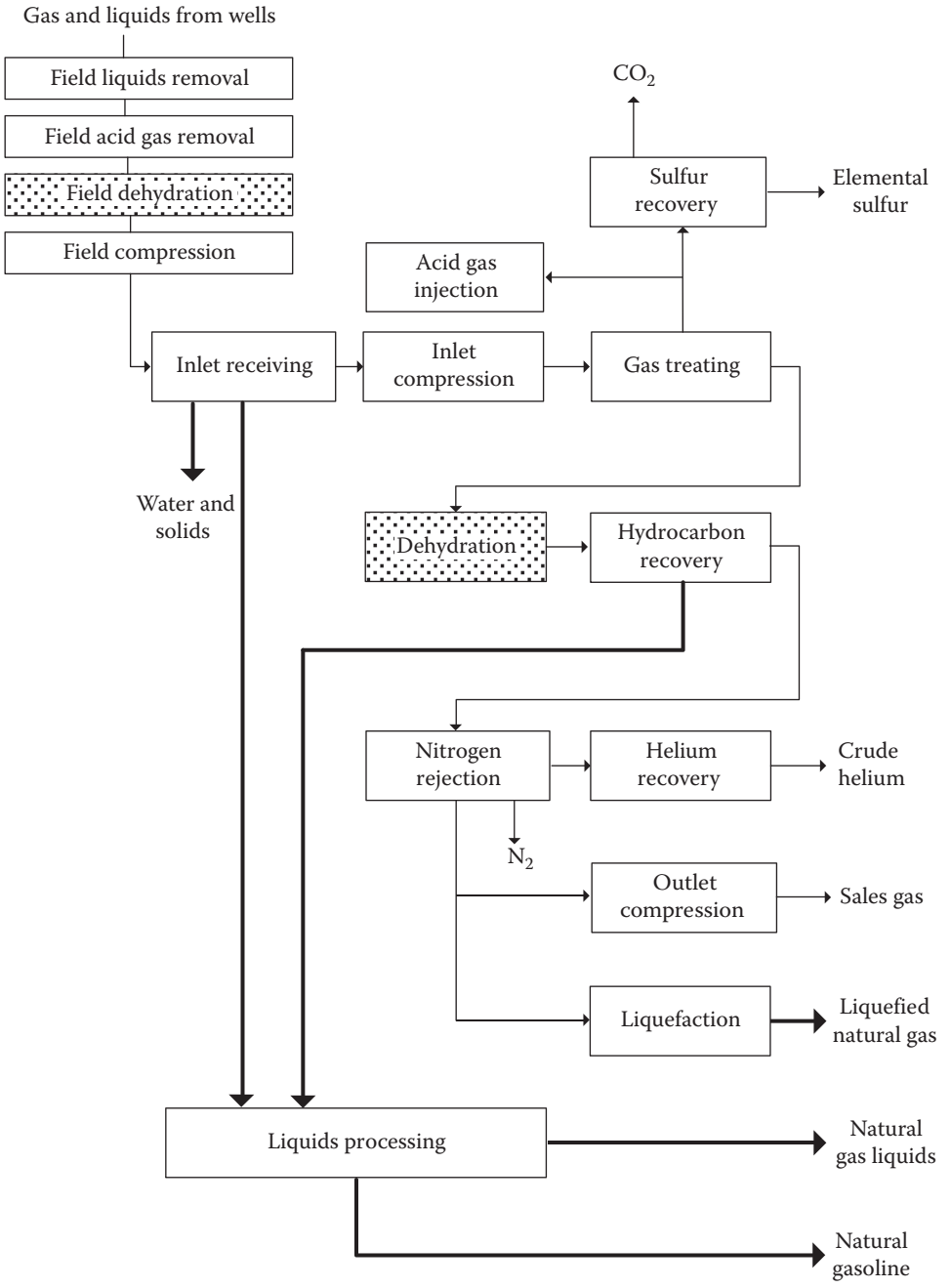
James, R., and Arshad, A., High efficiency contaminant removal improves new and existing sweetening processes, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2017.

Johnson, J.E., Selexol® solvent process reduces lean, high-CO_2 natural gas treating costs, *Energy Progr., 4*(4), 241, 1984.

Johnson, J.E., Trace components: An overview, *Hydroc. Eng., 11*(12), 43, 2006.

Johnson, J.E., Trace components: Gas treatment & conditioning, *Hydroc. Eng., 12*(5), 29, 2007a.
Johnson, J.E., Trace components: GTU solvent selection, *Hydroc. Eng., 12*(2), 43, 2007b.
Johnson, J.E., Trace components: The SRU, *Hydroc. Eng., 12*(4), 81, 2007c.
Jou, F.Y., Otto, F.D., and Mather, A.E., Vapor liquid equilibrium of carbon dioxide in aqueous mixtures of monoethanolamine and methyldiethanolamine, *Ind. Eng. Chem. Res., 33*, 2002, 1994.
Judd, D.K., Selexol® unit saves energy, *Hydroc. Proc., 57*(4), 122, 1978.
Kent, R.L., and Eisenberg, B., Better data for amine treating, *Hydroc. Proc., 55*(2), 87, 1976.
Klinkenbijl, J.M., Dillon, M.L., and Heyman, E.C., Gas pre-treatment and their impact on liquefaction processes, *Proceedings of the Seventy-Eighth Gas Processors Association Convention*, Tulsa, OK, 1999, p. 229.
Kohl, A., and Nielsen, R., *Gas Purification*, 5th edn. Gulf Publishing, Houston, TX, 1997.
Lemmon, E.W., McLinden, M.O., and Friend, D.G., Thermophysical properties of fluid systems, *NIST Chemistry WebBook, NIST Standard Reference Database Number 69,* Linstrom, P.J. and W.G. Mallard (eds.), National Institute of Standards and Technology, Gaithersburg, MD, 2017. http://webbook.nist.gov (Retrieved April 2019).
Leppin, D., Fisher, K., and Matonis, D., Modeling direct injection of H_2S scavenger in pipelines: Laboratory investigations and improved computer model. *Eighty-Eighth Annual Gas Processors Association Convention*, Tulsa, OK, 2009.
Linde, Linde molecular sieves non-hydrocarbon materials data sheets, Form 9691-F, undated.
Lyddon, L., and Nguyen, H., Analysis of various flow schemes for sweetening with amines, *Proceedings of the Seventy-Eighth Annual Convention of the Gas Processors Association*, Tulsa, OK, 1999, p. 177.
McJannett, J., Using Selexol® solvent for multiple applications. A discussion of flow schemes and case studies, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2012, p. 17.
Meyer, H.S., Volume and distribution of subquality natural gas in the United States, *Gas TIPS, 6*(1), 10, 2000.
Moritis, G., More EOR projects start but production continues to decline, *Oil Gas J., 106.15*, 41, 2008.
Mortko, R.A., Remove H_2S selectively, *Hydroc. Proc., 63*(6), 78, 1984.
Northrop, P.S., and Bialek, R., Cryogenic sour gas process attractive for acid gas injection application, *Eighty-Third Annual Gas Processors Association Convention*, Tulsa, OK, 2004.
Oberding, W., et al., Lessons learned and technology improvements at the Lost Cabin gas plant, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2004, p. 273.
Raney, D.R., Remove carbon dioxide with Selexol®, *Hydroc. Proc., 55*(4), 73, 1976.
Rollenhagen, T., et al., Sulfur removal from CO_2, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2010, p. 279.
Schulz, M., Developments in H_2S scavenging, *Pet. Technol. Q. Gas*, 2018.
Seagraves, J., Quinlan, M., and Corley, J., Fundamentals: Gas sweetening, *Laurance Reid Gas Conditioning Conference*, Norman, OK, 2010.
Shah, V.A., Integrated gas treating and hydrocarbon recovery process using Selexol® solvent technology, *Proceedings of the Sixty-Eighth Annual Convention Gas Processors Association*, Tulsa, OK, 1989, p. 197.
Simmons, C.V., Reclaiming used amine and glycol solutions, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 1991, p. 335.
Smith, W.A., Good operating practices for amine treating systems, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 1996, p. 303.
Spillman, R.W., and Cooley, T.E., Membrane gas treating, *Proceedings of the Eighty-Eighth Annual Gas Processors Association Convention*, Tulsa, OK, 1989, p. 186.
Sterner, A.J., Acid gas fractionation, *Laurance Reid Gas Conditioning Conference*, Norman, OK, 2001.
Sweny, J.W., High CO_2-H_2S removal with Selexol® solvent, *Proceedings of the Sixty-Ninth Annual Gas Processors Association Convention*, Tulsa, OK, 1980, p. 163.
Sweny, J.W., and Valentine, J.P., Physical solvent stars in gas treatment/purification, *Chem. Eng., 54*(19), 77, 1970.
Tennyson, R.N., and Schaaf, R.P., Guidelines can help choose proper process for gas-treating plants, *Oil Gas J., 75*(2), 78, 1977.
Veroba, R., and Stewart, E., Fundamentals of gas sweetening, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2003.
Warren, G.L., and Bertrand, T., Triazine based H_2S scavengers: the facts to date, *Laurance Reid Gas Conditioning Conference*, Norman, OK, 2015.

11 Gas Dehydration



11.1 INTRODUCTION

Typically, dehydration is important in three areas:

- Gas *gathering*. Water needs to be removed to reduce pipeline corrosion and prevent line blockage caused by hydrate formation. The water dew point should be below the lowest pipeline temperature to prevent free-water formation. Chapter 8 discusses field operations and gas hydrates.
- *Product dehydration*. Both gas and liquid products have specifications on water content. Sales gas that leaves a plant is usually dry if cryogenic hydrocarbon liquid recovery is used. Liquid and gas streams may be water saturated after amine treatment or coming from underground storage. Most product specifications, except for propane, require that no free water be present (*Engineering Data Book*, 2016a). This requirement puts the maximum water in sales gas at 4–7 lb_m/MMscf (60–110 mg/Nm^3). For liquids, the water content is 100–200 ppmw. Fuel grades of propane require lower water content (see Chapter 6) but as a practical matter, all propane product is produced to be able to be sold as a fuel grade.
- *Hydrocarbon recovery*. Most plants use cryogenic processes to recover a C_2^+ liquid NGL product from inlet gas. If acid gases are removed using amine processes, the treated gas is water saturated. To prevent hydrate formation in cryogenic hydrocarbon recovery sections the water concentration should be 0.1 ppmv or less. Chapter 12 discusses hydrocarbon recovery processes.

The first two areas are less demanding, and a variety of processes are available to meet the need. However, the third application, as well as gas liquefaction and cryogenic nitrogen rejection units, requires water contents two orders of magnitude lower than the other two. Only molecular sieves can provide dehydration to this level.

Water content is stated in a number of ways:

1. Mass of water per volume of gas, lb_m/MMscf (mg/Nm^3)
2. Water dew point temperature, °F (°C), which is the point that liquid water will condense out of the gas phase
3. Concentration, parts per million by volume (ppmv)
4. Concentration, parts per million by mass (ppmw)

The first three water-content values are commonly used with gases, and the second and fourth values are used with liquids. The first and third values are convenient, as they are easily related. All conversions between concentration values require knowing the molar mass of the gas mixture.

Unfortunately, the dew point is commonly used because it makes practical sense. However, no simple conversion method exists between dew point and the other concentration units. There is little agreement in the literature on the correct relation between dew point and water vapor content. A dew point table based on U.S. Bureau of Standards, Circular 564, Table 9.9 (Hilsenrath et al., 1955), correlates dew point with parts per million of water vapor on a volume basis. This table often forms the commercial basis for conversion and is often reproduced although Circular 564 has long been out of print.

This chapter provides ways to estimate the water content of gases and then discusses the common processes used for its removal. The same basic processes apply to drying liquids, but a liquid, which has a higher density, alters the processes slightly. Chapter 15 discusses dehydration of liquids.

11.2 WATER CONTENT OF HYDROCARBONS

Determining the saturation water content of a gas (the dew point) is a standard but complex problem in thermodynamics, and excellent discussions of phase equilibria calculations are given in many thermodynamics texts (e.g., Prausnitz et al., 1999; Smith et al., 2018). We first assume ideal behavior, and then present a commonly used engineering correlation based on experimental measurements.

In any mixture, where both the gas and liquid phases are in equilibrium, each component, i, in the mixture obeys the relationship

$$x_i \gamma_i P_i^{\text{Sat}} = y_i \varphi_i P \tag{11.1}$$

where

x_i is the mole fraction in the liquid phase
γ_i is the activity coefficient
P_i^{Sat} is the saturation or vapor pressure
y_i is the vapor phase concentration
φ_i the vapor phase fugacity coefficient
P the total pressure

(This is Equation 4.2 with the fugacity coefficient added to account for real gas behavior in the vapor phase.) The vapor pressure is temperature dependent, whereas the activity and fugacity coefficients are temperature, pressure, and composition dependent. If three of the four variables, temperature, pressure, liquid composition, and vapor composition, are known, the fourth variable can be calculated (flash calculation). The activity and fugacity coefficients can be calculated by use of equations of state and empirical equations. However, many commonly used equations of state have difficulty modeling the strong polar nature of water in hydrocarbon–water mixtures; calculations from different simulators can give different results, especially in prediction of water content in the liquid phase. If the mixture contains methanol or brine, the calculations become more uncertain.

However, reasonably good estimates of the concentration of water in the vapor phase in equilibrium with liquid water can be made at pressures below 500 psia (35 bara). If we make the good assumption of negligible hydrocarbon in the liquid water phase, which, thus makes both x_i and γ_i unity for water and assume the gas phase to be ideal, which makes φ_i unity, we obtain

$$y_{H_2O} = \frac{P_{H_2O}^{\text{Sat}}}{P} \tag{11.2}$$

Equation 11.2 provides reasonably good values for gas-phase water content, provided that the gas contains less than a few mol% of either CO_2 or H_2S. Water vapor pressure as a function of temperature can be found in steam tables or the NIST WebBook (Lemmon et al., 2017).

A more accurate way to determine the water content is to use Figure 11.1a. Figure 11.1a gives the water content for a hydrocarbon gas as a function of temperature and pressure. Figure 11.1b provides corrections for gas gravity and for salinity if the water phase contains brine. The chart is widely used in the gas industry and gives good results, provided the gas contains less than about 5 mol% CO_2 plus H_2S. (Appendix B[1] provides a color-coded version of Figure 11.1a.) The *Engineering Data Book* (2016b) provides an empirical method to predict water concentrations when the gas contains higher concentrations of the acid gases. Note that the dashed lines in

[1] See Appendix B on publisher website: www.crcpress.com/Fundamentals-of-Natural-Gas-Processing-Third-Edition/Kidnay-Parrish-McCartney/p/book/9781138612792

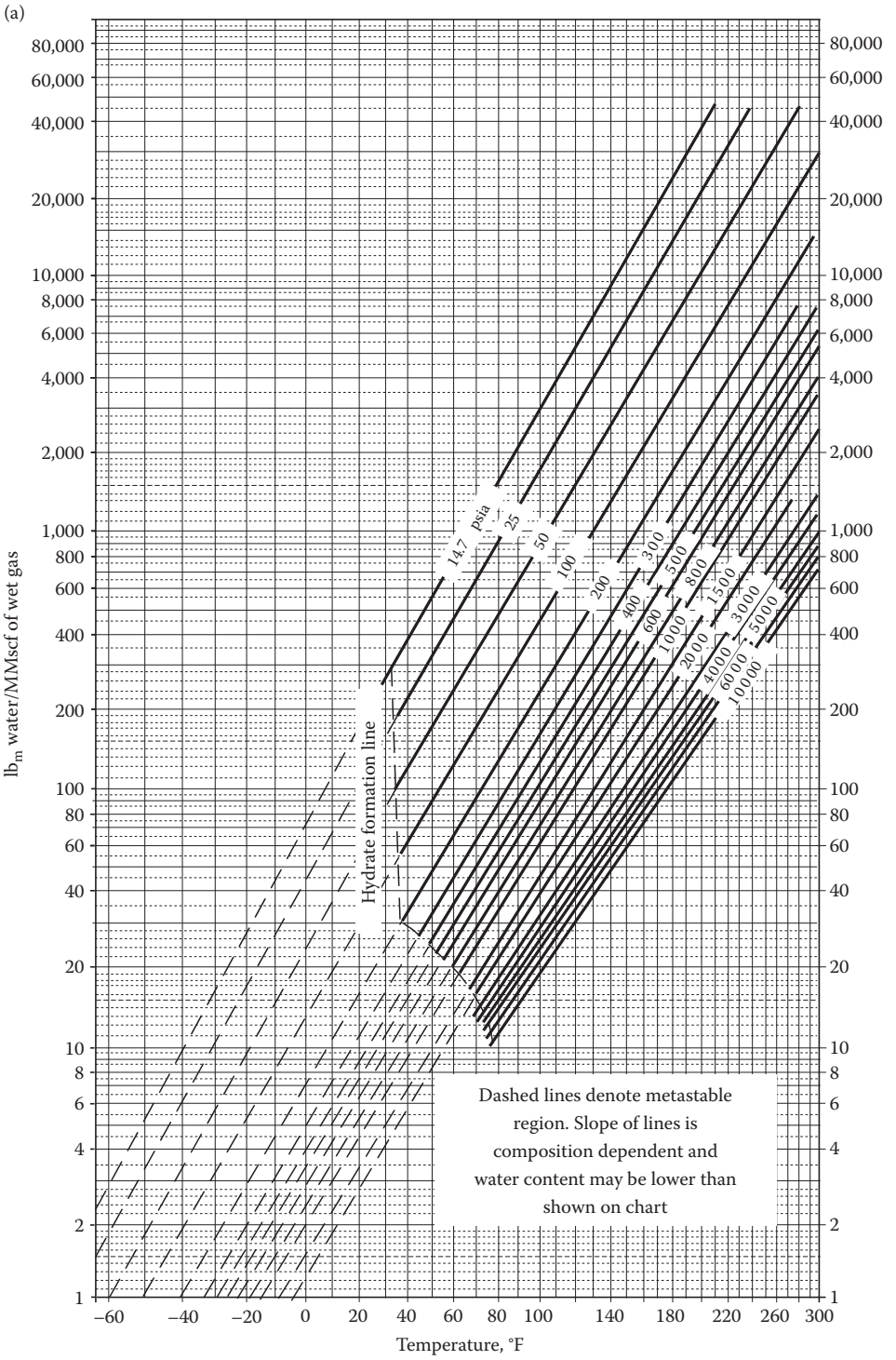


FIGURE 11.1a Water content of hydrocarbon gases as a function of temperature and pressure (lb water/MMscfd can be converted to mg water/Nm^3 by multiplying by 16.9). (Adapted from *Engineering Data Book*, 2016b, with permission.)

(*Continued*)

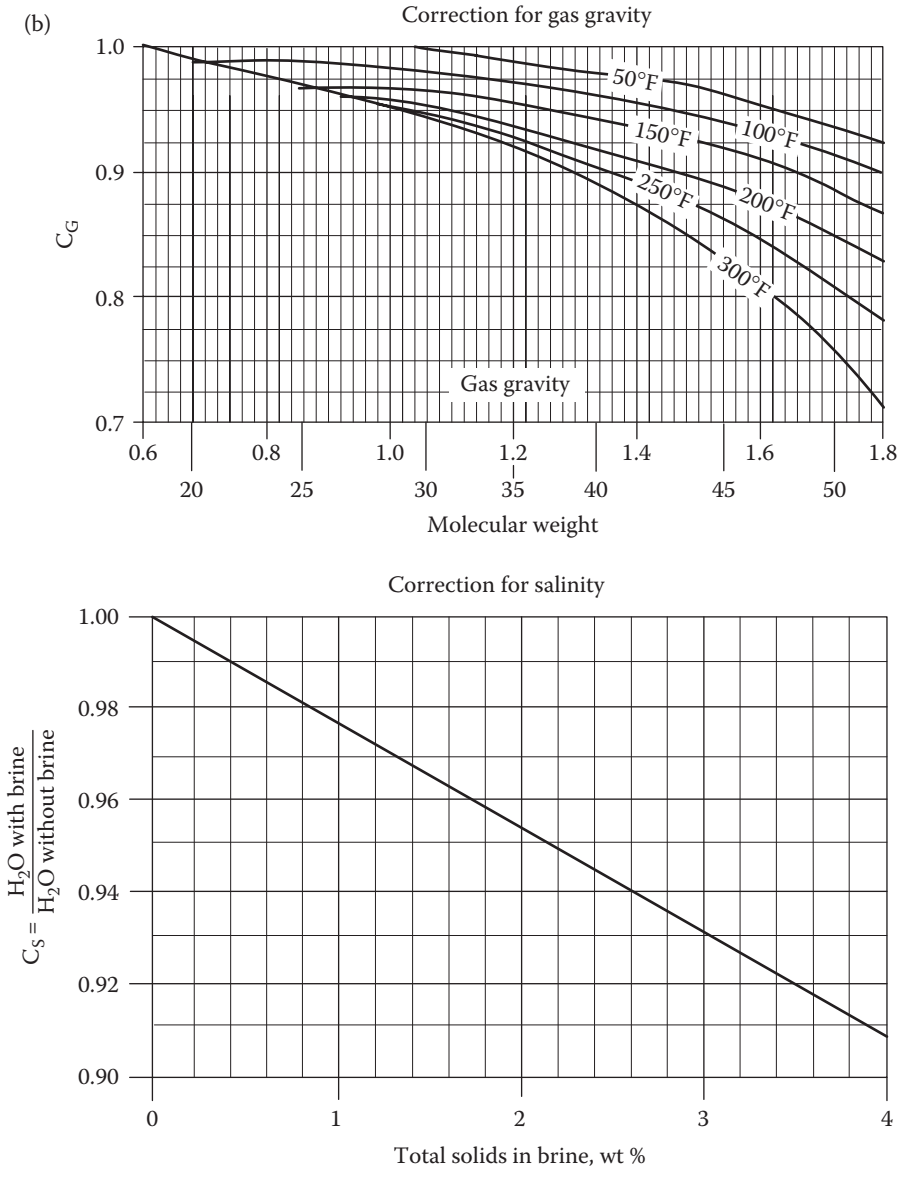


FIGURE 11.1b Gas gravity and salinity corrections to water content in hydrocarbon gases. (Adapted from *Engineering Data Book*, 2016b, with permission.)

Figure 11.1a represent the water phase in equilibrium with either ice or gas hydrate, depending upon the gas composition and pressure. Actual gas phase water contents can be lower than that obtained from the chart. GPA Research Report RR-174 (Ng et al., 2001) reports water content in gases containing H_2S and CO_2.

Example 11.1

Calculate the water content of the sweet natural gas shown in Table 11.1 at 300 psia (20.7 bara) and 80°F (26.7°C) by use of Equation 11.2 and Figure 11.1a

TABLE 11.1
Gas Composition for Example 11.1

Component	Mole Fraction	Molar Mass	Mol Fraction × Molar Mass
N_2	0.01	28.013	0.28
CH_4	0.90	16.043	14.44
C_2H_6	0.04	30.070	1.20
C_3H_8	0.03	44.097	1.32
n-C_4H_{10}	0.02	58.123	1.16
Totals	1.00		18.41

Solution

Equation 11.2 using vapor–pressure data from the NIST WebBook (Lemmon et al., 2017) gives

$$y_{H_2O} = \frac{P^{Sat}_{H_2O}}{P} = \frac{0.507\,\text{psia}}{300\,\text{psia}} = 0.0017\,\text{mol fraction}$$

Convert to lb_m water/MMscf:

$$W_{Sat} = \left(0.0017\frac{\text{mol}\,H_2O}{\text{mol gas}}\right)\left(18\frac{lb_m\,H_2O}{\text{lb-mol}}\right)\left(\frac{1\,\text{lb-mol}}{379.5\,\text{scf}}\right)10^6 = 81\frac{lb_m\,H_2O}{\text{MMscf}} = 1{,}300\frac{\text{mg}}{Nm^3}$$

From Table 11.1, the molar mass (MW) of the gas mixture is 18.41 and the specific gravity is

$$\text{SpGr} = \frac{\text{MW gas}}{28.9625} = \frac{18.41}{28.96} = 0.636$$

From Figure 11.1a W_{Sat} = 85 lb_m/MMscf (1,440 g/Nm^3). Correct for specific gravity by obtaining C_G from Figure 11.1b (C_G = 0.99), and multiplication gives

$$W_{Sat} = (0.99)(85) = 84\,lb_m/\text{MMscf}\,(1{,}420\,\text{g/Nm}^3)$$

The values differ by 4%.

Increasing the pressure to 1,000 psia (70 bara), Equation 11.2 gives a value 27% below the value obtained from Figure 11.1a.

Both Equation 11.2 and Figure 11.1 show that at a given temperature the water content decreases with increasing pressure. Also, at a given pressure, water content increases with increasing temperature because the vapor pressure of water increases with temperature. These trends are valid as long as CO_2 and H_2S (acid gases) concentrations are low. The pressure effect on water content becomes complex if acid gas concentrations are higher. (*Engineering Data Book*, 2016b). Water content of gases containing high concentrations of H_2S and/or CO_2 such as the acid gas from an amine regenerator is discussed in Chapter 16.

11.3 GAS DEHYDRATION PROCESSES

This section discusses the conventional methods for drying natural gas, and then briefly describes some less conventional methods. Two processes, absorption and adsorption, are the most common and are discussed in detail. Chapter 4 provides some background on the two processes.

11.3.1 Absorption Processes

11.3.1.1 Overview of Absorption Process

Water levels in natural gas can be reduced to the 10 ppmv range in a physical absorption process in which the gas is contacted with a liquid that preferentially absorbs the water vapor. The solvent used for the absorption should have the following properties:

- A high affinity for water and a low affinity for hydrocarbons
- A low volatility at the absorption temperature to reduce vaporization losses
- A low viscosity for ease of pumping and good contact between the gas and liquid phases
- A good thermal stability to prevent decomposition during regeneration
- A low potential for corrosion

In practice, the glycols, ethylene glycol (EG),[2] diethylene glycol (DEG), triethylene glycol (TEG) and propylene glycol are the commonly used absorbents. TEG is the most frequently used because it offers the best compromise between solvent losses and initial cost. However, in cold climates DEG is sometimes used because of its lower viscosity at the lower contactor temperatures. For operations in which frequent brine carryover into the contactor occurs, operators use EG because it can hold more salt than the other glycols. The solubility of sodium chloride in EG water mixtures is around 20 wt% (Masoudi et al., 2004; Parrish, 2000; Trimble, 1931), whereas it is only around 5 wt% in TEG (Kruka, V.R., Private Communication, 2005).

Appendix B gives some of the more important properties of the commonly used glycols and glycol–water mixtures. Table 11.2 shows their formulas, along with the maximum recommended regeneration temperature. Smith (2004) reports temperatures for onset of slow thermal degradation as 328°F (164°C) and 385°F (196°C) for DEG and TEG, respectively. However, Smith (2004) gives typical maximum regenerator temperatures of about 350°F (175°C) and 400°F (204°C) for DEG and TEG, respectively. Manufacturer's literature (Dow Chemical Company, 2007) gives an onset of initial decomposition temperature of 464°F (240°C) for TEG. They note that long-term exposure of glycols to temperatures above 120°F (50°C) results in glycol degradation.

Figure 11.2 shows a typical, simplified, flow diagram for a glycol absorption unit. The wet gas passes through an inlet scrubber to remove solids and free liquids, and then enters the bottom of the glycol contactor. Gas flows upward in the contactor, while lean glycol solution (glycol with little or no water) flows down over the trays or packing. The glycol absorbs water and leaves as rich glycol at the bottom of the column while dry gas exits at the top. The rich glycol flows through a heat exchanger at the top of the still (regenerator) where it is heated and provides the coolant for the still

TABLE 11.2
Glycols Used in Dehydration

Name	Formula	
Ethylene glycol (EG)	$HO–(CH_2)_2–OH$	$C_2H_6O_2$
Diethylene glycol (DEG)	$HO–((CH_2)_2–O)–(CH_2)_2–OH$	$C_4H_{10}O_3$
Triethylene glycol (TEG)	$HO–((CH_2)_2–O)_2–(CH_2)_2–OH$	$C_6H_{14}O_4$
Propylene glycol	$HO–(CH_2)_3–OH$	$C_3H_8O_2$

Source: Sheilan (2016).

[2] EG is sometimes called monoethylene glycol (MEG).

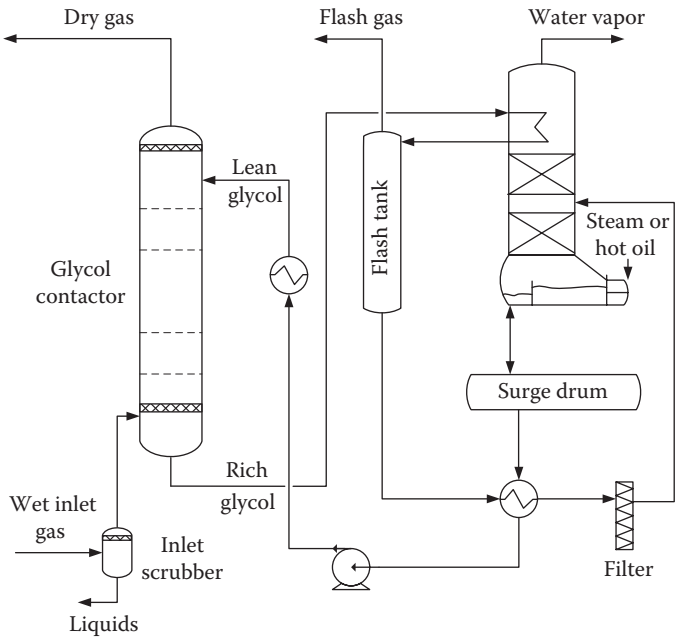


FIGURE 11.2 Schematic of typical glycol dehydrator unit.

condenser. The warmed solution goes to a flash tank, where dissolved gas is removed. The rich glycol from the flash tank is further heated by heat exchange with the still bottoms, and then becomes the feed to the still. The still produces water at the top and a lean glycol at the bottom, which goes to a surge tank before being returned to the contactor. Figure 11.2 shows a steam or hot oil heated reboiler but direct fired units are also common. Essentially all field units are direct fired.

The pump which delivers the lean glycol to the contactor is often driven by energy recovered from the pressure reduction of the rich glycol between the contactor and the flash tank. This style of pump is commonly called a "Kimray" pump after the manufacturer who popularized their use. They are particularly suited for remote field locations where electric power is unavailable or unreliable. At first glance, using the energy from the pressure reduction to create a comparable pressure increase appears to violate the first law of thermodynamics. The key is that there is dissolved gas in the rich glycol which, upon expansion, provides more energy than is available from the simple hydraulic expansion of a liquid glycol stream. See Sheilan (2016) for more details.

Operating conditions for glycol units are governed principally by the degree of dehydration required, the physical properties of the glycol solutions, and the inlet pressure of the gas to the processing unit. Some typical operating conditions for TEG absorbers are given in the next section. The articles of Hernandez-Valencia et al. (1992), Parrish et al. (1986), and Wieninger (1991), along with the *Engineering Data Book* (2016b), provide detailed information on absorber design and operation. Although many design references refer to trays, most modern TEG absorbers use structured packing instead of trays.

11.3.1.2 Representative Operating Conditions for TEG Absorbers

As noted above, TEG is the most common absorbent for dehydration, although some operations in colder climates (e.g., the North Sea) will use DEG because of its lower viscosity. Tetraethylene glycol has a lower vapor pressure and withstands higher regeneration temperatures than does TEG, but the additional cost outweighs the marginal increased benefits. Smith (2004) reports about 20,000 TEG dehydration units operating in the United States.

Gas flow rates, compositions, inlet pressures and temperatures, and the required degree of dehydration vary widely. However, Table 11.3 provides some typical service conditions.

Figure 11.3 shows the equilibrium dew points that can be achieved with TEG solutions of different concentrations as a function of contactor temperature. For example, if an equilibrium dew point of –15°F (–26°C) is required and the contactor operates at 80°F (27°C), then a TEG solution of 99.3 wt% is required. However, this assumes that the dry gas exiting is in equilibrium with the incoming lean glycol (i.e., infinite number of contactor trays). To account for nonequilibrium concentrations, the *Engineering Data Book* (2016b) suggests use of an equilibrium temperature that is 10°F–20°F (5°C–10°C) below the desired dew point temperature. Therefore, to obtain the –15°F (–26°C) exit dew point temperature, the lean glycol concentration should be about 99.8 wt%.

The *Engineering Data Book* (2016b) notes that Figure 11.3 is based upon equilibrium between water vapor and a liquid water phase. At lower temperatures, the true equilibrium condensed phase is gas hydrate, which will form at higher temperatures than does subcooled water. Therefore, solids formation could be as much as 15°F–20°F (8°F–10°C) higher than the dew point value obtained from Figure 11.3. The actual error depends upon temperature, pressure, and gas composition. However, the pressure effect is minimal, and the chart can be used to 1,500 psia (100 bara). At higher pressures the chart is conservative. For more information on equilibrium considerations in TEG unit design, refer to Clinton et al. (2008).

The required lean glycol concentration dictates still reboiler operating conditions. Higher reboiler temperatures yield leaner glycol. At a 400°F (204°C), the typical maximum regeneration temperature, TEG has a lean glycol concentration of 98.6 wt% (*Engineering Data Book*, 2016b) at sea level. Higher purity requires reduction of the partial pressure of water in the reboiler vapor space. There are three ways used to increase glycol concentrations above 99.5 wt% (Sheilan, 2016; Smith and Humphrey, 1995):

- Vacuum distillation
- Stripping gas
- Drizo™ process

TABLE 11.3
Typical Operating Conditions of TEG Dehydrators

	Contactor
Inlet pressures	<2,000 psig (140 barg)
Inlet gas temperature	60°F–100°F (15°C–40°C)
Pressure drop	5–10 psi (35–70 kPa)
Glycol circulation rate	2–4 gal/lb_m H_2O removed, with three common (15–30 L/kg)
Tray efficiencies	25%–30%
Dew points	>–25°F (–32°C)
Glycol losses	0.1 gal/MMscf (14 L/10^6 Nm^3)
	Regenerator (Still and Reboiler)
Column internals	Packed equivalent to three or four theoretical trays
Reboiler temperature	385°F–400°F (195°C–205°C)
	Flash Tank
Pressure	50–75 psig (3.5–5 barg)
Temperature	150°F (65°C)

For dehydration of gas streams which contain high concentrations of C_4^+, adequate time needs to be allowed for removal of the less-volatile components from the glycol to minimize hydrocarbon losses in the still overhead. The flash tank should be designed to provide three-phase separation.

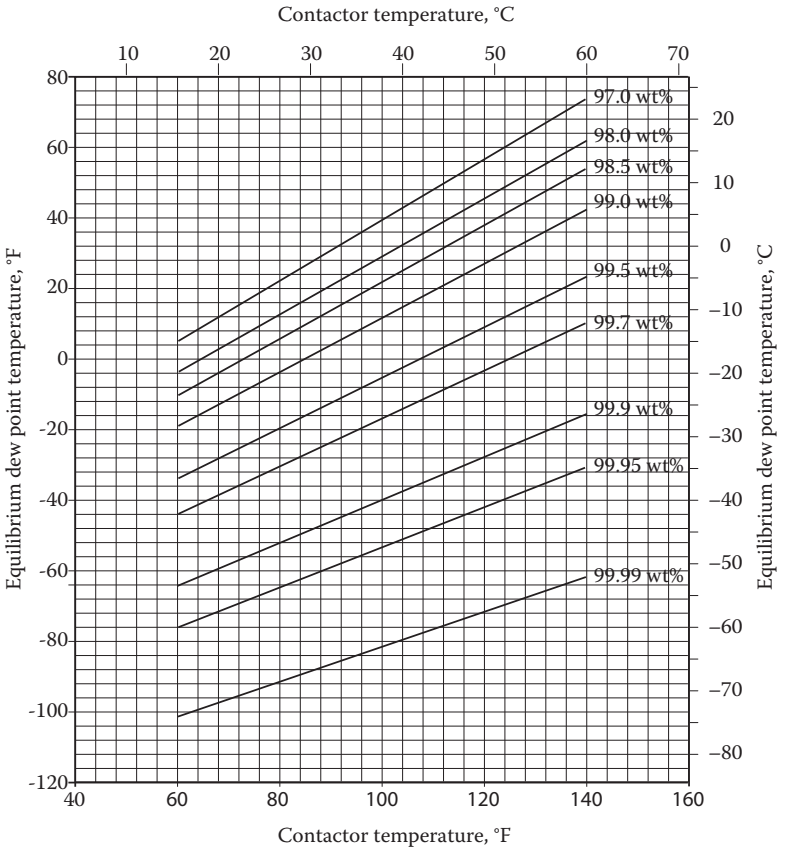


FIGURE 11.3 Equilibrium water dew point as a function of contactor temperature and TEG concentration in wt%. (Adapted from *Engineering Data Book*, 2016b, with permission.)

Adding a vacuum pump to lower regenerator pressure can be an effective means of raising the TEG concentration to about 99.98 wt%. However, Smith and Humphrey (1995) note that it is effective only on lean gas streams. Although the solubility of hydrocarbons in TEG is small, higher concentrations of C_3^+ or the presence of BTEX can make maintaining the low pressure difficult.

The most common way to reduce the water partial pressure is to use a stripping gas[3] which can yield lean glycol concentrations of 99.96–99.98. The major drawback of this approach is the volume of stripping gas required. To obtain 99.96 wt%, TEG requires 10 scf/gal TEG (0.07 Nm^3/L) and blowers are usually required to return the low-pressure gas to inlet compression (Smith and Humphrey, 1995). This option becomes more attractive when the gas can be used as low-pressure fuel gas or the regenerator off-gas is captured as part of an emissions control process. Sheilan (2016) discusses stripping gas recovery systems.

The Drizo™ process uses a complex system of liquid hydrocarbon recycles to produce a very high-purity TEG, which is then used to achieve very low outlet dew points. Outlet water levels to less than 1 ppm have been claimed for this process. One advantage of this process is that it has significantly lower hydrocarbon emissions, including BTEX, than other TEG systems.

The *Engineering Data Book* (2016b) and Smith and Humphrey (1995) describe the three methods in more detail.

[3] A stripping gas is a noncondensing gas at operating conditions that is used to strip the more volatile solutes from a liquid.

Figure 11.3 shows that lower absorption temperatures improve dehydration. As a general guideline, absorber inlet gas temperatures can be as high as 150°F (65°C), although temperatures above 100°F (40°C) may result in unacceptable vaporization losses for the glycol solutions (*Engineering Data Book*, 2016b). Because the contactor inlet gas mass flow rate is typically much higher than that of the TEG, the gas inlet temperature sets the contactor temperature. Being a physical absorption process with a low heat of absorption the contactor temperature varies little from top to bottom. At inlet temperatures below approximately 50°F (10°C), the viscosities of the glycol solution (see Appendix B) is sufficiently high to reduce contactor efficiencies and increase pumping costs. Typical maximum operating pressures are around 2,000 psig (140 barg).

TEG losses from a properly operating plant, excluding spillage, should be minimal. The *Engineering Data Book* (2016b) estimates about 0.1 gal/MMscf (14 L/10^6 Nm^3) from carryover, if a standard mist eliminator is used. Other losses range between 0.05 gal/MMscf (6 L/10^6 Nm^3) for high-pressure, low-temperature dehydration and 0.3 gal/MMscf (40 L/10^6 Nm^3) for low-pressure, high-temperature dehydration. Losses from vaporization are negligible. Higher losses can result from foaming problems in either the contactor or regenerator, or from glycol solution degradation due to high reboiler temperatures.

11.3.1.3 Acid Gas Dehydration

For gas streams with a high CO_2 concentration, equilibrium glycol losses can be much higher and should be considered when selecting the glycol. Glycerol has been used to dehydrate some very high-concentration CO_2 streams (Wallace, 1985) for EOR. The solubility of CO_2 in glycol solutions was reported in Research Report RR-183 (Davis et al., 2002).

Sour gases can be dried with glycol solutions if appropriate anticorrosion measures are taken. Figures 11.4–11.6 show the solubility of the acid gases in TEG as a function of temperature and pressure in lean glycol. These figures are used to estimate the acid gas volume in addition to the absorbed hydrocarbon gas. At 1,000 psig and 100°F (70 barg and 40°C), the estimated hydrocarbon gas solubility is 1 scf/gal (7 Nm^3/m^3) of TEG. It should be noted that H_2S emissions from the still

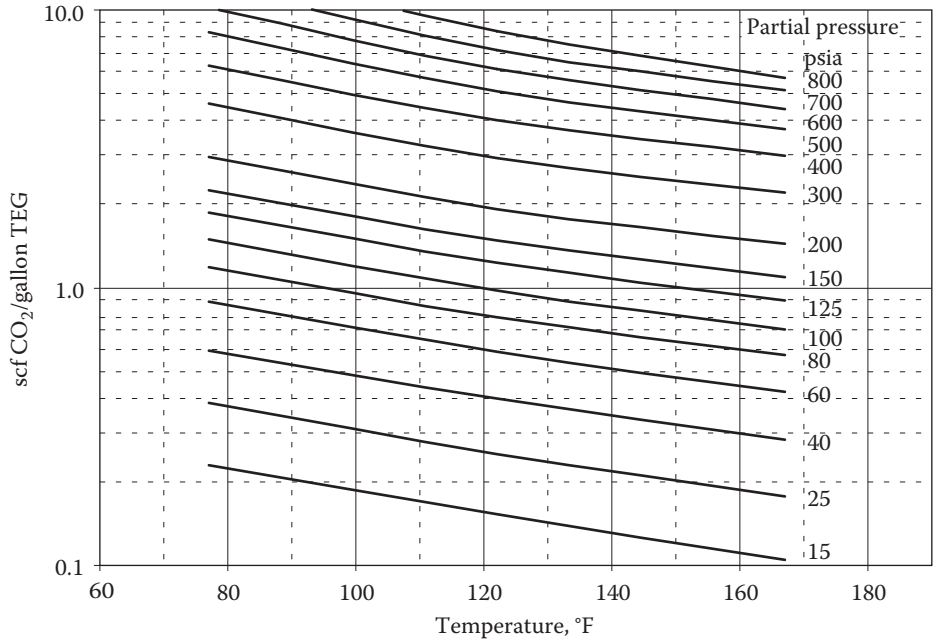


FIGURE 11.4 Solubility of CO_2 in lean TEG as a function of temperature and partial pressure (Wichert and Wichert, 2004).

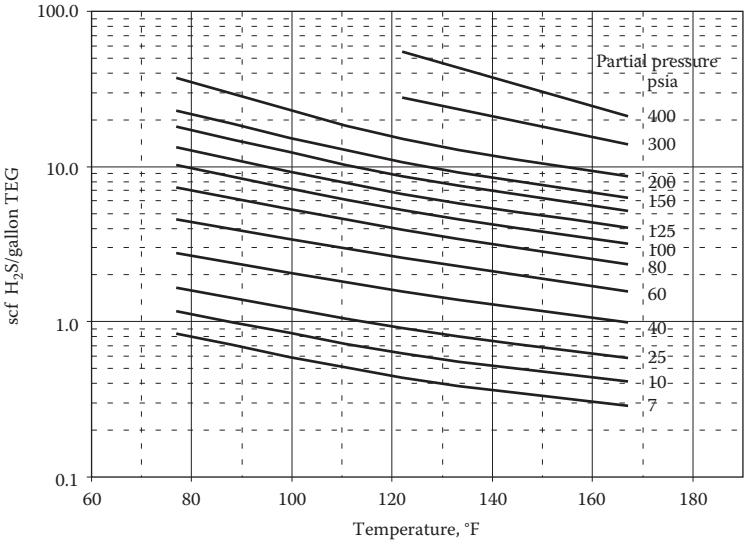


FIGURE 11.5 Solubility of H_2S in lean TEG as a function of temperature and partial pressure (Wichert and Wichert, 2004).

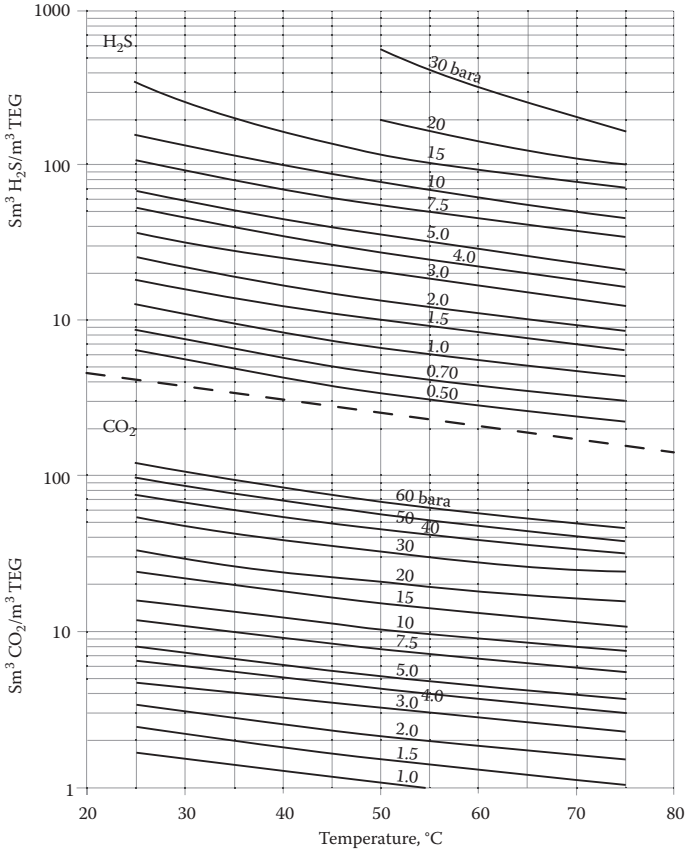


FIGURE 11.6 Solubility of H_2S and CO_2 in lean TEG as a function of temperature and partial pressure (Wichert and Wichert, 2004).

can be quite high when dehydrating sour gas. Solubility of sulfur species in TEG were reported in Research Reports RR-189 (Marriott et al., 2005), RR-204 (Afzal et al., 2008), and RR-209 (Mamrosh and Fisher, 2012). Also, because aromatic hydrocarbons are readily absorbed in TEG, BTEX emissions from the still need to be considered. An extensive study of BTEX and other hydrocarbon solubility in glycols has been conducted. This work was reported in Research Report RR-214 (Horstmann et al., 2011) and is summarized in Research Report RR-206 (Mamrosh and Fisher, 2012) based on several GPA research reports and selected literature references.

11.3.1.4 Other Factors that Affect Glycol Dehydrator Performance

Oxygen reacts with the glycols to form corrosive acidic compounds. These compounds also increase the potential for foaming and glycol carryover (Wieninger, 1991). A dry natural gas blanket is often put over surge tanks to minimize air intrusion. An inert gas is recommended when storing glycols (Dow Chemical, 2007). The *Engineering Data Book* (2016b) suggests that precautions be taken if oxygen is present in the gas as aldehydes can be formed and emitted from the still. These emissions are undesirable both from the standpoint of toxicity and odor.

The *Engineering Data Book* (2016b) notes that low pH accelerates glycol decomposition and recommends addition of trace amounts of basic hydrocarbons (e.g., alkanolamines). For glycol units downstream of amine treaters, the trace amount of amine carryover tends to mitigate the acidity problem.

Glycol dehydration units in many gas plants are downstream of the amine treaters and process a relatively clean gas stream that contains no H_2S and reduced CO_2 levels. Excessive amine carryover is the main concern in these situations. Dehydrators in gathering systems can be in more demanding situations where they may process streams that contain acid gases and methanol or other hydrate inhibitors. They also may be subjected to oil slugs, liquid water slugs, and compressor oil mist. Water-soluble components increase the regenerator duty, and hydrocarbon impurities can cause foaming in the system. Proper sizing of inlet scrubbers is critical in these situations. In some cases, filter separators or coalescing filters are required to prevent fine mists from entering the absorber.

Offshore producers sometimes use EG instead of TEG when produced water is carried over to the contactor. In these situations, the purpose of dehydration is hydrate prevention. With EG, to meet the 4–7 lb_m H_2O/MMscf (60–110 mg/Nm^3) specification, either stripping gas or running the still at a vacuum is required. The higher EG losses are considered acceptable. In some cases, reclaimers, which distill the EG from the brine are on the platform.

The *Engineering Data Book* (2016b) reports that glycol removes 40%–60% of the methanol added to the gas as a hydrate inhibitor. The increased liquid loading places an additional heat load on the reboiler and an added vapor load on the regenerator. Even with adverse conditions many unattended glycol systems function well in the field.

11.3.2 Adsorption Processes

11.3.2.1 Overview of Adsorption

Chapter 4 discusses the principles of adsorption and gives an overview of the general process. This section discusses the application of adsorption to dehydration. Solid-bed desiccants are commonly the only way to achieve the level of water removal required by downstream cryogenic processes. Physical adsorption is an equilibrium process like vapor–liquid equilibria and equations analogous to Equation 11.1 apply. Thus, for a given vapor phase concentration (partial pressure) and temperature, an equilibrium concentration exists on the adsorbent surface that is the maximum concentration of the condensed component (adsorbate) on the surface. Figure 11.7 shows the equilibrium conditions for water on a commercial molecular sieve as a function of partial pressure of water and temperature. These curves are called isotherms. The figure is based upon a water–air mixture but

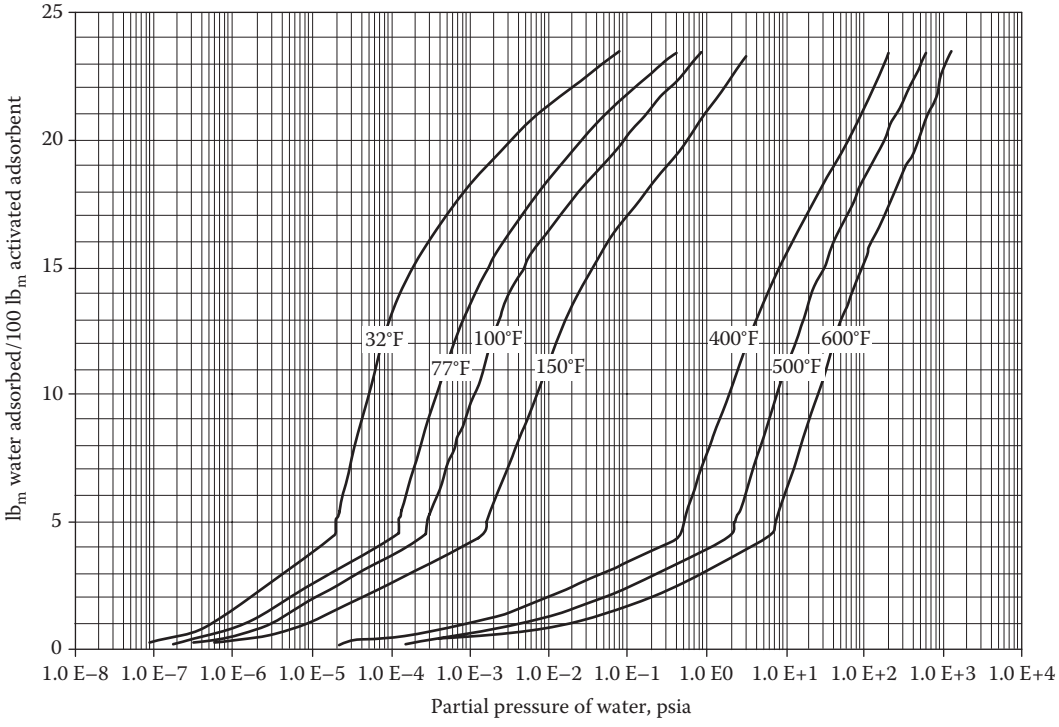


FIGURE 11.7 Water loading on UOP Adsorbent 4A-DG MOLSIV Pellets. Activation conditions for the adsorbent were 662°F (350°C) and <10 μm Hg. (Adapted from *Engineering Data Book*, 2016b. Used with permission of UOP LLC, A Honeywell Company.)

is applicable to natural gas systems. The important parameter is the partial pressure of water; total pressure has only a minor effect on the adsorption equilibrium.

11.3.2.2 Properties of Industrial Adsorbents for Dehydration

Three types of commercial adsorbents are in common use in gas processing plants:

- Silica gel, which is a granular highly porous form of silica
- Activated alumina, which is made of Al_2O_3
- Molecular sieves, which are made of alkali aluminosilicates and can be altered to affect adsorption characteristics.

Table 11.4 lists some important properties of three adsorbents compiled primarily from commercial literature. The properties are representative and vary among manufacturers.

Silica gels are used mostly where a high concentration of water (>1 mol%) vapor is present in the feed, and low levels of water in the dehydrated gas are not needed. They are relatively noncatalytic when compared to alumina and molecular sieve. Alumina is very polar and strongly attracts water and acid gases. They are used for moderate levels of water in the feed when low levels of water in the product are not required. They have the highest mechanical strength of the adsorbents considered here. However, for gas going into cryogenic processing, the only adsorbent that can obtain the required dehydration is a molecular sieve. Molecular sieve is a composite of tiny alkali aluminosilicate crystals bound together with a more porous clay binder. The 4A molecular sieve is the most common, but the smaller pore 3A is sometimes used. It has the advantage of being a poorer catalyst

TABLE 11.4
Representative Properties of Commercial Silica Gels, Activated Alumina and 4 A Molecular Sieve

	Silica Gel	Activated Alumina	4 A Molecular Sieve
Typical shape	Spherical beads and granular	Spherical beads	Pellets (extruded cylinders) and beads
Bulk density lb_m/ft^3 (kg/m^3)	45–49 (720–780)	47–53 (750–850)	45 (720)
Particle size	4–8 mesh (2–5 mm)	7–14 mesh, 1/8 in., 3/16 in., 1/4 in. (3, 5, and 6 mm)	1/16 in., 1/8 in., 1/4 in. diameter cylinders (1.6, 3.2, and 6 mm)
Packed bed % voids	40	40	35
Specific heat Btu/lb_m-°F (kJ/kg-°C)	0.20–0.22 (0.84–0.92)	0.24 (1.00)	0.25 (1.05)
Surface area (m^2/g)	650–830	210–360	600–800
Pore volume (cm^3/g)	0.36–0.43	0.2–0.4	0.28
Regeneration temperature, °F (°C)	480–540 (250–280)	320–430 (160–220)	400–600 (200–315)
Typical pore diameter (Å)	22	NA	4
Dew point temperature of effluent, °F (°C)[a]	−80 (−60)	−100 (−75)	−140 (−95)
Typical moisture content of effluent gas (ppmv)	10–20	5–10	0.1

[a] As reported by Blachman and McHugh (2000).

for generation of COS if both H_2S and CO_2 are present[4] because a portion of the more active sodium cations in 4A has been replaced with potassium. If both oxygen and H_2S are present, 3A reduces the production of elemental sulfur that can block adsorbent pores. However, operators usually have little incentive to use the more expensive 3A for dehydrating gas going to hydrocarbon recovery. Blachman and McHugh (2000) discuss use of multiple adsorbents in the same bed for applications in which both higher water concentrations and acid gases are present.

11.3.2.3 Adsorption Process

Although this discussion uses molecular sieve as the example of an adsorbent to remove water, with the exception of regeneration temperatures, the basic process is the same for all gas adsorption processes. Figure 11.8 shows a schematic of a two-bed adsorber system. One bed, Adsorber 1 in Figure 11.8 dries gas while the other bed, Adsorber 2, goes through a regeneration cycle. The wet feed goes through an inlet separator to catch any entrained liquids before the gas enters the top of the active bed. Flow is top-down to avoid bed fluidization. The dried gas then goes through a dust filter to catch fines before the gas exits the unit. This filter must be kept working properly, especially if the gas goes on to a cryogenic section with plate-fin heat exchangers, as dust can collect in the exchangers, reducing heat transfer and dramatically increasing pressure drop. Two dust filters are used in parallel so that one can be in service while the other filter elements are being replaced. Pressure drops are monitored with typical 5–10 psi drop (0.3–0.7 bar). Filters are changed out at higher pressure drops; low pressure drops may indicate filter cartridge rupture. Winston et al. (2013) provide additional best practices.

[4] Carbonyl sulfide (COS) can be formed in the following reaction: $H_2S + CO_2 \leftrightarrow H_2O + COS$. The equilibrium constant for the reaction is of the order of magnitude of 10^{-6} at adsorption temperatures but increases to 10^{-4} at regeneration temperatures (Trent et al., 1993). Its concentration in feed gas is normally extremely low.

Figure 11.8 shows a slip stream of dry gas returning to the bed that is being regenerated. (Sales gas is sometimes used instead of a slip stream. The sales gas stream has the advantage of being free of heavier hydrocarbons that can cause coking.) This gas is usually about 10% of gas throughput.

Figure 11.9 shows the inlet and outlet temperature profiles for regeneration using a common 4-h heating step. Regeneration involves heating the bed, removing the water, and cooling. For the first two steps, the regeneration gas is heated to about 450°F–550°F (230°C–290°C) to both heat the bed (and adsorber vessel walls if external insulation is used) and remove adsorbed water from the

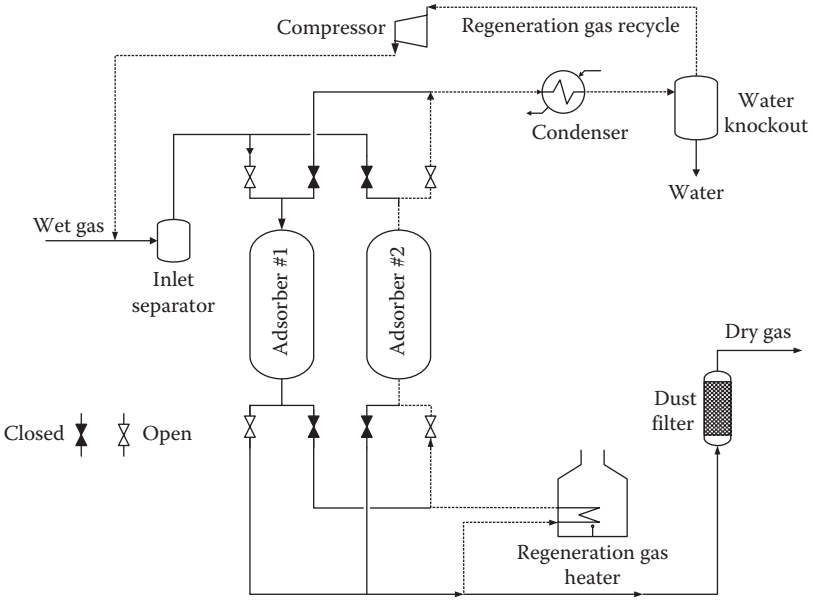


FIGURE 11.8 Schematic of a two-bed adsorption unit. Valving shown is with adsorber 1 in drying cycle and adsorber 2 in regeneration cycle.

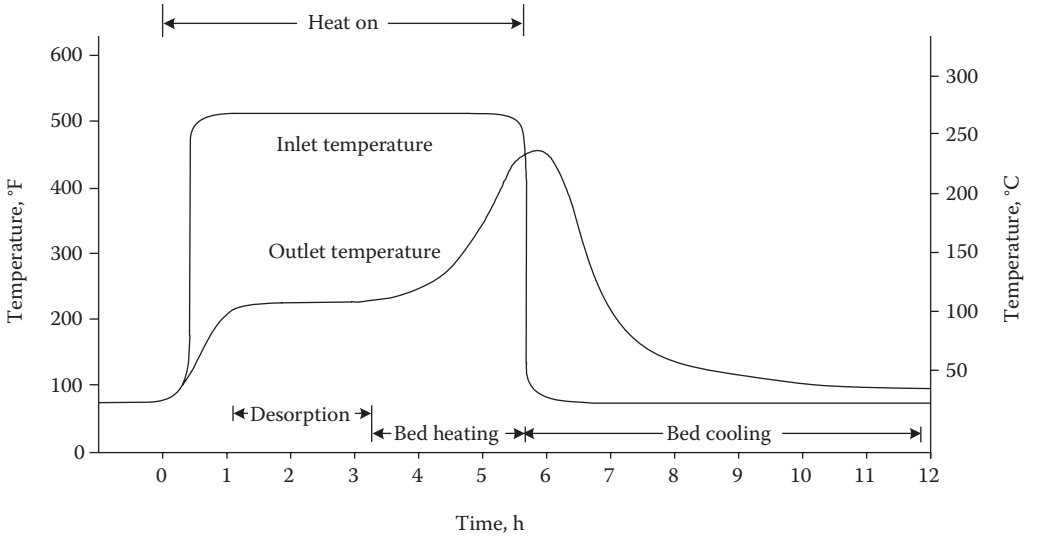


FIGURE 11.9 Qualitative temperature profile in the heating step of a molecular sieve used for dehydration.

adsorbent. If COS formation is a problem, it can be mitigated by lowering regeneration temperature to 400°F–450°F (200°C–230°C) or lower, provided sufficient time for regeneration is available, or by switching to 3A. Regeneration gas enters at the bottom of the bed (reverse of flow during adsorption) to ensure that the lower part of the bed is the driest and that any contaminants trapped in the upper section of the bed stay out of the lower section. The high temperature required makes this step energy intensive and in addition to furnaces, other heat sources (e.g., waste heat from gas turbine exhaust) are used when possible. The hot, wet regeneration gas then goes through a cooler and separator to condense water before being recompressed and mixed with incoming wet feed. To complete the regeneration, unheated regeneration gas passes through the bed to cool it before it is placed in drying service. Gas flow during this step typically is in the direction opposite of drying.

The bed pressure during regeneration is dictated by the regeneration gas pressure. Ideally, it will be near the adsorption pressure to avoid pressure swings in the bed. Pressure changes in the bed can cause bed movement and adsorbent attrition. To avoid attrition problems, the *Engineering Data Book* (2016b) recommends that the bed pressure not be changed more than 50 psi/min (6 kPa/s). As Malino (2004) points out, higher regeneration pressures increase the amounts of water and hydrocarbons that condense at the top of the bed and fall back onto the adsorption bed. Modeling results indicate that refluxing likely occurs into and during the plateau region when the bulk of the water is being removed (Rastelli and Stiltner-Shadden, 2008). Refluxing is a major cause of bed aging, as it leads to adsorbent breakdown and subsequent caking of fines (Rastelli and Stiltner-Shadden, 2008). Condensation at the bed walls can also occur and lead to caking. The caking leads to higher pressure drop and reduced bed capacity. Some manufacturers offer molecular sieves that are more resistant to the attrition caused by refluxing at the top of the bed (Rastelli and Stiltner-Shadden, 2008).

Using a two-step regeneration process provides another alternative to minimizing refluxing and subsequent caking (*Engineering Data Book*, 2016b). Initially, the bed and walls are heated to about 200°F (93°C) using regeneration gas at about 250°F (120°C), the regeneration then proceeds as usual using gas at 450°F–550°F (230°C–290°C). Having the whole bed at higher temperature minimizes water condensation at the top when most of the water is being desorbed.

Table 11.5 lists design parameters that are guidelines for typical molecular sieve dehydrators (Chi and Lee, 1973; Cummings and Chi, 1977; *Engineering Data Book*, 2016b; Kohl and Nielsen, 1997; Lukchis; Petty, 1976; Trent, 2001). Both the *Engineering Data Book* (2016b) and Trent (2001) give extensive details on designing adsorber systems.

The combination of feed rate, pressure drop, and adsorbent crush strength dictates the adsorption bed geometry. To minimize the mass transfer zone[5] length (L_{MTZ}), the bed diameter should be kept

TABLE 11.5
Typical Design Parameters for Molecular Sieve Dehydration Units

Feed Rate	**10–1,500 MMscfd (3–500 Nm³/s)**
Superficial velocity	Approximately 30–40 ft/min (9–12 m/min)
Pressure drop	Approximately 5 psi (35 kPa), not to exceed 10 psi (70 kPa)
Cycle time	4–24 h
Temperatures and pressures	
Adsorption	Temperature: 50°F–115°F (10°C–45°C)
	Pressure: up to 1,500 psig (100 barg)
Regeneration	Temperature: 450°F–550°F (230°C–290°C)
	Pressure: Adsorption pressure or lower

[5] For a discussion on mass transfer zones, see Section 4.5.1.

small. This also reduces the wall thickness of the high-pressure vessels and increases the superficial velocity. It does not affect intraparticle mass transfer, which is the limiting step. Thus, higher velocities can increase the L_{MTZ}. Accurate calculation of the L_{MTZ} is complex. Trent (2004) suggests the following dimensioned equation for estimating the L_{MTZ} of 4 × 8 (1/8 in. [3 mm] diameter) mesh beads:

$$L_{MTZ}(\text{ft}) = 2.5 + 0.025V_S(\text{ft/min}) \tag{11.3a}$$

$$L_{MTZ}(\text{m}) = 0.76 + 1.4V_S(\text{m/h}) \tag{11.3b}$$

where V_S is the superficial gas velocity. For 8 × 12-mesh (1/16 in.) beads, the length is about 70% of the values calculated by Equation 11.3. The *Engineering Data Book* (2016b) suggests the following equation:

$$L_{MTZ}(\text{ft}) = F\left[\frac{V_S(\text{ft/min})}{35}\right]^{0.3} \tag{11.4a}$$

$$L_{MTZ}(\text{m}) = F\left[\frac{V_S(\text{m/h})}{640}\right]^{0.3} \tag{11.4b}$$

where the factor F = 1.70 ft for a 1/8 in. sieve and 0.85 ft for 1/16 in. material (F = 0.62 and 0.26 m for 3 and 1.5 mm adsorbents). Over the typical gas flow ranges, Equation 11.3 gives an L_{MTZ} double that of Equation 11.4.

As noted above, higher velocities increase pressure drop through the bed. This pressure drop has two adverse effects:

- Higher inlet compression discharge pressures to maintain the same outlet pressure
- Increased mechanical load on the adsorbent, which can lead to particle breakdown and a further increase in pressure drop

The adsorbent beds typically have a 6-in. (15 cm) deep layer of inert 1/2 to 1-in. (13–25 mm) diameter alumina or ceramic balls (density of about 80 lb_m/ft^3[1,200 kg/m^3]) resting on a floating screen at the top of the bed. This layer is sometimes on top of another floating screen-supported layer of 1/8 in. (3 mm) diameter beads. These layers help distribute the incoming gas flow but, more importantly, help keep the bed from shifting. The screens float to account for thermal expansion during regeneration.

The bottom of the bed has a similar layering, with the smaller beads on top of the larger ones, which are supported by a fixed screen. An important consideration is proper design of the bottom bed support. The bed support design must account for temperature changes during regeneration and for the static and dynamic loads due to gas flow. In addition to proper design, it is critical that the installation of the bottom support screen be supervised and inspected by a knowledgeable person.

The most common reasons for replacing a bed are loss of adsorbent capacity and unacceptable pressure drop, which usually occur simultaneously. The rate of loss of capacity with time varies considerably, but common rates used for molecular sieves in dehydration service are a 35% capacity loss over a 3- to 5-year period or approximately 4,000 cycles. Typically, a rapid loss occurs in the beginning and a gradual loss thereafter. The adsorbent decays primarily because of carbon and sulfur fouling, and caking caused by instability in the clay binder. These effects occur during bed regeneration. de Bruijn and van Grinsven (2001) provide a complete discussion of these phenomena.

Increased pressure drop is usually caused by breakdown of adsorbent into finer particles and by caking at the top of the bed because of refluxing. Attrition usually occurs with bed pressure changes before and after regeneration. Monitoring the pressure drop is important, as it provides a good

diagnostic to bed health. The *Engineering Data Book* (2016b) recommends a modified form of the Ergun equation to compute pressure drop:

$$\frac{\Delta P}{L}(\text{psi/ft}) = B\mu V_S + C\rho V_S^2 \tag{11.5}$$

where
viscosity, μ, is in centipoises
density, ρ, in lb_m/ft^3
superficial velocity, V_S, in ft/min (multiply psi/ft by 22.62 to obtain kPa/m and divide ft/min by 197 to obtain m/s)

The coefficient values for typical adsorbents are given in Table 11.6.

A number of factors affect bed capacity. For the commonly used 4A molecular sieve, the *Engineering Data Book* (2016b) suggests that the design water content of a molecular sieve when at equilibrium with saturated gas at 75°F (24°C) will be 13 lb_m H_2O/100 lb_m sieve. A new molecular sieve holds about 20 lb_m H_2O/100 lb_m sieve. Two factors affect the design capacity: water content of entering gas and adsorption temperature. Figure 11.10 provides a correction for the capacity as a function of percent relative saturation. Figure 11.11 gives a correction for the decrease in bed capacity at temperatures greater than 75°F (24°C). The effect of unsaturated gas and higher temperature can be computed by

TABLE 11.6
Equation 11.5 Coefficient Values for Typical Adsorbents

Particle Type	*B*	*C*
1/8 in. (3 mm) bead	0.0560	0.0000889
1/8 in. (3 mm) pellets	0.0722	0.000124
1/16 in. (1.5 mm) bead	0.152	0.000136
1/16 in. (1.5 mm) pellets	0.238	0.000210

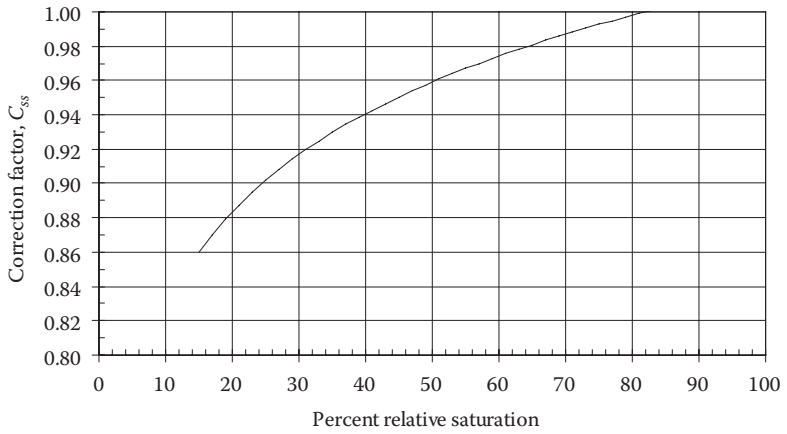


FIGURE 11.10 Molecular-sieve capacity correction for unsaturated inlet gas. (Adapted from *Engineering Data Book*, 2016b, with permission.)

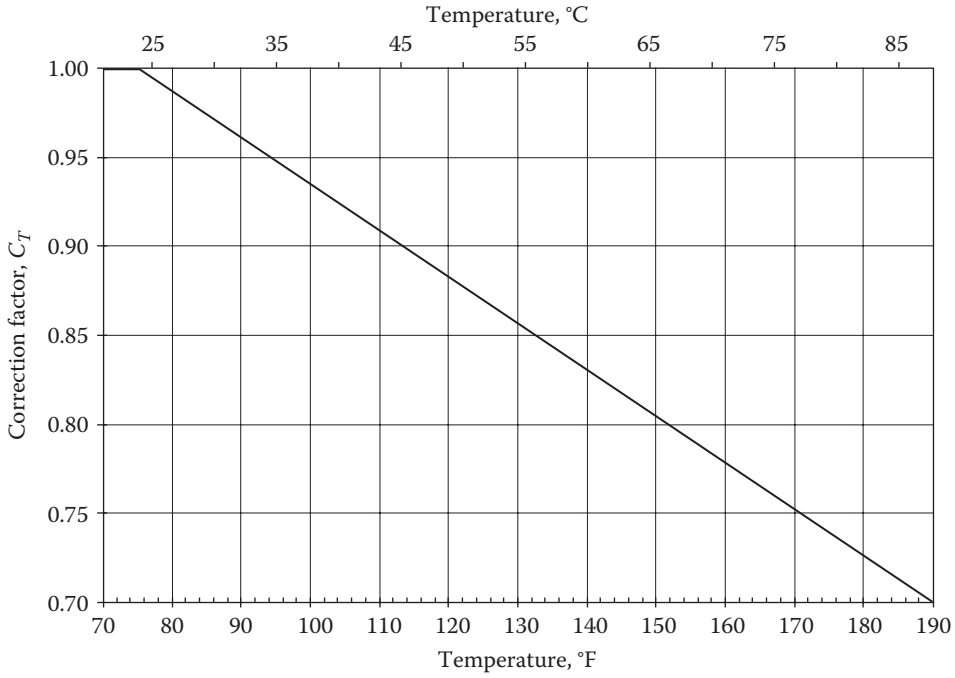


FIGURE 11.11 Correction for decrease in adsorption capacity caused by inlet gas temperature in molecular sieve. (Adapted from *Engineering Data Book*, 2016b, with permission.)

$$C_{SS} = 0.636 + 0.0826 \ln(\text{Sat}) \tag{11.6}$$

and

$$C_T = 1.20 - 0.0026t(°\text{F}) \tag{11.7a}$$

$$C_T = 1.11 - 0.0047t(°\text{C}) \tag{11.7b}$$

where

C_{SS} and C_T are correction factors for subsaturation and temperature, respectively
Sat is the percent of saturation.

Example 11.2

An existing 4 A molecular sieve bed has been processing 80 MMscfd (25 Nm^3/s) on a 12 h cycle with two beds. Exit gas goes to a cryogenic turboexpander section. Gas flow is increased to 100 Mscfd (30 Nm^3/s). Estimate the increased pressure drop and determine whether the bed capacity allows continued operation on a 12 h cycle or the cycle time should be changed.

The gas enters the bed at 120°F (50°C) and 950 psig (65 barg). Water content is 60% of saturation at 120°F (50°C). The molar mass of the gas is 18.5, with a viscosity of 0.014 cP and a compressibility factor of 0.84.

The adsorption bed contains 41,000 lb_m (18,600 kg) of 1/8 in. (3 mm) diameter beads with a bulk density of 44 lb_m/ft^3 (700 kg/m^3). The inside wall diameter of the bed is 7.5 ft (2.3 m). The adsorbent was installed 2 years ago.

Solution

PRESSURE DROP CALCULATION

Determine the height of the adsorption bed. The volume of adsorbent V = mass/adsorbent density = 41,000/44 = 932 ft^3 (26.4 m^3). The cross-sectional area of the bed $A = \pi D^2/4 = \pi(7.5)^2/4 =$ 44.2 ft^2 (4.1 m^2). The bed height then is V/A = 932/44.2 = 21.1 ft (6.43 m).

Gas density, ρ = MW $P/(zRT)$ = 18.5 × (950+14.7)/[0.84 × 10.73 (460+120)] = 3.41 lb$_m$/ft^3 (54.6 kg/m^3).

To obtain superficial velocity, first calculate actual volumetric flow rate, Q, using Equation 1.2:

$$Q = \text{scfm}\left(\frac{14.7}{P_1(\text{psia})}\right)\left(\frac{T_1(^\circ\text{R})}{520}\right)\left(\frac{z_1}{z_R}\right)$$

$$= \frac{100\times10^6}{1{,}440}\left(\frac{14.7}{950+14.7}\right)\left(\frac{460+120}{520}\right)\left(\frac{0.84}{1}\right) = 992\,\text{ft}^3/\text{min}\,(28.1\,\text{m}^3/\text{min})$$

The superficial velocity is then $V_S = Q/A$ = 992/44.2 = 22.4 ft/min (6.8 m/min).

Use of Equation 11.5, $\Delta P/L\,(\text{psi/ft}) = B\mu V_S + C\rho V_S^2$, with B = 0.0560 and C = 0.0000889 gives

$$\frac{\Delta P}{L} = (0.0560)(0.014)(22.4) + (0.000089)(3.41)(22.4)^2 = 0.170\,\text{psi/ft}\,(0.35\,\text{kPa/m}).$$

Total bed pressure drop is 0.170 psi/ft × 21.1 ft = 3.58 psi (0.25 bar), which is in a good operating range.

BED CAPACITY CALCULATION

To determine the capacity, first calculate the capacity per pound of absorbent. The bed has aged, so at 75°F (24°C) the absorbent should hold 13 lb$_m$ water/100 lb$_m$ of sieve, if the entering gas is saturated with water vapor. However, the gas enters at 60% of saturation. With either Figure 11.10 or Equation 11.6, the absorbent holds only 97% of capacity or 12.6 lb$_m$ water/100 lb$_m$ sieve. The temperature effect from Figure 11.11 or Equation 11.7 is to reduce capacity to 88%, so the bed should hold 12.6 × 0.88 = 11.1 lb$_m$ water/100 lb$_m$ sieve in the equilibrium zone.

The length of the MTZ is calculated by either Equation 11.3a or 11.4, but use the former because it is more conservative

$$L_{\text{MTZ}}\,(\text{ft}) = 2.5 + (0.025\times22.4) = 3.1\,\text{ft}\,(0.9\,\text{m})$$

This value represents 15% (3/21) of the bed height. Assume the MTZ holds 50% of the equilibrium loading and remaining 85% of bed contains the equilibrium loading; the bed could hold

$$11.1/100\times41{,}000(0.85+0.15\times0.5) = 4{,}210\,\text{lb}_m\,(1{,}900\,\text{kg})\,\text{of water}.$$

From Figure 11.7, the water content at saturation for a gas at 950 psig (65 barg) and 120°F (50°C) is 100 lb$_m$/MMscf (1.7 g/Nm^3). Essentially, all water into the bed must be removed. The gas enters at 60% of saturation, which is 0.6 × 100 = 60 lb$_m$/MMscf (1.0 g/Nm^3). For a 12 h cycle, the water adsorbed is 60 × 100 × 0.5 = 3,000 lb$_m$ water (1,360 kg). This loading would require 59% of the bed be at equilibrium loading using assumptions made. The bed is slightly oversized but can remain on a 12 h cycle.

The major operating costs of adsorption are the energy required for regeneration and the compression power required to overcome bed pressure drop in adsorption and regeneration. To minimize the heat

load, the adsorption beds are insulated. Insulation may be external or internal. Internal insulation saves energy during bed regeneration because it eliminates heating of the vessel walls and reduces the regeneration time. However, insulation imperfections and cracks may cause wet gas to bypass the adsorbent. Internal insulation also requires a larger diameter pressure vessel, which adds to capital costs.

Regeneration usually takes eight or more hours with 50%–60% of the time involved in heating and driving off water. The balance of time is in cooling down the bed and having about 30 min of standby and switching.

The *Engineering Data Book* (2016b) recommends the following simple and conservative technique for estimating the heat required for regeneration, q.

$$q_W = \left(1{,}800\ \text{Btu/lb}_m\right)\left(\text{lb}_m\ \text{of water on the bed}\right) \tag{11.8a}$$

$$q_W = \left(4{,}200\ \text{kJ/kg}\right)\left(\text{kg of water on the bed}\right) \tag{11.8b}$$

$$q_{si} = \left(\text{lb}_m\ \text{of sieve}\right)\left(0.24\ \text{Btu/lb}_m - °\text{F}\right)\left(t_{rg} - t_1\right) \tag{11.9a}$$

$$q_{si} = \left(\text{kg of sieve}\right)\left(1.0\ \text{kJ/kg K}\right)\left(t_{rg} - t_1\right) \tag{11.9b}$$

$$q_{st} = \left(\text{lb}_m\ \text{of steel}\right)\left(0.12\ \text{Btu/lb}_m - °\text{F}\right)\left(t_{rg} - t_1\right) \tag{11.10a}$$

$$q_{st} = \left(\text{kg steel}\right)\left(0.5\ \text{kJ/kg K}\right)\left(t_{rg} - t_1\right) \tag{11.10b}$$

$$q_{hl} = 0.10\left(q_W + q_{si} + q_{st}\right) \tag{11.11}$$

where

q_W, q_{si}, q_{st}, and q_{hl} represent the heat required to desorb the water, heat the adsorbent, heat the vessel walls, and heat loss to surroundings assuming external insulation, respectively.

t_{rg} is the regeneration temperature of the gas that enters the bed minus 50°F (28°C)

t_1 is the gas temperature during adsorption

t_{rg} accounts for the temperature approach between the heating gas and the final heated bed temperature. The total estimated heat of regeneration is then

$$q = 2.5\left(q_W + q_{si} + q_{st} + q_{hl}\right) = 2.75\left(q_W + q_{si} + q_{st}\right) \tag{11.12}$$

where the factor of 2.5 corrects for the change in temperature difference (in–out) across the bed with time during the regeneration cycle; 40% of the heat is actually transferred to the bed and walls and the rest is lost in the exiting gas. Note that this includes the heat loss in the regeneration gas from the heater to the bed. Regeneration furnaces are usually gas-fired and located away from the process units. Therefore, the hot gas line between the furnace and the adsorption bed can be long. It is important that the pipe insulation be specified based on the regeneration gas heat balance rather than an economic insulation thickness criteria.

Example 11.3

Estimate the heat required to regenerate an adsorption bed that holds 40,000 lb_m (18,100 kg) of 4 A molecular sieve and 4,400 lb_m (2,000 kg) of water. The vessel contains 55,000 lb_m (25,000 kg) of steel, and the regeneration temperature gas is 600°F (315°C) to the bed. The bed adsorbs at 100°F (38°C). Estimate the gas flow rate under the assumption that the C_P for the gas is 0.68 Btu/lb_m-°F (1.7 kJ/kg-K), that 60% of the regeneration time involves heating the bed, and that the bed is on an 8-h cycle. Allow 30 min for standby. Cooling gas is available at 100°F (38°C) and the bed should be cooled to 150°F (65°C) before returning to adsorption service.

Solution

Use Equations 11.8–11.12 to compute the heat load. $t_{rg} = 600 - 50 = 550°F$ (288°C).

Water:

$$q_W = \left(1{,}800\ \text{Btu/lb}_m\right)\left(\text{lb}_m\ \text{of water on the bed}\right) = 1{,}800 \times 4{,}400 = 7{,}920\ \text{MBtu}\ (8.4\ \text{GJ})$$

Sieve:

$$q_{si} = \left(\text{lb}_m\ \text{of sieve}\right)\left(0.24\ \text{Btu/lb}_m\text{-°F}\right)\left(t_{rg} - t_1\right) = 40{,}000 \times 0.24\left(550 - 100\right)$$
$$= 4{,}320\ \text{MBtu}\ (4.6\ \text{GJ})$$

Steel:

$$q_{st} = \left(\text{lb}_m\ \text{of steel}\right)\left(0.12\ \text{Btu/lb}_m\text{-°F}\right)\left(t_{rg} - t_1\right) = 55{,}000 \times 0.12\left(550 - 100\right)$$
$$= 2{,}970\ \text{MBtu}\ (3.1\ \text{GJ})$$

Use Equation 11.12 to obtain the total heat requirement.

$$q = 2.75\left(q_W + q_{si} + q_{st}\right) = 2.75\left(7{,}920 + 4{,}320 + 2{,}970\right) = 41{,}800\ \text{MBtu}\ (44.1\ \text{GJ})$$

REGENERATION GAS FLOW RATE CALCULATION

Time allocated for heating is 60% of 8 h = 4.8 h. Then the gas flow rate is

$$\dot{m} = \frac{q}{\left[C_P \times \text{Time} \times \left(t_{rg} - t_{ad}\right)\right]} = \frac{41{,}800{,}000}{0.68 \times 4.8 \times \left(550 - 100\right)} = 25{,}600\ \text{lb}_m\text{/h}\ (11{,}600\ \text{kg/h})$$

Time remaining for cooling (allowing 30 min of standby) is 7.5 − 4.8 = 2.7 h.

Using the same approach to calculate cooling load yields

$$q_{si} = 40{,}000 \times 0.24\left(550 - 150\right) = 3{,}840\ \text{MBtu}\ (4.0\ \text{GJ})$$

Steel:

$$q_{st} = 55{,}000 \times 0.12\left(550 - 150\right) = 2{,}640\ \text{MBtu}\ (2.8\ \text{GJ})$$

$$q = 2.5\left(q_{si} + q_{st}\right) = 2.5(3{,}840{,}000 + 2{,}640{,}000) = 16{,}200\ \text{MBtu}\ (17.0\ \text{GJ})$$

$$\dot{m} = \frac{q}{\left[C_P \times \text{Time} \times \left(\Delta t\right)\right]} = \frac{16{,}200{,}000}{\left[0.68 \times 2.7 \times \left(550 - 150\right)\right]} = 22{,}100\ \text{lb}_m\text{/h}\ (10{,}000\ \text{kg/h})$$

Note that the 1.10 factor in Equation 11.12 is not used as heat loss aids cooling. Since the calculated cooling gas rate is lower than the required heating gas rate, a typical design would cool the gas at the same rate for slightly less than 2.7 h or achieve a cooler bed temperature before returning the bed to adsorption service.

The regeneration gas must be of good quality. If it contains heavy hydrocarbons or lube oil those components are likely to crack at regeneration heater temperature and deposit coke. This coke can both block active sites in the molecular sieve and potentially cause hot spots in the regeneration gas heater tubes.

Occasionally, the adsorbent beds produce increased fines in the exit gas. The fines usually result from attrition of the molecular sieve. Bottom support balls or molecular sieve beads in the downstream dust filter may indicate a failure of the mechanical supports at the bottom of the bed (Richman, P., Private Communication, 2005).

The most common bed configuration is the two-bed system shown in Figure 11.8. Trent (2004) notes that some three-bed systems are set up such that two beds are run in series with the downstream bed used as a guard bed. Due to the higher pressure drop with two beds in series this arrangement is typically only used where the inlet water content and flow vary significantly.

Another three-bed arrangement has one bed adsorbing and two being regenerated. The primary advantage of this arrangement is that regeneration gas heating requirements are reduced. This three bed arrangement transfers heat from a cooling bed to a warming bed. Trent (2004) suggests the best approach for four-bed systems is to run two beds in parallel. For a given gas throughput, the pressure drop is reduced to one-eighth of the two-bed system. Finally, some older plants may have required multiple beds because the units originally used activated alumina. Activated alumina has a longer MTZ than molecular sieve and a guard bed was required to maximize bed loading.

11.3.2.4 Other Factors that Affect the Adsorption Process

Trace amounts of oxygen affect bed life and performance in a variety of ways. At the normal regeneration gas temperature of 600°F (315°C) for molecular sieves, 2 mol of oxygen react with methane to form 2 mol of water and 1 mol of CO_2. This reaction is exothermic and high concentrations of oxygen in the gas can lead to temperatures above the design temperature of the molecular sieve vessel. Therefore, when oxygen is present, the temperature of the beds during regeneration must be monitored for safety reasons. Clark et al. (1975) found that oxygen undergoes partial oxidation reactions with heavier hydrocarbons, which are adsorbed in the binder to form alcohols and carboxylic acids that ultimately turn to water and CO_2. If H_2S is present, it can undergo oxidation to elemental sulfur, sulfur dioxide, and water. Trent (2001) points out that oxygen concentrations greater than 20 ppmv also generate olefins that become coke in the bed. These reactions reduce molecular sieve capacity by forming solid deposits and by causing incomplete removal of water during regeneration because the partial pressure of water is higher (see Figure 11.7). To avoid the above reactions as well as COS formation, regeneration temperatures are lowered to the 300°F–375°F (150°C–160°C) range. However, this range increases the required regeneration time and the amount of regeneration gas used, which can increase compression cost. A paper by Schendel (2015) details the testing of different types of molecular sieve and regeneration temperatures when drying gas containing oxygen.

Another means of dealing with low concentrations of oxygen in the gas being dehydrated is to use a closed-loop regeneration system which is essentially oxygen free. These special designs should only be undertaken with the aid of a molecular sieve manufacturer or an engineering contractor with experience on these systems.

Ensuring that the beds are protected from entrained water and hydrocarbons is critical. Even trace amounts of entrained water load the bed quickly and increase the regeneration heat load. If the gas comes to the dehydration unit fully saturated, which is often the case, cooling the gas and removing the condensed water before the gas enters the bed lowers water loading and potentially increases the drying-cycle time. Trent (2004) notes that cooling a water-saturated gas by 20°F (10°C) drops the saturated gas phase water content by 50%.

Methanol is a commonly used hydrate inhibitor (see Chapter 8) coming in from the field and may be carried over from amine treating providing an additional load on the mole sieve. Information on the removal of methanol can be found in Chapter 14.

Example 11.4

Gas, with a molar mass of 23, leaves an amine treater water saturated at 100°F (38°C) at 1,000 psia (70 bara) and enters a molecular sieve dehydrator. How much would the water load on the adsorption bed be decreased if the gas were cooled to 80°F (27°C) before entering the adsorber? Assume that none of the condensed water enters the adsorption bed.

Solution

Figure 11.1a shows the water content of gas at 1,000 psia (70 bara) and at 100°F (38°C) and 80°F (27°C) to be 64 and 33 lb_m/MMscf (1.1 and 0.56 g/Nm^3), respectively. The molar mass and temperature are low enough that the gravity correction is only 1% and can be neglected. The reduction in water content is (64–33)/64 = 0.48. Thus, if all condensed water is removed, a 48% reduction of the water load would occur on the adsorption bed. Recall from Figure 11.11 or Equation 11.7 that the cooler gas also increases the bed capacity as the temperature correction factor increases from 0.94 to 0.99. Thus, cooling the gas by 20°F (11°C) would essentially double the adsorption time.

11.3.3 Nonregenerable Desiccant Processes

In some situations, such as remote gas wells, use of a consumable salt desiccant, usually $CaCl_2$, may be economically feasible but can be unattractive compared with a regenerative process in a plant situation. The system can reduce the water content to 20 ppmv. Typical salt capacities are 0.3 lb_m $CaCl_2$ per lb_m H_2O. The *Engineering Data Book* (2016b) provides a brief description of a vertical bed contactor, initially charged with $CaCl_2$ pellets. The moist stream enters near the bottom of the pellet bed. As the salt removes the water, it first forms various solid salt hydrates and then becomes a brine slurry which is drained from the bottom. The hydrocarbon stream leaves in equilibrium with dry salt. There are often multiple beds in series so that when all salt is expended in the first bed it can be removed from service for recharging without generating a wet product. This process is now less used because of disposal problems, but at least one installation used this approach to dehydrate a high pressure CO_2 stream before delivery to a pipeline. The commercial product selected is said to overcome some of the handling issues with older formulations.

Beds using $CaCl_2$ are sometimes used at small remote compressor stations to dry gas or instrument air when power is unavailable or unreliable.

11.3.4 Membrane Processes

Membranes offer an option for cases in which drying is required to meet pipeline specifications (Bikin et al., 2003). Their modular nature, light weight, large turndown ratio, and low maintenance make them competitive with glycol units in some situations.

Feed pretreatment is a critical component of a membrane process (see Chapter 4). The inlet gas must be free of solids and droplets larger than 3 μm. Inlet gas temperature should be at least 20°F (10°C) above the dew point of water to avoid condensation in the membrane.

Units operate at pressures up to 1,000 psig (70 barg) with feed gases containing 500–2,000 ppmv of water. They produce a product gas stream of 20–100 ppmv and require minimal pressure drop. The low-pressure (7–60 psig (0.5–4 barg)) permeate gas volume is about 3%–5% of the feed gas volume. This gas must be recompressed or used in a low-pressure system such as fuel gas.

Smith (2004) suggests that membranes used for natural gas dehydration are economically viable only when dehydration is combined with acid gas removal. On the basis of commercial units installed and several studies (Bikin et al., 2003; Binci et al., undated), membranes are economically attractive for dehydration of gas when flow rates are less than 10 MMscfd (0.3×10^6 Nm^3/d). Binci et al. (undated) claim that membrane units are competitive with TEG dehydrators on offshore platforms at flows below 56 MMscfd (1.5×10^6 Nm^3/d). The reliability and simplicity of membranes may make

them attractive for offshore and remote-site applications, provided the low-pressure permeate gas is used effectively and extensive pretreatment is not required. An added benefit compared with TEG units is the absence of BTEX emissions.

11.3.5 Other Processes

Two relatively new processes are worth mentioning. The first process is a refrigeration process that mixes methanol with the gas and cools the gas to very low temperatures. The water–methanol mixture drops out and the methanol is recovered in a stripper column. The process has several major advantages:

- It can obtain dew points in the −100°F to −150°F (−70°C to −100°C) range.
- It requires no heat input other than to the methanol regenerator.
- It requires no venting of hydrocarbon-containing vapors.

However, it requires external refrigeration to cool the gas, and minimal methanol losses occur in the stripper. The *Engineering Data Book* (2016b) provides more details.

The second process is the Twister technology, which is discussed in Chapter 12. It has been considered attractive in offshore applications (Wilson and Yuvancic, 2004) for dehydration because of its simplicity (no moving parts) along with its small size and weight. Brouwer et al. (2004) discuss the successful implementation on an offshore platform. Some offshore operations exceed 2,000 psi (140 bar), so recompression is not needed with the unit where overall pressure drop is 20%–30%.

11.3.6 Comparison of Dehydration Processes

A number of factors should be considered in the evaluation of a dehydration process or combination of processes. If the gas must be dried for cryogenic liquids recovery, molecular sieve is the only long-term, proven technology available. It has the added advantage that it can remove CO_2 at the same time. If CO_2 is being simultaneously removed, because water displaces CO_2, the bed must be switched before the CO_2 breaks through, which is well before water breakthrough (see Section 10.4 for discussion of CO_2 adsorption). Enhanced TEG regeneration systems may begin to compete with molecular sieve. Skiff et al. (2003) claim to have obtained less than 0.1 ppmv water by use of the Drizo™ process with a modified regeneration system that uses about 70% of the energy required for molecular sieves.

High inlet water vapor concentrations make molecular sieve dehydration expensive because of the energy consumption in regeneration. As can be seen from Example 11.3, over 50% of the overall energy required is related to the amount of water adsorbed. In addition to the previously mentioned cooling the gas and removing condensed water, there are two approaches used to reduce the amount of water going to the molecular sieve bed.

The first option is to use another dehydration process (e.g., TEG dehydration) in front of the molecular sieve bed. Currence et al. (2014) evaluate this option on both a CAPEX and OPEX basis. The second option is to have combined beds with silica gel or activated alumina on top of the molecular sieve. The bulk of the water is removed with the first adsorbent, and the molecular sieve removes the remaining water. This configuration reduces the overall energy required for regeneration by taking advantage of the higher water capacity of silica gel or activated alumina. The higher capacity allows the use of a smaller adsorbent bed and vessel which lowers regeneration energy required.

If dehydration is required only to avoid free-water formation, hydrate formation, or to meet the pipeline specification of 4–7 lb_m/MMscf (50–100 mg/Nm^3), any of the above-mentioned processes may be viable. Traditionally, glycol dehydration has been the process of choice. System constraints dictate which technology is the best to use. Smith (2004) and Huffmaster (2008) provide an overview of natural gas dehydration technology, with an emphasis on glycol dehydration.

When considering susceptibility to inlet feed contamination, replacing a solvent is much easier and cheaper than changing out an adsorbent bed. However, prevention of contamination by use of

properly designed inlet scrubbers and coalescing filters, if required, is the best solution to avoid feed contamination problems. In a conventional gas plant, where inlet feed fluctuations are handled in inlet receiving, feed contamination is generally limited to possible carryover from the sweetening unit. However, in field dehydration, the possibility exists of produced saline water, solids, oil, and well-treating chemicals entering the dehydrator. Wieninger (1991) discusses how these components detrimentally affect glycol dehydrators.

11.4 SAFETY AND ENVIRONMENTAL CONSIDERATIONS

Dehydration processes require few safety considerations outside of having high-temperature and high-pressure operations. Probably the most unique safety consideration is when bed adsorbents are being changed. The bed must be thoroughly purged, preferably with nitrogen, to remove adsorbed hydrocarbons before the adsorbent is dumped. A potential exists for hydrocarbons on the adsorbent to ignite when exposed to air because the adsorbent heats as it adsorbs moisture from the air. Either a highly trained company expert or an adsorbent company representative should be present to ensure safe dumping and filling operations. The dumping process produces dust, and operators should wear protective clothing and dust masks.

A major environmental concern in dehydration with glycol solutions is BTEX emissions. Chapter 14 discusses this issue in more detail. Disposal of spent $CaCl_2$ brine must be in accordance with local environmental regulations. Spent adsorbents, if properly regenerated, may be discarded into normal landfills. EG is toxic to humans and must be handled properly.

DISCUSSION QUESTIONS

1. Why is there a correction for factor brine content when using Figure 11.1a?
2. What are the common ways to report water content in gases and liquids? Why are some more convenient for gases than liquids?
3. There are a range of decomposition temperatures given for the decomposition of TEG. What are the important factors in deciding the bottoms temperature for the TEG regenerator?
4. Glycol dehydration units are used in field operations and in plant operations. Which type of service is more prone to operational problems? Explain your answer.
5. Why is a flash tank required in a glycol dehydrator?
6. Figure 11.2 shows steam or hot oil as the heat source for the regenerator reboiler. What other way could the reboiler be heated? Which is the most likely heat source of heating for a field unit?
7. Compare qualitatively the energy costs for adsorption to those of TEG absorption. Which are higher and why?
8. What causes refluxing of water in an adsorption bed being regenerated and why might it be important?
9. List at least three potential reasons for adsorption bed capacity decreasing over time.
10. Explain why the slopes in Figures 11.10 and 11.11 are in opposite directions (one increasing and one decreasing).
11. Why is oxygen a potential problem in TEG and molecular sieve dehydration units?

EXERCISES

11.1 A gas contract specifies that the water content must be 4 lb_m/MMscf or lower. What is this specification in mg/Nm^3, ppmv, and ppmw? Assume the molar mass of the gas is 18.

11.2 Estimate the water content of a natural gas (molar mass of 18) at 1,000 psia (69 bara) and 100°F (38°C) by using Figure 11.1a and by using Equation 11.2. The vapor pressure of water at 100°F is 0.95 psia.

11.3 Determine the correction needed for molar mass of the gas in Exercise 11.2 using Figure 11.1b. What is the additional correction needed if the gas is in contact with produced water containing 2% by weight brine?

11.4 A field TEG unit is required to produce a gas (molar mass of 22) that will not condense water at 40°F and 500 psia (4°C and 34 bara). Gas to the glycol unit is water saturated at 110°F (43°C) and 300 psia (21 bara) and the flow rate is 80 MMscfd (89×10^3 Nm^3/h).

a. Using a TEG rate of 3 gal/lb_m (0.025 m^3/kg) of water removed, what will be the minimum glycol circulation rate in gpm (m^3/h)?

b. The TEG unit has a regeneration duty equal to the heat required to vaporize the removed water with an overall efficiency of 33%. Assume a TEG regeneration temperature of 400°F (204°C). Fuel costs are $5.00 per MMBtu ($4.75/GJ). Assume heat of vaporization for water is 1165 Btu/lb (2.707 kJ/g).
Compute the daily heater fuel energy cost.

11.5 A two-bed field molecular sieve system is used to dry a gas (molar mass of 22) to a dew point of 40°F and 500 psia (4°C and 34 bara). Gas to the unit is water saturated at 110°F (43°C) and 300 psia (21 bara) and the flow rate is 80 MMscfd (89×103 Nm^3/h). The loading averages 10% (by weight) of water on each adsorbent bed, the superficial velocity in the adsorbent vessel is 40 ft/min (0.20 m/s). The dehydrator uses an adsorption cycle time of 8 h, and heats and cools in 4 h each.

a. What mass of adsorbent is needed to remove the water?

b. Assuming ideal gas behavior, what are the dimensions of the adsorbent bed?
For the adsorbent system, assume the vessel wall thickness is 2″ (50 mm) and uses steel with a density of 500 lb_m/ft^3 (6.4 kg/m^3). The heat capacity of the steel is 0.12 Btu/lb_m-°F (0.5 kJ/kg-K). Ignore the vessel heads but include 5 ft (1.5 m) of extra shell for bed supports and screens. Ignore heat losses to the surroundings and assume the heat of adsorption is equal to the heat of vaporization of water (see Appendix B[1]).

c. What is the required regeneration duty to heat the bed to 450°F (230°C)?
Assume the regeneration gas heater has an efficiency of 75%.

d. Compute the daily energy cost for both heater fuel and compression (see Chapter 9 for compression). The adsorbent system has a pressure drop of 15 psi (1 bar). Utility costs are $0.04 per kWh for the compressor motor and $5.00 per MMBtu ($4.75/GJ) for fuel gas.

REFERENCES

Afzal, W., et al., Impact of sulfur species on glycol dehydration (GPA 992-3): Solubility study of certain sulfur species in glycol aqueous solutions experimental vapor-liquid equilibrium data for (COS/H_2S/MEG/H2O) and (COS/H_2S/TEG/H_2O) systems, Research Report RR-204, Gas Processors Association, Tulsa, OK, 2008.

Bikin, B., et al., Novel composite membranes and process for natural gas upgrading, Annual Report to Department of Energy, DE-FC26–99FT40497, 2003. www.osti.gov/servlets/purl/823967 (Retrieved April 2019).

Binci, F., et al., Natural gas dehydration in offshore rigs. Comparison between traditional glycol plants and innovative membrane systems, undated. www.researchgate.net/publication/266585508_Natural_gas_dehydration_in_offshore_rigs_comparison_between_traditional_glycol_plants_and_innovative_membrane_systems (Retrieved April 2019).

Blachman, M., and McHugh, T., Sour gas dehydration technology and alternatives, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2000.

Brouwer, J.M., et al., Supersonic gas conditioning first commercial offshore experience, *Eighty-Third Annual Gas Processors Association Convention*, Tulsa, OK, 2004.

[1] See Appendix B on publisher website: www.crcpress.com/Fundamentals-of-Natural-Gas-Processing-Third-Edition/Kidnay-Parrish-McCartney/p/book/9781138612792.

Chi, C.W., and Lee, H., Natural gas purification by 5A molecular sieves and its design method, *AIChE Sym. Ser., 69*(134), 95, 1973.

Clark, K.R., et al., Molecular sieve treating of natural gas containing oxygen, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 1975.

Clinton, P., et al., A review of TEG-water equilibrium data and its effect on the design of glycol dehydration units, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2008, p. 393.

Cummings, W., and Chi, C.W., Natural gas purification with molecular sieves, *Canadian Chemical Engineering Conference*, Calgary, Alberta, Canada, 1977.

Currence, K., et al., Dehydration systems for natural gas, *Laurance Reid Gas Conditioning Conference*, Norman, OK, 2014.

Davis, P.M., et al., The impact of sulfur species on glycol dehydration: A study of the solubility of certain gases and gas mixtures in glycol solutions at elevated pressures and temperatures, Research Report RR-183, Gas Processors Association, Tulsa, OK, 2002.

de Bruijn, J.N.H., and van Grinsven, P.F.A., Optimising the on stream time of a mol sieve dehydration unit, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2001.

Dow Chemical Company, Triethylene glycol, 2007. https://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_0952/0901b80380952386.pdf?filepath=ethyleneglycol/pdfs/noreg/612-00004.pdf&fromPage=GetDoc (Retrieved April 2019).

Engineering Data Book, Section 2, Product specifications, GPSA Midstream Suppliers, Tulsa, OK, 2016a.

Engineering Data Book, Section 20, Dehydration, GPSA Midstream Suppliers, Tulsa, OK, 2016b.

Hernandez-Valencia, V.N., et al., Design glycol units for maximum efficiency, *Seventy-First Annual Convention Gas Processors Association*, Tulsa, OK, 1992.

Hilsenrath, J., et al., Bureau of standards circular No. 564: Tables of thermal properties of gases, 1955. archive.org/details/circularofbureau564hils (Retrieved April 2019).

Horstmann, S., et al., Solubility of non-aromatic hydrocarbons in TEG solutions, Research Report RR-214, Gas Processors Association, Tulsa, OK, 2011.

Huffmaster, M., Gas dehydration fundamentals: Part 1: Introduction to dehydration, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2008, p. 3.

Kohl, A., and Nielsen, R., *Gas Purification*, 5th edn. Gulf Publishing, Houston, TX, 1997.

Lemmon, E.W., et al., Thermophysical properties of fluid systems, *NIST Chemistry WebBook, NIST Standard Reference Database Number 69,* Linstrom, P.J. and W.G. Mallard (eds.), National Institute of Standards and Technology, Gaithersburg, MD, 2017. http://webbook.nist.gov (Retrieved April 2019).

Lukchis, G.M., Adsorption systems, Part I: Design by mass transfer zone concept, Part II: Equipment design, Part III: Adsorbent regeneration, UOP Brochure XF–04A.

Malino, H.M., Fundamentals of adsorptive dehydration, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2004, p. 61.

Mamrosh, D., and Fisher, K., Solubility of H_2S and CO_2 in EG and TEG, Research Report RR-209, Gas Processors Association, Tulsa, OK, 2012.

Marriott, R.A., et al., The impact of sulfur species on glycol dehydration: A study of the solubility of certain gases and gas mixtures in glycol solutions at elevated pressures and temperatures, Research Report RR-189, Gas Processors Association, Tulsa, OK, 2005.

Masoudi, R., et al., Experimental measurement and thermodynamic modeling of clathrate hydrate equilibria and salt solubility in aqueous ethylene glycol and electrolyte solutions, *Fluid Phase Equil., 219*, 157, 2004.

Ng, H.-J., et al., Water content of natural gas systems containing acid gas, Research Report RR-174, Gas Processors Association, Tulsa, OK, 2001.

Parrish, W.R., Thermodynamic inhibitors in brines, Final Report, DeepStar CTR 4210, DeepStar.org, 2000.

Parrish, W.R., et al., Phase behavior of the triethylene glycol-water system and dehydration/regeneration design for extremely low dew point requirements, *Proceedings of the Sixty-Fifth Annual Convention Gas Processors Association*, Tulsa, OK, 1986, p. 202.

Petty, L.E., Practical aspects of molecular sieve unit design, *Proceedings of the Fifty-Fifth Annual Convention Gas Processors Association*, Tulsa, OK, 1976, p. 10.

Prausnitz, J.M., et al., *Molecular Thermodynamics of Fluid-Phase Equilibria*, Prentice-Hall Publishers, Englewood Cliffs, NJ, 1999.

Rastelli, H., and Stiltner-Shadden, J., Use of modeling to optimize severe service natural gas dehydrators, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2008, p. 417.

Schendel, R., Plant experience -molecular sieve dehydration of gas containing oxygen, *Laurance Reid Gas Conditioning Conference*, Norman, OK, 2015.

Sheilan, M., Gas dehydration fundamentals, Part 3: TEG unit operations, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2016, p. 95.

Skiff, T., et al., Drizo unit competes with solid bed desiccant hydration, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2003, p. 213.

Smith, J.M., et al., *Introduction to Chemical Engineering Thermodynamics*, 8th edn. McGraw-Hill Higher Education, New York, 2018.

Smith, R.S., Fundamentals of gas dehydration inhibition/absorption section, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2004.

Smith, R.S., and Humphrey, S.E., High purity glycol design parameters and operating experience, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 1995, p. 142.

Trent, R.E., Dehydration with molecular sieves, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2001.

Trent, R.E., Dehydration with molecular sieves, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2004, p. 75.

Trent, R.E., et al., The practical application of special molecular sieves to minimize the formation of carbonyl sulfide during natural gas dehydration, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 1993, p. 239.

Trimble, H.M., Solubilities of salts in ethylene glycol and in its mixtures with water, *Ind. Eng. Chem., 23*, 165, 1931.

Wallace, C.B., Dehydration of supercritical CO_2, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 1985.

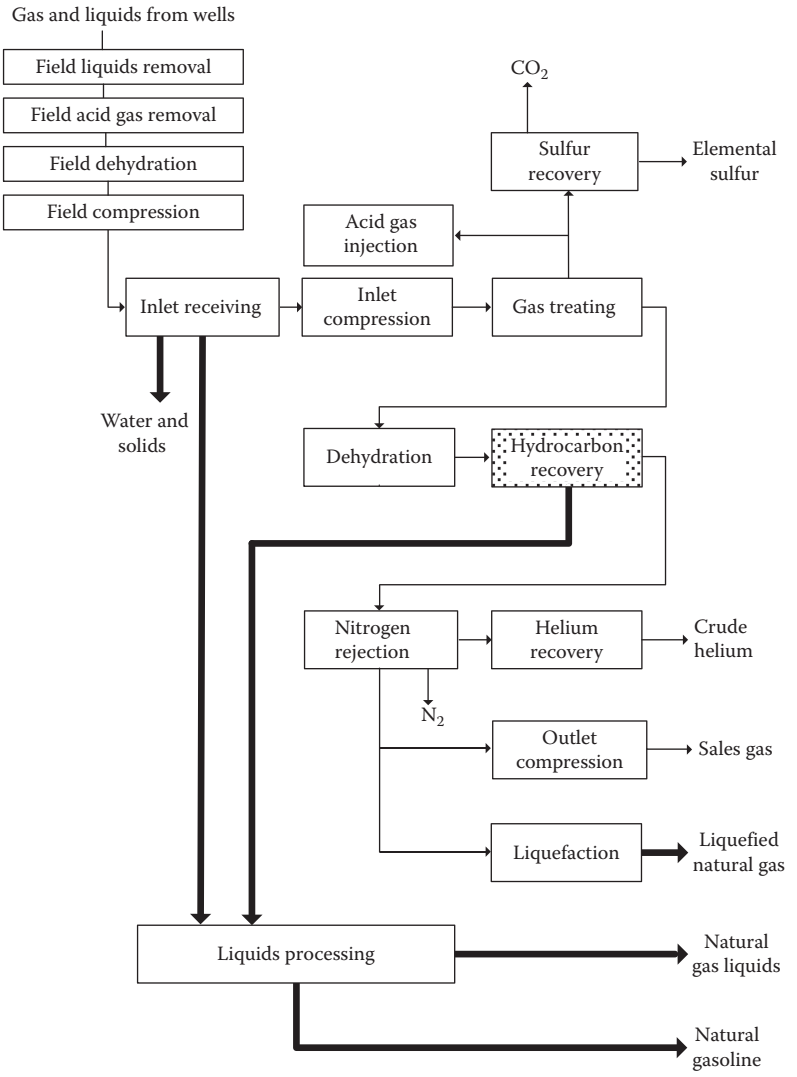
Wichert, E., and Wichert, C.G., New charts estimate acid gas solubility in TEG, *Hydroc. Proc., 83*(1), 47, 2004.

Wieninger, P., Operating glycol dehydration systems, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 1991, p. 23.

Wilson, J.L., and Yuvancic, J., Process selection for dehydrating Gulf of Mexico offshore platform gas, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2004.

Winston, K., et al., Fundamentals of separation filtration & activated carbon, *Laurance Reid Gas Conditioning Conference*, Norman, OK, 2013.

12 Hydrocarbon Recovery



12.1 INTRODUCTION

Pipeline-quality natural gas specifications (see Chapter 6) include limits on acid gases, water content, and higher heating value, which is typically in the range of 950–1150 Btu/scf (35.4–42.8 MJ/Nm^3) (*Engineering Data Book*, 2016a; NGC+ Interchangeability Work Group, 2005). In addition, many pipeline tariffs[1] include hydrocarbon dew point or cricondentherm temperature

[1] Tariffs are documents filed with regulatory authorities that define the conditions for the transportation of gas, including gas specifications.

(defined in Section 12.1.1) specifications. In the United States, specifications are set by negotiation between the processor and the purchaser. In some countries, exact limits are set by national standards.

The previous two chapters addressed acid gas and water content. Nitrogen, a diluent that lowers heating value, may require removal; Chapter 13 discusses these removal processes. This chapter considers processes that remove C_2^+ hydrocarbons. They affect both heating value and dew point. There are fundamentally two motivations for removing C_2^+ hydrocarbons from natural gas in the gas plant:

- To generate revenue by selling higher value natural gas liquids (NGLs)
- To condition the gas for sale or use as fuel

This chapter discusses hydrocarbon recovery methods to both lower the heating value and/or create NGL liquid hydrocarbon products. Of all the activities associated with gas processing, liquids recovery often provides the major income for gas processors. In the early years of gas processing, the sole purpose was recovering liquids. The residue gas was commonly flared. Gas became a valuable product only after the gas pipeline infrastructure was built.

Hydrocarbon recovery is sometimes required in field operations for fuel conditioning or to prevent liquid formation in gathering lines (dew point control). As noted in Chapter 8, booster station compressor fuel may be raw gas taken directly from the gathering pipeline. However, raw gas is usually too rich, and simple systems are used to lower the heating value (i.e., condition the fuel) by removing heavier hydrocarbons.

Dew point control is necessary when liquid formation reduces gas throughput, causes excessive slugging, and/or interferes with gas metering. Condensation can be a problem for offshore production, where several operators share a common gas line to shore. These lines may operate at 1,800 psig (125 barg) or higher and are at seafloor temperatures of 40°F (4°C). Dew point control may also be necessary if a downstream pressure drop cools the gas enough to cause liquid condensation.

After a brief discussion of retrograde condensation, this chapter discusses some common process elements used in hydrocarbon recovery, and then describes some common processes that utilize these elements. Many process variations are available, and this chapter illustrates only a few simple process configurations. Regardless of the process employed, expenditure of energy is required to condense and separate a portion of the inlet gas as a liquid NGL product. Also included are brief descriptions of some newer technologies.

12.1.1 Retrograde Condensation

One reason for dew point control is the fact that rich natural gas mixtures containing heavier hydrocarbons exhibit unintuitive behavior called retrograde condensation. Figure 12.1 shows the pressure–temperature relationship for a typical natural gas mixture that contains 85 mol% methane, 10 mol% ethane, and 5 mol% of C_3^+ with trace components up to heptane. The phase envelope (solid line) is the bubble point–dew point line of the mixture. At any temperature and pressure combination outside the envelope, the mixture is single phase. At temperatures and pressures inside the envelope, two phases exist. The dashed curve represents the vapor-phase line at 95% quality (i.e., 95% vapor).

Three points on the envelope are important:

- Point A: The cricondentherm, which is the maximum temperature at which two phases can exist
- Point B: The cricondenbar, which is the maximum pressure at which two phases can exist
- Point C: The critical point, which is the temperature and pressure where the liquid and vapor phases have the same concentration

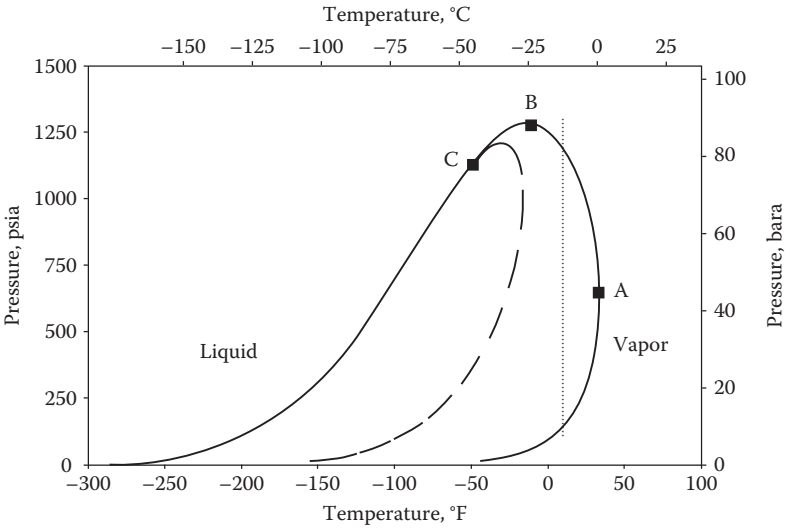


FIGURE 12.1 Pressure–temperature diagram for a natural gas that contains predominately methane, with trace components up to heptane. The dashed curve represents the vapor-phase line at 95% quality.[2] Points A, B, and C denote the cricondentherm, cricondenbar, and critical point of the mixture, respectively.

The retrograde condensation effect can be seen by following the vertical dotted line in Figure 12.1. For the mixture at the temperature and pressure at the top of the line, a single phase exists. Dropping the pressure causes a liquid phase to form (retrograde condensation), and two phases exist until the pressure is below the envelope. The dotted-line path is similar to what can happen in a pipeline at constant temperature because of line pressure drop.

The dashed curve inside the envelope denotes the pressure and temperature of the mixture at 95 mol% vapor. Removing the 5% liquid would create a gas mixture with a narrower envelope bound by the dashed curve. This curve shows the dramatic difference in the phase behavior of the new gas mixture if only the 5% condensed liquid is removed from the raw gas. The cricondentherm of this mixture is approximately 50°F (30°C) lower than the original mixture, and for this mixture condensation does not occur at typical pipeline temperatures.

The cricondentherm of a mixture strongly depends on the presence of the heavy components. The cricondentherm increases with increased mixture molar mass. Concentration of the heavy components present is relatively less important than their molar mass. A mixture that contains methane and 10 mol% propane has a cricondentherm comparable to a methane–heptane mixture with only 0.06 mol% heptane.

12.2 PROCESS COMPONENTS

The process components involved in hydrocarbon recovery vary, depending upon the desired products and gas volume being processed as well as inlet composition and pressure. Not all components listed here will be found in all plants, and different combinations of components provide the same results. Factors that dictate the optimum process configuration include inlet compositions, temperatures, and pressures.

12.2.1 Refrigeration System

A refrigeration system plays a major role in many hydrocarbon recovery processes, as it is used to cool the gas stream to recover a significant amount of C_2^+ and to lower gas temperatures as the gas

[2] Quality is the percentage vapor in a vapor–liquid mixture.

goes into other stages of hydrocarbon recovery. It may be the only source of refrigeration when inlet pressure is low. Vapor compression refrigeration using propane as the working fluid is the most common in gas plants and is discussed here. (LNG facilities also use nitrogen, ethane, or ethylene, as well as hydrocarbon mixtures as refrigerants. See Chapter 18 for details.) The basic refrigeration cycle is discussed first and is then followed by a look at process variations. The *Engineering Data Book* (2016c) provides valuable design guidelines that are not repeated here.

12.2.1.1 Basic Propane Refrigeration Process

As described in any basic thermodynamics book (e.g., Smith et al., 2018), the refrigeration cycle consists of four steps that are depicted on the pressure–enthalpy chart in Figure 12.2:

1. Compression of refrigerant vapor from point A to point B, which is a pressure well above its vapor pressure (for this illustration, the compression is assumed to start with saturated vapor).
2. Condensation to point C by heat exchange with a cooling fluid, usually air or water.
3. Expansion to a lower pressure through a valve—Joule–Thomson (J–T) expansion—to cool the refrigerant to point D.
4. Heat exchange with the fluid to be cooled by evaporation of the refrigerant back to point A.

Figure 12.3 shows the flow diagram for a propane refrigeration cycle, with typical operating conditions. Each of the steps is described below.

Compression step (point A to point B in Figure 12.2): Cycle analysis begins with propane vapor entering the compressor as a vapor at 14.5 psia (1 bara) and approximately −40°F (−40°C), where it is compressed to 250 psia (17 bara). The power required and compressor discharge temperature depend upon compressor efficiency (see Chapter 9 for details).

The work of compression is simply

$$w_S = \frac{(h_B - h_A)}{\eta_{IS}}, \tag{12.1}$$

where η_{IS} is the isentropic efficiency of the compressor (see Chapter 9) and w_s is the work per unit mass (or mole). Taking into account compressor nonideality, the actual enthalpy at the end of the compression is

$$h_{B'} = h_A + w_S. \tag{12.2}$$

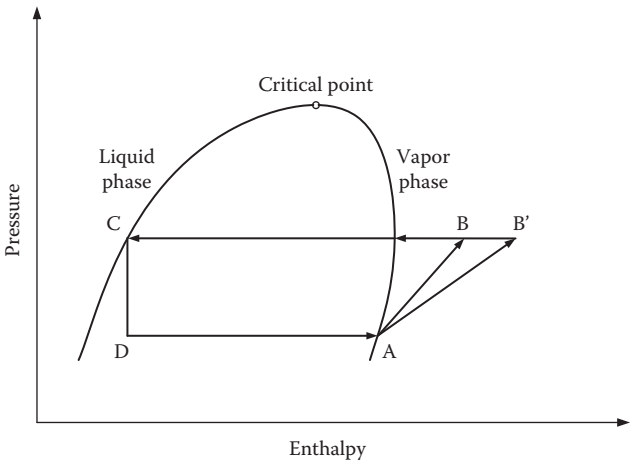


FIGURE 12.2 Schematic of refrigeration cycle on a pressure–enthalpy chart.

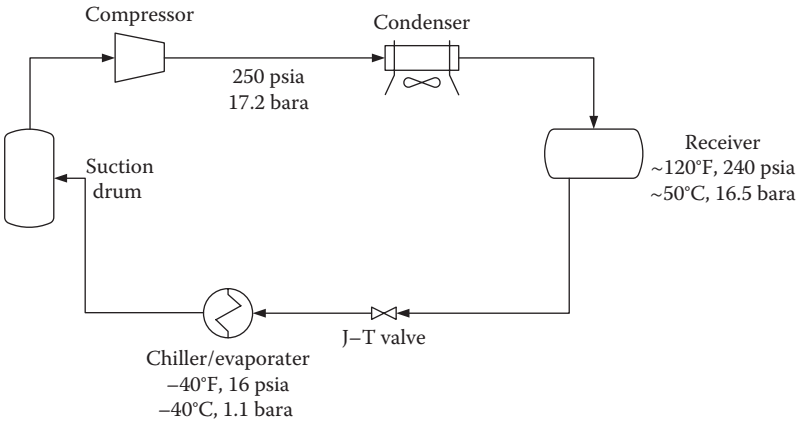


FIGURE 12.3 Single-stage propane refrigeration system. (Adapted from *Engineering Data Book*, 2016c. With permission.)

Compressor power to the refrigeration system is the product of the mass flow rate and shaft work

$$bhp = \dot{m} \cdot w_S \tag{12.3}$$

Condensation step (point B' to point C in Figure 12.2): The warm gas goes to an air or water-cooled condenser, where the propane cools to 100°F–120°F (40°C–50°C), totally condenses, and collects in a receiver. This step is simply

$$q_{Cond} = h_C - h_{B'}. \tag{12.4}$$

Expansion step (point C to point D in Figure 12.2): Propane liquid leaves the receiver and flashes through a J–T valve, where the temperature and pressure drop to –40°F (–40°C) and 16 psia (1 bara). No change occurs in the enthalpy, but the temperature drops to the saturation temperature of the liquid at the expansion discharge pressure and, if there are no heat leaks, $h_C = h_D$. If there is a heat leak, q_L, then

$$h_D = h_C + q_L \tag{12.5}$$

The fraction, f, of propane liquid is computed knowing the initial enthalpy and liquid and vapor enthalpies at the evaporation temperature, which for the given case is

$$h_D = h_D^L f + \left(1 - f\right) h_D^V.$$

Assuming the vapor leaves the chiller as a saturated vapor,

$$\begin{aligned} h_D^V &= h_A, \\ f &= \frac{\left(h_A - h_D\right)}{\left(h_A - h_D^L\right)}. \end{aligned} \tag{12.6}$$

Refrigeration step (point D to point A in Figure 12.2): The cold propane then goes to a heat exchanger, the chiller, where liquid propane cools the process stream by evaporation. Because the propane in the chiller is evaporating and minimal heat exchange occurs between cold propane vapor and the inlet gas, the inlet and outlet propane temperature remain constant. The propane returns to the compressor suction slightly above –40°F (–40°C). The heat absorbed by the propane is simply $h_A - h_D$.

In the past, most chillers were the kettle type in which propane is on the shell side and the liquid level is maintained above the tube bundle. Often other high-performance heat exchangers (e.g., plate-fin) are used (see Section 3.4.5 for more details). The chiller typically has two zones of heat transfer. The first is exchange of boiling propane with gas above its dew point and will involve only sensible heat on the gas side. The second zone has condensing vapors from the process stream and boiling propane, which gives a much higher overall heat transfer coefficient (*Engineering Data Book*, 2016c).

To complete the cycle, the propane vapors leave the chiller and go to the suction drum before being compressed.

The cycle described here is ideal and ignores some important factors: heat leak through insulation and compressor suction frictional pressure drop. For real, functioning refrigeration cycles, both of these must be taken into account by appropriate adjustment of the ideal cycle described above.

Example 12.1

Compute the fraction liquid for the propane refrigeration system on the basis of the conditions given in Figure 12.3. Ignore heat leak into the system and assume the compression efficiency is 77%. Use the PH diagram for propane given in Appendix B[3] for the calculations.

Solution

Compression step: Following the cycle as given above, first calculate the work of compression. To compute compressor work, we use Equation 12.1 and assume that the inlet gas condition is saturated vapor at –40°F (–40°C). The work per unit mass (assuming reversible compression) required to compress the propane from 14.5 to 250 psia (1–17 bara) using Appendix B is

$$w_S = \frac{(h_B - h_A)}{\eta_{IS}} = \frac{\left(h_{250\,\text{psia}} - h_{14.5\,\text{psia},\ -40°\text{F}}\right)}{\eta_{IS}}.$$

Therefore, $w_S = (367 - 311)/0.77 = 73$ Btu/lb_m (169 kJ/kg).

Because of the compressor inefficiency, using Equation 12.2, the enthalpy of the vapor that leaves the compressor is

$$h_{B'} = h_{250\,\text{psia}} = h_{14.5\,\text{psia},\ -40°\text{F}} + w_S = 311 + 73 = 384\,\text{Btu/lb}_\text{m}\ (891\,\text{kJ/kg}),$$

which corresponds to approximately 180°F at 250 psia. (Note that the compression ratio of 17 to 1 would require a two-stage compressor. See Chapter 9 for multistaging.)

Condensation step: Pressure drop between the condenser inlet and receiver is usually around 8–10 psi (0.55–0.7 bar). The heat load on the condenser is the change in enthalpy from the heated vapor to condense to all liquid and cool it to 120°F. On the basis of the PH diagram in Appendix B. (B.22, B.23), this value is

$$q = h_{B'} - h_C = h_{250\,\text{psia}} - h_{242\,\text{psia},120°\text{F}} = 384 - 228 = 156\,\text{Btu / lb}_\text{m}\ (362\,\text{kJ / kg}).$$

To calculate the mass fraction liquid, use Equation 12.6

$$f = \frac{(h_A - h_D)}{\left(h_A - h_D^L\right)} = \frac{\left(h^V_{-40°\text{F}} - h_{240\,\text{psia},120°\text{F}}\right)}{\left(h^V_{-40°\text{F}} - h^L_{-40°\text{F}}\right)},$$

$$f = \frac{(311 - 228)}{(311 - 129)} = 0.46.$$

[3] See Appendix B on publisher website: www.crcpress.com/Fundamentals-of-Natural-Gas-Processing-Third-Edition/Kidnay-Parrish-McCartney/p/book/9781138612792

12.2.1.2 Alternate Process Configurations

Thermodynamics dictates that to minimize the refrigeration work (i.e., compression required), heat from the chiller should be removed at as high a temperature as possible. One way to reduce compressor duty per unit of refrigeration duty is to multistage the refrigeration process by the removal of process heat at more than one temperature. Figure 12.4 shows a two-stage system, with representative operating conditions. In this system, the condensed propane stream expands to approximately 62 psia (4.3 bara) and 25°F (–4°C) in two parallel J–T valves. One of the expanded streams goes to a chiller and is vaporized before going to the compressor second stage.

A properly designed two-stage refrigeration system has the highest efficiency when a heat exchanger is used on the first stage as shown. However, higher efficiency compared to the system shown in Figure 12.3 can still be obtained using only a single J–T expansion into the economizer. Gas plants commonly omit the first-stage heat exchanger for cost purposes. However, when high efficiencies are critical, such as in an LNG plant, the heat exchanger is used and three stages of refrigeration are common.

The interstage liquid goes through a second J–T expansion to provide the low-temperature cooling. Pressures are adjusted so that the compression ratio is equal in both compressor stages. Table 12.1 shows the significant savings in going to two stages, but less of a benefit when going to three stages.

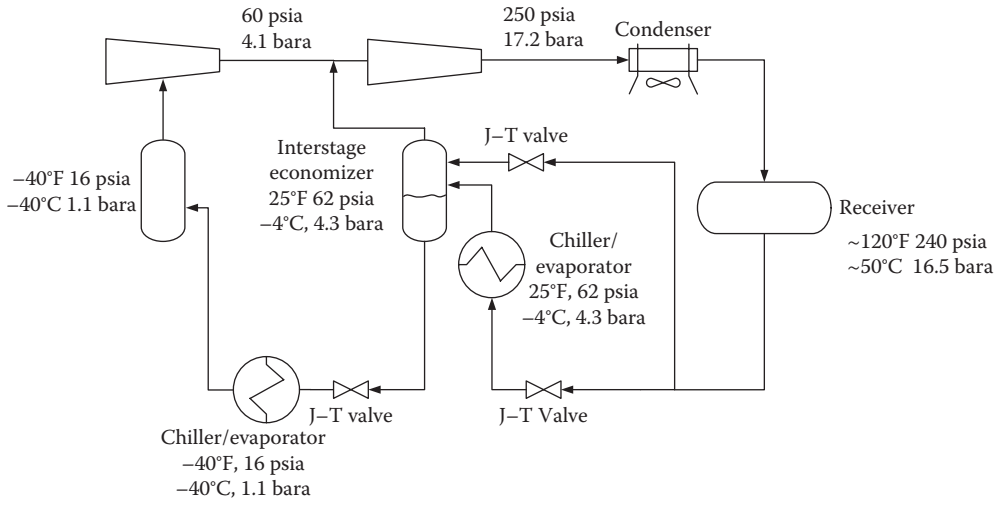


FIGURE 12.4 Two-stage propane refrigeration system, with second chiller and interstage flash economizer. Refrigeration cycles often omit this chiller with expansion directly to the interstage economizer.

TABLE 12.1
Effect of Stages on Condenser and Compression Duty for Constant Refrigeration Duty with Propane Refrigerant

	Number of Stages		
	1	**2**	**3**
Change in compressor power (%)	Base	–17.6	–21.8
Change in condenser duty (%)	Base	–7.7	–9.5

Source: Author calculations using ProMax® 5.0 (Bryan Research & Engineering LLC, 2019).
Refrigeration temperature is –40°F (–40°C), condensing temperature is 100°F (38°C) and only a single, low-temperature chiller is used.

Multistaging reduces work requirements by removing heat from the process stream at different temperatures. An alternative is removal of heat from the refrigerant before it is expanded. Refrigerant subcooling is sometimes used by exchange of the propane that leaves the receiver with cold propane. An *Engineering Data Book* (2016c) example shows that an 8% reduction in recirculation rate to the second stage of two-stage refrigeration is obtainable when the propane from the condenser is cooled by 10°F (5°C).

External refrigeration can be used to cool the process stream to much lower temperatures. A common way is to use cascade refrigeration. In this option, one refrigerant (e.g., propane) is used to remove heat from another refrigerant (e.g., ethane), which then cools the process gas down to as low as –120°F (–85°C). This technique is commonly used in LNG plants and is discussed in Chapter 18. Many gas plant process stream temperatures go well below –120°F (–85°C), but usually rely upon propane refrigeration and process gas expansion for cooling instead of additional external cooling.

Many combinations are possible for making refrigeration more efficient. However, each must be balanced with the associated additional capital cost, realizable operating cost savings, and operating complexity. Little incentive exists for complex refrigeration systems in gas processing. However, LNG plants make extensive use of complex cycles, as discussed in Chapter 18, to reduce refrigeration (i.e., compression) costs.

12.2.1.3 Effect of Operating Variables on Refrigeration Performance

A number of other process variables affect refrigeration capacity. An obvious one is the condenser outlet temperature, which is limited by the heat removed in the condenser and dictates compressor discharge pressure. If air cooling is used, the temperature can exhibit wide swings, both seasonal and daily, in ambient and condenser temperatures. Table 12.2 shows the importance the condensing temperature plays on both condenser and compressor duties to maintain a constant refrigeration capacity.

Another factor that affects performance is refrigerant purity. Propane commonly contains small amounts of ethane. Low concentrations pose no problem. If ethane accumulates in the propane receiver, condensation pressure increases for a given temperature. When refrigeration capacity becomes adversely affected, the refrigeration loop is purged into a low-pressure plant gas stream and propane with a lower ethane content is added to the system.

Whereas light ends affect performance, heavy components are less of a problem, but still must be removed. The most common heavy material is compressor oil. Heavy liquids are removed by periodically taking a slipstream from the bottom of the chiller, which goes to a small heated vessel where the propane is evaporated and returned to the suction of the compressor. The heat source is usually hot propane vapor from compressor discharge. Butanes may also be present, but unless they are in large quantities they will not significantly increase chiller temperature.

12.2.2 Turboexpansion

Until the 1960s, J–T expansion was the only way used to cool gas plant streams by pressure drop. Herrin (1966) describes the first turboexpander gas processing plant. The J–T valve, which is essentially a control valve with a variable or fixed orifice, is an extremely simple, inexpensive, and widely

TABLE 12.2
Effect of Condensed Refrigerant Temperature on Condenser and Compression Duty for Constant Refrigeration Duty with Propane as the Refrigerant

Condensing temperature, °F (°C)	60 (15)	80 (27)	100 (38)	120 (49)	140 (60)
Change in compressor duty (%)	–33.2	–17.7	Base	21.0	47.6
Change in condenser duty (%)	–12.9	–6.9	Base	8.2	18.5

Source: Author calculations using ProMax® 5.0 (Bryan Research & Engineering LLC, 2019).

used means to reduce gas temperature. Although still used extensively to produce refrigeration, J–Ts have been supplanted by turboexpanders in gas plants for process stream cooling. Turboexpanders are, in essence, centrifugal compressors that run backwards. Unlike J–T expansion, they extract work from the stream. While J–T expansion is essentially an isenthalpic process, an ideal, thermodynamically reversible turboexpander is isentropic. The maximum reversible work required for compression is isentropic; conversely, the maximum reversible work removed by a turboexpander system is also isentropic. Turboexpansion provides the maximum amount of heat removal from a system for a given pressure drop while generating useful work. The work can be used to drive compressors or electrical generators. The equations in Chapter 9 for isentropic compression apply to the turboexpander. Chapter 1 contrasts the amount of cooling between J–T and isentropic expansion.

The major breakthrough for turboexpanders came when the design and materials made it possible for condensation to occur inside the expander. The fraction condensed can be up to 50% by weight (Jumonville, 2004). However, the droplets must generally be 20 μm in diameter or less, as larger droplets can cause erosion of internal components.

Most turboexpanders drive centrifugal compressors to provide a portion of the outlet compression. In situations where inlet pressures are very high (e.g., offshore), turboexpanders are sometimes used in pressure letdown to provide refrigeration for dew point control and to generate power.

Like compressors, expanders can be positive displacement or dynamic; dynamic expanders can be radial or axial. However, the only type used in gas processing is the radial unit with inward (centripetal) flow, and discussion here is limited to this type.

Figure 12.5 shows a cutaway view of a typical turboexpander used in gas processing. The expander is the unit on the right, and the compressor is the unit on the left. Gas enters the expander through the nozzle at the top right and is guided onto the wheel by the aerodynamically shaped adjustable guide vanes, which completely surround the expander wheel. The swirling high-velocity inlet gas turns the wheel and transfers part of its kinetic energy to the wheel and shaft and exits to the right through the tapered nozzle. Because part of the energy of the gas has been transferred to the wheel, the exit gas is at a much lower temperature and pressure than the gas entering. The expander wheel, directly coupled to the compressor wheel, provides the work necessary to drive the centrifugal compressor on the left. Low-pressure gas enters on the left, is compressed by the compressor wheel, and exits at the top of the unit. Lubricating oil enters in the top port shown in the center of the unit.

Approximately 50% of the enthalpy change occurs in the turbine (Jumonville, 2004). The increase in velocity over the vanes results in the other 50% of the total pressure and temperature drop across the expander unit. Thus, the inlet guide vanes are a vital part of the energy conversion process in a turboexpander. The high velocity of the gas that exits the vanes and enters the expander wheel greatly improves overall turboexpander efficiency (Peranteaux, J., Private Communication, 2005).

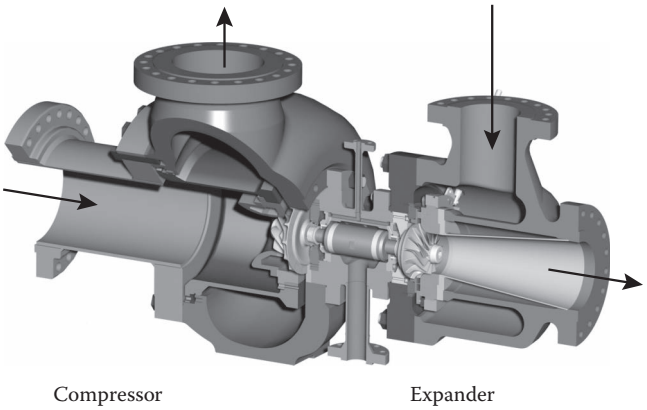


FIGURE 12.5 Cutaway view of a turboexpander. (Courtesy of Atlas Copco Mafi-Trench Company LLC.)

Figure 12.6 shows a large turboexpander used in a large LNG plant. Operating conditions for turboexpanders vary, depending on the process application and the composition of the gas being processed. However, Tables 12.3 and 12.4 provide a general idea of turboexpander operations in a gas plant. Note the size of the wheel in Table 12.3 and the rotating speeds in both tables.

Although simple in principle, turboexpanders are sophisticated yet extremely reliable pieces of rotating machinery. In addition to the complex aerodynamic design of the expander and compressor components of the system, the unit must be equipped with low drag but 100% effective shaft seals. These seals operate under high pressure and at temperatures that range from cryogenic to well above ambient. By injecting clean, dry "seal gas" into the shaft seals, lube oil is prevented from escaping the bearing housing and the bearings are protected from the cold process gas. Fluid-film bearings that support the shaft that connects the expander and compressor sections are traditionally supplied with oil by use of a pressurized recirculating system. The *Engineering Data Book* (2016c) provides more details.

FIGURE 12.6 Turboexpander in large LNG plant which shows the compressor on the right side of the unit. The turboexpander processes 30,500 lb/min (830,000 kg/h) and recovers approximately 9.2 MW (12,000 hp) of power. (Courtesy of Atlas Copco Mafi Trench Company LLC.)

TABLE 12.3
Expander–Compressor Design Conditions

	Expander	Compressor
Inlet gas rate, MMscfd (10^6 Nm^3/d)	250 (7.1)	187 (5.3)
Molar mass	22.80	19.69
Inlet pressure, psia (bara)	1,590 (109.7)	855 (58.9)
Inlet temperature, °F (°C)	30 (–1.0)	34 (1.0)
Outlet pressure, psia (bara)	870 (60.1)	1,165 (80.3)
Outlet temperature, °F (°C)	–15 (–26.1)	78 (25.4)
Liquid formation, wt%	36	—
Power, hp (kW)	2,687 (2,004)	2,663 (1,986)
As tested efficiency (%)	85.0	78.5
Speed (rpm)	16,700	16,700
Wheel diameter, in. (mm)	7.75 (197)	10.9 (277)

Source: Lillard and Nicol (1994).

In principle, both the turboexpander and compressor can be multistaged. However, mechanical sealing problems have made multistaging impractical for both the expander and compressor (Peranteaux, J., Private Communication, 2005).

Some new units employ magnetic bearings instead of fluid-film bearings. Magnetic bearings keep the shaft in place by constantly adjusting the current in radial and axial electromagnets that support the shaft. Although the initial investment in magnetic bearings is higher than for comparably sized fluid-film bearings, this design provides substantial savings in lifetime utility operating costs when compared with conventional oil-lubricating systems. More importantly, they eliminate the potential for oil contamination in the cold section of the plant (Jumonville, 2004). Nonetheless, magnetic bearing systems still require seal gas. In this case, the seal gas protects the bearings from the cold process gas while simultaneously ensuring adequate cooling for the bearing coils (Peranteaux, J., Private Communication, 2005).

The *Engineering Data Book* (2016b) emphasizes some important points regarding turboexpanders:

- *Entrainment*: Gas entering the turboexpander must be free of both solids and liquids. Fine-mesh screens are used to protect the device, and the pressure drop across the screen should be monitored.
- *Seal gas*: This gas isolates process gas from the lubricating oil, or isolates process gas from the shaft if magnetic bearings are used, and must be clean and constantly available at the operating pressure. Sales gas is commonly used. Otherwise, a warmed inlet gas stream from the expander inlet separator is used. (The gas, if used, must be warmed to 70°F (20°C) or more to prevent thickening of the lube oil.)
- *Lubricant pumps*: These pumps must maintain a constant flow to lubricate the bearings if oil is used. A spare pump is mandatory. The *Engineering Data Book* (2016b) describes the lubrication system.
- *Shut-off valves*: A quick-closure inlet shut-off valve is used for shutdown.

As is the case for centrifugal compressors, turboexpander efficiency diminishes when operating off the design point. This variance can be approximately 5–7 percentage points when the flow increases or decreases by 50%. However, the turboexpander is normally driving a compressor, which also suffers loss in efficiency when off the design point. Therefore, the overall effect on the turboexpander–compressor unit efficiency will be larger. As is typical for centrifugal compressors, surge control is common on the compressor end of the unit but not always required because of the low head developed in the compressor.

Example 12.2

Use the inlet conditions and outlet pressure supplied in Table 12.4 to compute the outlet temperature and work generated per lb_m of gas inlet. For this example, assume the gas is pure methane, and use diagram from Appendix B (Figure B.16, B.17) to do the calculations. Compare this result to the outlet temperature and work done if a J–T expansion occurs over the same pressure drop and inlet temperature. (Only USES is used in this example to minimize confusion.)

Solution

Turboexpander: Inlet gas conditions are –50°F and 1,080 psia. At these conditions, for pure methane, the enthalpy is $h = 260$ Btu/lbm and the entropy is $s = 0.80$ Btu/lbm-°R. The ideal expansion is isentropic, so the constant entropy line is followed to the exit pressure of 480 psia, which is close to the saturation boundary of methane, where the temperature is –130°F and $h = 235$ Btu/lbm. The work done is $(260 - 235) = 25$ Btu/lbm. However, the expander is only 77% efficient, so the actual work done is $0.77\ (25) = 19.2$ Btu/lbm. The corrected final enthalpy is then $260 - 19.2 = 240$

TABLE 12.4
Turboexpander Design Conditions

	Expander	Compressor
Inlet flow rate, lb_m/h (kg/h)	221,000 (100,243)	208,000 (94,347)
Inlet gas rate, MMscfd (10^6 Nm^3/d)	115.6 (3.27)	115.2 (3.26)
Molar mass	17.46	16.5
Inlet pressure, psia (bara)	1,080 (74.5)	470 (32.4)
Inlet temperature, °F (°C)	–50 (–46)	60 (16)
Outlet pressure, psia (bara)	480 (33.1)	576 (39.7)
Outlet temperature, °F (°C)	–113.6 (–80.9)	93.5 (34.2)
Liquid formation (wt%)	19.3	—
Efficiency (%)	83	74
Speed (rpm)	22,000	22,000
Power, bhp (bkW)	1,380 (1,029)	1,350 (1,007)

Source: Agahi and Ershaghi (1992).

Btu/lbm at 480 psia, which corresponds to approximately –129°F. Therefore, the inefficiency did not greatly affect the final temperature in this example. The effect of the efficiency in plants that process large quantities of gas is significant, both in cooling and in lost power for recompression.

J–T expansion: The J–T expansion follows the constant enthalpy line down to the exit pressure of 480 psia, giving an exit temperature of –109°F. The work obtained during expansion is zero.

Therefore, use of a turboexpander with 77% efficiency provides an outlet gas that is 20°F (11°C) colder, and at the same time provides 19.2 Btu/lb_m (44.7 kJ/kg) of work. The benefit of turboexpansion compared with J–T expansion is noticeable in plants when the turboexpander is bypassed and J–T expansion is used. In such cases, the NGL production can drop significantly. Although this comparison is slightly unfair because the plant design is optimized for turboexpansion, it points out the value of turboexpanders. The general practice is to couple the turboexpander to a centrifugal compressor. The available expander work can be large. Swearingen (1970) states that a turboexpander handling 500 MMscfd (560×10^3 Nm^3/h) at pipeline pressure would develop 10,000 hp (7,500 kW). The turbine rotor would only be 18 in. in diameter. Expander–compressor combinations require considerable care in their selection and operation. Swearingen (1970) and the *Engineering Data Book* (2016b) discuss what must be considered in the selection, operation, and maintenance of turboexpanders. Working with the manufacturer is critical to ensure the unit's proper installation and operation, especially for off design cases.

12.2.3 Heat Exchange

Heat exchangers play an important role in all but the simplest hydrocarbon processes. Efficient heat exchange reduces compressor power and fuel consumption requirements in subambient processes by recovering some of the refrigeration. Most heat exchangers used in a gas processing plant are shell and tube, plate frame or brazed-aluminum plate-fin heat exchangers. Brazed aluminum plate-fin exchangers are extensively used in cryogenic processes. Section 3.4.5 discusses their advantages and disadvantages. For a more detailed discussion of these types of heat exchangers, refer to Chapter 3.

12.2.4 Gas–Liquid Separators

Refrigerated hydrocarbon recovery systems employ one or more gas–liquid separators, commonly called low-temperature separators or cold separators. These separators are comparable to the separators discussed in Section 5.1. Care is taken to minimize mist carryover when downstream equipment is a turboexpander or compressor. Additional liquid removal equipment (e.g., filter separator) is not

commonly used because of increased pressure drop and difficulty of servicing the filters. However, gas removal from liquid streams is less critical because it is tolerated downstream in the process.

12.2.5 Fractionation

In addition to conventional distillation columns, two other types of distillation columns are commonly found in gas plants: stabilizers and demethanizers. Both are stripping columns used to remove light ends from NGL streams. More information on fractionation is given in Chapters 4 and 15.

12.2.5.1 Stabilizers

The primary focus of dew pointing or fuel conditioning is to obtain a leaner gas. However, the byproduct is a liquid phase that contains a substantial amount of volatiles. To make the liquid product easier to store and to recover more light ends for fuel or sales gas, many of the systems will "stabilize" the liquid by passing it through a stabilizer column. Chapter 15 provides a more detailed discussion of these columns.

12.2.5.2 Demethanizer

A distinguishing feature of gas plants with high ethane recovery[4] is the demethanizer, as shown in Figure 12.7. The column differs from usual distillation columns in the following ways:

- It usually has an increased diameter at the top to accommodate the predominantly vapor feed near the top stage.
- It is primarily a stripping column, with no traditional condenser–reflux stream.
- It may have several liquid feeds further down the column that come from the cold separator.

FIGURE 12.7 Demethanizer column with molecular sieve adsorption beds in foreground.

[4] The term *recovery* in this context refers to the amount of a component in the feed gas that goes into the NGL product. For example, "60% ethane recovery" means that the NGL product contains 60% of the ethane in the feed gas to the process. It is the opposite of *rejection* which is the fraction of that goes to the residue sales gas.

- It may have several side reboilers, whose primary purpose is to cool the gas going through the reboiler to recover some of the refrigeration available.
- It has a large temperature gradient; up to 200°F (110°C) is common.

The column serves two main functions: it provides vapor/liquid separation of the methane-rich feed, which enters as a cold, two-phase stream, and it removes methane from the bottoms product. Depending on the plant configuration, there are multiple feed points coming from a turboexpander, a J–T valve, or a heat exchanger. In some configurations, the columns have reflux or a small liquid feed on the top stage, but many have no reflux. The NGL bottoms product is usually continuously monitored for methane content, which is typically controlled to a maximum of 0.5 LV% of the total product or 1.5 LV% of the ethane in the NGL.

The top of the column usually operates in the −175°F to −165°F (−115°C to −110°C) range, with pressures from 200 to 400 psig (14–28 barg). Operation of the demethanizer at higher pressures reduces compression costs. Shah and Stucky (2004) discuss the advantages and disadvantages of higher pressure operation.

To obtain high ethane recovery, the top of the column must operate at low temperature, which translates into a higher compression load. The demethanizer usually has 18–26 trays, with a tray efficiency of 45%–60%, or an equivalent packed bed (*Engineering Data Book*, 2016e).

12.3 LIQUIDS REMOVAL PROCESSES

This and the following sections discuss why hydrocarbon recovery is important, and how systems such as refrigeration, turboexpansion, and demethanizers are used to form NGL recovery systems. These systems are used by the gas processor to produce marketable products and to maximize revenue.

Many process configurations are used to recover hydrocarbons in gas processing. The best configuration depends upon many variables, including:

- Recovery level based on economics
- Gas volume
- Gas composition
- Pressures, both inlet and outlet
- Product slate

The product slate dictates the required lowest operating temperature of the gas.

If limited ethane recovery (<40%–60% ethane) is desired, the recovery process may be essentially a low-temperature separation (LTS) unit, with fractionation of the cold liquid to stabilize the NGL product. Although gas temperatures in an LTS may go down to −40°F (−40°C), only this is required to separate the light ends from the liquid.

Older plants using refrigerated lean oil absorption are sometimes capable of achieving up to 50% ethane recovery. Section 12.3.2.2 discusses these units.

For higher ethane recovery, temperatures must be lower, and may require a combination of external refrigeration and expansion. To increase recovery rates these plants use a demethanizer to strip methane from the NGL.

Plant inlet gas volumes, pressures, and compositions set the optimal plant configuration on an economic basis. This combination makes it difficult to set criteria for establishing the best plant configuration. However, higher gas volume and GPM content (gallons liquid per Mscf ($m^3/10^3$ Nm^3) discussed in Chapter 6) make high ethane recovery more attractive.

Inlet gas pressures make a major difference in plant configuration. High pressures may permit use of expansion, using a J–T valve or turboexpander, to provide all of the cooling if low ethane recovery is desired. For low inlet pressures, either external refrigeration or inlet compression

followed by expansion may be needed to achieve the desired level of ethane recovery. Required outlet pressure helps decide which approach should be taken.

The following sections discuss the hydrocarbon recovery objectives:

1. Dew point control and fuel conditioning
2. Low ethane recovery
3. High ethane recovery

In most gas processing processes, high ethane recovery results in high C_3^+ recoveries. Greater than 95% C_3^+ recovery occurs when ethane recovery levels are 60% or higher.

12.3.1 Dew Point Control and Fuel Conditioning

Both dew point control and fuel conditioning have the same main product—a gas with reduced C_3^+ fraction. Dew point control is sometimes a field operation, and stabilization of the produced liquid is site specific. Dew point control and fuel conditioning exist to remove heavy hydrocarbons from the gas stream. Less conventional technologies, such as Twister and membranes, are also discussed briefly for dew point control and fuel conditioning.

12.3.1.1 Low-Temperature Separation

A LTS unit, also called straight refrigeration or low-temperature extraction (LTX) unit, is commonly used for dew point control or fuel gas conditioning. The process consists of cooling and partial condensation of the gas stream, followed by a cold separator. When inlet pressures are high enough to meet outlet pressure requirements with some pressure drop, cooling is obtained by expansion through a J–T valve. Otherwise, external refrigeration is required. Water is often present in the gas, and injection of either ethylene glycol or methanol is used to prevent hydrate formation. For more information on the use of ethylene glycol and methanol for hydrate inhibition, see Chapter 8.

Figure 12.8 shows an LTS unit that uses ethylene glycol injection for hydrate inhibition and uses J–T expansion for cooling. The feed initially goes through a water knockout vessel to remove free water. The water-saturated hydrocarbon gas and liquids then mix with ethylene glycol before being cooled by exchange with cold gas from the cold separator. The mixture then passes through a J–T expansion valve and flashes into the cold separator to separate the gas, condensate, and glycol-water phases. The condensate goes to the condensate stabilizer for removal of remaining light ends.

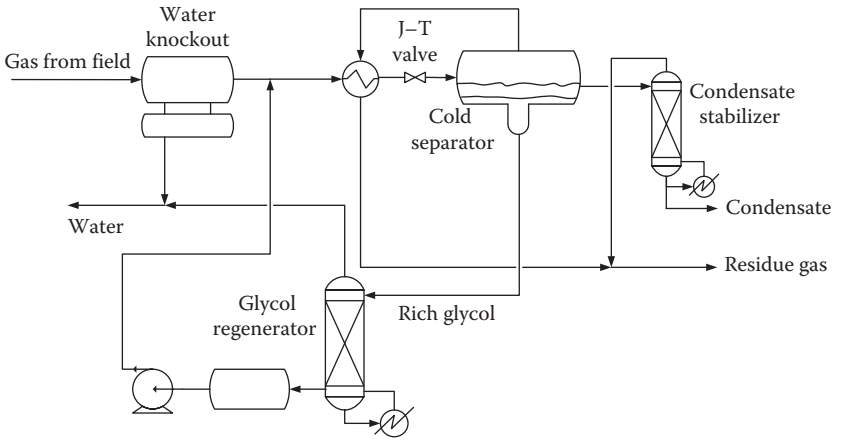


FIGURE 12.8 Low-temperature separation unit (LTS), with ethylene glycol injection and condensate stabilization.

Gas from the cold separator is heated in the gas-to-gas exchanger before being combined with the stabilizer overhead. The cold separator conditions and stabilizer operation set the dew point of the blended outlet gas.

Condensate from the stabilizer goes to product storage. The glycol–water mixture from the cold separator goes to the glycol regenerator for water removal and then reinjection into the feed.

If inlet pressures are too low for expansion, the stream is cooled by propane refrigeration. The advantage of direct refrigeration is that the pressure drop is kept at a minimum. Hydrate formation must be prevented either with feed dehydration upstream of the unit or inhibitor injection. Glycol injection is usually more cost effective, but if used, it increases the required refrigeration duty. The *Engineering Data Book* (2016d) provides additional details on these processes.

12.3.1.2 Twister

Okimoto and Betting (2001) reported use of a relatively new device, Twister, for dew point control and dehydration. It is used in one offshore facility (Brouwer et al., 2004), and has been favorably evaluated for other projects (Wilson and Yuvancic, 2004). Figure 12.9 shows a cutaway view of the device, and denotes the salient parts of the unit (Schinkelshoek and Epsom, 2008). Gas enters and expands through a nozzle at sonic velocity, which drops both the temperature and pressure and causes droplet nucleation. The two-phase mixture then contacts a wing that creates a swirl, and forces separation of the phases by centrifugal force. The gas and liquid are separated in the diffuser; the liquid is collected at the walls, and dry gas exits in the center.

Advantages of the system include:

- Simplicity. No moving parts and no utilities required.
- Small size and low weight. A 1 in. (24 mm) throat diameter, 6 ft (2 m) long tube can process 35 MMscfd (1×10^6 Nm^3/d) at 1,450 psia (100 bara).
- Driven by pressure ratio, not absolute pressure.
- Relatively low overall pressure drop. System recovers 65%–80% of original pressure.
- High isentropic efficiency. Efficiency is stated to be approximately 90%.

Drawbacks of the system include:

- Requires a clean feed. Solids erode the tubing and wing, necessitating an inlet filter separator.
- Limited turndown capacity. Flow variability is limited to ±10% of designed flow. This limitation is mitigated by the use of multiple tubes in parallel.
- Liquids exit with a "slip gas." This mixture is typically 20%–30% of the total flow volume (Epsom, H.D., Private Communication, 2005). The mixture can go to a gas–liquid separator for recovery of the gas, which may require recompression.
- Proprietary technology.

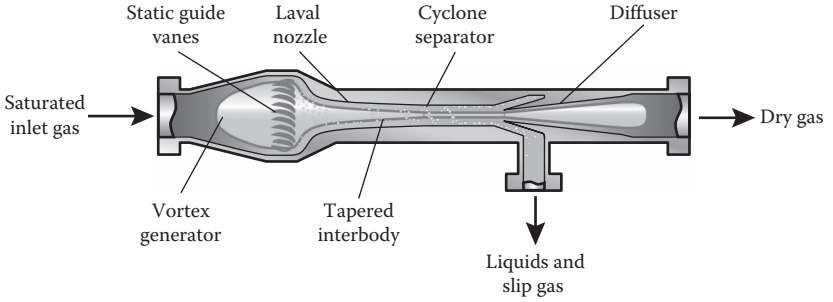


FIGURE 12.9 Cutaway view of Twister™ device. (Courtesy of Twister BV.)

Because of the limited turndown, the required pressure drop and the "slip gas" volume, application of Twister technology has been limited to a few installations.

12.3.1.3 Membranes

As discussed in Chapter 4, membranes are being used in several areas of gas processing, including dew pointing. Hale and Lokhandwala (2004) discuss using membranes for fuel conditioning. Membranes are ideal for this application, provided preconditioning is adequate to protect the membrane and little penalty exists for permeate compression. Figure 12.10 shows the flow configuration. Gas enters the membrane on the discharge side of the compressor, and the residual gas provides fuel to the compressor engine or gas combustion turbine. The low-pressure permeate is recycled to the suction for recompression. Table 12.5 provides results for one field unit. Gas rates to the membrane are low because only a small stream needs to be processed for fuel.

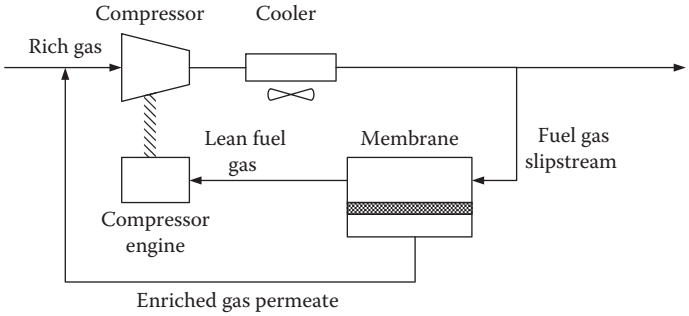


FIGURE 12.10 Schematic for membrane unit used as a fuel conditioner. (Adapted from Hale and Lokhandwala, 2004.)

TABLE 12.5
Operating Conditions and Composition of Natural Gas Stream Using Membrane for Fuel Gas Conditioning

	Membrane Feed	Lean Fuel Gas	Enriched Gas Permeate	
Temperature, °F (°C)	95 (35)	51 (10.5)	—	
Pressure psig (barg)	940 (65)	940 (65.0)	—	
Total flow lb-mol/h (kg-mol/h)	110.1 (50)	58.0 (26.3)	52.1 (23.7)	
Total volume MMscfd (10^3 Nm^3/d)	0.95 (27)	0.5 (14)	—	
Component mol%	**Feed**	**Fuel Gas**	**Permeate[a]**	**Percent Removed from Gas (%)**
Carbon dioxide	1.3	0.6	2.1	76
Methane	72.8	81.2	63.6	41
Ethane	9.6	9.0	10.3	51
Propane	9.9	7.1	13.0	62
i-Butane	2.4	0.8	4.2	82
n-Butane	2.5	0.9	4.3	81
n-Pentane	1.3	0.4	2.3	84
Water	0.11	0.0	0.2	100
Hydrocarbon dew point °F (°C)	95 (35)	38 (3.5)	—	

Source: Hale and Lokhandwala (2004).

[a] Composition of permeate and fraction removed from gas computed by material balance of normalized reported feed and fuel gas composition.

Like the previous technology, the process is simple and requires no moving parts. It too has the advantage of being relatively small and lightweight. The membrane unit described by Hale and Lokhandwala (2004) is 6 ft × 6 ft × 6 ft (2 m × 2 m × 2 m). The authors report this technology is used on several offshore installations. Unlike Twister, membranes have the advantage of a turndown ratio down to 50%, with no performance penalty.

The reported data were used to compute the permeate composition and fraction of feed removed from the feed. Table 12.5 points out the selectivity of the membrane, which may be poorer than that of Twister. In fuel conditioning, the selectivity is not a major issue because of the relatively small volume of gas that needs to be recompressed and the recycled enriched stream represents a negligible incremental load on the compressor.

A membrane that permeates heavy hydrocarbons preferentially to smaller molecules is counterintuitive. As stated in Chapter 4, membrane permeability is the product of the solubility and diffusion coefficient. For separation of light gases, the primary mode of selectivity is the diffusion coefficient. For dew pointing solubility drives the selectivity (Baker et al., 1998). These membranes are silicone rubber compounds that preferentially absorb the heavy components.

12.3.1.4 Adsorption

Another process capable of dew point control or fuel gas conditioning is adsorption with materials like silica gel, sometimes called "quick cycle" units. These units are temperature swing adsorption (TSA) units like those described in Chapter 4 but operate with adsorption cycles on the order of 30–120 min and recover mostly C_5^+ hydrocarbons. Mitariten (2007) provides an extensive review of the process.

12.3.2 Low Ethane Recovery

The focus of the previous section was removal of heavy components (C_3^+) to avoid condensation or improve fuel characteristics. This section discusses processes used in conventional gas plants where the objective is to produce a lean gas and recover up to approximately 60% of the ethane in the feed gas. Two process schemes are used to obtain this level of ethane recovery:

- Cooling by expansion or external refrigeration
- Lean oil absorption

As noted above, inlet pressure often dictates the best means of refrigeration. Lean oil was an early method used for hydrocarbon recovery but is now seldom used for new plants. Many of the refrigerated lean oil absorption plants in operation today are large facilities, where replacing them with a more modern turboexpander plant could be capital cost prohibitive. New gas processing facilities are almost exclusively cryogenic plants. Both approaches are described briefly below.

12.3.2.1 Cooling by Expansion or External Refrigeration

Figure 12.11 shows a plot for recovery of ethane and propane at 600 psig, with GPM based upon C_3^+ fraction. Recovery depends upon the relative amount of C_3^+ in the gas and the lowest gas temperature. Normally, recovery increases with increased richness of the gas. Variations in gas composition and pressure influence recoveries and Figure 12.11 should only be considered as a general guide for the temperature effect on recovery.

Figure 12.12 shows one commonly used direct refrigeration process that employs recycle from the fractionator to maximize liquids recovery. Inlet gas is cooled with cold residue gas and cold liquid from the separator before going to the propane chiller and then the cold separator. Vapor from the

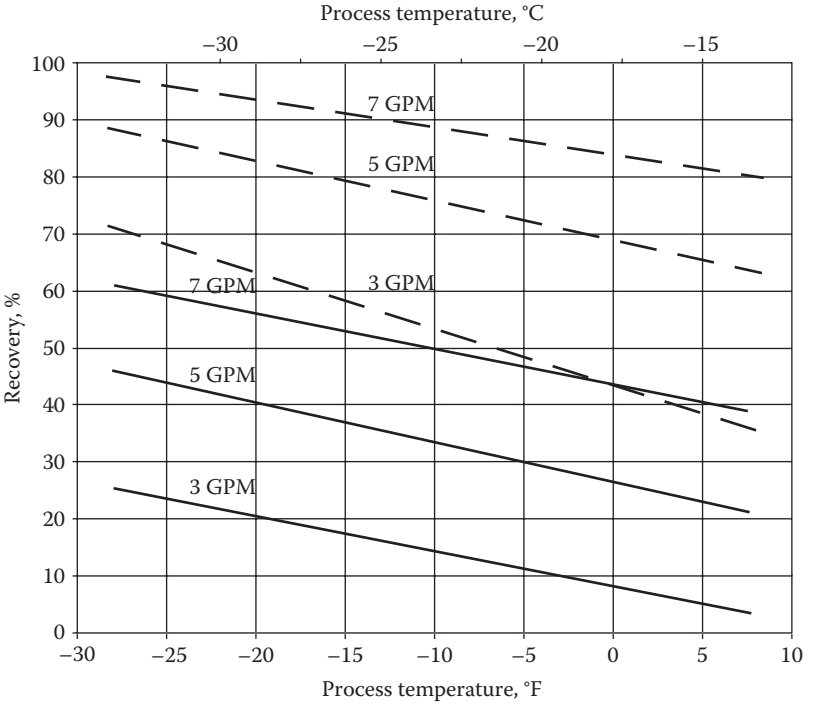


FIGURE 12.11 Recovery of ethane and propane as a function of the separation temperature and NGL content of feed. Operating pressure is 600 psig (41 barg) and GPM is based upon C_3^+. The solid and dashed lines represent ethane and propane recovery, respectively. Three, five, and seven GPM are equivalent to 0.4, 0.7 and 1 $m^3/10^3Nm^3$.

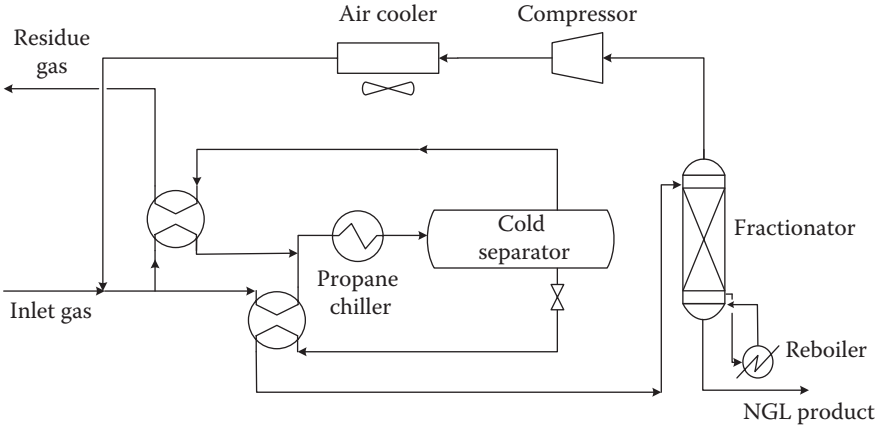


FIGURE 12.12 Schematic of a direct refrigeration process for partial recovery of C_2^+ fraction. (Adapted from *Engineering Data Book*, 2016d. With permission.)

separator is the sales gas and the liquid goes to a fractionator to strip out light ends and recover liquid product. The column operates at a lower pressure than does the cold separator. Because of system pressure drop and because the fractionator runs at the lower pressure the recycle stream must be compressed.

Alternatives to the process include:

- Reducing recycle by adding reflux to the fractionator
- Eliminating the recycle by sending the fractionator overhead out with residue gas
- Accepting lower NGL recovery and using the fractionator overhead as fuel
- Pumping liquid from the cold separator to the fractionator to eliminate the need for a recycle compressor

The *Engineering Data Book* (2016d) provides more details of process variations, and discusses how processing variables affect compressor and refrigeration requirements. The process shown in Figure 12.12 assumes that the gas enters sufficiently dehydrated to prevent hydrate formation. If the water content is higher, ethylene glycol injection can be added for hydrate inhibition, which increases refrigeration duty; however, temperatures are then limited by glycol viscosity.

Because the unit relies only on external propane refrigeration, the lower temperature limit on the feed to the LTS is approximately –35°F (–37°C). Unless the feed has a very high GPM, ethane recoveries will be below 60%. Expansion using J–T or turboexpanders is required to lower temperatures and increase recoveries.

With high inlet gas pressures, replacing the propane system with an expander is an attractive option. However, inlet compression may be necessary to obtain the temperatures required to obtain the desired recoveries. Both J–T and turboexpanders are used. Crum (1981) points out situations where a J–T system may be preferable to turboexpanders, although recent advances in turboexpander technology may temper some of them:

- *Low gas rates*: J–T is more economically viable at low gas rates. Crum (1981) maintains that at below 10 MMscfd (0.3×10^6 Nm^3/d), turboexpanders offer less economic advantage and they lose efficiency below 5 MMscfd (0.2×10^6 Nm^3/d).
- *Low ethane recovery*: For ethane recoveries of 10%–30%, J–T expansion may be sufficient.
- *Variable flow rates*: J–T is insensitive to widely varying flow rates whereas turboexpanders have lower efficiency when operating off of design rates.

Crum (1981) also points out that J–T plants are much simpler than turboexpander plants because J–T plants have no need for seal gas and lubricating oil systems. However, because of the inefficiency of J–T valves compared with turboexpanders, if any inlet compression is required, more is required with J–T expansion to obtain the same of recovery. The *Engineering Data Book* (2016d) suggests that use of J–T expansion for limited ethane recovery requires inlet pressures around 1,000 psi (70 bar).

Crum (1981) discusses five configurations in which J–T expansion is used to recover C_2^+ in plants ranging from 3 to 10 MMscfd ($0.1–0.3 \times 10^6$ Nm^3/d). Without external refrigeration, recovery rates were up to about 40%. A process that utilizes propane refrigeration in combination with J–T expansion obtained 80% recovery. Crum (1981) found that the fuel cost savings for compression failed to justify installation of turboexpanders in these small plants.

12.3.2.2 Lean Oil Absorption Process

Early gas processing plants used lean oil[5] absorbers to remove NGL components from natural gas (Cannon, 1993) and the process is still used in a number of gas plants. To improve recoveries later plants used external refrigeration to cool the feed gas and lean oil. Figure 12.13 shows a representative schematic of a propane-refrigerated lean oil system. The process involves three steps (*Engineering Data Book*, 2016d):

[5] Lean oil refers to a hydrocarbon mixture primarily made up of alkanes used to absorb NGL components from raw gas.

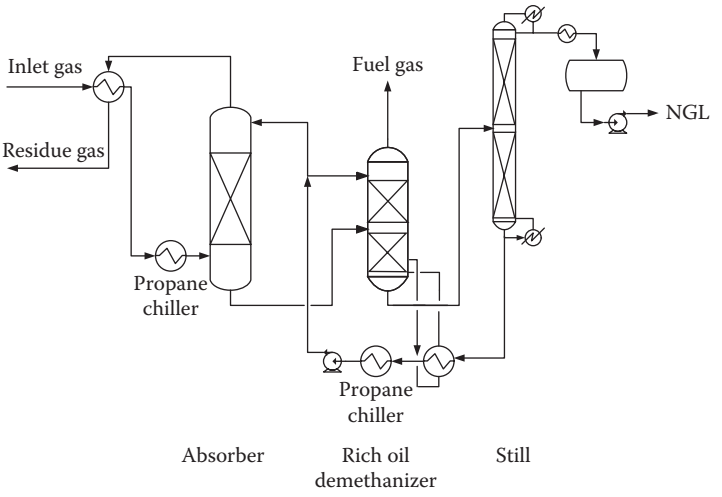


FIGURE 12.13 Refrigerated lean oil absorption process. (Adapted from *Engineering Data Book*, 2016d. With permission.)

1. *Absorption*: An absorber contacts gas with lean oil to absorb C_2^+ plus from feed gas.
2. *Stabilization*: The rich oil demethanizer (ROD) strips methane and lighter components from the rich oil.
3. *Separation*: The still separates the recovered NGL components as product from the rich oil and the lean oil then returns to the absorber and ROD.

Gas from the ROD is either blended with the exiting gas stream or used for fuel. Ambient temperature absorbers use lean oil with molar mass of 150–200, but refrigerated systems use molar masses of 100–130. The lower molar mass is an advantage, because the same mass flow of lean oil will absorb more NGL components from the gas.

If no refrigeration is used, and assuming the absorber runs at near ambient temperature, more than 75% of the propane and essentially the entire C_4^+ fraction are recovered. Using high solvent rates can increase the recoveries to 50% of the ethane and essentially all of the propane and heavier components. With propane refrigeration, typically more than 97% of the propane and up to 50% of the ethane is recovered. The *Engineering Data Book* (2016d) notes that refrigeration of the inlet gas and lean oil, along with heat to the still and ROD, are the key elements of an efficient lean oil system.

An advantage of lean oil absorption is that little pressure drop occurs through the absorber. However, the process is energy intensive and relies on numerous heat exchangers not shown in Figure 12.13 to reduce the energy load. For gas processing the whole process can be simplified by eliminating the lean oil and using external refrigeration, as discussed in the previous section. However, refrigerated lean oil absorption plants remain in operation with capacities of 1,000 MMscfd (30×10^6 Nm^3/d) or more. In new applications, lean oil plants have been replaced by cryogenic plants, but this process is still commonly applied in refineries.

12.3.3 High Ethane Recovery

The above processes provided limited recovery of ethane. To obtain 80%–90% or more ethane recovery requires temperatures well below what is obtainable by using propane refrigeration alone. In principle, direct refrigeration processes can be used by cascading propane cooling with ethane or ethylene refrigeration or by using a mixed refrigerant that contains methane, ethane, and propane. This may be attractive if significant inlet compression is required to produce refrigeration

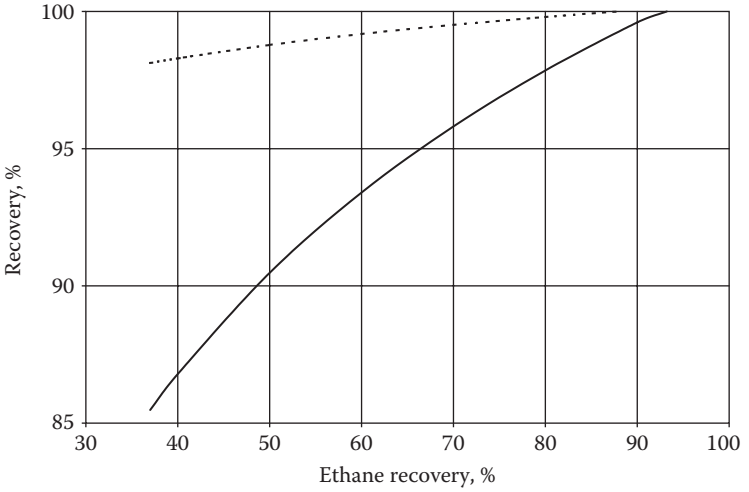


FIGURE 12.14 Recovery of propane and butanes as a function of ethane recovery rate. The solid and dashed lines represent propane and butanes recovery, respectively. See text for details.

by expansion. A primary motivation for the use of only direct refrigeration would be low inlet gas pressures. No matter which option is used, obtaining high ethane recoveries from low inlet-pressure feed streams requires substantial compression of the feed stream, the refrigerants, or both.

Figure 12.14 illustrates how ethane recovery affects propane and butane recoveries. These curves are simulations of recoveries for the Gas Subcooled Process (GSP) discussed below. The feed gas composition is shale gas No. 1 shown in Table 6.6; the simulator was ProMax 5.0 (Bryan Research & Engineering LLC, 2019). Recovery rates depend upon several factors including feed composition and process configuration. Because of minimum heating value specification for the residue sales gas, the amount of inerts in the feed can limit ethane recovery as well.

Example 12.3

Determine the maximum ethane recovery obtainable from an inlet gas containing 3.5% nitrogen, 7.0% ethane, and 2.5% propane (balance methane) when the residue sales gas must have a higher heating value of 1,000 Btu/scf (37.3 MJ/Nm^3) or higher. Assume all the inlet nitrogen and methane go to the residue sales gas, and the propane recovery is 100%.

Solution

BASIS: 1 SCF OF INLET GAS

The maximum ethane recovery is limited by the minimum heating value. The volume of nitrogen plus methane in the residue gas equals that in the inlet gas, 0.905 scf. The residue ethane volume is 0.07 scf minus the ethane removed in recovery. After renormalizing for all propane removal and the partial ethane removal, the residue gas must meet the 1,000 Btu/scf specification.

The residue volume, V_R, is the sum of (1 minus the fraction recovery) for each component times the component inlet volume:

$$V_R = 0.035\times(1-0)+0.87\times(1-0)+0.07\left(1-f_{C2}\right)+0.025\times(1-1)$$
$$= 0.905+0.07\left(1-f_{C2}\right)$$

where f_{C2} is the fraction ethane recovered.

The heating value of each component times the fraction of that component in the residue gas must equal 1,000. That gives

$$\frac{0.035\times 0+0.87\times 1{,}010\,\text{Btu/scf}+0.07\times\left(1-f_{C2}\right)\times 1{,}770\,\text{Btu/scf}}{0.905+0.07\times\left(1-f_{C2}\right)}=1{,}000\,\text{Btu/scf}$$

assuming all propane is recovered. Solving for f_{C2} yields 0.52 or 52%. Therefore, up to 52% of the inlet ethane can be recovered while meeting the residue sales gas heating value specification.

The following table summarizes the results.

Component	HHV[a] (Btu/scf)	Inlet Gas (mol%)	Percent Recovery (%)	Inlet × (1– Recovery) (%)	Residue (mol%)	HHV × mol%
Nitrogen	—	3.5	0	3.5	3.7	—
Methane	1,010	87.0	0	87.0	92.7	936
Ethane	1,770	7.0	52	3.4	3.6	64
Propane	2,516	2.5	100	0.0	0.0	–
Total		100.0		93.9	100.0	1,000

[a] Appendix Table B.1.

Figure 12.15 shows a simplified schematic for a conventional expander plant, circa 1975. It consists of gas heat exchangers, cold separator, turboexpander, and demethanizer. The figure shown is schematically oversimplified; in practice, the heat exchange is a more complex combination of exchangers. The inlet gas stream enters and splits into two streams with one going to heat exchange and to the cold separator. The other stream provides reboiler heat at the bottom, cools further in a side reboiler part way up the column, and rejoins the other feed stream before going to the cold separator. Liquid from the cold separator is flashed through a J–T valve and fed to the middle of the demethanizer. The cold separator vapor expands through a turboexpander. A J–T valve is installed parallel to the

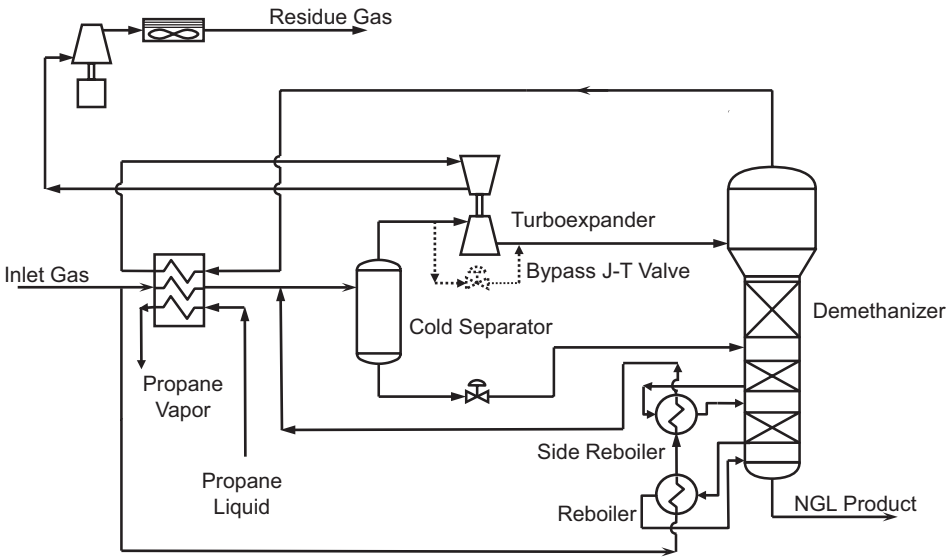


FIGURE 12.15 Schematic of early turboexpander process. Note that the one heat exchanger represents a network of exchangers.

turboexpander. This is required for plant start-up and for handling excess gas flow. It also allows continued operation at lower recoveries if the turboexpander is out of service.

The maximum ethane recovery with the turboexpander configuration shown in Figure 12.15 is approximately 80% (*Engineering Data Book*, 2016d). For this type of plant, the cold separator operates between 0°F and –30°F (–20°C to –35°C), depending on desired recovery level and gas composition. The demethanizer overhead typically operates in the range of –110°F to –170°F (–80°C to –110°C), and the bottoms is between 30°F and 0°F (0°C to –20°C). Design and operation limitations include:

- Operating the cold separator near the critical temperature and pressure of the mixture, which can make the plant unstable.
- Having carbon dioxide solidification and plugging.
- Requiring significantly more compression for incremental increases in C_2^+ recovery.

To overcome these and other limitations to high ethane recovery new processes were developed. These processes reduce ethane losses from the top of the demethanizer by the addition of a reflux-like liquid top feed. The first and most widely adopted process to be employed was the Gas Subcooled Process (GSP), illustrated in Figure 12.16. Because these new processes can operate the demethanizer at higher temperature, they can accept higher levels of CO_2. As can be seen from a comparison with Figure 12.15, a cold liquid stream is fed above the turboexpander inlet to improve recovery.

The *Engineering Data Book* (2016d) discusses a number of configurations that have been developed for high ethane recovery. Figure 12.17 illustrates the Recycle Split-Vapor (RSV) process. The RSV is a refinement of GSP that uses a slipstream of compressed sales gas as a second, leaner reflux stream for the demethanizer to increase recovery and improve efficiency. Like the GSP process, the vapor from the separator splits into two streams. Part goes to the turboexpander, and the balance goes through the overhead exchanger, where it is condensed to provide liquid reflux to the column. The turboexpander output enters further down the column. A small recycle stream of high-pressure residue gas is condensed and subcooled, then flashed down to be the top reflux stream for the demethanizer above the GSP feed. With the GSP feed providing "bulk" recovery of ethane in the column, only a small amount of lean reflux is needed

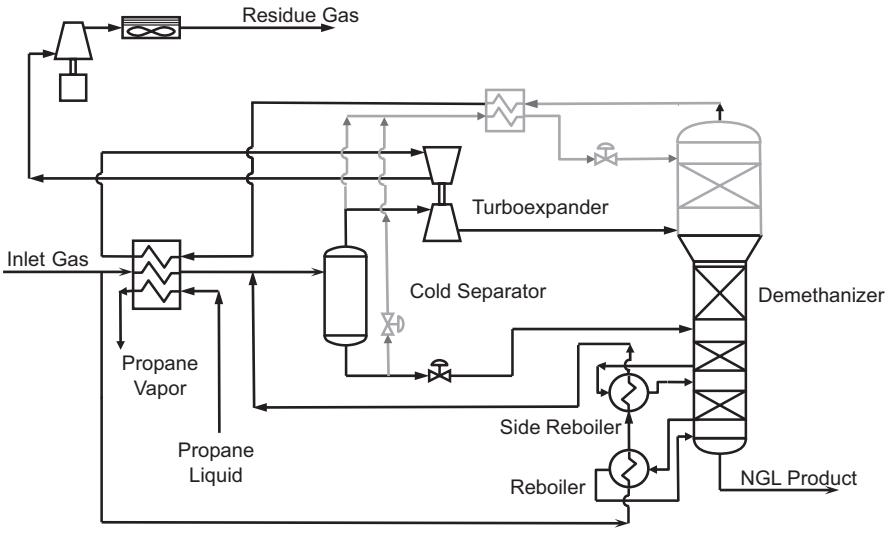


FIGURE 12.16 Schematic of GSP turboexpander process. Note that the one heat exchanger represents a network of exchangers. Lighter lines represent changes from the process shown in Figure 12.15. (Adapted from Hudson, et al., 2019).

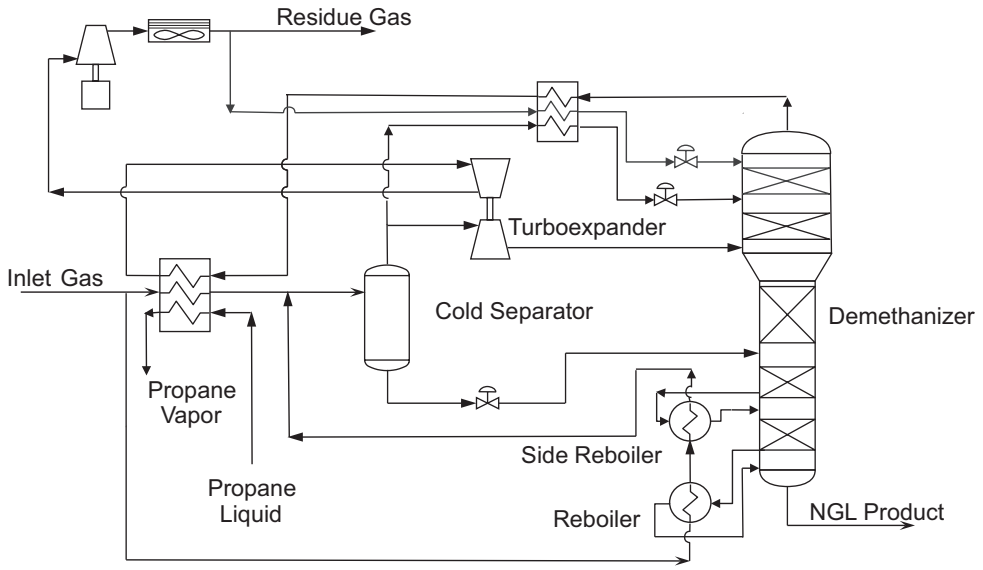


FIGURE 12.17 Schematic of RSV turboexpander process. The heat exchangers shown represent a network of exchangers (Adapted from Hudson et al., 2019).

to recover nearly all of the remaining ethane. For a thorough understanding of which process variations are best suited for what situations, the reader is referred to Wilkinson and Hudson (1992), Pitman et al. (1998), Pennybaker et al. (1999, 2000) and Hudson, et al. (2019).

12.4 SAFETY AND ENVIRONMENTAL CONSIDERATIONS

Safety considerations primarily exist because of the high pressures and low temperatures involved in hydrocarbon recovery. Plugging from insufficient removal of water, and carbon dioxide can be a processing hazard. Properly sized and functioning relief systems are critical to handle process streams in case plugging occurs or an outlet compressor shuts down.

Environmental concerns are relatively minor; lubricating oils along with methanol or glycol, if used, are the primary potential pollutants from spills.

DISCUSSION QUESTIONS

1. What are the major reasons for hydrocarbon recovery processes?
2. What is retrograde condensation, and why is it important in gas processing?
3. What is the difference between the critical point, cricondenbar, and cricondentherm of a natural gas mixture, and which is the most important to adjust to avoid pipeline condensation?
4. What are the relative merits of compressing the inlet gas and using propane refrigeration to provide the refrigeration needed for hydrocarbon recovery?
5. What is the maximum ethane recovery expected with a 5 GPM C_2^+ gas at 600 psig (41 barg) and –10°F (–23°C)?
6. What are the advantages and disadvantages of using J–T expansion versus turboexpansion?
7. When are fuel conditioning and dew pointing needed?
8. Why is glycol added to the gas in low-temperature separators, but not to cryogenic liquid recovery systems?

9. How does the membrane process for fuel conditioning differ from the membrane processes discussed in Chapter 4 for acid gas removal? Could the membrane material used in the two processes be interchanged? Why?
10. What are the key differences between the hydrocarbon recovery processes shown in Figures 12.15–12.17?

EXERCISES

12.1 For an inlet temperature of 32°F (0°C), compare the cooling obtained from a J–T expansion of methane from 1,000 to 200 psig to that obtained from a turboexpander with an adiabatic efficiency of 80%. What are the outlet temperatures, and how much work is produced for each expansion? Use the PH diagram available in Appendix B.[6]

12.2 Calculate the total flow rate of propane refrigerant needed (lb_m/h, kg/h) going through the single-stage propane chiller/evaporator (see Figure 12.3) and that needed for a two-stage system (see Figure 12.4). In both cases, assume the chiller/evaporator has a duty of 12,000 Btu/h (12.7 MJ/h). The chiller evaporates the propane at –40°F (–40°C) and it is condensed at 104°F (40°C). For the two-stage system the economizer is at 25°F (–4°C) and there is only one chiller.

Temperature	Saturated Vapor	Saturated Liquid
104°F (40°C)	–	219 Btu/lb_m (509 kJ/kg)
25°F (–4°C)	331 Btu/lb_m (770 kJ/kg)	168 Btu/lb_m (391 kJ/kg)
–40°F (–40°C)	311 Btu/lb_m (723 kJ/kg)	130 Btu/lb_m (302 kJ/kg)

Use the following enthalpy values (from Figures B.22 and B.23 in Appendix B) for your calculations:

12.3 In a simple turboexpander plant, similar to that shown in Figure 12.15, the bottom and side reboiler are heated by exchange with inlet gas. The total inlet gas flow rate is 10,000 lb-mol/h (4,536 kg-mol/h). The inlet gas, which is at 104°F (40°C), splits into two streams. One portion is cooled by cold residue gas. The other portion is cooled first in the reboiler and then the side reboiler. The liquid from the demethanizer to the side reboiler is at 0°F (–18°C). The side reboiler duty is 2.866 MMBtu/h (3.024 GJ/h) and the reboiler duty is 2.397 MMBtu/h (2.529 GJ/h). If the inlet gas has a molar heat capacity of 11.20 Btu/lb-mol (26.05 kJ/kg-mol) over the temperature range being considered and the minimum exchanger approach temperature[7] is 10°F (5.6°C), what fraction of the inlet gas is needed to provide the required demethanizer heating?

12.4 For the turboexpander plant described in Exercise 12.3, the residue gas to inlet gas exchanger has a duty of 5.263 MMBtu/h (5.553 GJ/h). How much refrigeration duty (MMBtu/h, GJ/h) must be supplied if the cold separator operates at –20°F (–29°C)?

12.5 Draw a sketch showing results from Exercises 12.3 and 12.4 in terms of heat exchanger arrangement.

[6] See Appendix B on publisher website: www.crcpress.com/Fundamentals-of-Natural-Gas-Processing-Third-Edition/Kidnay-Parrish-McCartney/p/book/9781138612792

[7] The approach temperature for a heat exchanger is the temperature difference between the two streams exchanging heat at any point in the heat exchanger.

REFERENCES

Agahi, R., and Ershaghi, B., Turboexpander redesign concepts and economics, *Proceedings of the Seventy-First Annual Convention Gas Processors Association*, Tulsa, OK, 1992, p. 29.

Baker, R.W., et al., The design of membrane vapor-gas separation systems, J. *Membrane Sci., 151*, 55, 1998.

Brouwer, J.M., et al., Supersonic gas conditioning first commercial offshore experience, *Eighty-Third Annual Gas Processors Association Convention*, Tulsa, OK, 2004.

Bryan Research & Engineering LLC, ProMax® 5.0, 2019.

Cannon, R.E., *The Gas Processing Industry, Origins and Evolution*, Gas Processors Association, Tulsa, OK, 1993.

Crum, F.S., Application of J-T plants for LP-gas recovery, *Proceedings of the Sixtieth Annual Convention Gas Processors Association*, Tulsa, OK, 1981, p. 68.

Engineering Data Book, Section 2, Product specifications, GPSA Midstream Suppliers, Tulsa, OK, 2016a.

Engineering Data Book, Section 13, Compressors and expanders, GPSA Midstream Suppliers, Tulsa, OK, 2016b.

Engineering Data Book, Section 14, Refrigeration, GPSA Midstream Suppliers, Tulsa, OK, 2016c.

Engineering Data Book, Section 16, Hydrocarbon recovery, GPSA Midstream Suppliers, Tulsa, OK, 2016d.

Engineering Data Book, Section 19, Fractionation and absorption, GPSA Midstream Suppliers, Tulsa, OK, 2016e.

Hale, P., and Lokhandwala, K., Advances in membrane materials provide new solutions in the gas business, *Eighty-Third Annual Gas Processors Association Convention*, Tulsa, OK, 2004.

Herrin, J.P., New process for liquid recovery, *Hydroc. Proc., 45*(6), 144, 1966.

Hudson, H., et al., How much CO_2 removal is enough for NGL recovery? (Revisited), *Laurance Reid Gas Conditioning Conference*, Norman, OK, 2019.

Jumonville, J., Tutorial on cryogenic turboexpanders, *Thirty-Third Turbomachinery Symposium*, 2004. https://oaktrust.library.tamu.edu/bitstream/handle/1969.1/163246/t33-15.pdf?sequence=1&isAllowed=y (Retrieved April 2019).

Lillard, J.K., and Nicol, G., An operating history of turboexpanders in the supercritical fluid regime, *Proceedings of the Seventy-Third Annual Convention Gas Processors Association*, Tulsa, OK, 1994, p. 270.

Mitariten, M., The Sorbead™ Quick-Cycle process for simultaneous removal of water, heavy hydrocarbons and mercaptans from natural gas, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2007, p. 125.

NGC+ Interchangeability Work Group, White paper on natural gas interchangeability and non-combustion end use, Federal Energy Regulatory Commission, 2005.

Okimoto, F.T., and Betting, M., TwisterTM supersonic separator, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2001.

Pennybaker, K., et al., A comparative study of propane recovery processes, *Seventy-Eighth Annual Convention of the Gas Processors Association*, Tulsa, OK, 1999.

Pennybaker, K., et al., A comparative study of ethane recovery processes, *Proceedings of the Seventy-Ninth Annual Convention Gas Processors Association*, Tulsa OK, 2000.

Pitman, R., et al., Next generation processes for NGL/LPG recovery, *Seventy-Seventh Annual Convention Gas Processors Association*, Tulsa, OK, 1998.

Schinkelshoek, P., and Epsom, H.D., Supersonic gas conditioning-commercialisation of TwisterTM technology, *Eighty-Seventh Annual Gas Processors Association Convention* Tulsa, OK, 2008.

Shah, K., and Stucky, B., Operation of high pressure cryogenic demethanizer at El Paso Eunice Gas Plant, *Eighty-third Annual Gas Processors Association Convention*, Tulsa, OK, 2004.

Smith, J.M., et al., *Introduction to Chemical Engineering Thermodynamics*, Eighth edn. McGraw-Hill Higher Education, New York, 2018.

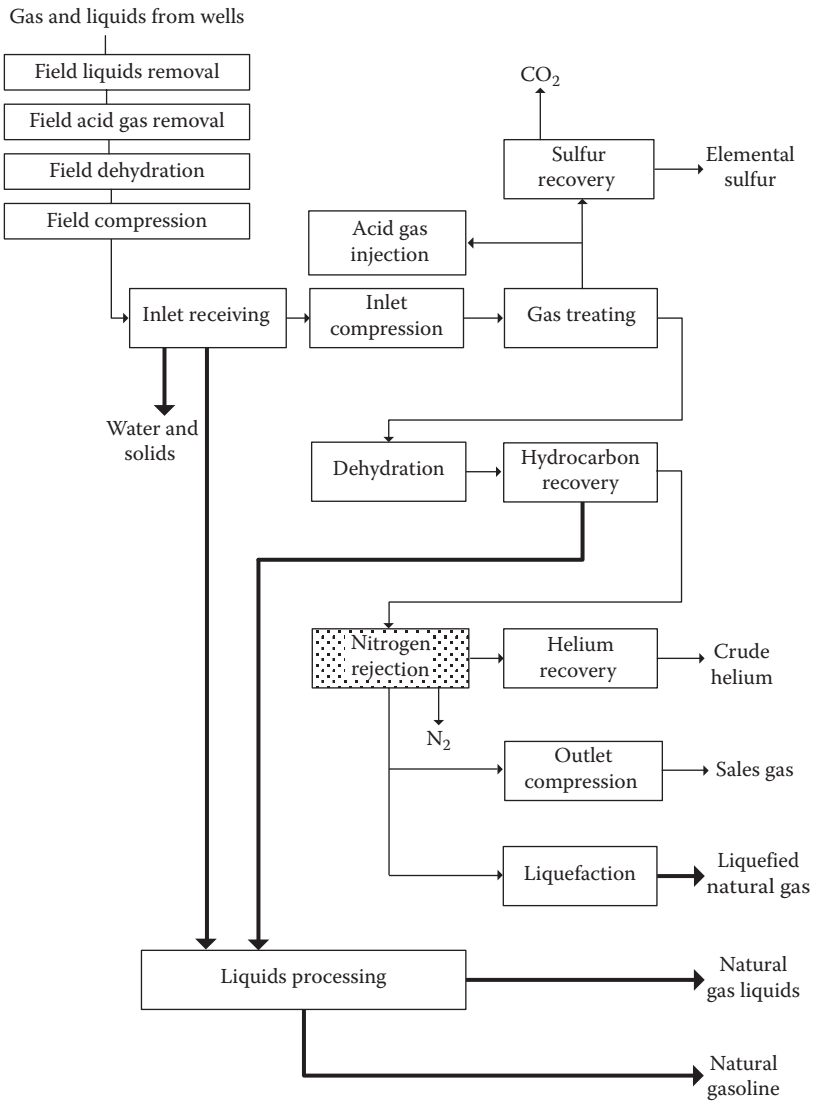
Swearingen, J.S., Engineers guide to turboexpanders, *Hydroc. Proc., 49*(4), 97, 1970.

Wilkinson, J., and Hudson, H., Improved NGL recovery designs maximize operating flexibility and product recoveries, *Seventy-First Annual Convention Gas Processors Association*, Tulsa, OK, 1992.

Wilson, J.L., and Yuvancic, J., Process selection for dehydrating Gulf of Mexico offshore platform gas, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman OK, 2004.

Taylor & Francis
Taylor & Francis Group
http://taylorandfrancis.com

13 Nitrogen Rejection



13.1 INTRODUCTION

Three sets of circumstances require nitrogen separation or rejection:

1. Processing high-nitrogen content gas to produce a pipeline-quality gas
2. Removing nitrogen from a natural gas so that the nitrogen can be used in an enhanced oil recovery (EOR) operation
3. Producing a nitrogen–helium feedstock mixture for helium recovery

This chapter discusses nitrogen rejection for EOR and for production of pipeline-quality gas, leaving a brief discussion of the helium–nitrogen separation to Chapter 14.

The Gas Research Institute's survey of U.S. reserves (GRI, 1993) found that approximately 24 Tcf ($670 \times 10^9 m^3$), 16% of the nonassociated reserves at that time were subquality in nitrogen and consequently will require blending to lower the nitrogen concentration or processing to remove the nitrogen to meet pipeline specifications (*Engineering Data Book*, 2016a).

Tannehill et al. (1999) discuss the processing of high-nitrogen gas. They also cover the location of high-nitrogen reserves, the number and types of plants used in the processing and summarize some of the economics.

13.2 NITROGEN REJECTION FOR GAS UPGRADING

When a natural gas has excessive nitrogen levels, three options are available (*Engineering Data Book*, 2016b):

1. Gas blending to meet pipeline specifications
2. Accepting a reduced price for the gas
3. Removing sufficient nitrogen to meet sales specifications

When options 1 and 2 are unavailable, a nitrogen rejection unit (NRU) can be employed.

The most common methods for removing nitrogen from natural gas are:

- Cryogenic distillation
- Pressure swing adsorption (PSA)
- Membrane separation

Table 13.1 provides a comparison of the three processes.

Cryogenic methods are the most economical at higher feed gas rates and nitrogen concentrations. At low gas volumes, membrane separation and PSA are economically feasible. (See Chapter 4 for description of these two processes.)

When PSA with molecular sieve is used, heavier hydrocarbons (all C_4^+ and part of the propane) go with the nitrogen stream. This is due to adsorption in the sieve binder as the heavier components are too large to enter the sieve pores. The binder also adsorbs water and CO_2. The loss of heavy hydrocarbons may or may not be beneficial.

TABLE 13.1
Comparison of Nitrogen Removal Processes

Process	Flow Range MMscfd (10^6 Nm^3/d)	Complexity	Heavy Hydrocarbons	Development Stage
Cryogenic distillation	>15 (0.4)	Complex	In product gas	Mature
PSA	2–15 (0.05–0.4)	Simple; batch operation, requires bed switching	In regeneration gas	Commercialized
Membrane	0.5–25 (0.01–0.7)	Simple continuous operation	In product gas	Commercialized

Source: Adapted from Hale and Lokhandwala (2004).

13.2.1 Cryogenic Distillation

The *Engineering Data Book* (2016b) notes that either a single- or double-column configuration is used for nitrogen rejection. A single column is used when the feed gas nitrogen content is below about 20 mol% and remains relatively constant. The process requires external refrigeration.

At higher concentrations, the double column is preferred because it requires no external refrigeration and can accommodate variable inlet nitrogen concentrations by changing operating conditions. Because the double-column design is more flexible, sometimes a small column or flash is used to concentrate the nitrogen in the feed going to the NRU. This approach makes the double-column design useable over almost the entire range of nitrogen concentrations. This section discusses only the double-column process. The Engineering Data Book (2016) provides details on the single-column configuration.

Figure 13.1 shows a simplified flow diagram of a classic double-column NRU. It is an adaptation of the process used in hundreds of air separation plants for many years. The feed gas is cooled by cross exchange with the product streams. Following a J–T expansion, the stream enters the high-pressure column, which typically operates between 300 and 400 psig (20–30 barg). The nitrogen–methane separation is relatively easy so the high-pressure column produces a nearly pure nitrogen overhead stream. The stream condenses in the low-pressure column reboiler and a small portion of the liquid returns as reflux to the high-pressure column. The majority of the liquid is subcooled, expanded through a J–T valve, and used as reflux for the low-pressure column.

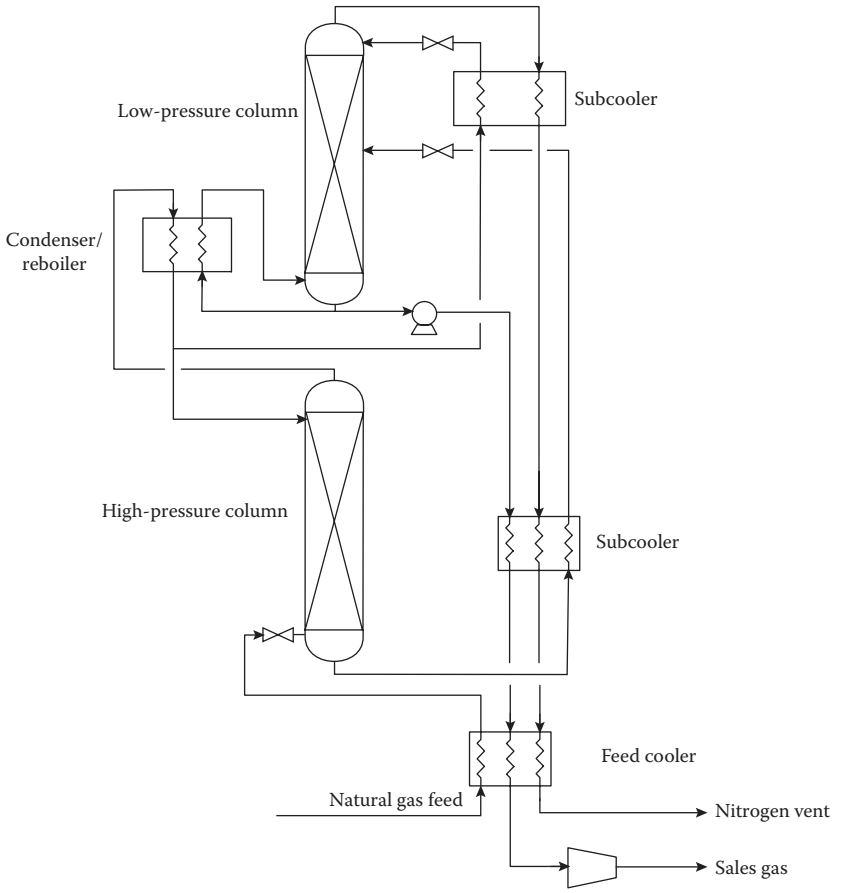


FIGURE 13.1 Schematic of a double-column NRU. (Adapted from *Engineering Data Book*, 2016b. With permission.)

The bottoms from the high-pressure column are cooled by heat exchange and J–T expansion and then fed to the low-pressure column. This column typically operates at approximately 10 psig (0.7 barg). The low-pressure column makes a high-purity nitrogen overhead and a liquefied sales gas bottoms product. The pumped bottoms and overhead nitrogen streams provide cooling for the high-pressure bottoms stream going to the low-pressure column. Ideally, the liquefied sales gas could be pumped to pipeline delivery pressure to avoid compression after regasification. However, the regasification temperature would be too high to provide adequate refrigeration for the process, making compression necessary.

The ability to change the high-pressure column operating pressure provides the flexibility to adjust the NRU to different nitrogen feed concentrations. This, combined with not needing external refrigeration, makes the double-column configuration attractive for many NRU applications.

Extremely low temperatures (lower than –240°F, –150°C) are involved in all the distillation processes; consequently, it is necessary to ensure that the feed to the unit has been treated to remove water, carbon dioxide, and mercury to acceptable levels; normally, 50 ppmv for carbon dioxide and ≤0.1 ppmv for water and <0.01 μg/Nm^3 for mercury.

The Hannibal gas plant of British Gas Tunisia (Jones et al., 1999) uses cryogenic distillation to reduce the nitrogen content of the feed gas from 16.9% nitrogen to the sales gas specification of 6.5% (see Chapter 20 for more details). Complete descriptions of the plant and its operations are given by Jones et al. (1999) and Howard (1998).

13.2.2 Pressure Swing Adsorption

After cryogenic distillation, PSA is probably the most widely used process for nitrogen rejection. The fundamentals of PSA are discussed in Chapter 4 and not repeated here.

D'Amico et al. (1993) describe a PSA unit that uses a specially treated carbon molecular sieve (CMS) for nitrogen rejection. The CMS is prepared by processing coal or wood carbon. Complete details as well as an economic study are presented in the original article. Shirley et al. (1996) discuss a PSA system using what they describe as a "special form of carbon" that adsorbs hydrocarbons while rejecting nitrogen. Bhattacharya et al. (2009) describe a small-scale unit to upgrade low-Btu gas to pipeline quality. The two distinctive features of the unit are the use of a nonpatented carbon produced from coconut husks, and the use of a vacuum system in the regeneration step.

Mitariten (2001), Mitariten et al. (2002), and Willis et al. (2003) describe a PSA process that uses the Molecular Gate sieve. According to these authors, conventional 3A and 4A molecular sieve have pore openings of 3.2 Å and slightly less than 4.2 Å, respectively. The Molecular Gate sieve is a titanium silicate with a pore opening of 3.7 Å, allowing better separation of nitrogen (3.6 Å in diameter) from methane (3.8 Å in diameter). Further information on the process is given by Mitariten (2009).

13.2.3 Membranes

Chapter 4 presented the basics of membrane separation, and that discussion applies to N_2 separation from natural gas. Baker and Lokhandwala (2008) present a comprehensive overview of natural gas processing using membranes. They conclude that the main use of membranes for nitrogen removal from natural gas is upgrading small quantities of wellhead gas to pipeline specifications.

Figure 13.2 shows such an application using the Nitrosep™ process. Values in the figure are approximate design values; Table 13.2 provides actual operating data. The objective was to take a low-heating value wellhead gas and produce a product gas, which could be blended with a low-nitrogen content gas to meet pipeline specifications. The properties of the feed gas varied but the values shown in the table are representative. The permeate from the first membrane unit was enriched in hydrocarbons and was the product gas. The permeate from the second membrane unit was also enriched in hydrocarbons and was recycled to the inlet, while the residue passed to a

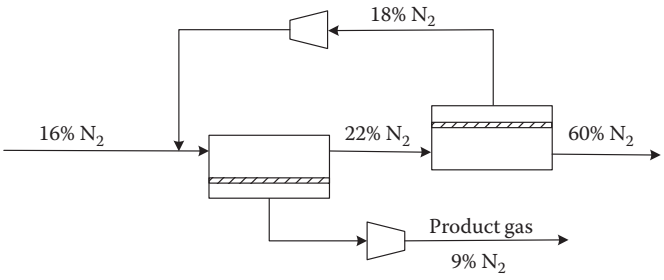


FIGURE 13.2 Nitrogen upgrading using membranes. (Adapted from Lokhandwala, 2007)

TABLE 13.2
Performance Data for Towne Exploration's Commercial Nitrogen Separation Unit

	Feed Gas	Product Gas	Vent Gas	Recycle Gas
Pressure, psig (barg)	847 (58.4)	821 (56.6)	828 (57.1)	840 (57.9)
Temperature, °F (°C)	76 (24)	87 (30.5)	63 (17)	104 (40)
Volume, MMscfd (10^3 Nm^3/d)	1.738 (46.5)	1.423 (38.1)	0.188 (5.04)	2.711 (72.6)
Heating value (Daily average) Btu/scf (MJ/Nm^3)	908 (35.8)	980 (38.6)	421 (16.6)	881 (34.7)
	Stream Compositions (Daily Average mol%)			
N_2	15.3	9.3	58.9	16.3
CO_2	0.3	0.3	0.1	0.2
CH_4	80.7	86.1	40.7	80.9
C_2H_6	2.0	2.2	0.2	1.4
C_3H_8	0.9	1.1	0.1	0.6
C_4^+	0.8	1.0	Negligible	0.6

Source: Adapted from Lokhandwala (2007).

third membrane unit to produce engine fuel and vent gas. Lokhandwala (2007) provides additional tabular data on both design and actual operating parameters.

13.3 NITROGEN REJECTION FOR ENHANCED OIL RECOVERY USING CRYOGENIC DISTILLATION

In a survey of EOR projects Moritis (2008) reported that the nitrogen EOR project servicing the offshore Cantarell reservoir in Mexico in 2008 produced about 1.8 MM bbl/d ($290 \times 10^3 m^3$/d). Kuo et al. (2001) described the four large air plants needed for the Cantarell project. When installed in 2000, the cryogenic nitrogen production facilities for the field were the world's largest; each of the four units was capable of generating 300 MMscfd (8×10^6 Nm^3/d) of nitrogen from air. The total compression power for air and nitrogen was 500,000 hp (375 MW).

A 2018 survey of worldwide EOR projects (IEA, 2019) listed over 230 projects with 161 of those located in North America. Approximately 19% of the total listed production was from gases such as nitrogen and natural gas. Total production listed accounted for 2.3 MM bbl/d ($370 \times 10^3 m^3$/day) of oil production. Neither a 2014 survey of EOR projects in North America (Kuuskraa and Wallace, 2014) nor the IEA 2018 survey list the Cantarell field as an active EOR project although the field still shows to be in production.

In conventional oil and gas production, the nitrogen content varies from well to well but remains relatively constant over time. By contrast, the nitrogen content of gas from an EOR project increases over the life of the project. In EOR, the N_2 is injected into the reservoir through a series of injection wells positioned to sweep the oil to the producing wells. Initially, there may be little or no N_2 in the produced gas, but inevitably N_2 breaks through to the producing wells. As the field becomes depleted, the N_2 content increases. Eventually, the N_2 level reaches a point where it is no longer economical to produce oil and the project is shut down.

In the EOR project described by McLeod and Schaak (1986), the anticipated inlet NRU nitrogen concentrations increased from 21% to 75%. As previously noted, feed concentration plays a major role in the process selection. Therefore, these NRU plants must be carefully designed to accommodate the wide range of inlet concentrations.

NRUs in EOR service can use double-column cryogenic distillation to handle the variable feed composition. The double-column NRU shown in Figure 13.1 and described in Section 13.2.1 is discussed in more detail by Vines (1986) and Alvarez and Vines (1985).

McLeod and Schaak (1986) give a detailed account of an EOR project using N_2 as the injection fluid. Figure 13.3 is a general schematic of the operation, which consisted of three separate units:

- An air separation plant to produce nitrogen
- A gas plant to recover liquids from the produced stream
- An NRU to produce a sales gas

The air separation plant produced liquid nitrogen and 30 MMscfd (800×10^3 Nm^3/d) of N_2 gas containing 5 ppmv of O_2. The oxygen from the unit was vented to the atmosphere. The N_2 gas was compressed to 4,900 psig (340 barg) in two sets of compressors and injected into the reservoir. The solution gas coming from the reservoir went to a conventional gas processing plant to produce a hydrocarbon product (LPG) and a residue gas that went to the NRU. The NRU produced a sales gas with a minimum heating value of 975 Btu/scf (38.4 MJ/Nm^3) from an NRU feed gas that contained from 20% to 75% N_2. The NRU used double-column cryogenic distillation for the separation, which is described in the paper. At the beginning of the project, there was little N_2 in the produced gas but the concentration continuously increased during the life of the project. In the later stages of the

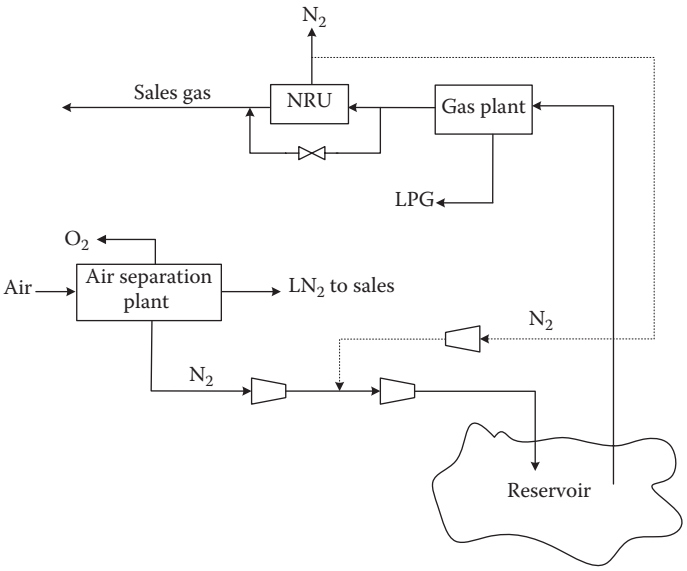


FIGURE 13.3 Schematic of an EOR system (McLeod and Schaak, 1986).

project, N_2 removed in the NRU was recompressed and reinjected into the reservoir thus reducing the need for N_2 from the air separation plant.

The Anschutz Ranch East NGL/NRU plant described by Davis et al. (1989) was designed to process 300 MMscfd (8×10^6 Nm^3/d) of gas with N_2 compositions varying from 2% to 80%. When built, it was the largest variable content NRU in the world.

Additional information on NRUs may be found in the papers of Goethe and Mawer (1987) and Young and Maloney (1989).

13.4 SAFETY AND ENVIRONMENTAL CONSIDERATIONS

Safety considerations are centered on the high pressures and extremely low temperatures generally encountered in NRUs. In addition, if there is a chance that low temperature nitrogen can be vented, it must be routed to a safe location so that it becomes more buoyant than the ambient air and is not allowed to accumulate in a confined space. This prevents the possibility of an accidental asphyxiation. Environmentally, all of the systems are benign.

DISCUSSION QUESTIONS

1. When is nitrogen rejection required in producing a sales gas?
2. Why are membrane and adsorption processes attractive at lower gas throughputs but not at high gas throughputs?
3. What is the major factor that differentiates NRU for gas cleanup from an NRU for EOR?
4. Would temperature swing adsorption be a viable process for NRU?
5. Figure 13.1 shows several places where J–T expansion is used to cool the stream. In which, if any, places could turboexpanders be used instead?
6. What makes the double-column NRU more versatile than the single-column NRU?

EXERCISES

13.1 It is possible to upgrade a natural gas stream by using membranes. Refer to Figure 13.2 and modify the schematic as follows:

- Add a third membrane unit at the end of the two-membrane train.
- The permeate from the third unit is compressor fuel and the residue goes to the flare.

Replace all values in Figure 13.2 as follows:

- The feed is 10 MMscfd (2.68×10^5 Nm^3/day), 15% N_2, 85% CH_4
- The product gas is 4% N_2, 7.6 MMscfd (2.04×10^5 Nm^3/day)
- The recycle stream is 8.7% N_2
- The compressor fuel (third membrane unit) is 26% N_2, 0.9 MMscfd (24×10^3 Nm^3/day)
- The flare is 65% N_2

a. What percent of the CH_4 is lost in the flare gas?
b. What is the total Btu (kJ) recovery in the product stream?

13.2 Bhattacharya et al. (2009) discuss upgrading high-nitrogen, low-quality natural gas to pipeline specifications using a PSA process for nitrogen rejection. The table below shows the results of one of their experimental runs.

	Heating value	Gas composition, Mol%	
	Btu/scf (MJ/Nm^3)	Hydrocarbons (CH_4^+)	N_2
Feed	687 (27.06)	63	37
Gas to flare	–	–	63.1
Sales gas	953 (37.53)	84	–

Calculate:

a. Efficiency of N_2 rejection (% N_2 removed)
b. Btu recovery

REFERENCES

Alvarez, M.A., and Vines, H.L., Nitrogen rejection/NGL recovery for EOR projects, *Energy Progr., 5*(2), 67, 1985.

Baker, R.W., and Lokhandwala, K., Natural gas processing with membranes: An overview, *Ind. Eng. Chem. Res., 47*, 2109, 2008.

Bhattacharya, C., et al., Field tests prove microscale NRU to upgrade low-btu gas, *Oil Gas J., 107*(40), 44, 2009.

D'Amico, J., et al., A PSA process for nitrogen rejection from natural gas, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 1993, p. 55.

Davis, R.A., et al., Integrated nitrogen rejection facility design and operation, *Proceedings of the Sixty-Eighth Annual Convention Gas Processors Association*, Tulsa, OK, 1989, p. 204.

Engineering Data Book, Section 2, Product specifications, GPSA Midstream Suppliers, Tulsa, OK, 2016a.

Engineering Data Book, Section 16, Hydrocarbon recovery, GPSA Midstream Suppliers, Tulsa, OK, 2016b.

Goethe, A., and Mawer, D.J., A new integrated nitrogen rejection process with NGL recovery, *Proceedings of the Sixty-Sixth Annual Convention Gas Processors Association*, Tulsa, OK, 1987, p. 89.

GRI, Chemical composition of discovered and undiscovered natural gas in the United States-1993 Update. *Volume 1: Project summary, GRI-93/0456.1*, Gas Research Institute, 1993.

Hale, P., and Lokhandwala, K., Advances in membrane materials provide new gas processing solutions, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2004.

Howard, I., Hannibal's experiences, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 1998, p. 194.

Inernational Energy Agency, World energy outlook, 2019. www.iea.org/weo/ (Retrieved April 2019).

Jones, S., et al., Simultaneous removal of water and BTEX from feed gas for a cryogenic plant, *Proceedings of the Seventy-Eighth Annual Convention Gas Processors Association*, Tulsa, OK, 1999, p. 108.

Kuo, J.C., et al., World's largest N_2-generation plant starts up for Cantarell reservoir pressure maintenance, *Oil Gas J., 99*(11), 41–47, 2001.

Kuuskraa, V.A., and Wallace, M., CO_2-EOR set for growth as new CO_2 supplies emerge, *Oil Gas J., 112*(5), 92, 2014.

Lokhandwala, K., Field demonstration of a membrane process to separate nitrogen from natural gas, final report, Department of Energy Award No.: DE-FCC26-01NT41225, 2007.

McLeod, R.P., and Schaak, J.P., A unique combination of natural gas processing with cryogenic technology in an enhanced oil recovery project, *Proceedings of the Sixty-Fifth Annual Convention Gas Processors Association*, Tulsa, OK, 1986, p. 71.

Mitariten, M., New technology improves nitrogen removal economics, *Oil Gas J., 99*(17), 42, 2001.

Mitariten, M., Nitrogen removal from natural gas with the Molecular Gate™ adsorption process, *Eighty-Eighth Annual of the Gas Processors Association Convention*, Tulsa, OK, 2009.

Mitariten, M., et al., Innovative Molecular Gate™ systems for nitrogen rejection, carbon dioxide removal, and NGL recovery, *Eighty-First Annual Gas Processors Association Convention* Tulsa, OK, 2002.

Moritis, G., More EOR projects start but production continues to decline, *Oil Gas J., 106*(15), 41, 2008.

Shirley, A., et al., Non-cryogenic nitrogen rejection from natural gas, *Proceedings of the Seventy-Fifth Annual Convention of the Gas Processors Association*, Tulsa, OK, 1996, p. 62.

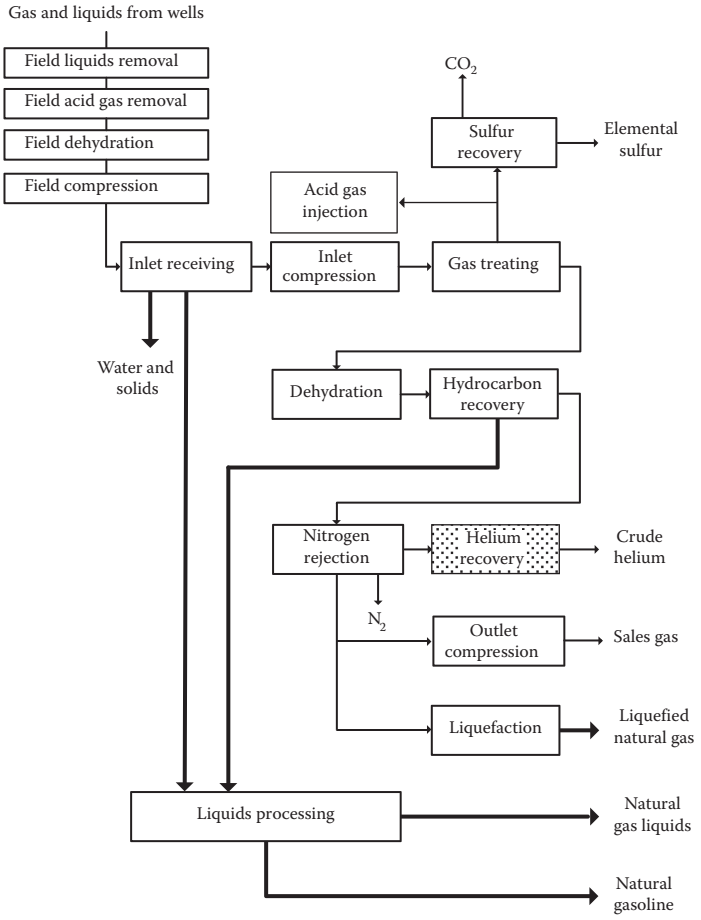
Tannehill, C.C., et al., High N_2 gas - snap shot of the present requirements for the future, *Proceedings of the Seventy-Eighth Annual Convention Gas Processors Association*, Tulsa, OK, 1999, p. 230.

Vines, H.L., Nitrogen rejection technology, *Chem. Eng. Progr., 82*(11), 46, 1986.

Willis, J., et al., The Molecular Gate® CO_2 removal process, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2003, p. 109.

Young, S.M., and Maloney, J.J., Enhanced reservoir value through nitrogen rejection, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 1989, p. 301.

14 Trace Component Recovery or Removal



14.1 INTRODUCTION

Chapters 10–13 discussed methods to remove the common natural gas impurities. A number of other trace components present processing, product quality, or environmental problems if concentrations are too high. These components include:

- Helium
- Hydrogen
- Oxygen
- Radon (naturally occurring radioactive material (NORM))
- Arsenic
- Mercury

- Benzene, toluene, ethylbenzene, and xylene (BTEX)
- Methanol

This chapter discusses helium recovery and briefly touches on hydrogen, oxygen, radon and arsenic. It then discusses mercury, BTEX, and methanol in more detail. Note that contracts rarely explicitly state specifications for any of these components other than oxygen, methanol, and crude helium.

14.2 HELIUM

14.2.1 Introduction

Helium, which has the lowest boiling point of all fluids, is a difficult diluent to remove in natural gas unless nitrogen rejection is used. When helium is present it concentrates in cryogenic nitrogen rejection units (NRU). See Chapter 13 for a discussion of NRUs. Literature indicates that unprocessed gases containing helium always have a significant concentration of nitrogen. However, not all unprocessed gases containing nitrogen contain helium. Unlike the other trace components discussed here, helium is a valuable product from natural gas processing, which makes high concentrations desirable. Recovery of helium from air is technically feasible but would be very expensive because the helium concentration is about 5 ppmv (Anderson, 2018). Anderson (2018) presents costs of between $1,000/Mscf and $9,000/Mscf (40–300 $/ 10^3 Nm^3) for helium when extracted from air.

A helium-rich gas is defined as one that contains more than 0.3% helium, and according to published field concentrations (Committee on the Impact of Selling the Federal Helium Reserve, 2000; Deaton and Haynes, 1961; Guccione, 1963; Johnson and Rydjord, 2001), a gas that contains more than 5% is rare. Traditionally, the source for helium is from select natural gas fields, and even the best of these gas fields contains relatively small concentrations of helium. A number of plants recover helium and are economically viable because of the helium produced. These plants typically recover helium from an NRU nitrogen vent stream. Helium is also recovered by processing the nitrogen stream rejected from liquefied natural gas (LNG) plants.

Anderson (2018) presents an overview of helium reserves and usage in the United States and the world. In 2015, the world production of grade-A helium (99.995% purity), excluding reserve withdrawals, was an estimated 3.8 Bscf (102×10^6 Nm^3); the United States produced 56% of the total, with the remainder coming from Algeria, Qatar, Russia, and Poland. Several new plants became operational between 2009 and 2015. Many of these are associated with LNG production. An Australian plant began producing up to 150 MMscf/year (4×10^6 Nm^3/year) in 2010 and Qatar has the capacity to produce 975 MMscf/year (26×10^6 Nm^3/year) of helium. Both facilities use nitrogen gas vented from LNG plants.

The uses of helium are limited but important. Its main applications stem from the fact that it is chemically inert and has the lowest boiling point of any substance. Figure 14.1 shows how helium was used in the United States in 2016. MRI stands for Magnetic Residence Imaging which requires liquid helium for the instrument's superconducting magnets.

14.2.2 Recovery Methods

Recovery of helium from natural gas requires refinement of the low concentrations into high-purity helium (99.995%). Helium is concentrated in the vent gas from NRUs and consequently, the traditional gas plant may produce only a raw helium stream mixture of helium and nitrogen. The low-purity helium, which may be up to 50 mol% helium, then goes to another facility for enrichment. Because the natural gas throughput from an LNG plant can be large, it can be economically attractive to recover helium even when the helium content is only a few percent in the vent gas. The helium recovery plants in Algeria, Qatar, and Australia use raw helium from LNG plant nitrogen vents. Often the helium production facility associated with an LNG plant is owned and operated by an industrial gas company rather than the LNG plant owner.

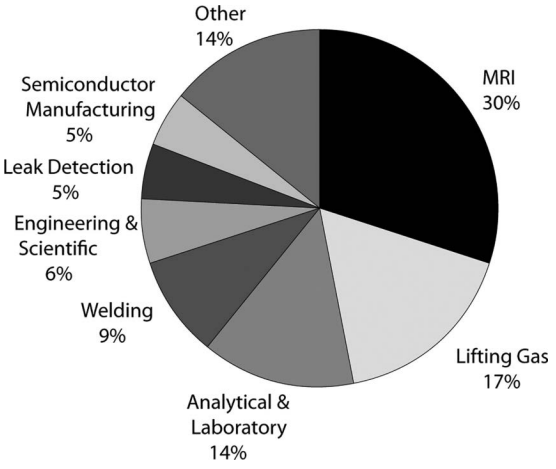


FIGURE 14.1 Grade-A Helium uses in the United States in 2016 (Anderson, 2018).

Early helium processing schemes (Deaton and Haynes, 1961; Guccione, 1963; Remirez, 1968) were cryogenic and involved cooling and condensing the natural gas and then recovering the helium by distillation as a crude product that was about 65%–80% helium. The crude helium was then stored or further refined in a series of low-temperature separations, followed by a final adsorption step using activated charcoal to produce the high-purity product.

Alternate technologies such as membranes and pressure swing adsorption (PSA) (see Chapter 4) for helium recovery are also used. Choe et al. (1988) present a discussion and analysis of hybrid cryogenic and membrane processes. Helium can be highly purified using PSA. Modern helium facilities employ a cryogenic distillation followed by PSA.

An example of the cryogenic/PSA process is the Ladder Creek Plant (Johnson and Rydjord, 2001). It is located in Eastern Colorado and started production in 1998. Figure 14.2 is a simplified block flow diagram of the plant. The inlet gas composition varies but the values in Table 14.1 are representative of the feed gases to the plant. With this poor quality of gas the plant was economically feasible only if the helium was recovered and sold.

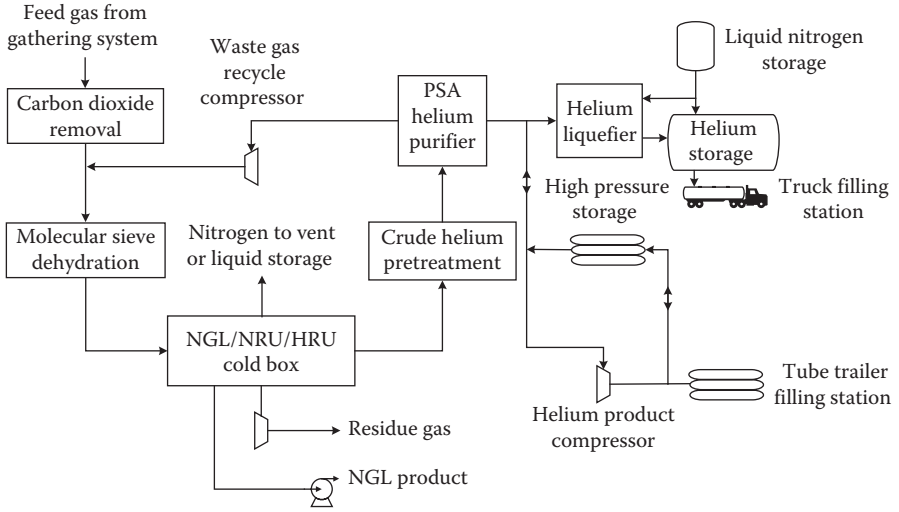


FIGURE 14.2 Schematic of Ladder Creek Helium Recovery Plant (Johnson and Rydjord, 2001).

TABLE 14.1
Range of Feed Gas Compositions to Ladder Creek Helium Recovery Plant

	Composition (mol%)	
Component	**Rich Helium Gas**	**Lean Helium Gas**
Nitrogen	61.93	31.58
Helium	3.54	1.81
Carbon dioxide	0.98	0.91
Methane	26.65	52.84
Ethane	2.60	6.40
Propane	1.95	3.64
i-Butane	0.37	0.46
n-Butane	0.88	1.09
Pentane+	1.10	1.27
Total	100.00	100.00

Source: Johnson and Rydjord (2001).

The plant was designed to process 35 MMscfd (0.94×10^6 Nm^3/d) of inlet gas, with expansion capability to 50 MMscfd (1.3×10^6 Nm^3/d). Helium recovery was set at 95%, with the ethane either rejected or recovered. The natural gas liquids (NGLs) are recovered while pipeline gas is produced.

In Figure 14.2, the carbon dioxide content is first reduced to less than 10 ppm, and then trace quantities of mercury present are removed before dehydration using molecular sieve beds. Details of the cold box are unavailable, but its products are:

- Crude helium stream (nitrogen plus helium)
- Small stream of liquid nitrogen
- Residue gas
- NGL

The liquid nitrogen is used to fill the nitrogen shields on the liquid helium trailers and the helium storage. The crude helium is purified to 99.997% by the use of PSA. The PSA adsorbers operate at ambient temperature and 240–280 psig (16.5–19 barg). Adsorbers are on-line for approximately 320 s and are then taken off-line, depressurized to approximately 40 psig (3 barg), and flushed with pure helium gas for reactivation. All flush gas is recycled to the cold box. The helium produced may be liquefied and stored and shipped by truck as a liquid or compressed and stored and shipped as a high-pressure gas. Details of the patented helium liquefier are not available, but it has a capacity of 1.7 MMscfd (46×10^3 Nm^3/d).

Tables 14.1 and 6.5 show that gases containing helium also have high nitrogen concentrations. However, many nitrogen-rich gases contain no helium.

Example 14.1

Compute the ratio of the minimum work required to separate pure He from air compared with that from a natural gas that contains 3 mol% He in the feed. Helium content in air is 5 ppmv. Assume the separation takes place at constant temperature and that the gases are ideal.

Solution

As shown in any engineering thermodynamics text (e.g., Smith et al., 2018), the theoretical minimum work to go from one state to another is $T\Delta s$, where T is the absolute temperature

and Δs is the change in entropy between the initial and final states. The entropy change per mole of ideal gas mixture formed from pure components is

$$\Delta s = -R\sum x_i \ln x_i,$$

where

R is the gas constant
x_i is the mole fraction of component i

Because the He concentration is so low in air (~5 ppmv), the mole fraction of the other components in air can be assumed to not change, so the change in entropy is assumed to be caused by the change in He concentration only. The ratio of work per mole of He produced is based on one mole of initial gas mixture. Thus, the ratio of work is

$$\frac{T\Delta s_{\text{Air}}}{T\Delta s_{NG}} = \frac{\ln x_{\text{He,Air}}}{\left(\dfrac{x_{\text{He},NG}\ln x_{\text{He},NG} + x_{\text{He},NG}\ln\left(1-x_{\text{He},NG}\right)}{x_{\text{He},NG}}\right)}$$

$$= \frac{\ln\left(5\times10^{-6}\right)}{\left(\dfrac{0.03\ln 0.03 + 0.97\ln 0.97}{0.03}\right)} = 2.7$$

If the two separations are performed at 100% thermodynamic efficiency and at a constant temperature, the work required to obtain helium from air would be 2.7 times greater than extracting it from natural gas. However, most separation processes have low thermodynamic efficiencies so the actual ratio of work of separation could be five or more times greater. This is reflected in estimated recovery costs given in Section 14.2.1.

14.3 HYDROGEN

Hydrogen levels are rarely sufficiently high to cause a problem and no GPA Midstream Association specifications exist for maximum levels in sales gas. While a few fields produce gas containing hydrogen, the primary source is in gas streams from refineries delivered into gathering systems. Once mixed with produced natural gas the concentration of hydrogen is generally so low that it will not affect processing or product quality.

14.4 OXYGEN

Of the items listed above, oxygen and methanol are the only contaminants that do not occur naturally in natural gas. The best approach for treating oxygen is to prevent its introduction into the processing stream. The major sources of oxygen are leaking valves and piping in gathering systems that operate below atmospheric pressure. As fields age, gathering system maintenance becomes more critical to minimize oxygen contamination. Another common source of oxygen is a vapor recovery compressor on a production tank battery where suction pressures can be below atmospheric pressure. The *Engineering Data Book* (2016a) gives a 1.0 vol% maximum oxygen concentration in residue sales gas, but some pipelines have specifications as low as 10 ppmv.

Oxygen causes problems in gas processing at concentrations of less than 50 ppmv, such as:

- Enhancing pipeline corrosion if liquid water is present.
- Reacting with amines in gas treating, which ultimately leads to heat stable salt and corrosive compound formation.
- Reacting with glycols to form corrosive acidic compounds.
- Reacting with hydrocarbons during the high-temperature regeneration of adsorption beds to form water, which reduces regeneration effectiveness, and thus reduces bed capacity.

At low levels, oxygen can be removed using nonregenerative scavengers. Because many of these chemicals are expensive and some are toxic this approach is uncommon. For higher concentrations, the obvious removal method is to catalytically react it in the gas stream to produce water, which is then removed in a dehydration step. Oxidizing the process stream after treating generates CO_2, which can freeze out in cryogenic sections of the plant. Oxygen can be removed from residue sales gas with a NRU, but this step follows the processing steps most susceptible to oxygen damage. Also, few gas plants have NRUs.

Even if inlet gas contains no oxygen, trace amounts of oxygen cause problems in treating and dehydration as noted above. These problems are minimized by using deaerated makeup water and maintaining an inert blanket gas over amine and glycol solvents.

14.5 NORM

Some natural gases contain radon-222 (Rn-222), a naturally occurring radioactive material (NORM) generated by the decay of radium-226, which is the product of uranium-238 decay. It is present in low concentrations, and rarely poses a health problem unless it is in confined spaces. Figure 14.3 shows the primary decay path of Rn-222, which has a half-life[1] of about 3.8 days. After seven steps, Rn-222 decays into stable lead-206 (Pb-206) (Committee on Health Risks of Exposure to Radon (BEIR VI), 1999). Other minor decay paths occur but they contribute less than 1% of total activity. Lead-210 is the only major intermediate and Pb-206, the only stable progeny (daughter product). The Rn-222 progeny accumulate on surfaces to form a low-level radioactive scale, which may flake off and collect on filters. Storage vessels can accumulate the daughter products as sludge. Discarded piping with the scale generates low-level radioactive waste. The Environmental Protection Agency (EPA) calls these accumulations technology-enhanced NORM, TENORM, and has guidelines on handling and disposal (EPA, 2018).

Because the boiling point of radon is −79.2°F (−61.8°C), it tends to concentrate in propane and ethane–propane mixtures. Tan and Pelletier (2009) discuss procedures for removing NORM-contaminated adsorbent used to remove sulfur compounds from a depropanizer overhead stream.

Radon is usually in very low concentrations. However, radioactivity is an important health factor. It is measured in Curie, Ci, or Becquerel (Bq) where one Bq is one decay event per second and 3.7×10^{10} Bq equals 1 Ci. NORM concentrations in natural gases typically range from 30 to 41,000 pCi (10^{-12} Ci)/scf (40–57,000 Bq/Nm^3) (Gray, 1990). Because Rn-222 and the progeny are decaying simultaneously, there is no simple way to relate radioactivity directly to radon concentration or to rate of Pb-210 production in a process. Figure 14.4 shows the decay rates for Rn-222 and the longer-lived progeny if a gas containing one unit of Rn-222 is introduced into a container (McMichael, N., Private Communication, 2009). The activity of each short-lived progeny rises rapidly and is comparable to that of Rn-222 within 10 min. Figure 14.5 shows the sum of activities from all decays as

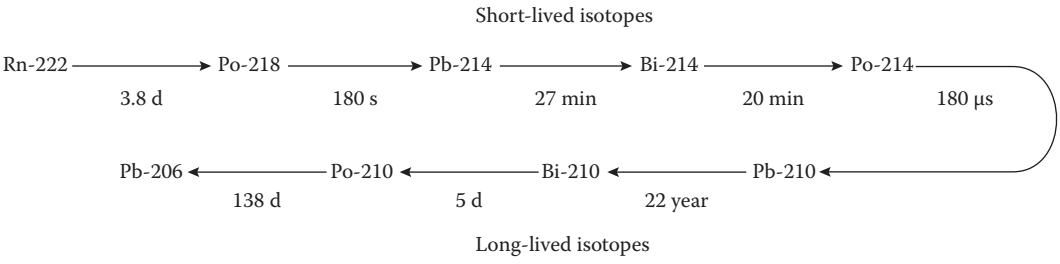


FIGURE 14.3 Primary radon-222 decay path to stable lead-206, along with half-life of each progeny.

[1] Half-life is the time required to reduce the amount of substance by one-half.

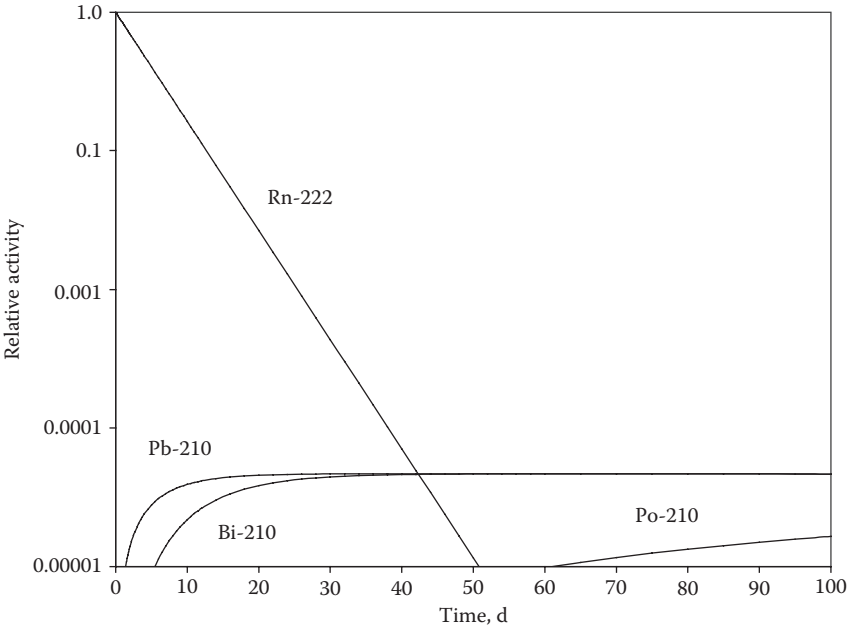


FIGURE 14.4 Relative activity of radon-222 and its long-lived progeny as a function of time.

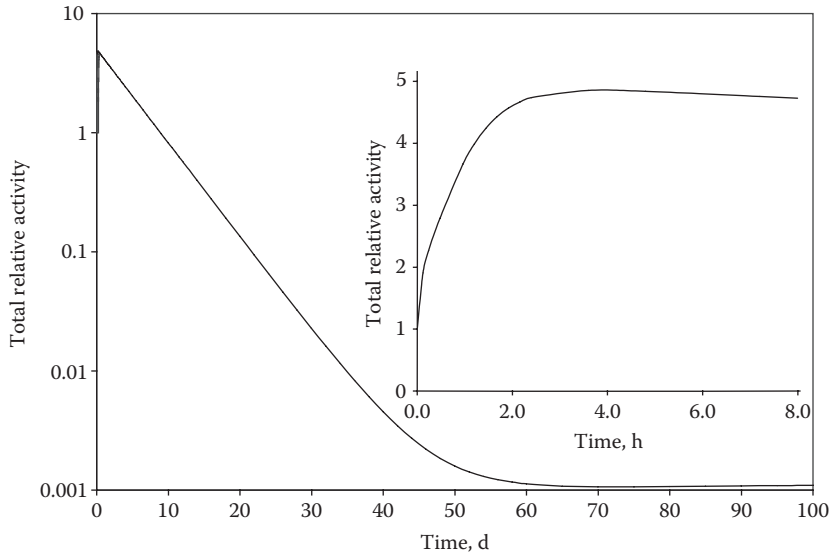


FIGURE 14.5 Total relative activity of radon-222 and progeny decay as a function of time. See text for description.

a function of time. Because of the rapid decay of the short-lived progeny, the total relative activity doubles within the first 10 min and reaches almost five times the initial value within 2 h. The rapid increase in activity makes radioactivity an inaccurate indication of radon content. Note that, after 60 days, the total activity is essentially constant at about 0.1% of the initial activity because of the slow Pb-210 decay. The two figures represent activities associated with a single pulse of gas containing Rn-222 into a container. The modeling of the activity of radon and progeny in a pipeline or vessel is much more complex and requires residence time data.

Example 14.2

A recently taken sample of natural gas has a radioactivity level of 15 pCi/L (a common measure of radioactivity) at 100°F (37.8°C) and 14.7 psia (1.01 bara). What is approximate Rn-222 concentration of the gas?

Solution

Basis: 1 s and 1 L of gas
Based upon the radioactivity level and assuming it all is due to Rn-222, the rate of decay of particles is

$$15\times10^{-12}\,\text{Ci / L}\times3.7\times10^{10}\,\text{decays / s}\left(\text{Bq}\right)=0.55\,\text{atoms / L.}$$

Assume ideal gas behavior to calculate the number of gas molecules:

At stated conditions have 22.4 L/mol × (273.15/(273.15 + 37.8)) = 20 L/mol (Temperature correction is included for completeness but unwarranted because of uncertainty of calculations.)

One mole contains 6.023×10^{23} molecules (Avogadro's Number). Thus, there are 1/20 mol × $6.023 \times 10^{23} = 3 \times 10^{22}$ gas molecules.

Radioactive decay is a random process, but in effect follows a first-order reaction. Then the rate of decay is given by

$$\ln\left(\frac{N}{N_0}\right)=-kt \tag{14.1}$$

where

N is the number of atoms at time t
N_0 the initial number of atoms
k is the rate constant

The relationship between the rate constant and half-life, $t_{1/2}$ is

$$k=\frac{\ln(2)}{t_{1/2}} \tag{14.2}$$

Therefore, the rate constant for Rn-222 decay is

$$k=\frac{\ln(2)}{3.8}=0.18\,\text{d}^{-1}=0.18\,\text{d}^{-1}\times\text{d}/86{,}400\,\text{s}=2.1\times10^{-6}\,\text{s}^{-1}$$

Then $\ln(N/N_0) = -kt = -2.1 \times 10^{-6}$/s and the number of decayed atoms is

$$1-\frac{N}{N_0}=1-\exp\left(-2.1\times10^{-6}\right)=2.1\times10^{-6}$$

Therefore, the initial number of Rn-222 atoms is

$$N_0=0.55/2.1\times10^{-6}=2.6\times10^{5}$$

Concentration of Rn-222, assuming that only it is decaying, is $2.6 \times 10^5/3 \times 10^{22} = 8.6 \times 10^{-18}$ mole fraction.

However, the actual Rn-222 mole fraction will be lower because progeny are decaying as well (see Figure 14.5) and depending upon how long the sample has aged, the actual concentration will be somewhere between ~2 and 8×10^{-18}.

14.6 ARSENIC

Arsenic is a toxic, nonvolatile solid but exists in natural gas predominantly as a more volatile trimethylarsine ($As(CH_3)_3$) (Trahan, 2008). It usually collects as a fine gray dust. High concentrations tend to be geographically localized. It can be successfully removed from gas using both regenerative and nonregenerative adsorption processes.

Several facilities reduce arsenic concentrations in sweet raw gas from around 1,000 to less than 1 μg/m^3 (Rhodes, Z., Private Communication, 2005). Without arsenic removal, the gas streams may not be marketable. Regenerative processes require dehydration of the gas to pipeline specifications before it goes to the removal process.

14.7 MERCURY

Two major problems are associated with the presence of mercury in natural gas: weakening of aluminum heat exchangers and environmental pollution. Aluminum heat exchangers are susceptible to amalgamation, corrosion of the amalgam, embrittlement, and weld cracking. Corrosion requires little mercury but does require water. The other problems require only liquid mercury (Ruddy et al., 2007). According to Rios et al. (1998), mercury may be present in elemental form or as organometallic compounds, such as dimethyl mercury, methylethyl mercury, and diethyl mercury, or as inorganic compounds such as $HgCl_2$. A comprehensive review of the impacts of mercury in natural gas streams is presented by McHenry and McCartney (2017) along with methods for removal.

Elemental mercury distributes between the gas and liquid phases. Whereas elemental mercury has an extremely low vapor pressure (~4×10^{-6} psia at 32°F, 3×10^{-7} bara at 0°C (Rios et al., 1998), vapor-phase concentrations are orders of magnitude higher than computed by Equation 4.2 because of the nonideal behavior of mercury at operating conditions. For example, Stiltner (2002) found gas from a pressurized inlet separator contained about 25% of the mercury that entered the plant. A sample from the separator liquid was flashed to ambient pressure. The remaining liquid contained less than 20% of the inlet mercury, whereas the flash gas, which was mostly ethane through pentane, contained over 50% of the inlet mercury. Thus, the majority of mercury goes to treating, dehydration, and then to the cryogenic section. What fraction would reach the cryogenic section was not stated.

The volatility of elemental mercury and the fact that it will accumulate as it condenses makes removal from the gas stream mandatory in cryogenic plants. As noted above, elemental mercury corrodes and weakens brazed-aluminum heat exchangers. The first reported instance of this problem occurred in an Algerian LNG facility in 1974 (Rios et al., 1998). Mercury is toxic to humans as well as a poison to many catalysts.

Organic mercury compounds concentrate in the hydrocarbon liquids, where they potentially can present environmental and safety hazards. The compounds are readily absorbed by most biological systems.

Although mercury in natural gas is normally at low levels, some gases contain sufficiently high mercury concentrations to cause both safety and health concerns. Table 14.2 shows the range of mercury levels in wellhead gas in a number of locations. Abbott and Oppenshaw (2002) state that much higher mercury levels have been detected in individual wells and that the highest known concentration is 4,400 μg/m^3 (500 ppbv) from a well in Germany. Rios et al. (1998) note that Southeast Asian gases tend to have higher elemental mercury levels, whereas the U.S. Gulf Coast gases are usually low, but a wide variation can occur within a given region.

14.7.1 Environmental Considerations

The environmental considerations of mercury and its compounds fall into two categories: (1) direct harm to individuals from inhalation of mercury vapors or compounds and (2) safe disposal of contaminated materials and equipment.

TABLE 14.2
Range of Elemental Mercury Levels in Wellhead Natural Gas from a Number of Countries

Location	Elemental Mercury Concentration in μg/m³ (ppbv)
South America	69–119 (8–13)
Far East	58–193 (6–22)
North Africa	0.3–130 (0.03–14)
Groningen (Netherlands)	180 (22)
Middle East	1–9 (0.1–1)
Eastern U.S. Pipeline	0.019–0.44 (0.002–0.05)
Midwest U.S. Pipeline	0.001–0.10 (0.0001–0.01)
North America	0.005–0.040 (0.0005–0.004)

Source: Abbott and Oppenshaw (2002).

From a health perspective, ingested mercury, particularly dimethyl mercury, permanently damages the brain and kidneys. Unfortunately, it concentrates in the tissue of both the fish and shellfish that are consumed by humans. According to the last EPA national database on fish advisories (2011), the United States had 4047 active advisories on eating fish and shellfish because they contained high mercury levels. Roughly 40% of the lake and river water area had mercury advisories. Mercury is by far the biggest chemical contaminant in United States' fresh water and comes from coal- and oil-fired power plants. In 2011, emission controls on mercury from coal- and oil-fired power plants at the federal level were in place (Environmental Protection Agency, 2017).

The mercury concentration in most natural gases is insignificant compared with the coals presently used in power plants (Wilhelm, 2005). As discussed below, elemental mercury is removed from natural gas to protect processing equipment and catalysts. However, some processes do not remove the mercury compounds. The U.S. gas industry has not come under any EPA regulations that require mercury removal. However, this situation could change in the future, especially for very large plants that process gases with higher than normal mercury levels.

The disposal of materials and equipment contaminated with mercury is a complex issue, and a discussion is beyond the scope of this book. Rios et al. (1998) and Müssig (1997) present excellent discussions of the problem.

14.7.2 Mercury Corrosion

The elemental form of mercury is apparently the cause of low-temperature failure in the commonly used plate-fin aluminum heat exchangers (Rios et al., 1998). If water is present, corrosion of the amalgam can be important (Ruddy et al., 2007). Elemental mercury attacks copper, zinc and brass, chromium, iron, and nickel as well. If the natural gas is to undergo cryogenic processing, the mercury must be removed to below 0.01 μg/m³ to avoid damage to low-temperature aluminum heat exchangers. Nelson (1994) gives a detailed discussion of the mechanism of mercury attack on brazed aluminum exchangers.

14.7.3 Removal Processes

Both regenerative and nonregenerative processes are available for the removal of mercury from gas and liquid streams, and both types will be discussed briefly. All of the processes take advantage of the reactivity of elemental mercury for removal. Complete removal of all mercury requires reduction of mercury compounds to elemental mercury. Processes that use chemisorption for removal may simultaneously remove the organic mercury compounds through physical adsorption. Some of

the processes remove arsenic and lead as well (*Engineering Data Book*, 2016c). Ruddy et al. (2007) give an excellent overview of the presently used methods for mercury removal from gas and liquid hydrocarbons. They provide some cost comparisons for removing mercury from gas and liquid streams. Eckersley (2010) discusses both regenerative and nonregenerative adsorption processes. McHenry and McCartney (2017) provide cost comparisons with pros and cons of different removal schemes.

14.7.3.1 Nonregenerative Processes

Rios et al. (1998) and *Engineering Data Book* (2016c) list a number of chemisorption processes for removal of elemental mercury from hydrocarbon streams to 0.01 μg/m^3 or lower. Bed capacities of 10% or higher are common. Most of these processes use sulfur impregnated on a support such as activated charcoal or alumina to provide a large surface area. Transition metal sulfides impregnated on adsorbents are also used. In these processes, the mercury reacts with the sulfur to form mercuric sulfide on the adsorbent surface.

Bourke and Mazzoni (1989) describe a sulfur-impregnated carbon adsorbent for mercury removal. The use of this type of mercury removal at the Anschutz Ranch East Plant in Wyoming is discussed in some detail by Lund (1996). Mock et al. (2008) provide some operating experiences using this removal technique in LNG plants.

Because the mercury levels are so low, the typical bed life can be up to 5 years (Bourke and Mazzoni, 1989) when treating gas streams. However, both condensing water and hydrocarbons can significantly reduce the bed life. Mercury removal units have historically been placed just before the gas enters the cryogenic portion of the gas plant and at temperatures above the dew point of the gas. The development of mercury removal materials which can be used upstream of treating and dehydration have caused many designers to review the location of removal beds in an attempt to limit exposure of equipment and personnel to mercury.

Organic mercury compounds are not removed by most of the adsorption processes and some treat only the gas phase. Vendors offer mercury removal beds containing catalysts to reduce the organic mercury to elemental mercury, which is adsorbed in the same bed.

14.7.3.2 Regenerative Process

Markovs and Corvini (1996) and Stiltner (2002) describe a regenerative process that utilizes silver on molecular sieve to chemisorb elemental mercury while providing dehydration at the same time. The advantage of silver is that the amalgam it forms with mercury decomposes at typical regeneration temperatures for dehydration (see Chapter 11). The silver-impregnated sieve is added to the standard molecular sieve dehydration bed, and the basic dehydration process remains unchanged. Essentially, all of the mercury condenses with the water on regeneration and forms a separate phase, which can be decanted. However, it can also be an undesired byproduct. Stiltner (2002) reports the solubility in water to be about 25 ppbw. Removal of the mercury from the water requires an additional adsorption step. After water and mercury removal, the regeneration gas can be recycled to the front of the bed without additional treatment, or it can be blended into the sales gas. If necessary, the regeneration gas can be further treated with a nonregenerative mercury-removal process to remove the last traces of mercury. For example, Traconis et al. (1996) describe the successful application of the silver-molecular sieve process in an 800 MMscfd (21×10^6 Nm^3/d) plant in Venezuela.

Although the silver-sieve process treats both gas and hydrocarbon liquid, how effective the process is in removing organic mercury compounds is unclear. Like the nonregenerative processes, this process can drop elemental mercury levels to 0.01 μg/m^3.

14.8 BENZENE, TOLUENE, ETHYLBENZENE, AND XYLENES

BTEX present two possible problems in gas processing: environmental concerns and potential freezing in cryogenic units. In most gas processing plants, BTEX is present in the volatile organic

TABLE 14.3
Fraction of BTEX Removed by TEG Dehydration Process

Absorber Process Conditions	
Pressure	1,000 psia (70 bara)
Temperature	100°F (38°C)
Glycol rate	3 gal TEG/lb_m water removed (25 L/kg)
Fraction BTEX Removed from Gas	
Benzene	10%
Toluene	14%
Ethyl benzene	19%
o-Xylene	28%

Source: Calculated from data in Ng and Robinson (1991)

compounds (VOCs) that must be controlled to meet EPA clean air regulations. Benzene is also classified as a carcinogen under U.S. regulations and is considered an air toxin. Emission limits for air toxins are lower than those for VOCs. BTEX concentrates in the glycols and amines used to dehydrate and sweeten the gas. Initially, industry interest was in glycol dehydration because it posed the larger problem, but now the amine sweetening process must be considered.

In glycol dehydration, the glycol absorbs some hydrocarbons as well as water. Although paraffinic compounds are removed in the flash tank, a fraction of the aromatic compounds are not completely removed because of their relatively low vapor pressures at the flash conditions and the affinity of glycols for them (see Chapter 11 for process description). Table 14.3 shows the fraction of BTEX removed at common TEG operating conditions.

When the rich glycol is regenerated, the BTEX exits the still in the vapor stream, and consequently this stream must be processed to recover or eliminate the BTEX before atmospheric venting. The methods presently used to control BTEX emissions to the atmosphere are:

- Adjustment of plant operating conditions to minimize the quantity of BTEX in the glycol absorber off gas
- Burning of still off gases before venting
- Condensation of the off gases and recovery of the BTEX as a liquid product
- Adsorption of the BTEX on a carbon adsorbent
- Absorption in solvent-enhanced glycol regeneration system

BTEX removal is thoroughly discussed in the paper by Rueter et al. (1992), and a summary of the main items in that paper is presented in the handbook by Kohl and Nielsen (1997). A summary of the U.S. regulations, along with suggestions on reducing BTEX emissions is given by the EPA (2006).

Amine treaters absorb BTEX along with the acid gases. Both acid gases and the BTEX are stripped in the regenerator and, traditionally, either flared if the H_2S level is low or sent to a Claus unit for sulfur recovery. Chapter 16 discusses BTEX poisoning of Claus catalysts. Bullin et al. (2008) show the effect of acid gas loading on BTEX absorption in various amines.

Collie et al. (1998) present a comparative study of emissions from glycol dehydrators and amine treaters. They used process simulations to model the behavior of both glycol and amine units and, on the basis of simulation results, came to the following conclusions:

- Reduction of the solvent circulation rate in both glycol and amine units and minimization of the lean-amine temperature were the most effective means of reducing BTEX emissions from the flash gas.

- A change of solvent type can also reduce emissions.
- For the cases studied, approximately 25% of the BTEX emissions came from amine units, and the remaining 75% came from glycol dehydrators.

Covington et al. (1998) present a similar paper that discusses how to minimize both operating costs and BTEX emissions from glycol dehydrators by the use of ethylene glycol (EG), diethylene glycol (DEG), and triethylene glycol (TEG). They conclude that emissions can be reduced by the use of either EG or DEG instead of TEG because of the lower solubility of BTEX in the lighter glycols. Operating costs may be reduced as well. However, this option may be attractive only when very low water contents are not required and the cost of glycol losses is not excessive.

Like carbon dioxide, both benzene and *p*-xylene can freeze and cause plugging problems in cryogenic NGL extraction units. If the feed contains significant quantities of BTEX, these compounds must be removed to a level that will prevent freezing in the low-temperature units. Jones et al. (1999) describe a plant that contains an NRU (see Chapter 20 for details) where the feed gas contains approximately 0.12% BTEX. The plant uses a glycol dehydrator (TEG) to remove water to a level of 7 lb_m /MMscf (120 mg/Nm^3) and at the same time remove more than half of the BTEX. The glycol unit is followed by a molecular sieve dehydrator to achieve the level of dehydration necessary for the NRU.

14.9 METHANOL

Although not naturally occurring in produced gas, methanol is often added to inhibit hydrate formation. It is also used in some acid gas removal processes. Therefore, methanol may be present in gas processing plants. Although not a problem within most processing plants themselves, downstream processing can be impacted by the presence of methanol. This caused limits to be imposed by many common carrier NGL pipelines with stiff penalties for concentrations exceeding the published specification which can range from below detectable limits to less than 200 ppmw. An excellent discussion of the issue is presented by O'Brien et al. (2016).

14.9.1 Methanol Removal

Most methanol removal in gas processing depends on a wash with existing amine or glycol systems and modified operating parameters. Some plants use dehydration equipment with different adsorbents. The choice of removal process depends on a number of factors but mostly depends on plant specific costs. For example, if amine unit makeup water is very expensive, an alternate approach might be chosen. These approaches are applied to both gas and liquid streams.

14.9.1.1 Amine Wash Removal

If the plant has an amine system it can often be operated to remove methanol. The aqueous amine solvent will readily absorb methanol but if the methanol concentration builds up in the circulating solution eventually methanol will be detected in the treated gas stream leaving the amine absorber and will be recovered with the NGL product. Successful removal with an amine has been accomplished by bleeding methanol laden water from the amine regenerator reflux system.

Removal can be accomplished either on the inlet gas as acid gases are removed or on the NGL product if it is amine treated. O'Brien et al. (2016) provide an excellent description of a plant with two trains—one removes acid gas from the feed gas and the other from the recovered NGL product. This provides a good comparison of the ability to remove methanol from both locations.

14.9.1.2 Adsorbent Removal

Adsorbent materials like the molecular sieve beds used for dehydration in a gas processing plant can also remove methanol. Most such systems do not have the capacity to remove methanol because adsorbed methanol is displaced by the more strongly absorbed water molecule (see Chapter 11). However, some plants have successfully been able to remove methanol by installing specialized

molecular sieve beds and/or adjusting the dehydration cycle to keep from displacing adsorbed methanol. In these plants the methanol removed from the gas stream is contained in the condensed water formed during regeneration.

14.9.1.3 Methanol Reuse

A few plants having high methanol content in the inlet gas have found it economically attractive to distill recovered methanol from water for reuse. The recovery system is relatively simple and can be used regardless of the methanol removal process. This approach is particularly attractive in areas where makeup water for amine systems is scarce and of poor quality.

DISCUSSION QUESTIONS

1. Which of the trace components discussed are not naturally occurring in natural gas? Do you expect them to become more or less of a problem in the future? Why?
2. What makes oxygen such a problem in gas processing?
3. What are NORM and TENORM?
4. When would you expect radon to be a health hazard and when would you expect the daughter products be a problem?
5. Some have stated that because helium naturally occurs in the atmosphere there is no reason to consider it a natural resource. Do you agree? Why?
6. What makes an LNG plant vent gas an attractive resource for helium?
7. What makes mercury a problem for gas processing?
8. What makes mercury a public health problem?
9. Which gas processing steps have potential BTEX emission problems?
10. List common ways by which BTEX emissions are controlled.

EXERCISES

14.1 A gas plant processes 140 MMscfd (43.4 Nm^3/s) of gas containing 500 ppmv of oxygen. How many lb_m (kg) of oxygen go into the plant per day?

14.2 Determine how long (d) it takes radon-222 and lead-210 to decay 90% of a given initial amount.

14.3 A helium plant processes a gas stream containing 3 mol% helium from an NRU at an LNG plant. The balance of the feed contains about 2 mol% methane and the remainder is nitrogen. (a) If the plant produces a nominal 150 MMscf/year, what is the feed daily gas rate to the plant? (b) How much air would have to be processed to obtain the same He production rate? Assume the helium content of air is 5 ppmv.

14.4 Estimate the size of a mercury removal bed to treat 100 MMscfd (2.68×10^6 Nm^3/d) entering the cryogenic section of a gas plant at 800 psig (55.1 barg) and 80°F (27°C). Because the mercury level is very low use the rule-of-thumb criteria (*Engineering Data Book*, 2016b) that the volume of nonregenerable material needed for Hg removal requires a 10 s residence time and maximum superficial velocity of 50 ft/min. Assume the void fraction of the adsorbent is 0.46 and ideal gas behavior.

14.5 A field TEG dehydrator processes 40 MMscfd (1.1×10^6 Nm^3/d) of gas. The operating conditions are comparable to those given in Table 14.3. An extended analysis of the gas shows the following concentrations of BTEX:

Benzene	0.050 mol%
Toluene	0.021 mol%
Ethyl benzene	0.001 mol%
Xylenes	0.007 mol%

Based upon the fraction of BTEX compounds removed from the gas, how many lb_m/year (kg/year) of each component are removed by TEG based upon 360 stream days per year? Use data from 14.3 and assume 28% of all xylenes are removed from the gas.

REFERENCES

Abbott, J., and Oppenshaw, P., Mercury removal technology and its applications, *Eighty-First Annual Gas Processors Association Convention*, Tulsa, OK, 2002.

Anderson, S.T., Economics, helium, and the u.S. Federal helium reserve: Summary and outlook, *Nat. Resour. Res., 27*(4), 455, 2018. doi:10.1007/s11053-017-9359–y.

Bourke, M.J., and Mazzoni, A.F., The roles of activated carbon in gas conditioning, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 1989, p. 137.

Bullin, J.A., et al., The impact of acid gas loading on the heat of absorption and VOC and BTEX solubility in amine sweetening units, *Eighty-Seventh Annual Convention Gas Processors Association Convention*, Tulsa, OK, 2008.

Choe, J.S., et al., Membrane/cryogenic hybrid systems for helium purification, *Proceedings of the Sixty-Seventh Annual Convention Gas Processors Association*, Tulsa, OK, 1988, p. 251.

Collie, J., et al., An analysis of BTEX emissions from amine sweetening and glycol dehydration facilities, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 1998, p. 175.

Committee on Health Risks of Exposure to Radon (BEIR VI), *Health Effects of Exposure to Radon: BEIR VI*, National Academy Press, Washington, D.C., 1999.

Committee on the Impact of Selling the Federal Helium Reserve, *The Impact of Selling the Federal Helium Reserve*, National Academy Press, Washington, D.C., 2000. www.nap.edu/catalog.php?record_id=9860 (Retrieved April 2019).

Covington, K., et al., Reduce emissions and operating costs with appropriate glycol selection, *Proceedings of the Seventy-Seventh Annual Convention Gas Processors Association*, Tulsa, OK, 1998, p. 4.

Deaton, W.M., and Haynes, R.D., How newest helium plant is working, *Petrol. Refin., 40*(3), 205, 1961.

Eckersley, N., Advanced mercury removal technologies, *Hydroc. Proc., 69*(1), 29, 2010.

Engineering Data Book, Section 2, Product specifications, GPSA Midstream Suppliers, Tulsa, OK, 2016a.

Engineering Data Book, Section 16, Hydrocarbon recovery, GPSA Midstream Suppliers, Tulsa, OK, 2016b.

Engineering Data Book, Section 21, Hydrocarbon treating, GPSA Midstream Suppliers, Tulsa, OK, 2016c.

Environmental Protection Agency, *Optimize glycol circulation and install flash tank separators in glycol dehydrators*, 2006. www.epa.gov/sites/production/files/2016-06/documents/ll_flashtanks3.pdf (Retrieved April 2019).

Environmental Protection Agency, National Listing of Fish Advisories » Historical Advisories, 2011. https://fishadvisoryonline.epa.gov/Advisories.aspx (Retrieved April 2019).

Environmental Protection Agency, Cleaner power plants, 2017. www.epa.gov/mats/cleaner-power-plants (Retrieved April 2019).

Environmental Protection Agency, *About TENORM*, 2018. www.epa.gov/radiation/tenorm/about.html#content (Retrieved April 2019).

Gray, P.R., Radioactive materials could pose problems for the gas industry, *Oil Gas J., 88*(26), 45, 1990.

Guccione, E., New approach to recovery of helium from natural gas, *Chem. Eng., 70*(9), 73, 1963.

Johnson, D.J., and Rydjord, K., Unique NGL/NRU/HRU plant processes new gas in eastern Colorado, *Eightieth Annual Convention Gas Processors Association*, Tulsa, OK, 2001.

Jones, S., et al., Simultaneous removal of water and BTEX from feed gas for a cryogenic plant, *Proceedings of the Seventy-Eighth Annual Convention Gas Processors Association*, Tulsa, OK, 1999, p. 108.

Kohl, A., and Nielsen, R., *Gas Purification*, Fifth edn. Gulf Publishing, Houston, TX, 1997.

Lund, D.L., Causes and remedies for mercury exposure to aluminum coldboxes, *Proceedings of the Seventy-Fifth Annual Convention Gas Processors Association*, Tulsa, OK, 1996, p. 282.

Markovs, J., and Corvini, J., Mercury removal from natural gas and liquid streams, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 1996, p. 133.

McHenry, R.C., and McCartney, D.G., Design considerations for mercury guard beds, *Laurance Reid Gas Conditioning Conference*, Norman OK, 2017.

Mock, J., et al., Experiences in the operation of dehydration and mercury removal systems in LNG trains, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman OK, 2008, p. 173.

Müssig, S., Experience in removing mercury from natural gas and subsequent mercury decontamination of process equipment, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 1997, p. 31.

Nelson, D.R., Mercury attack of brazed aluminum heat exchangers in cryogenic gas service, *Seventy-Third Annual Convention Gas Processors Association*, Tulsa, OK, 1994.

Ng, H.-J., and Robinson, D.B., The solubility of selected hydrocarbons in triethylene glycol, Research Report RR-131, Gas Processors Association, Tulsa, OK, 1991.

O'Brien, D., et al., Adjusting gas treatment strategies to resolve methanol issues, *Laurance Reid Gas Conditioning Conference*, Norman, OK, 2016.

Remirez, R., Cold-box design is key in Helium recovery unit, *Chem. Eng., 75*(27), 80, 1968.

Rios, J.A., et al., Removal of trace mercury contaminants from gas and liquid streams in the LNG and gas processing industry, *Proceedings of the Seventy-Seventh Annual Convention Gas Processors Association*, Tulsa, OK, 1998, p. 191.

Ruddy, T., et al., State of mercury removal technology, *Eighty-Sixth Annual Gas Processors Association Convention*, Tulsa, OK, 2007.

Rueter, C.O., et al., Research on emissions of BTEX and VOC from glycol dehydrators, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 1992, p. 187.

Smith, J.M., et al., *Introduction to Chemical Engineering Thermodynamics*, Eighth edn. McGraw-Hill Higher Education, New York, 2018.

Stiltner, J., Mercury removal from natural gas and liquid streams, *Eighty-First Annual Gas Processors Association Convention*, Tulsa, OK, 2002.

Tan, J., and Pelletier, D., Canadian gas plant handles NORM in replacing C_3 treater's mol sieve, *Oil Gas J., 107*(25), 59–65, 2009.

Traconis, B., et al., Mercury removal systems at Santa Barbara Extraction Plant, *Proceedings of the Seventy-Fifth Annual Convention Gas Processors Association*, Tulsa, OK, 1996, p. 123.

Trahan, D.O., Arsenic compounds in natural gas pipeline operations, *Pipeline Gas J., 149*, 95–97, 2008.

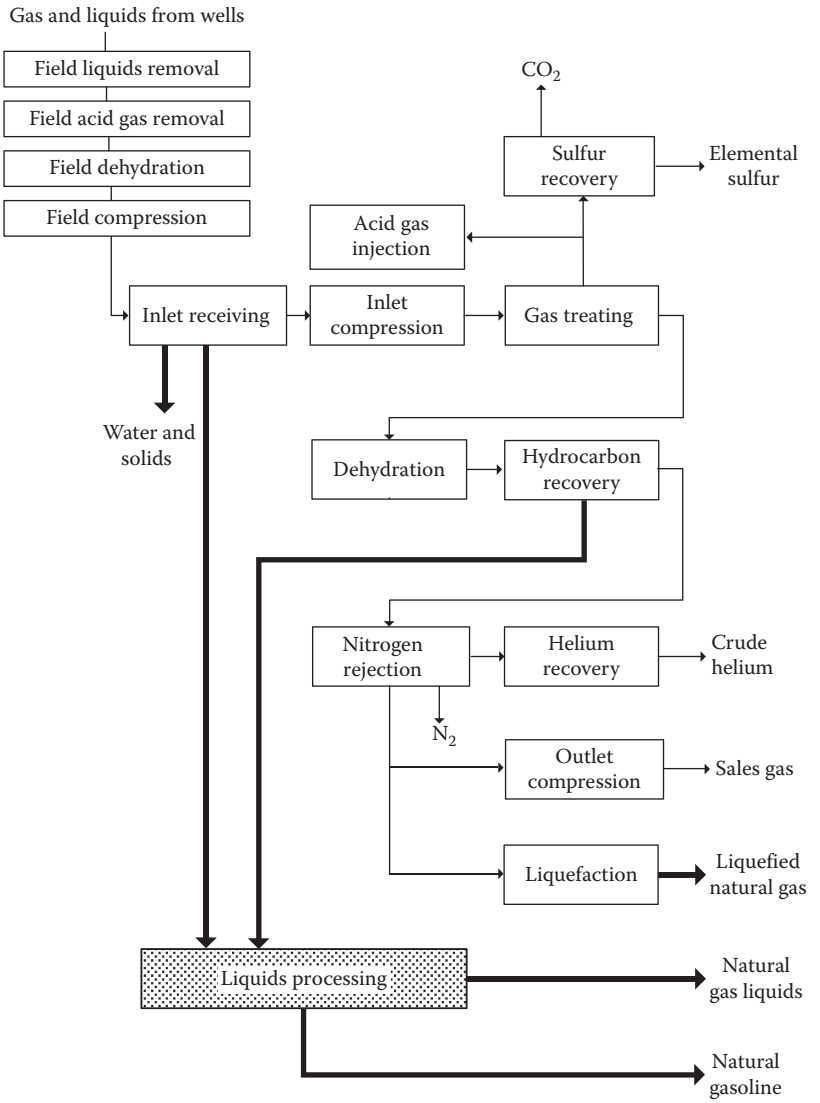
Wilhelm, S.M., Mercury in petroleum and natural gas: estimation of emissions from production, processing, and combustion, Mercury Technology Services, 2005. https://cfpub.epa.gov/si/si_public_record_Report.cfm?Lab=NRMRL&dirEntryId=55095 (Retrieved April 2019).

WEB SITES

Northeast Waste Management Officials Association: www.newmoa.org/—This site provides information on a variety of environmental problems, including mercury and hazardous wastes by an organization of environmental officials in northeastern United States, 2019.

Pollution Probe: www.pollutionprobe.org/publications/mercury-outreach-and-education-a-literature-review-of-best-practices/—This site provides a review of mercury and its health and environmental effects in North America, 2019.

15 Liquids Processing



15.1 INTRODUCTION

The previous chapters focused on processing gas streams. This chapter discusses processing hydrocarbon liquids. The two liquid streams processed in a gas plant are condensate and demethanizer bottoms NGL stream. Condensate can come from inlet separation and field locations. Condensate from field operations is often brought to the plant by truck. This condensate can go directly to storage and then to sale as natural gasoline without further processing if it meets the specifications given in Section 15.2. Otherwise, it requires processing or be sold as slop oil or crude oil. This chapter discusses the processing required to produce marketable liquid products.

15.2 CONDENSATE PROCESSING

Figure 15.1 shows a schematic of one scheme for handling condensate from the inlet receivers. In this example, processing the condensate involves two steps: water washing and condensate stabilization. Depending on the produced water quality, the condensate may require a water wash to remove salt and additives. If they are not a problem, then incoming water is removed in the inlet receiver and a water wash is unnecessary. Water received with the inlet gas often contains methanol or ethylene glycol, added in the field to prevent hydrate formation. Plants may recover the inhibitors on-site or ship the water off-site for inhibitor recovery before disposal. In most cases, wastewater is injected into disposal wells (Kuchinski, J., Private Communication, 2005). Section 14.9 discusses methanol handling.

After free water removal, the condensate goes to the stabilizer, where remaining lighter hydrocarbons are removed, compressed, and recombined with the gas from the inlet receiver. The primary purpose of the stabilizer is to produce a bottoms product that meets the specification for natural gasoline or "stabilized condensate." Both products have Reid vapor pressure specifications.

Specifications for Fractionation Natural Gasoline (Gas Processors Association, 2014) include:

- Reid vapor pressure of 14 psi (1 bar) or less as measured by ASTM D323-15a (2015). The common range is 9–12 psi (0.6–0.8 bar) (Kuchinski, J., Private Communication, 2005).
- Maximum of 6.0 LV% of C_4^- using ASTM D2163-14e1 (2014)
- No free water
- Color of +25 (Saybolt) as determined using ASTM D156-15 (2015).
- Reactive sulfur as determined by the Doctor test using ASTM D4952-12 (2017).
- Distillation end point of not more than 375°F (190°C) as determined using ASTM D86-18 (2018).

There are other likely specifications that are not standardized. For example, the density of the condensate from gas plants will be in the 65° to 85°API range. Also, if the condensate is not being sold as Fractionation Natural Gasoline, the water content is usually in the 0.5–1.0% BS&W (bottom sediment and water) range. If the distillation end point and/or color specifications are not met, additional

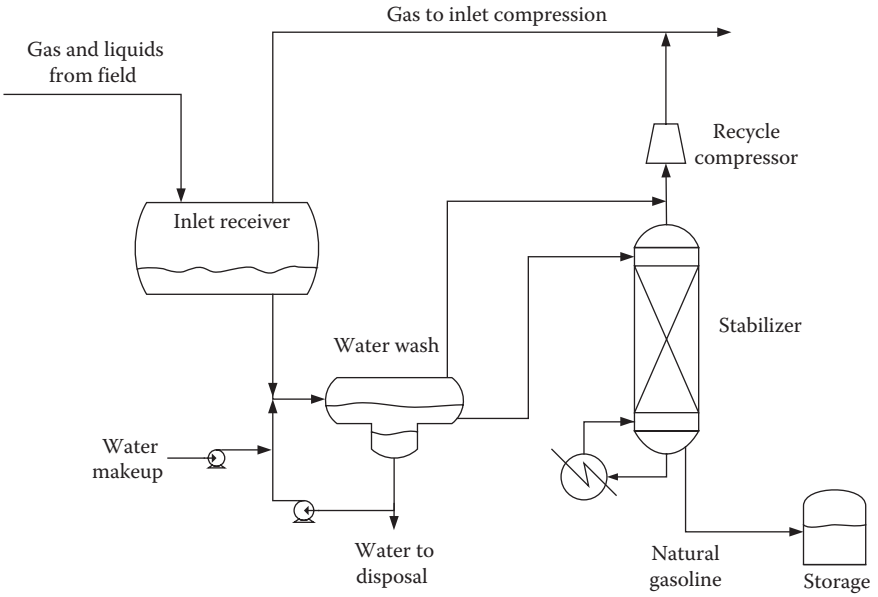


FIGURE 15.1 Condensate processing schematic.

processing is required to sell the material as natural gasoline. In lieu of additional processing, the material may be sold as stabilized condensate or slop oil at a discounted price.

Processing conditions in a condensate stabilizer vary widely from plant to plant and are a function of inlet condensate composition, plant operating conditions, and desired products. Variables include reboiler heating medium temperature and plant inlet pressure. The availability of compression also plays a major role.

If the objective is to maximize the production of condensate then a refluxed tower may be required. In general, to maintain bottoms product specifications, the stabilizer pressure is set by the reboiler temperature. A lower pressure stabilizer reduces the required bottoms temperature and reboiler duty but this requires more compression. For most gas processing facilities, the heating fluid system temperature determines the stabilizer pressure. Many stabilizers operate at 50 psig (3 barg) or less if low pressure inlet or recycle compression is available to handle the stabilizer overhead gas. Even at this relatively low pressure, the bottoms temperature can exceed 400°F (200°C), which could be near the limit of available heating medium. For lighter condensates, pressures up to 400 psig (28 barg) can be used.

15.2.1 Sweetening

Ideally, the sulfur compounds go with the light gases stripped in the stabilizer, so that they can be removed in gas treating. Most of the H_2S and CO_2 will be removed along with COS and some lighter mercaptans. To enhance acid gas removal, sweet natural gas can be used as a stripping gas. This process can reduce H_2S levels to the 10 ppm range (Webber et al., 1984). However, the cost is increased recycle compression.

If the natural gasoline is sour, the plant can either treat it or sell the liquid as sour crude. The price differential between sweet and sour crude drives the need for sweetening. In many cases, the liquid volumes are low and sweetening at the plant is not justified. Many of the sweetening processes for NGL, discussed in detail in Section 15.3.1, can be used. However, some form of caustic wash is the most common process.

Some newer processes have been developed for removal of mercaptans and other sulfur species from condensate and NGL streams. For more information, see Engel et al. (2016) and Collett (2016) for a discussion of some options. Please note that some of the claims made for these processes have not had widespread verification and should be considered only after a very thorough evaluation.

15.2.2 Dehydration

Dehydration of natural gasoline is seldom necessary. When in storage, free water drops out and the remaining low water content should meet customer requirements, provided the water layer is not included in the product delivery. However, emulsions of water and natural gasoline occur, which sometimes require emulsion breakers to obtain a good water–hydrocarbon separation. Water can accumulate in low points on lines containing water-saturated natural gasoline. The low points must be protected from freezing and possible line rupture.

15.3 NGL PROCESSING

Processing of NGL streams, if required, consists of sulfur compound removal and sometimes fractionation. Most sweetening processes involve contact with aqueous solutions and the product stream usually requires dehydration. Johnson et al. (2016) and Mokhatab et al. (2018) present overviews of sweetening and dehydration options. Mamrosh et al. (2017) discuss combinations of sweetening and dehydration for NGL streams. Mercaptans are difficult to remove because they are only slightly acidic in nature and amines do not readily react with mercaptans. Roberts (2016) compares caustic and adsorption methods for their removal.

Since the early 2000s, methanol in NGL has been characterized as a contaminant in some demethanizer bottoms streams. This is addressed in Chapter 14.

The following sections discuss sweetening, dehydration, and fractionation. Many of the treating processes discussed for natural gas apply but must be modified to properly function with liquids.

15.3.1 Sweetening

This section discusses commonly used processes to remove sulfur compounds and residual CO_2 from NGL. Thorough discussions of distribution of the various sulfur species in fractionation systems are presented by Harryman and Smith (1994), Likins and Hix (1996), and Granger et al. (2015). As noted above, many sulfur compounds are stripped into the gas phase, which, after any compression, typically goes to an amine treater. Ideally, the sulfur compounds would be removed during amine gas treating. This eliminates additional sweetening of the liquid products and dehydration if aqueous systems (i.e., amines or caustics) are used. As noted in Chapter 10, gas treating units are extremely effective at removing CO_2 and H_2S, but most do a poor job of removing other sulfur compounds, especially mercaptans and the more inert organic sulfides and disulfides. Also, acid gases and sulfur compounds not removed in gas treating concentrate in the demethanizer bottoms stream. Therefore, extremely low sulfur levels are required in gas treating to meet the liquid product specifications. If inlet gas contains both CO_2 and H_2S, COS may be present as well. Any COS present concentrates in the propane product stream (Mick, 1976). An overview study of sulfur species distribution in an NGL fractionation train was reported by GPA in 2015 (Granger et al., 2015).

15.3.1.1 Amine Treating

Amine treating of liquids is the same process used for treating gases. Most remove only CO_2 and H_2S. Two amines, DGA® and DIPA (see Chapter 10), can remove COS, but none remove CS_2 or significant amounts of mercaptans. Amine treating (Figure 15.2) is often used upstream of caustic treaters to minimize caustic consumption caused by irreversible reactions with CO_2.

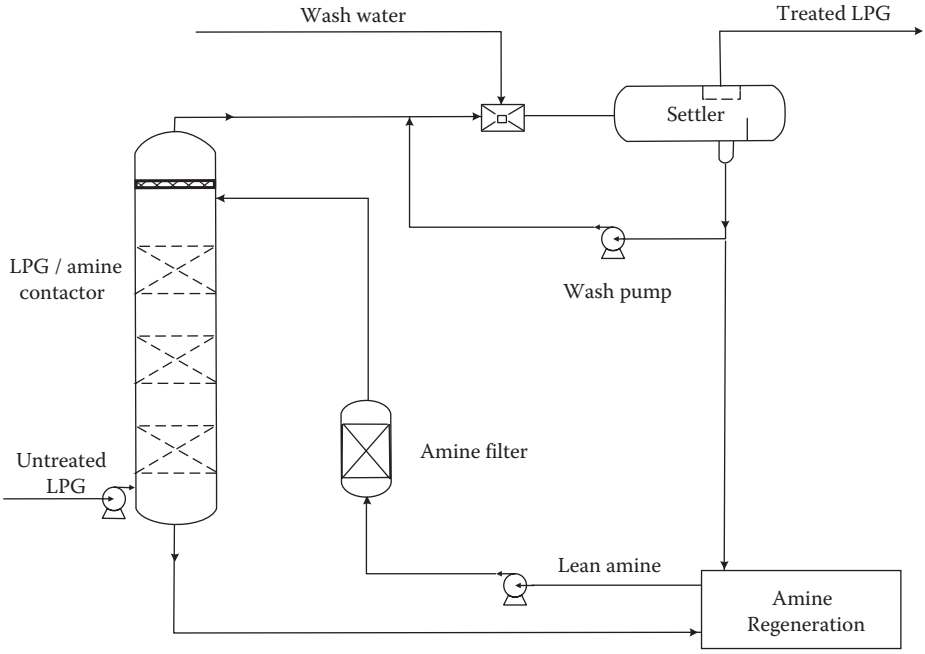


FIGURE 15.2 NGL amine treater.

Amine treating is usually conducted in a packed tower, although sieve trays are effective as well. To avoid vaporization, contactor operating pressure should be 100 psi (7 bar) above the liquid bubble point, and the entire contacting system should operate at least 50 psi (3.4 bar) above the bubble point (Nielsen, 1995). When operating near the bubble point pressure of the hydrocarbon stream, the scheme reported by Bacon (1972) should be considered as it provides mixing with the solvent without any pressure reduction. The *Engineering Data Book* (2016d) recommends a minimum contactor packing depth of 20 ft (6 m) and flow rates not exceeding 20 gpm per square foot of cross-sectional area (48.9 $m^3/h/m^2$).

Seagraves et al. (2014), Sargent and Seagraves (2003), and Veroba and Stewart (2003) provide additional details on contactor design. Nielsen (1995) notes that the lean amine viscosity should not exceed 2 cP to ensure good amine/hydrocarbon separation. Even so, the expected normal concentration of amine in the hydrocarbon stream that leaves the unit is about 100 ppmw. A water wash is recommended to both recover amine and protect downstream systems. Veroba and Stewart (2003) and Nielsen (1995) provide specifics on the water wash. The rich-amine regenerator step is identical to that discussed in Chapter 10 for gas treating.

15.3.1.2 Adsorption

Adsorption is commonly used for sweetening NGL and LPG streams. It has the advantage of being able to remove sulfur compounds down to low levels when no water is present, which makes it attractive for treating demethanizer bottoms. In contrast to the amine and caustic wash, downstream dehydration is often not necessary. Either promoted alumina, 13X or 5A molecular sieve will remove H_2S, COS, and mercaptans from LPG. The larger pore 13X is usually preferred because it has a higher capacity (Richman, P., Private Communication, 2005). Mick (1976) discusses the limitations of using molecular sieve for COS removal to the 2 ppm level when concentrations are in the hundreds of ppm.

Hydrocarbon flow can be up or down during adsorption. However, upflow is preferred, if possible, so that the regeneration can be down, to make recovery of all liquid from the bed easier (Richman, P., Private Communication, 2005). Liquid velocities are usually 3–5 ft/min (0.9–1.5 m/s), and bed height should be at least 5 ft (1.5 m), to allow good distribution (*Engineering Data Book*, 2016c). Liquid adsorption beds use the same graduated support packing used in gas adsorption.

The bed must be drained of liquid, and gas used for regeneration. If the fluid being treated is butane or lighter, sweet vapor of the fluid being treated can be used, which eliminates purging after regeneration. Refilling should be done with dry, sweet liquid. The filling rate must be slow to prevent bed movement. Also, the bed needs to be cool to avoid flashing and bed movement (Richman, P., Private Communication, 2005). Bed rearrangement is detrimental because it induces channeling and causes attrition; the generated dust leads to plugging in the bed or downstream filters.

The *Engineering Data Book* (2016c) indicates that new adsorbents capacity and performance data are usually presented on the basis of static measurements. However, under operating conditions, the actual bed capacity is typically about 50% of the static values, depending on the total amount of adsorbent in the bed. This difference is because of the mass transfer zone and bed aging (see Chapter 11 for details).

15.3.1.3 Caustic Treating

Johnson et al. (2016), Mokhatab et al. (2018), Mamrosh et al. (2017), and Roberts (2016) all discuss caustic processes. A number of caustic processes, both regenerative and nonregenerative, are used to remove sulfur compounds from NGL. The simplest process is the use of a nonregenerative solid potassium hydroxide (KOH) bed. It has the advantage of taking out H_2S and water as well. According to available literature, the nonregenerative solid KOH process is not commonly used. Sambrook et al. (1997) provide some discussion on the solid-bed KOH system. Mick (1976) found KOH effective for the removal of H_2S, but not other sulfur compounds. However, by the injection of methanol into the caustic bed, COS, mercaptans, and CS_2 can be removed. This blend is more used in refineries than in gas plants.

One of the most common processes for treating natural gasoline, and NGL, is the regenerative caustic wash with a sodium hydroxide solution. Frequently, it follows treating with an amine system. The amine pretreatment eliminates the acid gases and reduces the load on the caustic wash that removes or converts mercaptans.

The caustic wash process is used extensively for treating sour streams. For H_2S and mercaptan removal, the process can be regenerable, but CO_2 forms a nonregenerable carbonate salt. This by-product, along with the consumption of caustic for H_2S removal, is why an amine unit often precedes a caustic wash.

Figure 15.3 shows the process for a nonregenerative caustic wash. Many facilities with smaller amounts of organic sulfur to be removed use this process. The system shown in Figure 15.3 is often followed by a water wash to remove any entrained caustic and prevent embrittlement of downstream equipment. For larger facilities, a regenerated system is more commonly used to minimize caustic consumption and spent caustic disposal costs.

There are several regenerative caustic processes. Two will be discussed here. Typical of the regenerated caustic processes is the Merox™ process (Verachtert et al., 1990) shown in Figure 15.4.

Sour product is treated with caustic containing Merox™ catalyst to extract mercaptans. The caustic forms a water-soluble mercaptan salt. Air is added to the rich caustic to oxidize the mercaptan to a disulfide and regenerate the caustic:

$$RSH + NaOH \rightarrow RSNa + H_2O \tag{15.1}$$

$$2RSNa + \frac{1}{2}O_2 + H_2O \rightarrow RSSR + 2NaOH \tag{15.2}$$

The disulfide is water insoluble and separated from the caustic before the lean caustic returns to the wash. Verachtert et al. (1990) describe process alternatives that reduce the required amount of caustic and treat different hydrocarbon streams. Separation of caustic and disulfide phases is difficult because the two liquids have almost identical densities. To enhance separation, a coalescing medium, frequently anthracite coal, must be used. Even when treating streams with no CO_2 present, Merox™ caustic is spent by CO_2 in the regeneration air stream.

If complete sulfur removal is not required, Merox™ can also be used in a fixed-bed catalytic conversion process to convert mercaptans to disulfides. The disulfides remain with the liquid stream. However, the disulfide will pass the Doctor test (GPA Standard 3132-84, 2004), which detects the more reactive sulfur compounds H_2S and mercaptans.

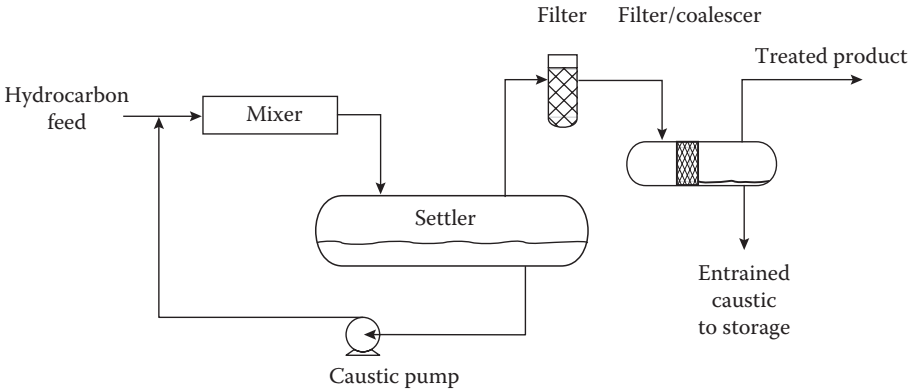


FIGURE 15.3 Nonregenerative caustic wash. Fresh caustic is added and spent caustic drained from the process on an as needed basis.

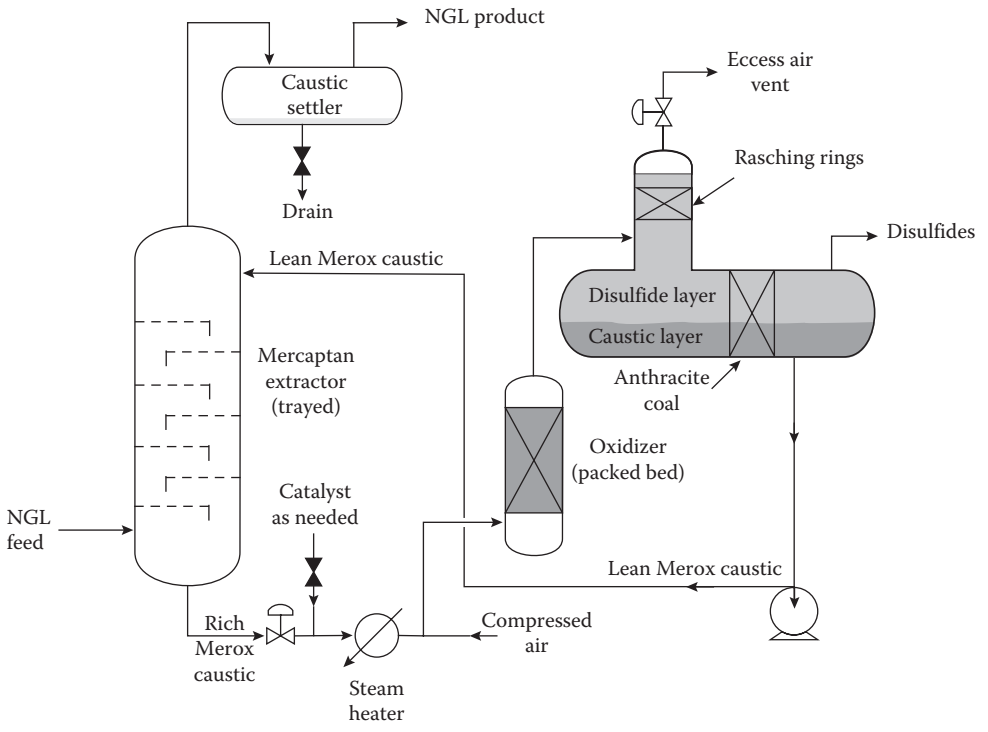


FIGURE 15.4 LPG Extractive Merox™ Treater.

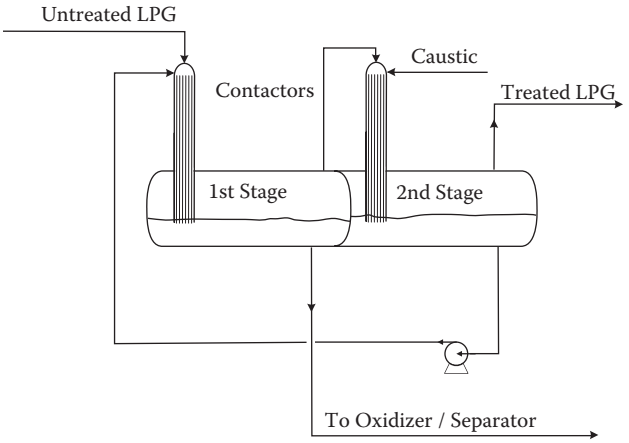


FIGURE 15.5 Two-stage THIOLEX™ system using FIBER FILM© Contactor. The disulfide formation/caustic regeneration step is not shown (Mokhatab et al., 2018).

A second regenerative caustic process is the THIOLEX™ system (Mokhatab et al., 2018) which is similar to Merox™ but uses a one or two stage FIBER FILM© Contactor to mix the caustic and LPG. The contactor is the vertical section shown in Figure 15.5 above the horizontal vessel of each stage and contains many small vertical metal fibers to provide good mass transfer between the two phases but allow easy separation in the horizontal vessel. The separation of disulfides and caustic is obtained by solvent extraction using the same proprietary contacting device.

15.3.1.4 Other Processes

Eckersley and Kane (2004) suggest that nonregenerative metal oxides, such as ZnO, are economically attractive if the sulfur rate into the bed is less than 400 lb_m/d (180 kg/d). These materials are effective for removal of H_2S and COS but are not as good for removing other sulfur species. For higher sulfur rates, sorbent bed replacement material costs become excessive. Older formulations of the material often required temperatures above ambient but newer materials are effective at H_2S and COS removal at ambient temperatures and below.

As noted in Chapter 11, COS hydrolyzes with water to form CO_2 and H_2S. However, COS does not affect the copper strip corrosion test. A properly run copper strip test includes the addition of water in an attempt to hydrolyze the COS (*Engineering Data Book*, 2016a). However, the test method does not reliably predict the presence of COS. Tests show the rate of hydrolysis to be extremely slow in the copper strip test apparatus. The GPA conducted a study of test reliability (Clark and Lesage, 2006). Because of the slow rate of hydrolysis, a shipment that contains water and COS can pass the test at departure but fail at delivery.

Carbonyl sulfide unfortunately is fairly difficult to remove with amines. Processes for its removal include treatment with either of the two amines DGA® or DIPA, or with adsorption using 3A molecular sieve, although the cheaper 4A will work if the regeneration gas contains no CO_2. Numerous nonregenerative metallic oxide processes are also available to remove COS from product streams. Some of these processes remove the COS directly and others require water to hydrolyze the COS to H_2S before it is reacted. With co-funding from the Propane Education and Research Council, GPA published a research report, which gives the relative cost of a number of the metallic oxide processes (Amiridis, 2006).

15.3.2 Dehydration

The acceptable water content in NGL streams varies from no free water present, for process streams, to product specifications of less than about 25 ppmw for commercial and HD-5 propane (Willman et al., 2014). The work by Willman et al. (2014) showed that there can be large variability in the commonly used freeze valve test (ASTM D2713-15e1, 2015) and that liquid propane containing over 36 ppmw passed the test. Figure 15.6, from the *Engineering Data Book* (2016c), gives the solubility of water in various hydrocarbon liquids as a function of temperature.

Customers sometimes require very dry liquid product, such as when it is used as feedstock to a process in which water is a catalyst poison.

Numerous processes are available for drying liquids, and many of the technologies discussed in Chapter 11 for dehydrating gases can be used for liquids. Therefore, this section presents only brief descriptions as needed and lists the pros and cons of each method as they apply to NGL.

15.3.2.1 Adsorption Processes

Section 15.3.1.2 described the use of adsorbents in liquid service. As stated earlier, adsorbent beds used in liquid service typically dry with hydrocarbon upflow to facilitate bed draining before regeneration. Any of the adsorbents described in Chapter 11 provide adequate drying if the specification requires removal below no free water. If extremely low water contents are essential, then molecular sieve may be required.

15.3.2.2 Nonregenerable Desiccant Dehydration

A consumable desiccant such as $CaCl_2$ is viable in remote situations, but disposal constraints can make it unattractive compared with a regenerative process in a plant situation where hydrocarbon liquids are dried. The *Engineering Data Book* (2016c) provides a brief description of a vertical bed contactor, initially charged with $CaCl_2$ pellets. The moist NGL enters near the bottom of the pellet bed. As the salt removes the water, it first forms various solid salt hydrates and then becomes a

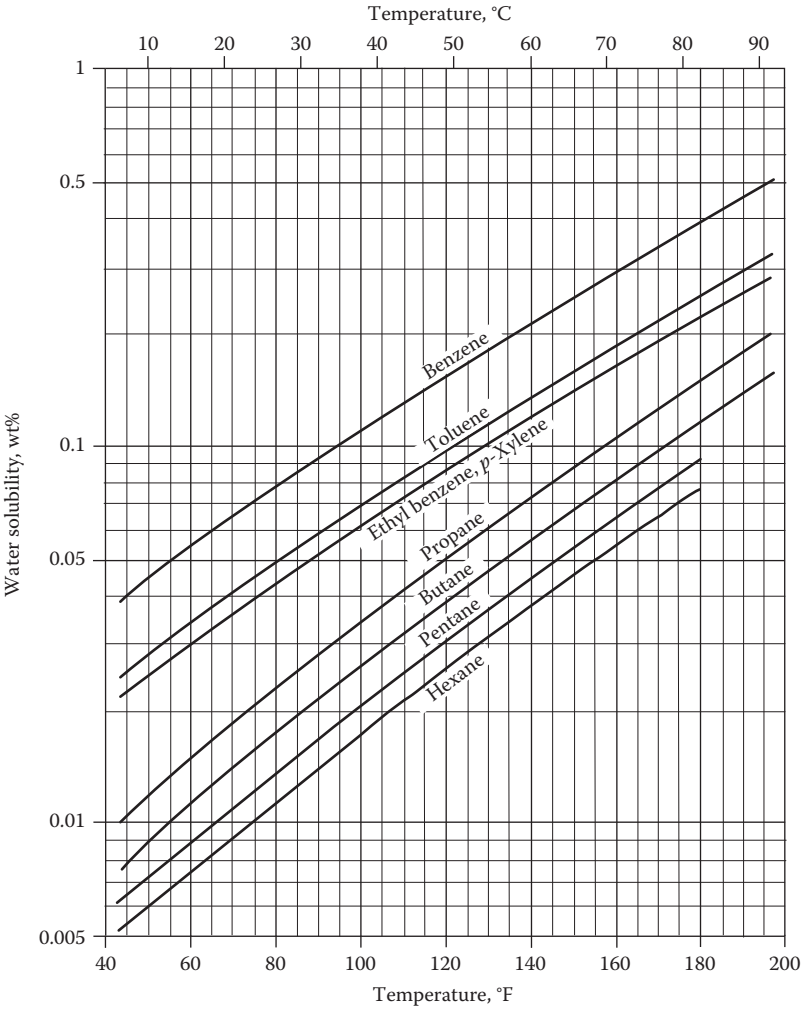


FIGURE 15.6 Solubility of water in hydrocarbons as a function of temperature. (Adapted from *Engineering Data Book*, 2016c, with permission.)

brine slurry which is drained from the bottom. The hydrocarbon stream is dispersed into the brine solution and leaves in equilibrium with dry salt. There are often multiple beds in series so that when all salt is expended in the first bed it can be removed from service for recharging without generating a wet product. This process is less used now because of disposal problems but at least one installation used this approach to dehydrate a high-pressure CO_2 stream before delivery to a pipeline. The commercial product selected for the project is said to overcome some of the handling issues with older formulations.

15.3.2.3 Gas Stripping

Gas stripping is a simple process for liquid dehydration and is frequently used offshore to dry condensates before they go to the production platform (*Engineering Data Book*, 2016c). The liquid is usually stripped with dry natural gas in a tower with trays or packing. As shown by Equation 4.2, the process is feasible because the activity coefficient, γ, for water in liquid hydrocarbons is in thousands, which makes the dissolved water more volatile than propane.

The process is low cost and space efficient. However, it requires a dry natural gas stream, which also strips some volatile hydrocarbons at the same time. This property makes it suitable for only condensates and natural gasoline. The stripping gas must be compressed and recycled to a dehydration unit or used as fuel gas.

15.3.2.4 Distillation

Propane and butane mixtures can be dried by the use of specially designed columns (*Engineering Data Book*, 2016c). In these columns, the water goes overhead with hydrocarbon and is decanted from the overhead reflux drum. The condensed hydrocarbon returns as reflux. The bottoms product will be bone dry, and even a side draw three or four trays from the top will meet product specifications. The *Engineering Data Book* (2016c) notes that the side-draw liquid must be cooled, but the process can be cost effective. This factor can make it attractive for narrow boiling fractions.

15.3.2.5 Absorption

Liquid product streams can be dehydrated using glycol contacting. These systems are very similar to gas dehydration with glycol, which is discussed in Chapter 11.

15.3.3 Fractionation

Figure 15.7 shows a typical processing configuration for demethanized NGL streams, commonly called raw product or "Y-grade." The processing required depends on the plant's feed composition and customer product requirements. Processing demethanized raw product ranges from no additional processing to sweetening, dehydration, and extensive fractionation. It is common in the United States for gas plants to pipeline NGL to another facility for fractionation. As noted in Chapter 7, transportation and fractionation fees (T&F) can affect the economics of ethane and propane recovery. However, these very large fractionation facilities are usually close to the end-user of the fractionated liquids. Directly pipelining Y-grade NGL from the plant eliminates storage and transportation costs of relatively small quantities of multiple products at individual gas processing plants.

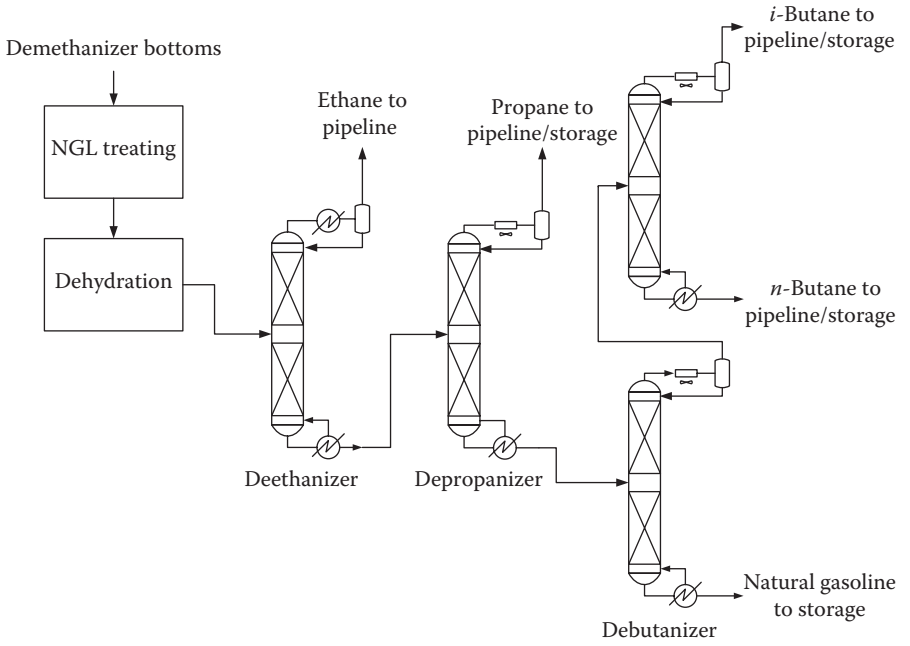


FIGURE 15.7 NGL fractionation train.

TABLE 15.1
Typical Fractionator Operating Conditions

	Operating Pressure, psig (barg)	Number of Actual Trays	Reflux Ratio[a]	Tray Efficiency (%)
Deethanizer	350–450 (24–30)	25–40	0.8–2.0	60–85
Depropanizer	240–270 (16–19)	30–45	1.8–3.5	80–90
Debutanizer	70–130 (5–9)	25–40	1.2–1.8	85–95
Deisobutanizer[b]	80–100 (5–7)	70–100	4–16	90–100
Condensate Stabilizer	50–400 (3–30)	16–24	Varies	30–50

[a] Reflux ratio relative to overhead mol/mol.
[b] Also called a butane splitter.

Figure 15.7 implies that all of the NGL is treated, which is not always the case. Feed quality and product slate dictate which streams require treating. In some cases, products are treated instead of the demethanized raw product stream and often dehydration of the feed is not required.

Table 15.1 provides typical operating conditions for the various columns. The condensate stabilizer is included for completeness. As noted previously, the fractionation train depends on the current economics and customer requirements. Sometimes, the first column takes an ethane–propane mixture (EP mix) overhead instead of pure ethane. If the deethanizer overhead system is producing an EP mix product instead of pure ethane, operating temperatures may be outside of hydrate formation conditions in the deethanizer column. Regardless of whether it is ethane or EP mix, this stream is usually pipelined to customers although some is exported in cryogenic ships. The other products can be shipped by tank car, truck, barge, or pipeline.

Distillation column design is beyond the scope of this book. However, the *Engineering Data Book* (2016b) provides extensive details on column design, column internals, and reboiler design.

15.4 SAFETY AND ENVIRONMENTAL CONSIDERATIONS

Major safety and environmental issues involved with treating the hydrocarbon liquids include the safe handling and disposal of the caustic compounds and solutions, if used. Other spent chemicals or by-products, such are organic disulfides and amine filter residue often require special attention.

For gas processing, storage and transport sulfur specifications are set on the basis of corrosion. The push for low sulfur levels in fuel affects the natural gasoline markets. When natural gasoline is used as a motor fuel blend stock, stringent levels of total sulfur may be required.

Natural gasoline may not be accepted as a motor gasoline blending stock unless the blended product contains 10 ppmw or less of sulfur. This level of sulfur content is often hard to achieve because many specifications only require the natural gasoline not contain reactive sulfur (i.e., pass the Doctor Test–ASTM D4952-12, 2017). Natural gasoline product with hundreds of ppmw of sulfur species is common.

Other considerations include VOC emissions from tanks and trucking operations, disposal of disulfide oil from mercaptan removal and disposal of spent treating chemicals like caustic, amine, and molecular sieve.

DISCUSSION QUESTIONS

1. Why is there a volatility (Reid vapor pressure) specification on natural gasoline and stabilized condensate?
2. Why is a water wash sometimes used on liquid condensate coming from the inlet receiver?

3. Why is the water specification on natural gasoline commonly less demanding than on sales gas?
4. What affects condensate stabilizer operating conditions?
5. Why is there such a large difference in number of trays and reflux ratios for the various column types in Table 15.1?
6. Compare the treating processes used for liquids and for gases.
7. What are the major differences between regenerating an adsorption bed in gas service and liquid service?
8. Will water come out of the top or bottom of a distillation column being used for removing water from propane? Why?
9. What is the major problem with COS being present in propane?
10. What are the pros and cons of using a stripping gas to remove a trace component?

EXERCISES

15.1 Using Equation 15.1, how much 15% by weight caustic (molar mass = 40) solution must be circulated (lb_m/h, kg/h) to remove 22 lb_m/h (10 kg/h) of methyl mercaptan (molar mass = 48) from an NGL mixture?

15.2 Assume the reaction of caustic and methyl mercaptan in Exercise 15.1 removes 100% of the mercaptan. Using Equation 15.2, how much air (lb_m/h, kg/h) is needed to regenerate the caustic solution?

15.3 The operator of the Merox™-type treating unit in Exercise 15.1 notices that the caustic slowly loses strength over time. Analysis of the spent caustic shows levels of Na_2CO_3. The inlet NGL has been washed with an MEA solution and does not contain CO_2. What is the source of the CO_2 that is reacting with the circulation caustic solution?

15.4 A deisobutanizer (butane splitter) contains 80 trays. Tray efficiency is approximately 100%. Because of the close boiling points of iC_4 and nC_4, high reflux flow and reboiler energy are needed to achieve the required product separation. The operator is considering installation of an additional deisobutanizer. What can be changed in the new tower to lower utility consumption?

15.5 The fractionation plant described in Exercise 15.4 feeds 10,000 bbl/d (66 m^3/h) of a mixture containing 25LV% iC_4 and 75LV% nC_4 to the deisobutanizer. The reflux rate is 40,000 bbl/d (265 m^3/h).

a. What is the reflux ratio for this column?
b. What is the reflux ratio if the feed is a 50/50 mixture of iC_4 and nC_4 and the reflux flow rate remains unchanged?

15.6 The NGL feed to a fractionator is 100,000 bbl/d. The feed consists of 35% ethane, 30% propane, 10% iC_4, 20% nC_4 and the balance is iC_5^+ (natural gasoline). The percentages are on a liquid volume basis. If the fractionator produces an 80/20 (LV%) ethane/propane mix, what are the approximate product rates (bbl/d, m^3/h) for EP mix, propane, iC_4, nC_4, and natural gasoline?

REFERENCES

Amiridis, M.D., Research Report RR-192 Carbonyl sulfide removal from propane, Gas Processors Association, Tulsa, OK, 2006.

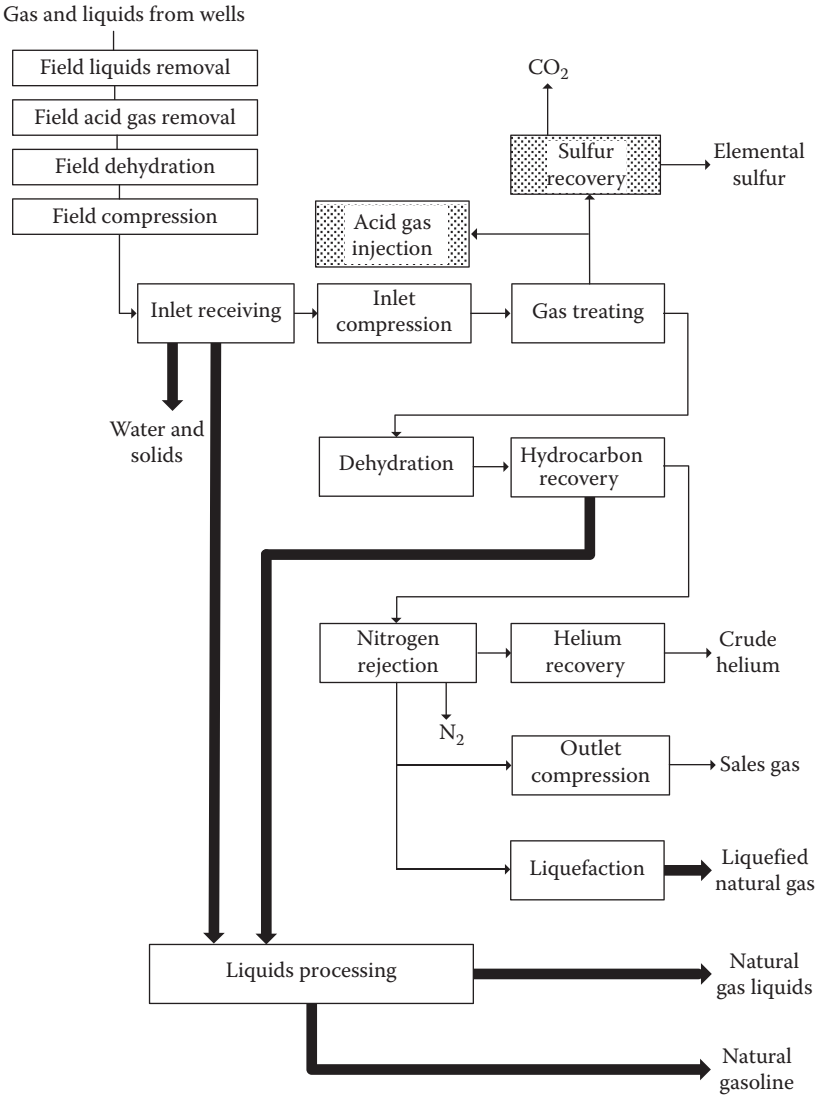
ASTM D86-18, Standard test method for distillation of petroleum products and liquid fuels at atmospheric pressure, ASTM International, West Conshohocken, PA, 2018. www.astm.org/Standards/D86.htm (Retrieved April 2019).

ASTM D156-15, Standard test method for Saybolt color of petroleum products (Saybolt chromometer method), ASTM International, West Conshohocken, PA, 2015. www.astm.org/Standards/D156.htm (Retrieved April 2019).

ASTM D323-15a, Standard test method for vapor pressure of petroleum products (Reid method), ASTM International, West Conshohocken, PA, 2015. www.astm.org/Standards/D323.htm (Retrieved April 2019).
ASTM D2163-14e1, Standard test method for determination of hydrocarbons in liquefied petroleum (LP) gases and propane/propene mixtures by gas chromatography, ASTM International, West Conshohocken, PA, 2014. www.astm.org/Standards/D2163.htm (Retrieved April 2019).
ASTM D2713-15e1, Standard Test Method for Dryness of Propane (Valve Freeze Method), ASTM International, West Conshohocken, PA, 2015. www.astm.org/Standards/D2713.htm (Retrieved April 2019).
ASTM D4952-12, Standard test method for qualitative analysis for active sulfur species in fuels and solvents (Doctor Test), ASTM International, West Conshohocken, PA, 2017. www.astm.org/Standards/D4952.htm (Retrieved April 2019).
Bacon, K.H., Liquid treating, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 1972.
Clark, P.D., and Lesage, K.L., An examination of interfering factors in the ASTM D-1838 Copper Strip Test, Research Report RR-190, Gas Processors Association, Tulsa, OK, 2006.
Collett, T., Improving condensate value, *Laurance Reid Gas Conditioning Conference*, Norman, OK, 2016.
Eckersley, N., and Kane, J.A., Designing customized desulfurization systems for the treatment of NGL streams, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2004, p. 313.
Engel, D.B., et al., Mercaptans removal from hydrocarbon condensates and NGL streams, *Laurance Reid Gas Conditioning Conference*, Norman, OK, 2016.
Engineering Data Book, Section 2, Product specifications, GPSA Midstream Suppliers, Tulsa, OK, 2016a.
Engineering Data Book, Section 19, Fractionation and absorption, GPSA Midstream Suppliers, Tulsa, OK, 2016b.
Engineering Data Book, Section 20, Dehydration, GPSA Midstream Suppliers, Tulsa, OK, 2016c.
Engineering Data Book, Section 21, Hydrocarbon treating, GPSA Midstream Suppliers, Tulsa, OK, 2016d.
Gas Processors Association, GPA Standard 3132-84: Natural gasoline specifications and test methods, Tulsa, OK, 2004.
Gas Processors Association, GPA Standard 2108-14, GPA Fractionation grade product specifications, Tulsa, OK, 2014.
Granger, L., et al., Sulfur species distribution in separators and fractionators, Research Report RR-228, Gas Processors Association, Tulsa, OK, 2015.
Harryman, J.M., and Smith, B., Sulfur compound distribution in NGL: Plant test data, GPA Section A committee, plant design, *Seventy-third Annual Gas Processors Association Convention*, Tulsa, OK, 1994.
Johnson, J.E., et al., Putting a trace on components, Part 3, *Hydroc. Eng., 21*(2), 31, 2016.
Likins, W., and Hix, M., Sulfur distribution prediction with commercial simulators, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 1996.
Mamrosh, D., et al., Technology Screening for Natural Gas Liquids Treatment, *Laurance Reid Gas Conditioning Conference*, Norman, OK, 2017.
Mick, M.B., Treat propane for COS removal, *Hydroc. Proc., 55*(7), 137, 1976.
Mokhatab, S., et al., Dealing with sour natural gas liquids in gas processing plants, *Laurance Reid Gas Conditioning Conference*, Norman, OK, 2018.
Nielsen, R.B., Principles of LPG amine treater design, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 1995, p. 229.
Roberts, P., State-of-the-art review of mercaptan removal technologies, Research Report RR-232, GPA Midstream Association, Tulsa, OK, 2016.
Sambrook, R.M., et al., A liquid propane desulfurization study, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 1997, p. 158.
Sargent, A., and Seagraves, J., LPG contactor design and practical troubleshooting techniques, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2003, p. 125.
Seagraves, J., et al., Fundamentals of gas sweetening—Amine treating, *Laurance Reid Gas Conditioning Conference*, Norman, OK, 2014.
Verachtert, T.A., et al., The UOP Merox™ process for NGL treating, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 1990, p. 267.
Veroba, R., and Stewart, E., Fundamentals of gas sweetening, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2003.
Webber, W.W., et al., Whitney Canyon Project, *Proceedings of the Sixty-Third Annual Convention Gas Processors Association*, Tulsa OK, 1984, p. 10.
Willman, T.J., et al., Freeze valve water content in LPG systems, Research Report RR-223, Gas Processors Association, Tulsa, OK, 2014.

Taylor & Francis
Taylor & Francis Group
http://taylorandfrancis.com

16 Acid Gas Processing and Disposal



16.1 INTRODUCTION

There are significant quantities of wellhead natural gases that do not meet pipeline specifications for the acid gases, H_2S and CO_2. In the past, only H_2S posed a significant disposal problem. Carbon dioxide was not considered a pollutant, and after removal from wellhead gas it was vented to the atmosphere or used in enhanced oil recovery (EOR). However, with the current emphasis on climate change, the venting of CO_2 will be an important issue in the future.

Acid gas processing and disposal is a primary topic at the annual Laurance Reid Gas Conditioning Conference held at the University of Oklahoma. Readers interested in more detail and current technology should consult the proceedings of that conference. Wichert (2018) provides a comprehensive reference on H_2S removal technologies and disposal.

Chapters 10 and 15 discuss processes to remove acid gases from natural gas and hydrocarbon liquids. This chapter addresses economically viable uses for acid gas and disposal in an environmentally sound manner. Acid gas generated from NGL processing can be considered the same as that obtained from natural gas treating.

16.1.1 Carbon Dioxide

From the perspective of the gas industry, CO_2 has four negative features, but only one positive one. The negative features are:

- In the presence of water, it forms a weak, corrosive acid.
- If present in a cryogenic process, it can precipitate as a solid.
- It is noncombustible, and thus reduces the heating value of the sales gas.
- It is classified as an atmospheric pollutant by the U.S. Environmental Protection Agency and has been cited as a major contributor to global climate change.

These problems are addressed by removing CO_2 from natural gas (Chapter 10) and venting it where allowed by environmental regulations or by sequestering it in underground reservoirs.

The positive feature is that it is an excellent fluid for miscible EOR.

16.1.2 Hydrogen Sulfide

H_2S is a highly undesirable component in natural gas because:

- It is extremely toxic.
- It is flammable.
- In the presence of water, it forms a weak, corrosive acid.

Only trace quantities of H_2S in gas plant products are permitted, and removal of large quantities of H_2S to meet specifications is expensive.

The positive feature of H_2S is that it can be converted into elemental sulfur, a major industrial chemical, and depending upon sulfur market price can be a saleable byproduct. In certain situations, it is also combined with CO_2 for EOR.

16.2 PROPERTIES OF SULFUR

To help the reader appreciate the sulfur conversion process, this section discusses some of the unique physical properties of sulfur. Sulfur is an unusual element. In the natural state, it does not exist as atomic S, but in a number of allotropic forms, S_n. The value of n changes significantly with temperature in the solid, liquid, and vapor phases, and has a pronounced effect on sulfur properties. A thorough discussion of the allotropic forms and their effect on thermodynamic and physical properties is beyond the scope of this text. This section gives some properties and illustrates the unique behavior of sulfur by showing the temperature-dependence of viscosity. For other properties, readers should refer to the *Engineering Data Book* (2016b), Meyer (1976), Tuller (1954), and West (1950).

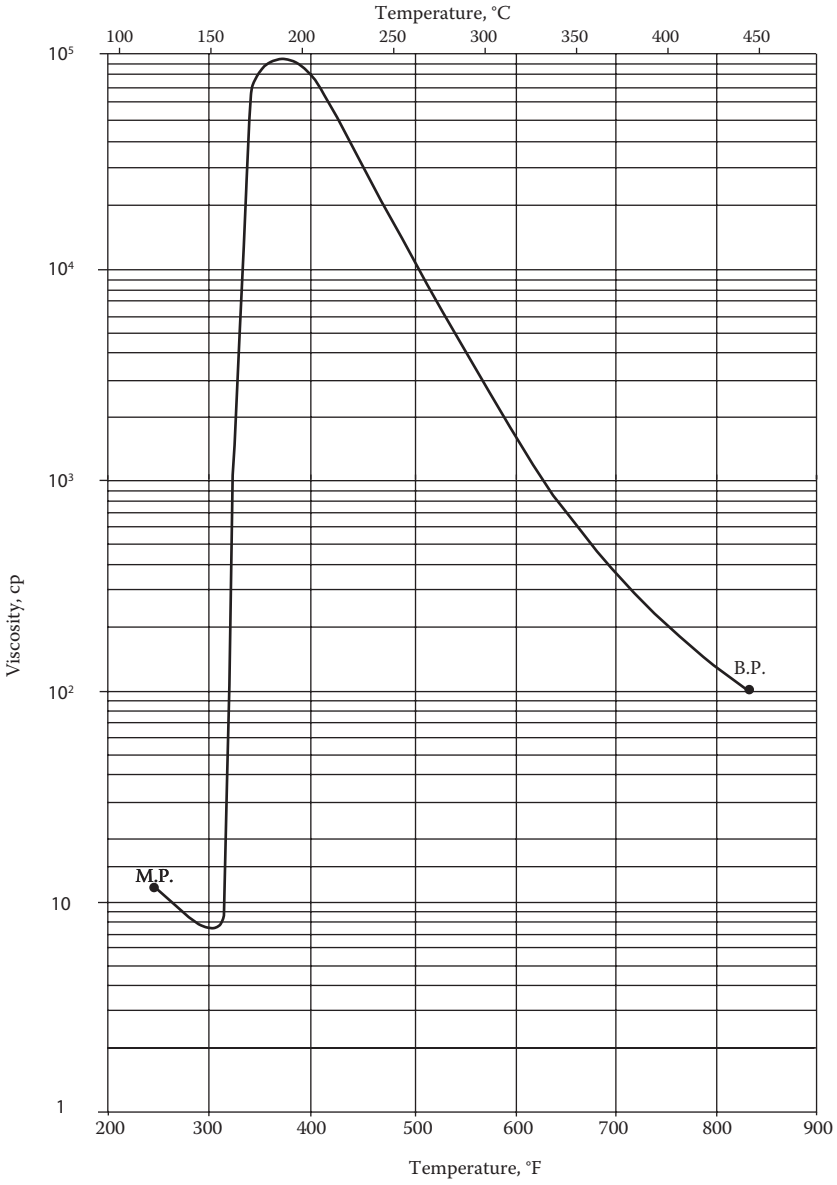


FIGURE 16.1 Viscosity of molten sulfur as function of temperature. (Adapted from the *Engineering Data Book*, 2016b, with permission.)

16.2.1 Solid State

The thermodynamically stable form of the solid is a function of temperature. One crystal form (orthorhombic) is stable up to 203.5°F (95.3°C). Above this temperature, the structure changes to another crystalline (monoclinic) form, which is stable up to the melting point at 247.3°F (119.6°C). Both crystalline forms are arranged in a ring structure composed of eight sulfur molecules (S_8). As the temperature is lowered, the monoclinic crystal slowly transforms to the orthorhombic form. The *Engineering Data Book* (2016b) presents correlations for heat capacity and discusses other properties of solid sulfur.

16.2.2 Liquid State

The principal allotropes in the liquid state are composed of 2, 6, and 8 sulfur molecules (S_2, S_6, and S_8). Note that S_2 is a dimer, and both S_6 and S_8 are ring structures at lower temperatures. According to Meyer (1976), in the vicinity of 316.5°F (158.1°C), designated the lambda point, λ, almost all properties of molten sulfur (e.g., heat capacity, density, viscosity and surface tension) experience a sudden change with temperature.

Figure 16.1 shows this unusual behavior for sulfur viscosity which has a maximum around this temperature. Shuai and Meisen (1995) present correlations of viscosity, density, vapor pressure, surface tension, thermal conductivity, and specific heat for sulfur. The *Engineering Data Book* (2016b) presents many of the same equations along with equilibrium properties needed to model the Claus reactors discussed in the following section.

The accepted explanation (Meyer, 1976; Tuller, 1954) for the unusual behavior is that as the temperature increases, the S_8 rings open to become S_8 chains, and the S_8 chains polymerize to form larger molecules. As the temperature is increased, the bonded chains break into single S_8 molecules, and sulfur gradually returns to its original state.

Pure molten sulfur has a maximum viscosity of over 90,000 cP, which would make it difficult to process (*Engineering Data Book*, 2016b). Fortunately, the viscosity is greatly reduced in the presence of H_2S. Of the commonly required physical properties, only thermal conductivity changes smoothly with temperature.

16.2.3 Vapor State

Sulfur vapor exists as S_x, where x can have values from 1 through 8. Figure 16.2 shows the distribution of the principal sulfur vapor species as a function of temperature. Note that at lower temperatures, S_8 dominates; however, at higher temperatures, S_8 converts to S_6, and finally to S_2. The sequence is not unexpected, because increased temperature means increased energy for the molecules, which leads to the breakup of the rings. Sulfur atoms, S_1, are not present in the equilibrium vapor below the critical point (Meyer, 1976). The formation of sulfur clusters has a very pronounced effect on the physical properties. However, the sulfur cluster effect occurs at much higher temperatures, and the changes are much less pronounced than those of the liquid (*Engineering Data Book*, 2016b).

16.3 SULFUR RECOVERY PROCESSES

Sulfur removal processes are the only processes in a gas plant that use reactor chemistry to generate a salable product. A survey of U.S. gas processing plants (True, 2015) shows that of the 666 natural gas plants, 84 (13%) report facilities for sulfur recovery. Processes to deal with the H_2S removed from natural gas may be loosely grouped into three categories, depending on the quantity of elemental sulfur produced:

- Large-scale, >25 long tons/d[1] (LT/d) of elemental sulfur
- Medium-scale, 0.2–25 LT/d of elemental sulfur
- Small-scale, <0.2 LT/d of elemental sulfur

Small-scale processes are primarily the nonregenerable scavengers discussed in Chapter 10. This chapter deals principally with large-scale processes (Section 16.3.1) with limited discussion of

[1] Sulfur production is commonly expressed in one of three different weight units: short tons (1 ton = 2,000 lb_m = 907 kg), long tons (2,240 lb_m = 1,016 kg), and tonnes (1 tonne = 1,000 kg = 2,204 lb_m). Plant capacities or production rates are stated in long tons or tonnes, and U.S. environmental regulations in tons.

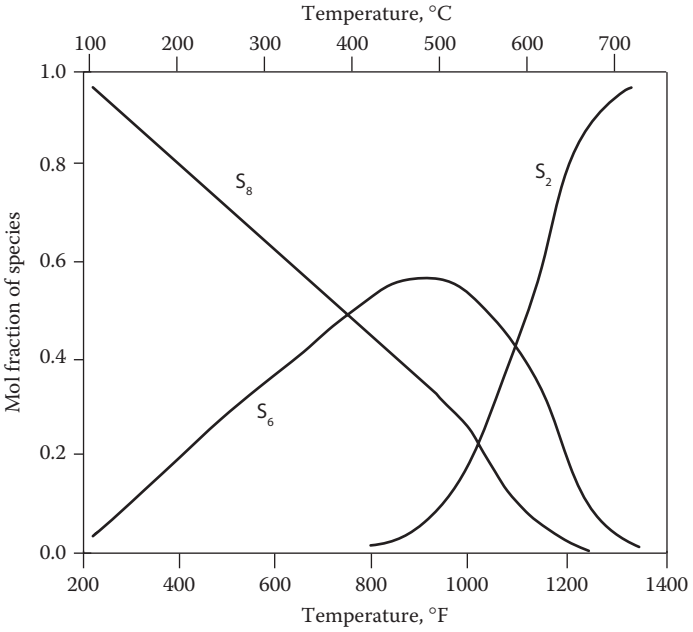


FIGURE 16.2 Distribution of sulfur vapor species as a function of temperature. (Adapted from *Engineering Data Book*, 2016b, with permission.)

medium-scale direct conversion redox processes (Section 16.3.2). Section 16.5 discusses acid gas injection (AGI) which is feasible for both medium- and large-scale quantities of sulfur.

Approximately 93% of the sulfur produced in the United States goes into production of sulfuric acid, which is used extensively in a wide variety of industrial products (U.S. Geological Survey, 2018).

The major source of elemental sulfur is recovered sulfur, obtained during the refining of crude oil and the processing of natural gas. In 2017, the United States produced approximately 9.0 million metric tons of elemental sulfur, 11% of the world's total. Of that total, approximately 93% came from the refining of petroleum and gas processing (U.S. Geological Survey, 2018).

The economics of sulfur production are unusual. Most commodities follow the traditional supply–demand scenario. When demand increases or decreases, manufacturers adjust production to match demand. Sulfur production is different because recovered sulfur from petroleum or natural gas is a byproduct of the process. Consequently, recovered sulfur production is only loosely linked to the supply–demand cycle. If demand for sulfur drops, the refiner or gas producer cannot decrease sulfur production because its recovery is required and becomes a cost of doing business. As a result, producers of recovered sulfur are sometimes faced with the problem of disposing of large sulfur surpluses.

The most comprehensive information on sulfur recovery processes is available in Hatcher et al. (2007), Maddox and Morgan (1998), *Engineering Data Book* (2016b), Kohl and Nielsen (1997), Echterhoff (1991), and Leppin (2001). Information on medium-scale sulfur processes is given in Echt et al. (2017). Strickland et al. (2001) provide a thorough discussion of tail gas treating unit (TGTU) processes (see following sction), along with cost comparisons.

16.3.1 Claus Process

True (2015) lists 199 natural gas plants worldwide that produce elemental sulfur, 84 in the United States, 86 in Canada, with the remaining 29 distributed in other countries. In 195 of the 199 plants (98%) the Claus process is listed as the sole or primary process for converting H_2S into sulfur; the

remaining processes are generally redox processes (see Chapter 10 for details). In most jurisdictions, the exit stream from Claus plants cannot meet environmental emission requirements, and a TGTU is required to remove the remaining sulfur compounds. The most commonly used Claus modifications are direct oxidation, e.g., SUPERCLAUS®, or sub-dew point processes, e.g., cold bed adsorption (CBA) process. There are also add-on processes, e.g., the Shell Claus Offgas Treating (SCOT®) process. The discussion of TGTU will be limited to these processes.

16.3.1.1 Chemistry

The Claus process consists of the vapor-phase oxidation of hydrogen sulfide to form water and elemental sulfur, according to the overall reaction (*Engineering Data Book*, 2016b)

$$3H_2S + \frac{3}{2}O_2 \leftrightarrow 3H_2O + \frac{3}{x}S_x \tag{16.1}$$

The above overall reaction is simply a mass balance and does not represent the reaction mechanism or show intermediate steps. In practice, the reaction is carried out in two steps:

$$H_2S + \frac{3}{2}O_2 \rightarrow H_2O + SO_2 \tag{16.2}$$

$$2H_2S + SO_2 \leftrightarrow 2H_2O + \frac{3}{x}S_x \tag{16.3}$$

The first reaction is a highly exothermic combustion reaction, whereas the second is a more weakly exothermic reaction promoted by a catalyst to reach equilibrium. The *Engineering Data Book* (2016b) and the articles by Hatcher et al. (2007) and Borsboom et al. (2003) provide additional information on Claus chemistry.

Figure 16.3 shows the equilibrium conversion obtained for H_2S into elemental sulfur by the Claus reaction. Kohl and Nielsen (1997) state that the unusual shape of the equilibrium curve is caused by the existence of different sulfur species at different reaction temperatures. They point out that at a sulfur partial pressure of 0.7 psia (0.05 bara) and temperatures below 700°F (370°C), the vapor is mostly S_6 and S_8, but at the same partial pressure and temperatures above approximately 1,000°F (540°C), S_2 predominates. This shift in species causes the reaction equilibrium curve to shift from a downward slope to an upward slope, as shown in Figure 16.3. This behavior has a significant effect on the operation of the Claus process.

Figure 16.3 shows that the maximum conversion to sulfur is obtained at temperatures near the melting point of sulfur (248°F, 120°C). To prevent solids from forming, temperatures above the melting point are maintained in the equipment where liquid sulfur is present. In the catalytic reactors, the temperatures are above the sulfur dew point because liquid deposition reduces catalyst activity. To avoid sulfur condensation the catalytic reactors operate at temperatures above the optimum equilibrium conversion. This is the reason for having a series of reactors, with sulfur product withdrawn from the reacting mixture between reactors. Withdrawing sulfur product causes the reaction (16.3) to shift to the right, which results in more sulfur produced. The CBA process discussed in Section 16.3.1.3 operates close to maximum conversion but allows liquid sulfur deposition in the catalytic bed.

16.3.1.2 Process Descriptions

Process descriptions and operating data for the Claus processes are given in Kohl and Nielsen (1997), Parnell (1985), and Hatcher et al. (2007). Although there are many variations of the Claus process, there are two principle approaches: straight-through and split-flow. When the H_2S concentration is sufficiently high, the straight-through Claus process is preferred. However, the split-flow

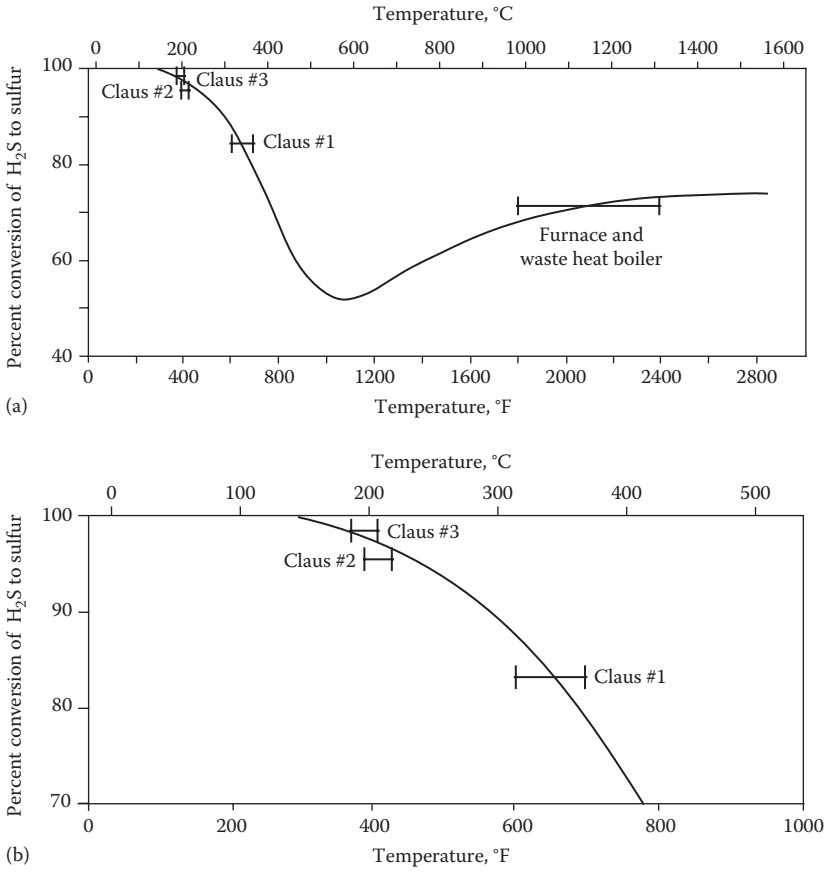


FIGURE 16.3 Equilibrium conversion of hydrogen sulfide to sulfur, typical operating range of Claus furnace and typical reactor inlet temperatures (Adapted from *Engineering Data Book*, 2016b, with permission.)

Claus process may be required at lower H_2S concentrations. The following paragraphs describe both types and when each type is used. For all Claus processes, the combustion air flow rate is controlled to maintain the proper H_2S/SO_2 ratio of 2:1 at the final reactor outlet (see equations in Section 16.3.1.1).

Table 16.1 summarizes ranges for using the various Claus options. Note that the table concentration values are approximate and the process variations are typical, not definitive.

TABLE 16.1
Claus Options for Different H_2S Feed Concentrations

H_2S Feed Concentration (mol%)	Process
55–100	Straight-through
30–55	Straight-through plus acid gas and/or air preheat
15–30	Split-flow or straight-through plus acid gas and/or air preheat
10–15	Split-flow with acid gas and/or air preheat
5–10	Split-flow with fuel added, oxygen enrichment, or with acid gas and air preheat

Source: *Engineering Data Book* (2016b)

16.3.1.2.1 Straight-through Claus

Figure 16.4 shows a simplified flow diagram for the straight-through Claus unit. This is the preferred configuration because all the acid gas feed flows through the reaction furnace, thus allowing the destruction of hydrocarbon or other impurities present in the feed. Impurities absorbed by treating solvents like aromatic hydrocarbons foul catalyst beds and ammonium compounds can cause plugging.

Figure 16.3 shows the approximate inlet temperature of the three Claus reactors and the furnace temperatures in the Claus process on the H_2S to sulfur equilibrium curve. The necessity to maintain temperatures above the sulfur dew point governs the catalytic reactor temperatures. The necessity to maintain a stable flame requires a furnace temperature above approximately 1,700°F (925°C). This requirement sets the operation of the furnace and waste heat boiler (WHB).

The first reaction (16.1) takes place in a reaction furnace operating near ambient pressure (3–8 psig; 0.2–0.6 barg) and at temperatures of 1,800°F–2,500°F (1,000°C–1,400°C). The air flow rate is adjusted to react one-third of the H_2S to SO_2, along with any other combustibles such as hydrocarbons and mercaptans. The H_2S reaction is exothermic and heat is used to produce high-pressure steam in a WHB. Reactions (16.2 and 16.3) take place in the reaction furnace and WHB. The gases exit the WHB in the range of 500°F–650°F (260°C–340°C) (Parnell, 1985), which is above the sulfur dew point, so sulfur does not condense in the boiler.

The WHB is followed by catalytic stages where only the second reaction takes place because all O_2 has been consumed in the furnace. The catalysts used are generally alumina (Al_2O_3) or titania (TiO_2). Each catalytic reactor is followed by a condenser to remove the sulfur formed. The gas is cooled to 300°F–400°F (150°C–200°C) in the condenser to remove elemental sulfur as a liquid. The condenser is generally cooled by boiling water to produce low-pressure steam. Vapor leaving the condenser is at the sulfur dew point and is reheated before entering the next converter to prevent sulfur deposition on the catalyst. Typical inlet temperatures to the three catalytic stages are 650°F (340°C), 410°F (210°C), and 390°F (200°C). Because Equation 16.3 is exothermic, the reactor outlet temperature is higher and is a function of H_2S concentration.

Gas reheating between stages is normally done using one of the following methods (Grekel et al., 1965; Valdes, 1964):

- Mixing the reactor inlet gas with gas from the outlet of an upstream reactor

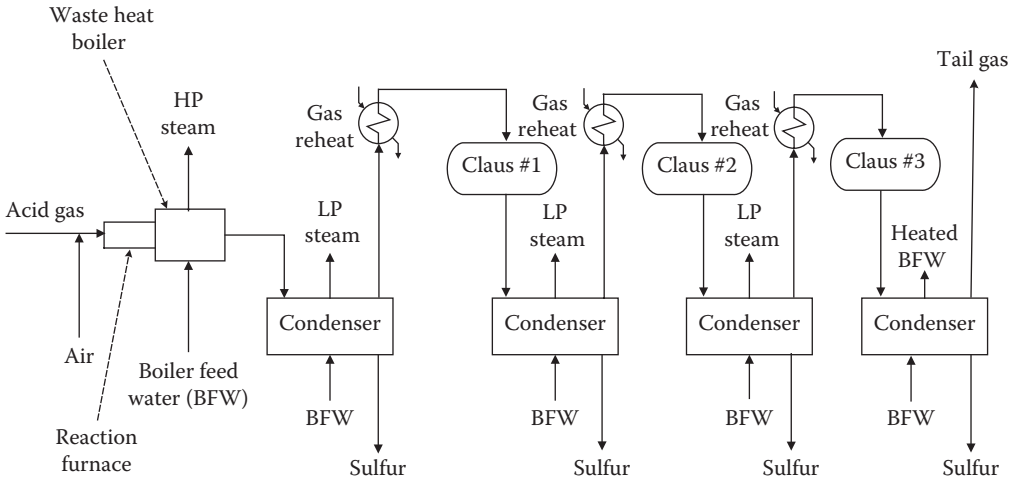


FIGURE 16.4 Simplified flow diagram for the straight-through Claus process.

- Using steam heat exchange or fuel gas-fired heaters
- Using heat exchange between reactor inlet and exit streams

It is important to maintain a combustion furnace flame temperature of 1,700°F (930°C) or higher, because the flame is not stable at lower temperatures. Consequently, the straight-through configuration cannot be used at lower H_2S concentrations because the feed gas heating value is too low. Common solutions to this problem include:

- Preheating the air and/or acid gas feed
- Adding fuel gas to the reaction furnace burner
- Enriching the combustion air with oxygen
- Using the split-flow process
- Further enriching the acid gas stream in H_2S (Acid Gas Enrichment)

Slavens et al. (2010) and Tonjes et al. (2010) provide a thorough discussion of sulfur recovery options from lean acid gases, including a detailed discussion of acid gas enrichment.

Figure 16.5 shows a two-reactor Claus unit. Only two beds are used because the sulfur recovery unit uses a SCOT-type tail gas cleanup process (see Section 16.3.1.3). The reaction furnace is on the left, and the two reactors are in the center above their respective condensers. The covered sulfur pit is at grade on the lower right side of the photo.

16.3.1.2.2 Split-Flow Claus

Figure 16.6 shows the split-flow configuration for H_2S acid gas feed concentrations below approximately 30 vol%. In this scheme, the feed is split; at least one-third of the feed goes to the furnace, and the remainder joins the furnace exit gas before entering the first catalytic converter. Sufficient acid gas is bypassed so that the flame is stable, but the maximum feed bypass is two-thirds, because one-third of the H_2S must be reacted with combustion air to form SO_2. (Note the stoichiometry in Equations 16.1–16.3.)

FIGURE 16.5 Two reactor Claus unit.

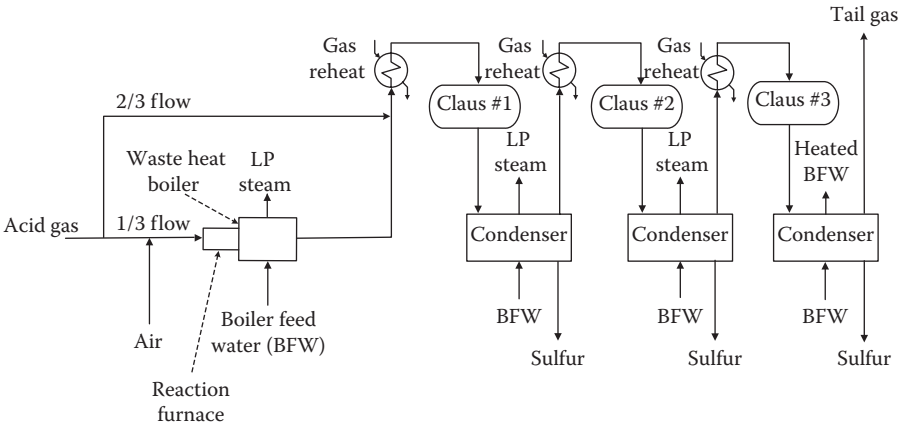


FIGURE 16.6 Split-flow Claus process. (Adapted from Echterhoff, 1991)

If preheating is used with the split-flow configuration, gases with as little as 7% H_2S can be processed. However, a major disadvantage of split-flow is that up to two-thirds of the contaminants in the feed bypass the reaction furnace and reach the first catalytic converter where they can deactivate the catalyst.

Aromatic compounds such as benzene, toluene, ethylbenzene, and xylenes (BTEX) poison the Claus catalyst. In a straight-through Claus unit, aromatic compounds in the acid gas feed are destroyed by the flame temperatures in the reaction furnace. As the H_2S content of the gas becomes lower, the flame temperature in the furnace drops, and some BTEX may reach the catalyst in the first reactor. In a split-flow Claus unit, up to two-thirds of the acid gas bypasses the furnace and the contained aromatic compounds reach the first Claus reactor. Consequently, lean acid gases containing significant quantities of BTEX may require BTEX removal prior to the Claus unit.

The effect of aromatic components on the Claus catalyst has been investigated by Crevier et al. (2007, 2001). They discuss removing the BTEX by using regenerable carbon beds before the Claus unit.

Generally, the sulfur recovery in the conventional plants discussed above is in the order of 94%–95% for two catalytic stages, and may reach 98% for three stages. The addition of a fourth stage is usually not economical, because overall sulfur recovery is increased by less than 1%.

16.3.1.3 Tail Gas Cleanup

Sulfur emission regulations and required recovery levels vary around the world. In the United States, recoveries of up to 99.95% may be required. Recovery regulations often consider such factors as plant location, size, and the percent H_2S in the sulfur recovery unit feed. These regulations forced development of tail gas cleanup technology. Tail gas cleanup entails either an add-on downstream of the Claus unit or a modification of the Claus unit itself. Catalytic reactor processes for this final sulfur removal are generally divided into three categories (Kohl and Nielsen, 1997):

- Direct oxidation of H_2S to sulfur (SUPERCLAUS®)
- Sub-dew point Claus processes (CBA, MCRC, Sulfreen™)
- SO_2 reduction and recovery of H_2S (SCOT-type)

This section provides an example process in each category.

SUPERCLAUS® is an example of selective oxidation of H_2S to sulfur for final cleanup. The process, as described by Lagas et al. (1988, 1994, 1989) and by Goar and Meyer (2008), involves a slightly modified two-stage Claus unit followed by a third-stage catalytic reactor to oxidize the

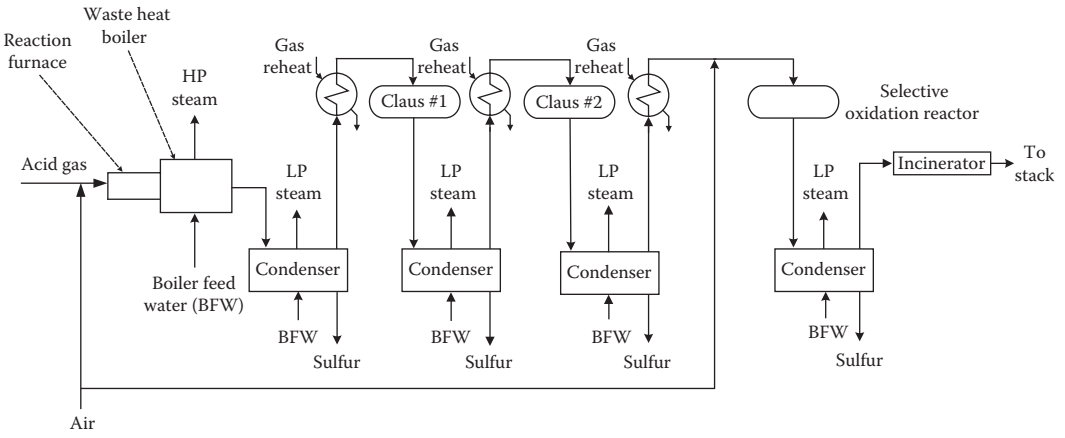


FIGURE 16.7 SUPERCLAUS® unit. (Adapted from d'Haêne, 2003.)

remaining H_2S to elemental sulfur. Figure 16.7 shows the overall process. Other selective oxidation processes have been developed and for more information on these processes consult the Laurance Reid Gas Conditioning Conference proceedings.

The first and second reactors use a Claus catalyst, whereas the third reactor contains the selective oxidation catalyst. The Claus unit itself is operated with a deficiency of air, so that the gas that exits the second reactor contains 0.8–3 vol% H_2S. Sufficient air is added to this exit gas to keep the oxygen level in the 0.5–2 vol% range. The mixture then goes to the third reactor, where the catalytic reaction occurs:

$$3H_2S + \frac{3}{2}O_2 \leftrightarrow 3H_2O + \frac{3}{x}S_x \tag{16.1}$$

The selective oxidation catalyst in the third reactor does not promote the reaction

$$H_2S + \frac{3}{2}O_2 \leftrightarrow H_2O + SO_2 \tag{16.2}$$

or the reverse reaction of sulfur with H_2O vapor (Equation 16.4)

$$\frac{3}{x}S_x + 2H_2O \leftrightarrow 2H_2S + SO_2 \tag{16.4}$$

Consequently, a total recovery rate of 99% or higher can be reached. Lagas et al. (1988) describe a modification of SUPERCLAUS® that can theoretically reach a sulfur recovery rate of 99.5%.

The CBA process is an example of a widely used sub dew point process. Figure 16.8 shows one of its many possible variations. The front end of the unit is a Claus reactor, and the sub-dew point process takes place in one of the final two catalytic reactors, CBA #1 and CBA #2. One converter is in service, while the other is being regenerated. After the gas leaves the final condenser, it is not reheated but is sent to the third reactor (CBA #2), which is operated at a temperature well below the sulfur dew point. As can be seen from Figure 16.3, this results in a better equilibrium conversion, but liquid sulfur is deposited on the catalyst and causes a gradual loss of activity. While CBA #2 is in service, CBA #1 is being heated and regenerated with a slipstream from Claus #1. After regeneration is complete, the reactor can be cooled with a slipstream from the final condenser. When the catalyst in CBA #2 is exhausted, valves (not shown in the figure) are switched, and CBA #1 becomes

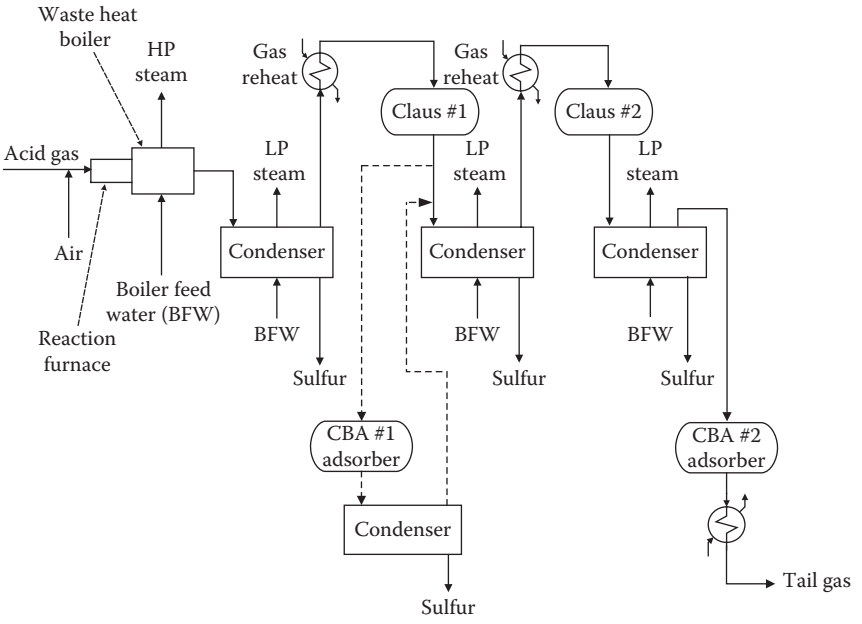


FIGURE 16.8 CBA unit. Drawing shows CBA #1 bed in regeneration mode. (Adapted from Goddin et al., 1974.)

the adsorbing reactor while CBA #2 undergoes regeneration. Total sulfur recoveries greater than 99% have been obtained with CBA processes (Clark et al., 2002).

The SCOT® process is an example of a process that reduces the SO_2 in the Claus plant off-gas back to H_2S. It then uses amine treating to selectively absorb the H_2S, which is recycled back to the Claus plant for conversion to elemental sulfur. The process can produce an exit gas that contains 10–250 ppmv of total sulfur, while increasing total sulfur recovery to 99.97% or higher. Figure 16.9 shows a simplified process flow diagram of the SCOT® process. Figure 16.10 shows a photograph of a SCOT-type unit. From left to right are the inline burner, catalytic reactor, quench tower, absorber, and regenerator.

The following description of the process has been adapted from Echterhoff (1991). The feed, off-gas from the Claus unit, is heated to 575°F (300°C) in an inline burner that is operated substoichiometrically to produce a reducing gas mixture containing H_2 and CO. The mixture then flows to a catalytic reactor (cobalt-molybdenum on alumina), where sulfur compounds, including SO_2, CS_2,

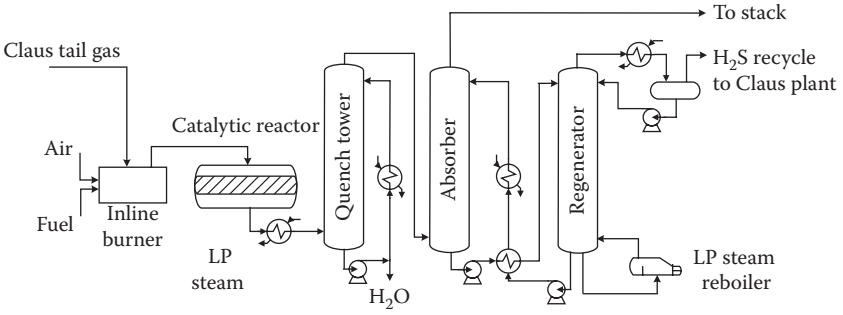


FIGURE 16.9 Shell Claus Offgas Treating (SCOT®) unit. (Adapted from Echterhoff, 1991.)

FIGURE 16.10 SCOT-type tail gas cleanup unit.

and COS, are reduced to H_2S. The gas leaving the reactor goes to a waste-heat exchanger, where it is cooled to approximately 320°F (160°C) and produces low-pressure steam.

The gas from the waste-heat exchanger then flows through a quench tower, where it is cooled to approximately 100°F (40°C) by externally cooled recycle water in countercurrent flow. The water from the tower is condensed, and the excess water is sent to a sour water stripper. Gas from the quench tower then contacts an aqueous amine solution in the absorption column. The amine is generally methyldiethanolamine (MDEA) or diisopropylamine (DIPA) to absorb H_2S while slipping CO_2. When extremely high selectivity is required, FLEXSORB™ solvent may be used (Crevier et al., 2009). The gas exiting the top of the absorber contains 10–250 ppm H_2S and is incinerated. The rich amine that leaves the bottom of the absorber flows to the regenerator, where heat is applied to strip the H_2S from the amine solution. The overhead from the regenerator is cooled to condense the water, and the H_2S is recycled to the Claus unit feed. Lean amine is cooled and returned to the absorber.

Advances in catalysts have allowed the substoichiometric inline burner to be replaced with a steam-heated exchanger operating at lower temperatures. This has the advantage of eliminating problems associated with the burner and the introduction of fuel gas into the system. Crevier et al. (2009) provide a more detailed discussion of low-temperature SCOT-type processes.

16.3.2 Small- to Medium-Scale Recovery Processes

A number of processes have been developed for small- to medium-sized sulfur recovery operations, those dealing with sulfur production in the approximate range of 0.2–25 LT/d of sulfur. As mentioned previously, for small amounts of H_2S, nonregenerable scavengers such as iron sponge may be cost effective, and for large quantities of H_2S the Claus process or one of its modifications is most often chosen. This section discusses two processes that are attractive at intermediate sulfur capacities: LO-CAT II® and CrystaSulf™. Kohl and Nielsen (1997) discuss a broader range of processes. Biological processes are discussed in Chapter 10.

16.3.2.1 LO-CAT II®

This is a direct conversion process (Hardison, 1984; Hardison and Ramshaw, 1991; Heguy and Nagl, 2003; Kohl and Nielsen, 1997) using a patented aqueous solution of ferric ion held in solution by organic chelating agents. The product is elemental sulfur. There are three basic LO-CAT® configurations:

- Aerobic
- Anaerobic
- Autocirculation

The aerobic configuration will not be discussed, because it is used for situations like odor control in landfills. Figure 16.11 shows a simplified flow sheet of the conventional anaerobic process, and Figure 16.12 illustrates the autocirculation unit. The chemistry of both processes is the same. The anaerobic process is the most widely used in gas processing; the autocirculation process can be used when the unit is treating the acid gas from an amine unit.

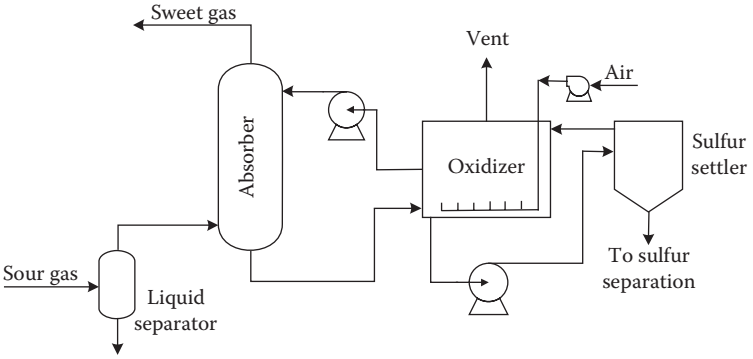


FIGURE 16.11 Simplified LO-CAT II® anaerobic process. (Adapted from Hardison and Ramshaw, 1991; Heguy and Nagl, 2003)

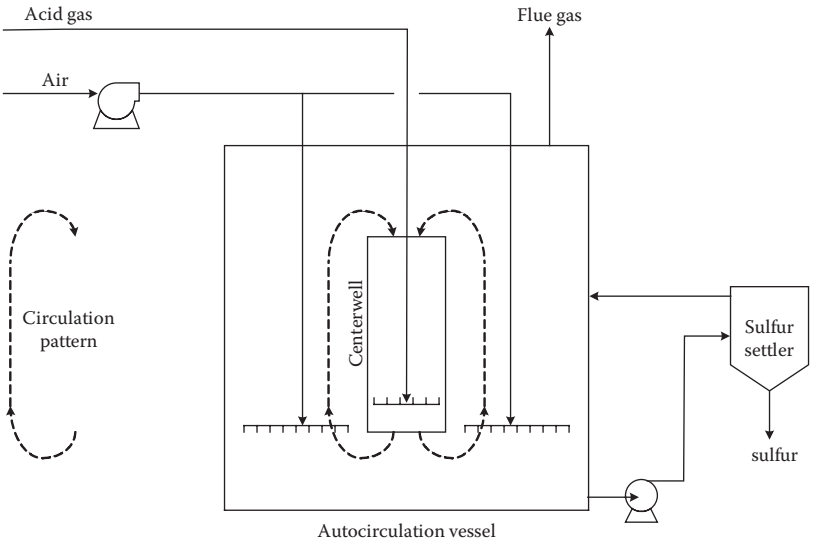


FIGURE 16.12 LO-CAT II® autocirculation unit. (Adapted from Heguy and Nagl, 2003)

The LO-CAT II® process takes place in five steps (Heguy and Nagl, 2003):

1. Absorption of the H_2S into an aqueous catalyst solution

$$H_2S(g) + H_2O(1) \leftrightarrow H_2S(aq)$$

2. Ionization of the H_2S

$$H_2S(aq) \leftrightarrow H^+ + HS^-$$

3. Oxidation of HS^- to S^0 and reduction of Fe^{+++} to Fe^{++}

$$HS^- + 2Fe^{+++} \rightarrow S^0 + 2Fe^{++} + H^+$$

4. Absorption of O_2 into aqueous solution

$$\frac{1}{2}O_2(air) + H_2O(1) \leftrightarrow \frac{1}{2}O_2(aq)$$

5. Oxidation of Fe^{++} to Fe^{+++}

$$2Fe^{++} + \frac{1}{2}O_2(aq) + H_2O(1) \rightarrow 2Fe^{+++} + 2OH^-$$

The overall stoichiometry of the process is

$$H_2S(g) + \frac{1}{2}O_2(g) \rightarrow S(s) + H_2O(l)$$

The iron, held in aqueous solution with proprietary chelating agents, acts as a catalyst and also serves as an electron donor and acceptor. Steps 2, 3, and 5 are rapid; steps 1 and 4 are slower and are rate controlling. The process is designed to run at a high pH (7–8.5) that would normally not allow the iron to stay in solution, but the proprietary chelating agent maintains the iron solubility and prevents the formation of $Fe(OH)_3$ and FeS (Holub and Sheilan, 2000).

LO-CAT II® has the following characteristics:

- It is specific to H_2S, and does not react with COS, CS_2, mercaptans, or CO_2.
- It is capable of 99.99% sulfur removal, thus making it suitable as a tail gas unit for the Claus process.
- It has a nontoxic catalyst solution.
- It requires the continuous addition of chemicals to control pH and replenish those lost to the product sulfur cake.

Note that in Figure 16.11, steps 1, 2, and 3 are performed in the absorber, and steps 4 and 5 takes place in the oxidizer. In this configuration, a pump is required to circulate liquid to the absorber from the oxidizer.

In the autocirculation configuration, the circulating pump is eliminated, and all five steps take place in the autocirculation unit. Circulation of the liquid is accomplished due to density differences between the rich and regenerated solutions. The centerwell is a piece of pipe, open at both ends, that acts as the absorber. The volume of air is larger than that of the acid gas, and thus there is a density difference between the liquid in the centerwell and that outside of it, creating a natural liquid flow.

Both configurations typically produce a wet sulfur cake. This cake can be used directly as a fertilizer product or upgraded to marketable sulfur.

16.3.2.2 CrystaSulf

The CrystaSulf™ process uses a proprietary nonaqueous solution to carry out the Claus reaction. Figure 16.13 shows a simplified process flow diagram.

The process operates as follows:

- Sour gas is fed to the absorber, where it contacts the sorbent, a nonaqueous solution containing dissolved SO_2.
- Elemental sulfur is formed in the absorber via the Claus reaction, but remains soluble in the organic solution.
- Sorbent containing the dissolved sulfur is cooled and fed to the crystallizer, where further cooling causes the sulfur to crystallize.
- Regenerated sorbent is then recycled back to the absorber.
- Sulfur slurry is then fed to the settler and filtration system, where the sulfur is recovered as a filter cake.
- SO_2 is added to the solution either from an external source of SO_2 or by burning a portion of the product sulfur to produce SO_2 on-site.

CrystaSulf™ has the following features (Dalrymple et al., 1999, 2005):

- It is capable of up to 99.8% sulfur removal.
- It can tolerate high concentrations of CO_2.
- It tolerates oxygen contamination.
- It does not react with mercaptans.
- It is unaffected by liquid hydrocarbon slugs because it is hydrocarbon based.
- It can be applied directly to sour streams or Claus unit tail gas.

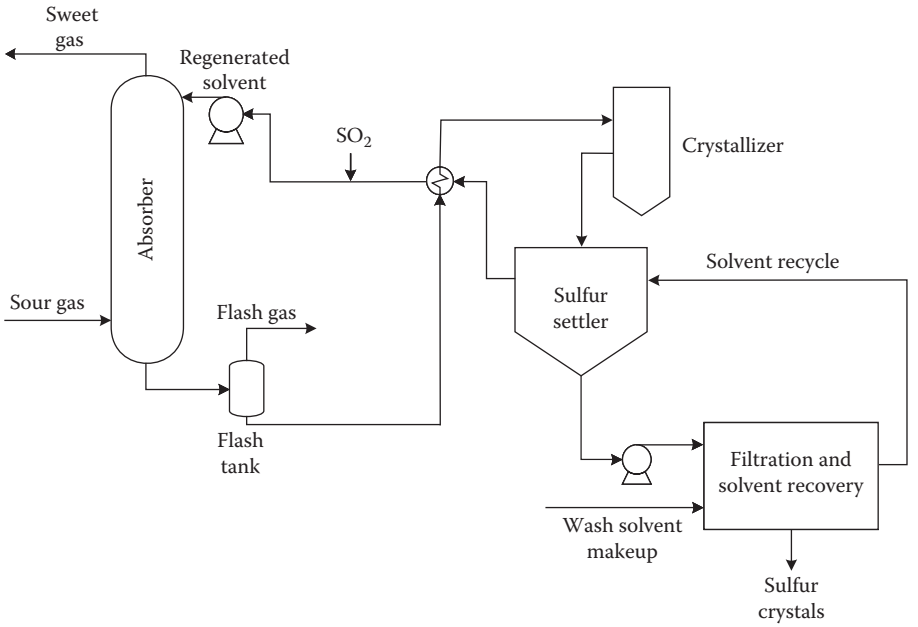


FIGURE 16.13 Simplified diagram of the CrystaSulf™ process.

As of 2019 there were no commercial units operating and therefore the process is not completely proven in the field. Pilot scale units are in operation.

Additional information on the process is available from McIntush et al. (2000, 2001).

16.4 SULFUR STORAGE

Sulfur from the Claus unit is withdrawn as a liquid, and is generally stored in the molten state. Sulfur is transported in the molten form or converted to a granular material. For longer-term storage, sulfur is often stored in huge blocks. A number of potential problems are associated with sulfur storage. A brief summary relating primarily to molten sulfur, adapted from Johnson and Hatcher (2003b), is given below:

- Sulfur fires: Uncommon, but they can produce large amounts of highly toxic SO_2.
- H_2S: Any dissolved H_2S in the molten sulfur from the condensers may be a significant hazard if appropriate degassing techniques are not used.
- Corrosion: A wet sulfidic atmosphere can lead to severe corrosion of carbon steel.
- SO_2: Formed from the oxidation of H_2S and sulfur is highly toxic, and forms highly corrosive sulfurous acid in the presence of water.
- Static discharge: Because of the excellent insulating properties of molten sulfur, static discharge may occur under certain conditions and lead to possible fires or explosions.

A comprehensive discussion of sulfur storage and degassing is beyond the scope of this book, but Johnson and Hatcher (2003a, b) give an excellent presentation.

16.5 ACID GAS INJECTION

Section 16.3 discusses processes for converting H_2S into elemental sulfur, a valuable industrial chemical. Presently, there are no comparable processes for turning CO_2 into useful products, although research is underway. The discussion here deals only with using the acid gases in EOR operations or sequestering by injection into a suitable underground reservoir. The use of CO_2 in EOR is common and using a mixture of H_2S and CO_2 is practiced in a few situations. These injection methods will be briefly reviewed.

16.5.1 Enhanced Oil Recovery

EOR embraces a number of processes for recovering oil from known reserves beyond that are recoverable by conventional primary and secondary methods. EOR techniques include injection of miscible solvents (hydrocarbon gases, CO_2), immiscible gases (nitrogen (discussed in Chapter 13), air and flue gas), thermal methods (steam injection or partial combustion of *in situ* hydrocarbons), and chemicals (addition of wetting agents, etc. to water flooding).

Data available in 2014 (Kuuskraa and Wallace, 2014b) lists 218 active EOR projects in the United States, divided into four categories: thermal, chemical, gas, and other. Carbon dioxide accounted for 171 of the total, compared to 57 CO_2 EOR projects in 1988. In the United States, EOR accounted for 435 thousand barrels per day (Mbbl/d) (69,000 m^3/d) of oil production, with CO_2 contributing 300 Mbbl/d (48,000 m^3/d).

Modeling studies conducted by Duda et al. (2010) state that current best EOR practices have a potential for recovering more than 47 billion bbl of oil (7.5×10^9 m^3), and that next generation technologies may be capable of recovering an additional 30 billion bbl (5×10^9 m^3).

Several projects use a mixture of H_2S and CO_2 as the EOR fluid. Because these are often reported in the literature as "CO_2 floods" it is difficult to identify the fields involved. Because projects are

sometimes limited by availability of CO_2 (Kuuskraa and Wallace, 2014a) the use of mixed AGI fluids for EOR has increased.

16.5.2 Injection Wells

AGI is a viable disposal method for H_2S in some areas. In the United States, AGI started in 1986, with a small project to inject 0.5 MMscfd (600 Nm^3/h) of gas. By 2005, there were an estimated 84 projects worldwide, processing approximately 55 MMscfd (1.5×10^6 Nm^3/d) (Carroll et al., 2005). Since that time additional projects have been installed but the authors found no documentation on the number of projects.

The AGI concept is simple, but the implementation is not. Basically, AGI requires finding a suitable geologic formation in close proximity to the source of the acid gas, compressing the gas, and permanently sequestering it underground. Some of the more obvious difficulties associated with implementation are:

- Locating a suitable geologic formation.
- Obtaining the necessary federal, state, and local permits.
- Compressing low-pressure wet acid gas, which may be toxic and corrosive, to high wellhead injection pressures.
- Dehydrating to avoid liquid water or gas hydrates (see Chapter 8).

Removal of water to prevent corrosion during compression requires knowing the saturated water content of the mixture. Figure 16.14 shows that predicting the maximum water content of acid gas mixtures is difficult. For data in the figure at 100°F (38°C) the symbols denoting gas mixture compositions (in mol percent) are as follows:

▲ 30% CH_4 + 60% + 10% H_2S
▫ 90% CH_4 + 10% CO_2
◆ 9% CH4 + 10% CO_2 + 81% H_2S.

At 200°F (93°C):

▲ 5.5% CH_4 + 0.3% C_3H_8 + 25% CO_2 + 69.2% H_2S
▫ 43.7% CH_4 + 30% CO_2 + 26.3% H_2S
◆ 5.4% CH_4 + 0.3% C_3H_8 + 49.5% CO_2 + 44.8% H_2S

Depending on composition and temperature, the maximum water content can have a minimum value at relatively low pressure. This allows dehydration by compression and cooling. Figure 16.14 shows that even a small amount of methane has a significant effect on the saturated water content of an acid gas stream. Also, the literature on water content of acid gases above hydrates is uncertain. As of the time of publication, work is ongoing to resolve this uncertainty.

Figure 16.15 illustrates the compression path for a typical acid gas mixture being injected into a deep reservoir. Four stages of compression are required to deliver the acid gas to the wellhead at 1,200 psig (83 barg). The zigzag lines in the figure trace the compressor suction and discharge temperatures and pressures for each stage. The compressor must be designed and operated to avoid condensation of liquid and formation of hydrates. Because the gas may be corrosive it is common for corrosion-resistant materials to be used and dehydration installed on compressor interstages.

A detailed discussion of AGI is beyond the scope of this book; interested readers should refer to Carroll et al. (2005) and Wichert (2018) for good overviews of AGI. Ariyapadi et al. (2006) evaluate designs for high-capacity CO_2 AGI.

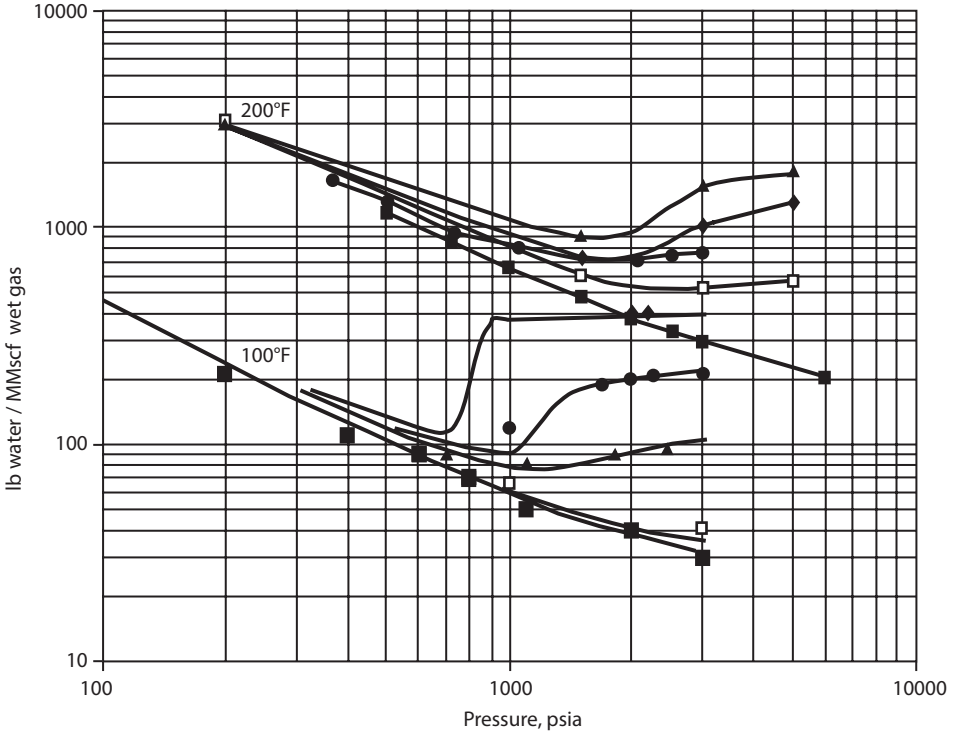


FIGURE 16.14 Saturated water content of acid gas mixtures as a function of temperature, pressure, and gas composition. The symbols ● and ■ denote pure CO_2 and pure CH_4, respectively. See text for other gas compositions. (Adapted from *Engineering Data Book*, 2016a, with permission.)

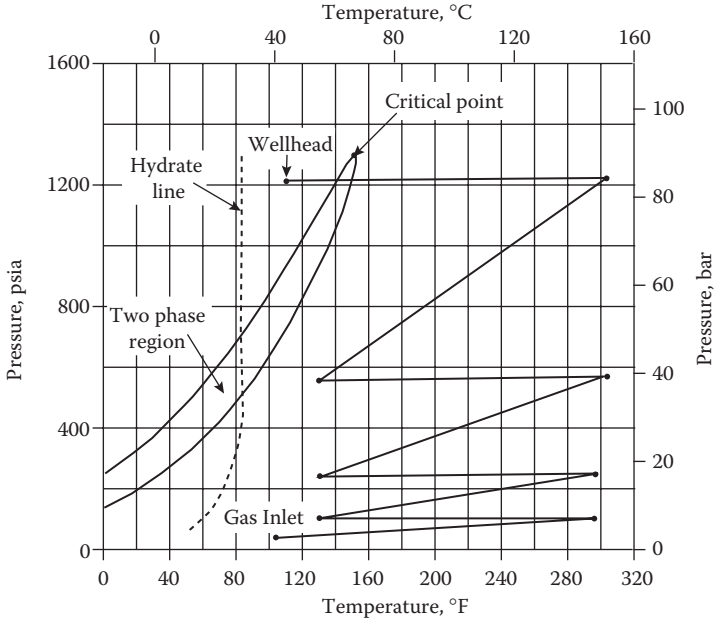


FIGURE 16.15 Compression path for a wet acid gas mixture. (Adapted from Carroll et al., 2005)

16.6 SAFETY AND ENVIRONMENTAL CONSIDERATIONS

Tables 16.2–16.4, adapted from Johnson and Hatcher (2003a), summarize the more important physical properties of molten sulfur, hydrogen sulfide, and sulfur dioxide. The tables also address safety and environmental concerns.

The primary safety and environmental concerns for AGI include:

- Equipment and piping integrity, which includes multistage compressors
- Reservoir and casing integrity for many years
- Presence of high-pressure, toxic gas mixtures if H_2S is present.

In addition to the issues with sulfur compounds highlighted, wet CO_2 can be corrosive to equipment and CO_2 can be an asphyxiant. Also, because CO_2 forms a solid at low temperatures, maintenance blowdown procedures and relief design must consider the potential for blockages with solids even with dry systems.

TABLE 16.2
Important Properties, Safety, and Environmental Concerns for Molten Sulfur

Physical Property or Characteristic	Hazards
Melts at 240°F (116°C)[a]	Possible severe burns
Boils at 851°F (455°C)[a]	Exhibits measurable vapor pressure at molten sulfur handling process conditions
Flash point 334°F–369°F (168°C–187°C)	Not much higher than normal storage temperatures
Autoignites at 478°F–511°F (248°C–266°C)	Sulfur fires can easily occur in the presence of oxygen
Viscosity transition at 318°F (159°C)	Increasingly difficult to pump above this temperature Magnitude is dependent upon H_2S content of the molten sulfur
Highly flammable in air	Sulfur fires
Solid dust cloud autoignites at 375°F (191°C)	Important variable in solid-forming operations Deflagration possible
Excellent insulator	Static discharge at 11% or higher oxygen atmosphere
Toxicity	Highly toxic at low concentrations

Source: Johnson and Hatcher (2003a).

[a] For S_8, Georgia Gulf Sulfur Corporation (2015) gives a melting point of 230°F–246°F (110°C–119°C) and boiling point of 832°F (444°C).

TABLE 16.3
Important Properties, Safety, and Environmental Concerns for H_2S

Physical Property or Characteristic	Hazards
Toxicity	Highly toxic at extremely low concentrations
Highly flammable in air between approximately 3.4% and 45% at process conditions	Deflagration possible
Exposed carbon steel forms iron sulfide corrosion product under wet, reducing conditions	Excessive corrosion in carbon steel piping Iron sulfides are highly pyrophoric

Source: Johnson and Hatcher (2003a).

TABLE 16.4
Important Properties, Safety, and Environmental Concerns for SO_2

Toxicity	Highly toxic at low concentrations
Corrosive when wet	Forms sulfurous acid in the presence of water at low temperatures

Source: Johnson and Hatcher (2003a).

DISCUSSION QUESTIONS

1. What is the reason for the unusual behavior of some physical properties of liquid and vapor sulfur?
2. What makes sulfur as a commodity different from most other commodity chemicals?
3. Why does H_2S feed composition dictate the type of Claus unit, and what are the methods used to make the process work at different H_2S concentrations?
4. Why is only one-third of the H_2S burned in the furnace of the straight-through Claus unit?
5. Why are tail gas cleanup units preferred to adding more reactors to conventional Claus units?
6. How does SUPERCLAUS® differ from conventional straight-through Claus unit?
7. What is a unique feature of the CBA process?
8. How do the SCOT-type processes differ from other sulfur recovery processes?
9. What are some of the major similarities and differences between the LO-CAT II® and CrystaSulf™ sulfur conversion processes?
10. What do you think could be some of the difficulties with AGI?

EXERCISES

16.1 An amine unit treats 100 MMscfd (2.7×10^6 Nm^3/day) of natural gas (composition below) to remove essentially all the H_2S and CO_2 which are then sent to a Claus unit. The Claus feed is at 100°F (38°C) and 8 psig (0.6 barg), and the unit removes 99.5% of the H_2S as elemental sulfur.

How much elemental sulfur (lb_m) is produced per day?

Component	mol%
CH_4	92.5
C_2H_6	1.4
C_3H_8	0.9
C_4^+	0.5
CO_2	2.0
H_2S	2.7

16.2 The tail gas from the Claus unit in Exercise 16.1 is the feed to a TGTU to remove remaining H_2S. With the addition of this processing step, the overall sulfur recovery increases to 99.9%. What is the H_2S recycle (lb-moles/day) (kg-moles/day) to the Claus unit? State any assumptions.

16.3 If environmental regulations on sulfur allow incineration, what would be the SO_2 emissions (lb_m/d, kg/d) from the Claus unit in Exercise 16.1 if the H_2S was incinerated? State any assumptions.

16.4 The gas entering an MDEA treating unit contains 0.5 mol% H_2S and 8 mol% CO_2. Inlet flow rate is 120 MMscfd (3.22×10^6 Nm^3/day). The treater uses a 50 wt% MDEA solution and has an inlet pressure of 1,000 psig (70 barg). The plant then dehydrates the gas and sells it as pipeline-quality gas. The pipeline specification requires that the gas contain no more than 0.25 grains/100 scf (6 mg/Nm^3) of H_2S and a maximum of 2% mol CO_2.
   a. What problem might be encountered in the operation of the Claus unit?
   b. What alternate methods of gas treating might be suitable for dealing with this problem?

REFERENCES

Ariyapadi, S., et al., Study evaluates design of high-capacity CO_2 injection plants, *Oil Gas J., 104*(33), 74, 2006.

Borsboom, H., et al., New insights into the Claus thermal stage, chemistry and temperatures, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2003.

Carroll, J.J., et al., Fundamentals of acid gas injection (AGI), *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2005.

Clark, P., et al., Enhancing the performance of the CBA process by optimizing catalyst macroporosity, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2002, p. 79.

Crevier, P.P., et al., Saudi Aramco eliminates Claus catalyst deactivation caused by aromatics using activated carbon, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2007.

Crevier, P.P., et al., Quantifying the effect of individual aromatic contaminants on Claus catalyst, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman OK, 2001.

Crevier, P.P., et al., TG 107 Low temperature tail gas treating catalyst is hot stuff, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2009, p. 379.

d'Haêne, P.E., Tail gas treating, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2003, p. 89.

Dalrymple, D.A., et al., CrystaSulf™ process for recovering small amounts of sulfur from gas streams, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 1999, p. 391.

Dalrymple, D.A., et al., CrystaSulf™—One-step H2S to sulfur conversion or high-pressure natural gas, *Eighty-fourth Annual Gas Processors Association Convention*, Tulsa, OK, 2005.

Duda, J.R., et al., Modeling exercises assess US CO2-EOR potential, *Oil Gas J., 108*(13), 52, 2010.

Echt, B., et al., Fundamentals of low-tonnage sulfur removal and recovery, *Laurance Reid Gas Conditioning Conference*, Norman, OK, 2017.

Echterhoff, L.W., State of the art of natural gas processing technologies, GRI -91/0094, Gas Research Institute, 1991.

Engineering Data Book, Section 20, Dehydration, GPSA Midstream Suppliers, Tulsa, OK, 2016a.

Engineering Data Book, Section 22, Sulfur recovery, GPSA Midstream Suppliers, Tulsa, OK, 2016b.

Georgia Gulf Sulfur Corporation, Sulfur properties, 2015. www.georgiagulfsulfur.com/sulfur/chemical-properties (Retrieved April 2019).

Goar, B.G., and Meyer, S.E., Claus gas cleanup can now be better, easier, and less expensive to meet federal EPA restrictions, *Eighty-Seventh Annual Gas Processors Association Convention* Tulsa, OK, 2008.

Goddin, C.S., et al., CBA process up's Claus recovery, *Hydroc. Proc., 53*(10), 122, 1974.

Grekel, H., et al., Package plants for sulfur recovery, *Chem. Eng. Progr., 61*(9), 70, 1965.

Hardison, L.C., Applications of the Lo-Cat™ process to sweetening natural gas, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 1984, p. 373.

Hardison, L.C., and Ramshaw, D.E., New developments in the Lo-Cat® hydrogen sulfide oxidation process, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 1991.

Hatcher, N., et al., Sulfur recovery fundamentals, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2007.

Heguy, D.L., and Nagl, G.J., Consider optimized iron-redox processes to remove sulfur, *Hydroc. Proc., 82*(1), 53, 2003.

Holub, P.E., and Sheilan, M., Fundamentals of gas sweetening, *Laurance Reid Gas Conditioning Conference*, Norman, OK, 2000.

Johnson, J.E., and Hatcher, N.A., A comparison of established sulfur degassing technologies, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2003a.

Johnson, J.E., and Hatcher, N.A., Hazards of molten sulfur storage and handling, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2003b, p. 109.
Kohl, A., and Nielsen, R., *Gas Purification,* Fifth edn. Gulf Publishing, Houston, TX, 1997.
Kuuskraa, V., and Wallace, M., EOR set for growth as new CO2 supplies emerge, *Oil Gas J., 112*(5), 92, 2014a.
Kuuskraa, V.A., and Wallace, M., CO2-EOR set for growth as new CO2 supplies emerge, *Oil Gas J., 112*(5), 92–105, 2014b.
Lagas, J.A., et al., The SUPERCLAUS® process, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 1988, p. 41.
Lagas, J.A., et al., SUPERCLAUS®, five years of operating experience, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 1994, p. 192.
Lagas, J.A., et al., Claus process gets extra boost, *Hydroc. Proc., 68*(4), 40, 1989.
Leppin, D., Large-scale sulfur recovery, Gas TIPS*, 7*(1), 26, 2001.
Maddox, R.N., and Morgan, D.J., Gas treating and sulfur recovery, *Gas Conditioning and Processing*, Norman, OK, 1998.
McIntush, K.E., et al., Results of pilot plant testing the CrystaSulf™ process, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2000.
McIntush, K.E., et al., CrystaSulf™ process fills H2S scavenging and sulfur recovery gap, *Gas TIPS, 7*(1), 19, 2001.
Meyer, B., Elemental sulfur, *Chem. Rev., 76*(3), 367, 1976.
Parnell, D., Look at Claus unit design, *Hydroc. Proc., 64*(9), 114, 1985.
Shuai, X., and Meisen, A., New correlations predict physical properties of elemental sulfur, *Oil Gas J.,* 93(42), 50, 1995.
Slavens, A., et al., Enhanced sulfur recovery from lean acid gases containing COS and mercaptans, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman OK, 2010, p. 257.
Strickland, J.F., et al., Relative capabilities and costs of tail gas clean-up processes, *Gas TIPS, 7*(1), 9, 2001.
Tonjes, M., et al., New approaches to processing lean acid gases, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 2010, p. 105.
True, W.R., Despite downturn, US, Canada shales drive gas production, processing growth, *Oil Gas J., 113*(6), 50, 2015.
Tuller, W.N. (ed.) *The Sulfur Data Book*. McGraw Hill, New York, 1954.
U.S. Geological Survey, Sulfur, 2018. https://minerals.usgs.gov/minerals/pubs/commodity/sulfur/mcs-2018-sulfu.pdf (Retrieved April 2019).
Valdes, A.R., New look at sulfur plants Part 1: Design, *Hydroc. Proc., 43*(3), 104, 1964.
West, J.R., Thermodynamic properties of sulfur, *Ind. Eng. Chem., 42*(4), 713, 1950.
Wichert, E., *The Sour Gas, Sulfur and Acid Gas Book: Technology and Application in Sour Gas Production, Treating and Sulfur Recovery,* Gray Jay Ventures Inc., 2018.

Taylor & Francis
Taylor & Francis Group
http://taylorandfrancis.com

17 Transportation and Storage

17.1 INTRODUCTION

As illustrated in Figure 17.1 pipeline-quality raw gas and processed natural gas must be transported from the source to the end user, industrial or residential. Except for the uncommon situation where the gas plant is dedicated to a single commercial customer, storage may be required. For natural gas, transportation and storage problems are more difficult than with other common fuels, such as coal and gasoline. Being a gas, it has low energy density at ambient temperatures and pressures. For an equal volume of these three fuels at ambient temperature and pressure, the energy content of gasoline is approximately 1,000 times greater than that of natural gas. The same volume of coal contains 700 times more energy as a fuel. These large differences in energy density highlight two major issues with natural gas. First, a relatively high pressure is required to increase the gas density and raise the energy content per unit volume so that the gas can be transported economically by pipeline (common pressures are approximately 800–1,500 psig [60–100 barg]). Second, large quantities of natural gas cannot be stored in relatively simple and inexpensive aboveground facilities similar to those used for less volatile liquid petroleum products. Note that for methane, the primary component of natural gas, the critical temperature is –118°F (–83°C), and consequently, no amount of pressure can convert methane into a liquid at 60°F (15°C). Natural gas is converted to liquefied natural gas (LNG) at ~–250°F (~–155°C). Chapter 18 discusses the unique issues associated with producing, transporting, and storing LNG.

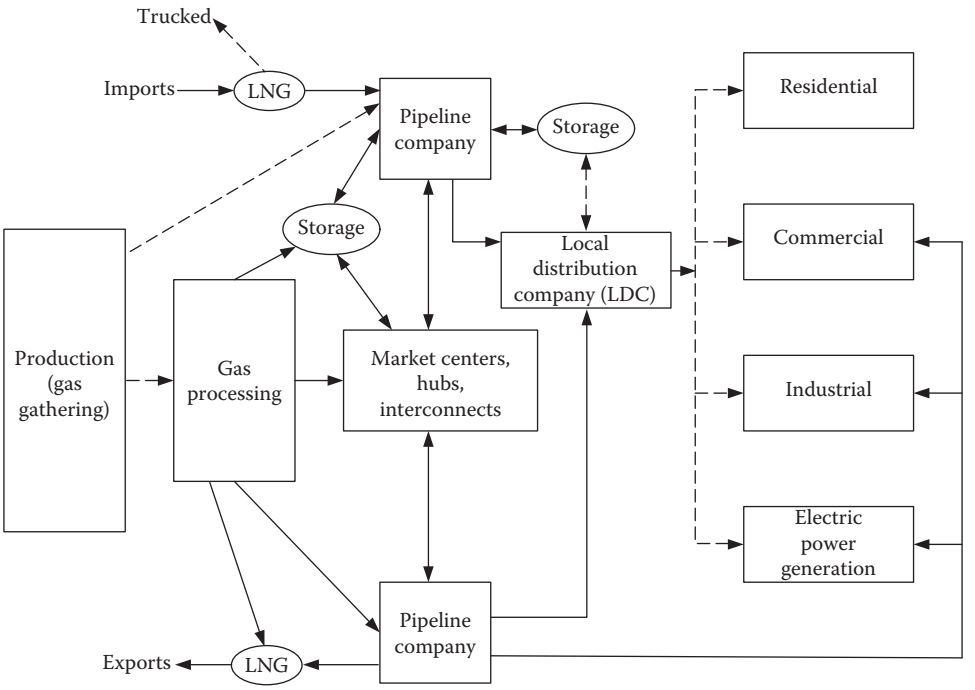


FIGURE 17.1 Overview of U.S. natural gas distribution system. Solid lines and dotted lines denote large and small pipe diameters, respectively. (Adapted from Energy Information Administration, undated-c.)

As discussed in Chapter 6, many natural gases contain significant quantities of hydrocarbons that are removed to produce the dry natural gas distributed to industrial and residential customers and valuable natural gas liquids (NGLs) product. (Dry in this context means that the C_2^+ content is sufficiently low to prevent liquid condensing at pipeline temperatures and pressures.) Although more volatile, NGL is transported by pipeline in much the same way as crude oil and refined petroleum products. The transportation and storage of natural gas and NGL will be discussed separately.[1]

17.2 GAS

17.2.1 Transportation

Depending on the gas plant's function, any of several possible gas streams may be transported from the plant to customers (see Figure 6.10). Although some plants have a single dedicated customer for the sales gas, most sales gas goes into an extensive pipeline network dedicated to natural gas service. Because product quality is so uniform within the United States, many different gas processors utilize the same trunk pipelines, and many gas plants are connected to multiple transmission lines.

The transportation system is composed of many parts; most important are pipelines and compressor or pumping stations. This chapter provides a general overview of the U.S. gas pipeline and compressor station system. Discussion of liquid pipelines, pumping stations and SCADA are beyond the scope of this text. Interested readers may refer to texts such as Mohitpour et al. (2007) and McAllister (2013).

17.2.1.1 Gas Pipelines

Natural gas pipelines can loosely be divided into three categories:

- Gathering systems
- Transmission systems
- Local distribution company (LDC) systems

Gathering systems consist of lines that transfer the gas from wellheads to a processing plant. If the gas can be made pipeline quality by field conditioning, it may be tied to a transmission line.

Transmission systems are both interstate (subject to federal regulation) and intrastate (subject to state regulation). They are composed of larger diameter lines designed to move large quantities of gas over significant distances.

The LDCs generally assume gas ownership at the city-gate and are responsible for transfer to the end user. Brokers, producers, and marketers can purchase and make retail sales. However, the LDCs are the primary marketers of retail gas.

The Energy Information Administration (undated-a) reports that the U.S. transmission and distribution grid in 2018 consisted of:

1. More than 210 gas pipeline systems
2. About 305,000 miles (490,000 km) of interstate and intrastate transmission lines
3. More than 11,000 delivery points, 5,000 receipt points, 1,400 interconnection points
4. More than 1,400 compressor stations
5. 24 market centers or hubs
6. 400 underground gas storage facilities

[1] Note that there are a few "dense phase" pipelines that operate at pressures above the cricondenbar (see Chapter 12) of the mixture to keep the fluid in one phase.

7. 49 locations where gas can be imported or exported via pipeline
8. 8 LNG import facilities, 59 peakshaving plants[2], and 41 satellite LNG facilities[3]

Maps for items 4 through 8 are available in the reference cited above.

Figures 17.2–17.4 show that 2008 was an exceptional year for the United States; there were 35 pipeline projects put into service, totaling approximately 3,600 (5,800 km) miles and with a capacity of 32.7 Bcf/day (0.88×10^9 Nm^3/d) added to the lower-48 pipeline grid (Energy Information Administration, 2018d). These figures do not include gathering lines. The values given include all data reported. There are about 20% of the projects having incomplete data. Figure 17.3 shows no net mileage increase in 2014 because a 500 mile (800 km) interstate pipeline with designed capacity of 255 MMscfd (6.83×10^6 Nm^3/d) was shutdown. While Figure 17.2 shows no major change in capacity in 2017, Figures 17.3 and 17.4 show significant increases in pipeline mileage and capital expenditures. Almost all projects that year were in the northeast where the Marcellas shale play is located.

Smith (2018b) provides cost data on 11 major interstate pipeline construction projects in the United States in the 2017–2018 time frame. They included both gas and liquid lines. The cost on a per unit length varies depending upon total length, pipe diameter, and locale. Below is a breakdown for rough cost estimates in the four major cost categories:

1. *Materials*: 1.3 MM$/mi ($810,000/km) or 13% of total cost. This cost includes pipe materials, pipe coatings, and cathodic protection.
2. *Labor*: 4.0 MM$/mi ($2,500,000/km) or 41% of total cost.
3. *Miscellaneous*: 4.2 MM$/mi ($2,600,000/km) or 43%. These include engineering costs and surveying, telecommunications equipment, freight, taxes, allowances for funds used during construction, supervision, administration and overheads, regulatory filing fees, and contingencies.
4. *Right-of-way and damages*: 370 M$/mi ($230,000/km) or 4%. These include right-of-way costs and damages during construction.

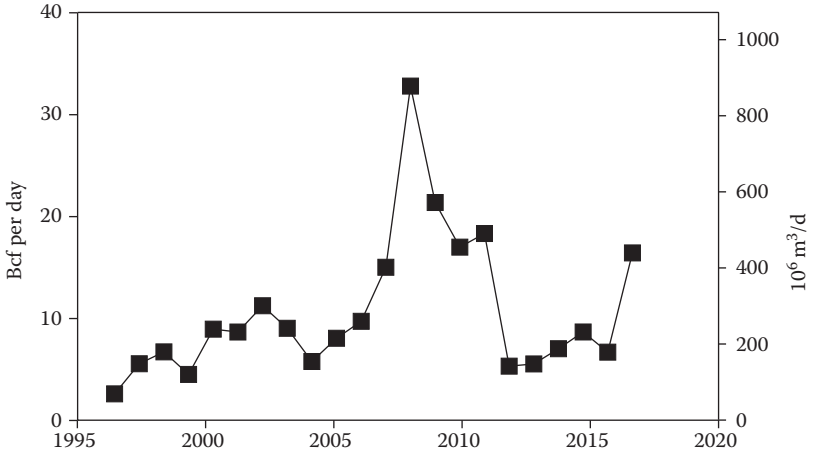


FIGURE 17.2 Net additions to capacity in the United States gas transmission system for 1996 to 2017. See text for more details (Energy Information Administration, 2018d).

[2] A peakshaving plant is a small LNG plant that liquefies natural gas for storage during low-gas demand periods and regasifies liquid when gas demand is high. They are discussed in Chapter 18.

[3] A satellite LNG facility stores LNG and dispenses vaporized liquid. All LNG is trucked to facility.

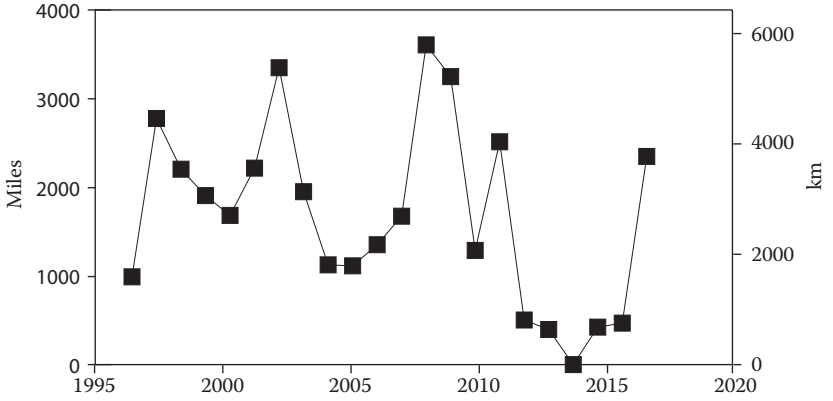


FIGURE 17.3 Net additions to pipeline mileage in the United States gas transmission system for 1996–2017. See text for more details (Energy Information Administration, 2018d).

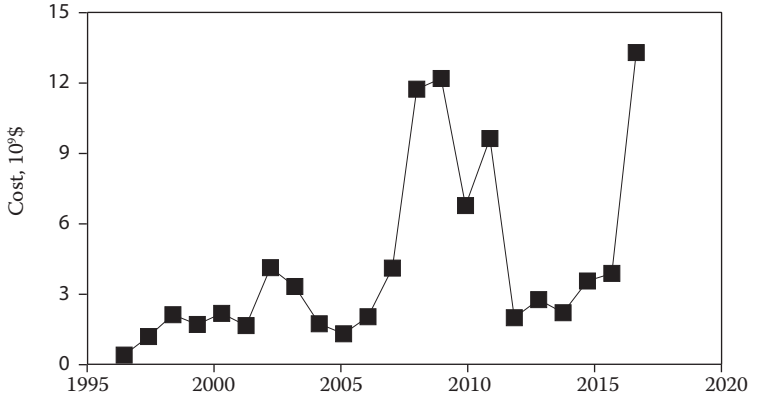


FIGURE 17.4 Cost of new pipelines mileage in the United States gas transmission system for 1996–2017. See text for more details (Energy Information Administration, 2018d).

Figure 17.5 shows planned pipeline construction in 2019 and beyond around the world. Planned construction in the United States is roughly 3,600 miles (Smith, 2018a) which is significant. Whereas in 2009 the United States construction dominated, the Asia-Pacific regions, especially China and Europe have even more mileage planned.

Information on operating pressures for the lines was not available. The larger and longer lines are normally built with 30 in. or larger (760 mm) diameters and run at 1,000 psig (70 barg) or higher. For example, an 800 mile (1,287 km) gas pipeline from the North Slope of Alaska to southcentral Alaska will be 42 in. (1,066 mm) will operate at 2,075 psig (143 barg). It will have eight compressor stations with 3.3 bcfd (88×10^6 Nm^3/d) capacity. Some gas will be locally consumed but the majority will be liquefied for overseas export (The Pipeline, undated). There is a planned 1,230 km (770 mile) pipeline transporting gas from Russia to Germany. The capacity will be 55×10^9 m^3/yr (2.1 Tcf/yr) (Anonymous, 2018). Major interstate pipelines are usually 24–36 in. (610–910 mm) in diameter, and the lateral lines that connect to the mainline are typically 6–16 in. (150–410 mm). More detailed information on pipeline transportation is available in the books by Manning and Thompson (1991) and McAllister (2013). The *Engineering Data Book* (2016) provides equations for calculating flow rates in transmission lines.

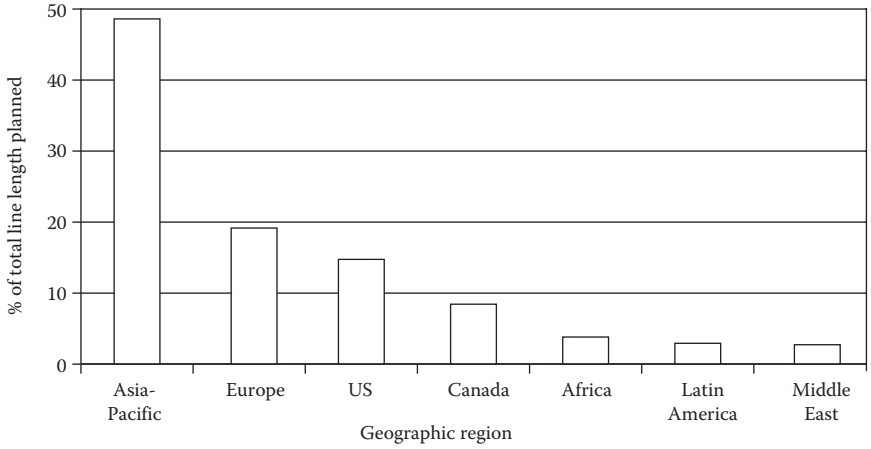


FIGURE 17.5 Distribution of planned gas pipeline mileage additions around the world. (Modified from Smith, 2018a).

17.2.1.2 Compressor Stations

In 2017, there were 1,500 compressor stations in the United States, an increase of 12 from the previous year. Interstate pipeline transmission service accounted for 1,272 stations (85%) and 228 (15%) were used in other activities (Smith, 2018b).

Smith (2018b) provides detailed cost figures for 23 compressor stations added to interstate transmission lines (all onshore) in the United States in 2017. The average cost was $2,744 $/hp. Percentage costs of each of the four major cost categories are:

- Equipment and materials, 35%
- Labor, 25%
- Land, 1%
- Miscellaneous (surveys, engineering, supervision, administration and overhead, etc.), 39%

The 23 stations were built in 14 states and the total cost (materials, labor, land, and miscellaneous) differs between locations. Figure 17.6 shows the total cost normalized in terms of compressor power. The trend to lower costs with increasing power requirement is clear until 20,000 hp (15 MW) is reached, where there is no longer an economy of scale.

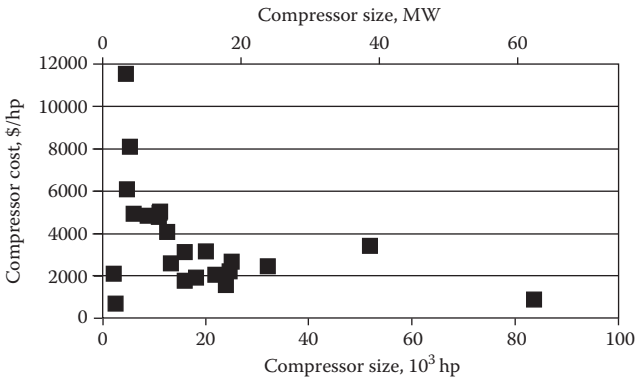


FIGURE 17.6 Unit cost for compressor stations (Smith et al., 2018).

17.2.1.3 Odorization

Natural gas has a faint, if any, odor when purified to pipeline quality. To detect gas leaks, an odorant must be added. The Department of Transportation code Title 49 Part 192, Section 192.625 (a) states "A combustible gas in a distribution line must contain a natural odorant or be odorized so that at a concentration in air of one-fifth of the lower explosive limit, the gas is readily detectable by a person with a normal sense of smell." For natural gas, this is 1% gas in air. However, it applies only to pipelines located in populated areas where the gas is not used as a chemical feedstock. Therefore, the odorant typically has been added at the city-gate by gas utilities.

The "normal sense of smell" criterion is open to interpretation. To be on the safe side, most utilities inject more than enough to meet the code. The most common odorants are blends of *tert*-butyl mercaptan (TBM) with other propyl and butyl mercaptans, tetrahydrothiophene (THT, thiophane), dimethyl sulfide, or methyl ethyl sulfide. The odor is readily recognized by the public as "the natural gas odor." Typical injection rates are 0.5–1 lb_m/MMscf (8–16 mg/Nm^3) (Jacobus and Roberts, 1996).

The commonly used odorants are detectable in extremely low concentrations, e.g., TBM is detectable at 0.3 ppb (Roberts, 2004). However, they are subject to "odorant fade" where the mercaptan is depleted from the gas. There are four common causes of fade in gas systems (Roberts, 2004):

- Adsorption
- Absorption
- Oxidation
- Masking

17.2.1.3.1 Adsorption

Although the surface area of pipelines is relatively small so are odorant levels. New pipelines, which can be many miles long, may initially need additional odorant injection to account for adsorption on the new metal surfaces. However, because mercaptans react with iron oxide surfaces to form much less odiferous disulfides, adsorption decreases with time but never completely stops.

Adsorption is more of a problem in summer months because utility gas demands are lower and the residence time in pipelines is longer. (Note that utility gas lines are buried so pipeline temperature changes little between summer and winter.) One option is to increase mercaptan injection rates, although, whenever feasible, dropping line pressure is a good option because it reduces gas residence time.

Adsorption can be a factor for gas escaping from buried lines because the odorant can be adsorbed by soils, especially clays. Roberts (2004) provides a number of references on this topic.

17.2.1.3.2 Absorption

The DOT regulations require that odorants be insoluble in water. Being hydrocarbon based, the odorants can condense in hydrocarbon liquids and reduce odorant levels. The obvious solution is to prevent condensation in the pipelines. Roberts (2004) notes that increasing the isopropyl mercaptan concentration helps because it is more volatile than TBM. This should be a temporary measure until the real problem (pipeline liquids) is solved.

17.2.1.3.3 Oxidation

As noted earlier, mercaptans react on the wall of rusty pipe to form disulfides. Rust (Fe_2O_3) on the walls provides the necessary reactive sites. When the Fe_2O_3 sites are depleted by the formation of Fe_3O_4 by reduction (and concomitant mercaptan oxidation), pipeline oxidation diminishes. Oxidation is especially important in a new pipe, which always contains rust.

Ozone generators have become increasingly popular in homes. Roberts (2001) discusses how ozone generators can oxidize all common odorants thus making them ineffective.

17.2.1.3.4 Masking

Household and workplace air fresheners are an example of where masking can prevent detecting a gas leak. Roberts (2001) points out that odors from landfills could mask odorants added to pipelines drawing gas from the landfills.

17.2.2 Market Centers

Figure 17.1 shows that market centers, or hubs, play a major role in bringing gas to the end user from storage, pipelines, and processing facilities. They are usually located near the intersection of several major pipelines. Market centers are an outgrowth of the U.S. market restructuring in the 1980s, and the requirement that interstate gas companies transport gas but not buy or sell the gas. They exist in the United States, Canada, and in other countries. According to the Energy Information Administration (Tobin, 2009) "The defining characteristics of a natural gas market center are that it provides customers (shippers and gas marketers primarily) with receipt/delivery access to two or more pipelines systems, provides transportation between these points, and offers administrative services that facilitate that movement and/or transfer of gas ownership." In 2018, 43 operational hubs existed in the United States (Federal Energy Regulatory Commission, 2018). Market center services vary widely between facilities, and no two hubs are identical, but Table 17.1 lists typical services provided (Tobin, 2009). The business is highly competitive, and like any business, has had closings and mergers.

The best known (but not the largest) of the U.S. market centers is undoubtedly the Henry Hub, located in southwestern Louisiana. It serves numerous commercial customers each day through 13 interconnecting pipeline systems. The hub transportation capacity is 1,800 MMscfd (48×10^6 m^3/d) of gas. Henry Hub has two salt dome storage sites with a working capacity of 15 Bcf (420×10^6 m^3). It has two compressor stations which can compress 520 MMscfd (14×10^6 m^3/d). It is best known as the delivery point for New York Mercantile Exchange (NYMEX) natural gas futures contracts.

Market centers are valuable in facilitating the management of transportation and storage of natural gas in the United States; their numbers and importance will undoubtedly increase in the future. Additional information can be obtained from the Energy Information Administration (Tobin, 2009) and Beckman and Determeyer (1997). The Energy Information Agency (undated-b) has a map showing all hub locations.

17.2.3 Gas Storage Facilities

17.2.3.1 Introduction

Storage can be either baseload or peakshaving. Baseload storage provides a large volume of gas (working gas) for a long-term steady withdrawal of the gas (typically 3–5 months), followed by a long-term injection period (typically 5–7 months). Peakshaving facilities are designed to provide large quantities of gas over a relatively short time frame (hours or days). Prior to having peakshaving facilities, gas utilities sometimes had to resort to curtailing service to commercial customers to provide residential service.

Before 1992, the U.S. natural gas market was regulated, and natural gas storage had two main purposes:

- To provide baseload storage to meet seasonal, weather-sensitive, demands above normal pipeline delivery capability
- To provide peak (or peakshaving) storage to smooth out the demand curve

After deregulation, storage facilities were open for additional uses, such as storing gas when prices were low and selling gas when prices were higher.

TABLE 17.1
Services Arranged and Coordinated in Market Hub Centers

Transportation/wheeling: Transfer of gas from one interconnected pipeline to another through a header (hub), by displacement (including exchanges), or by physical transfer over the transmission of a market center pipeline.

Parking: A short-term transaction in which the market center holds the shippers gas for redelivery at a later date. Often uses storage facilities, but may also use displacement or variations in linepack.

Linepack: Refers to the gas volume contained in a pipeline segment. Linepack can be increased beyond the pipeline's certificated capacity temporarily and, within tolerances, by increased compression.

Loaning: A short-term advance of gas to a shipper by a market center that is repaid in kind by the shipper a short time later. Also referred to as advancing, drafting, reverse parking, and imbalance resolution.

Storage: Storage that is longer than parking, such as seasonal storage. Injection and withdrawal operations may be separately charged.

Peaking: Short-term (usually less than a day and perhaps hourly) sales of gas to meet unanticipated increases in demand or shortages of gas experienced by the buyer.

Balancing: A short-term interruptible arrangement to cover a temporary imbalance situation. The service is often provided in conjunction with parking and loaning.

Title transfer: A service in which changes in ownership of a specific gas package are recorded by the market center. Title may transfer several times for some gas before it leaves the center.

*Electronic nomination**: Customers may connect with the market center electronically to enter natural gas transportation nominations, examine their account position, and access bulletin board services. Such systems may also facilitate trading among buyers and sellers and support direct negotiation among parties and access bulletin board services.

Administration: Assistance to shippers with the administrative aspects of gas transfers, such as nominations* and confirmations.

Compression: Provision of compression as a separate service. If compression is bundled with transportation, it is not a separate service.

Risk management: Services that relate to reducing the risk of price changes to gas buyers and sellers, e.g., exchanges of futures for physicals.

Hub-to-hub transfers: Simultaneous receipt of a customer's gas into a connection associated with one center and an instantaneous delivery at a distant connection associated with another center.

Source: Tobin (2009).

* A nomination is a specified quantity of gas being exchanged between buyer and seller at a set price on a specified day.

Figure 17.7 illustrates the wide swings that occur in gas demand, and the relatively constant combined U.S. gas plant production and net imports (now exports), clearly showing the necessity for large-volume storage to adjust the supply curve to match demand. Note that the spike in the summer month's demand results primarily from electric utilities that use gas turbine driven generators to meet peak electric power demands for air conditioning. Also, the net demand continues to increase due to replacing coal with natural gas in baseload power plants. In ten years up to 2018, coal usage dropped by 49% while natural gas usage increased by 69% (Energy Information Administration, 2018e).

17.2.3.2 Storage Facilities

In common with all engineering processes, storage gas reservoirs have their own terminology. Table 17.2 summarizes the most important terms.

Basically, two types of storage facilities exist for natural gas:

- Small capacity (to ~15 MMscf [0.4×10^6 Nm^3]) aboveground, floating-roof gas holders that operate at near ambient pressure.
- Large underground facilities (depleted oil and gas fields, salt caverns, and aquifers) that operate at elevated pressures.

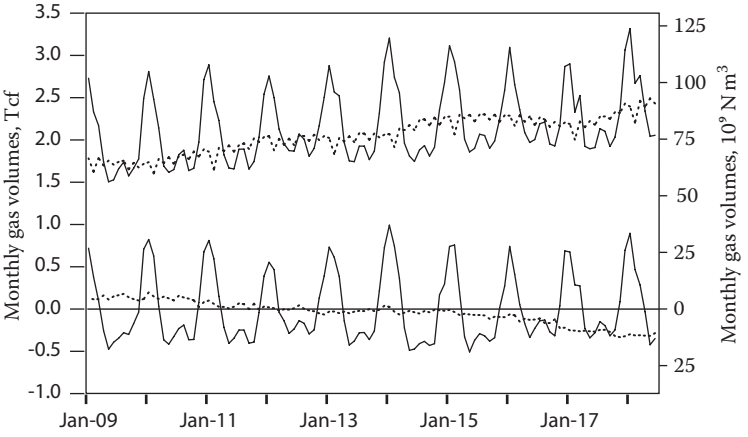


FIGURE 17.7 United States' monthly natural gas supply and demand. Upper solid line shows demand and upper dotted line is net production. The lower solid line denotes gas withdrawals and dotted line the total net gas imports (Energy Information Administration, 2018d).

TABLE 17.2
Important Terminology for Underground Storage

Total gas storage capacity	Maximum volume of gas that can be stored in an underground storage facility
Total gas in storage	Volume of storage in the reservoir at a particular time
Base gas (or cushion gas)	Volume of gas intended as a permanent inventory in a storage reservoir to maintain adequate pressure and deliverability rates throughout the withdrawal season
Working gas capacity	Total gas storage capacity minus cushion gas, i.e., available gas for withdrawal without diminishing deliverability rates
Deliverability	Most often expressed as measure of the amount of gas that can be delivered (withdrawn) from a storage facility on a daily basis; deliverability is variable and depends on such factors as the amount of gas in the reservoir at any time, the reservoir pressure, and compression capability available to the reservoir
Injection capacity (or rate)	Amount of gas that can be injected into a storage facility on a daily basis; injection rate is also variable and depends on the same factors as deliverability

Source: Energy Information Administration (2015).

Overall, underground storage is far more important and the discussion here is limited to that topic.

The United States Geological Survey first proposed use of underground storage for natural gas in 1909. The first North American facility was a depleted gas reservoir in Welland County, Ontario, Canada converted to storage use in 1915. This facility was followed by the Zoar field in Concord, New York in 1916 (Cates, 2001). In 1916, a German patent was issued on solution mining of salt caverns for storage of crude oil and distillates, and in 1950, this concept was applied to storage of NGL in the Keystone field, West Texas. The first use of a salt cavern for natural gas storage came in 1961, in Marysville, Michigan, and the first use of a leached salt dome for storage was in 1964, at Eminence, Mississippi (Beckman and Determeyer, 1997). The number of underground gas storage facilities has been relatively constant in recent years varying from 407 in 2002 to 419 in 2013 to 414 in 2017. The 2017 distribution is primarily depleted fields (328) with aquifers numbering 47 and salt caverns 39 (Energy Information Administration, 2018c). Figure 17.8 shows the percentage of

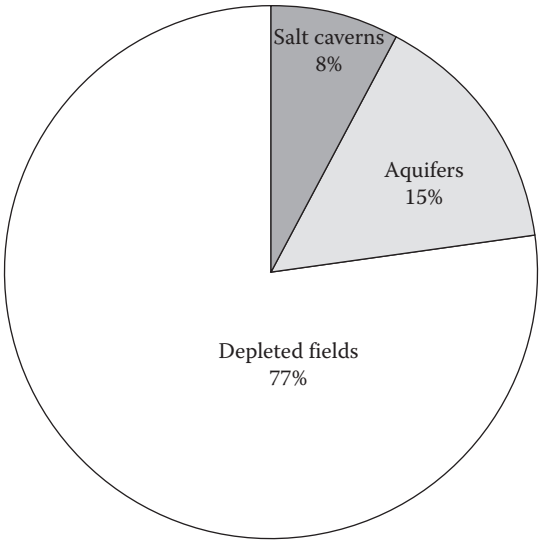


FIGURE 17.8 Distribution of underground storage capacity in the United States in 2017 (Energy Information Administration, 2018c).

total capacity (9.26 Tcf [248×10^9 Nm^3]) in 2017 for each type of underground facility in the United States (Energy Information Administration, 2018c). However, the estimated working gas capacity in 2017 was estimated to be 4.85 Tcf (130×10^9 Nm^3).

Figure 17.9 shows underground storage volumes. The lower line denotes the base (cushion) gas volume which increased by 3% in ten years. The top line represents the total storage capacity, which increased 11% over the 10-year period. The base gas volume is required to maintain sufficient reservoir pressure so that proper delivery rates are possible. The middle line denotes stored gas volume.

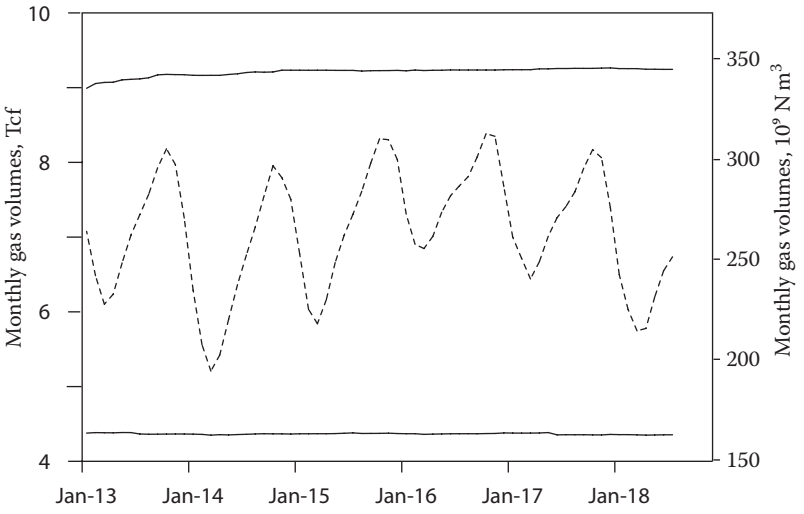


FIGURE 17.9 Gas volumes in underground storage. Upper line is total available storage capacity, middle line is stored gas volume, and lower line is cushion gas volume (Energy Information Administration, 2018b).

The total base gas and storage capacity values shown in Figure 17.9 are not absolute and are subject to change and interpretation. For example, in practice, a storage facility may be able to exceed certified total gas storage capacity by exceeding certain operational parameters. Also, the distinction between base and working gas is somewhat arbitrary, so facilities can withdraw some base gas for supply to markets in times of heavy demand. As expected, the shape of the storage curve follows that for the demand shown in Figure 17.7.

The majority of gas storage occurs in depleted reservoirs and is preferred, if available, for two obvious reasons:

- The geology of the reservoir is known
- The facilities for withdrawing and injecting gas are basically in place

When depleted reservoirs are unavailable, the two most common techniques are aquifers and salt caverns. Aquifers are underground natural water reservoirs that can, under the right circumstances, be used for gas storage. However, aquifer storage is usually the most expensive and, thus, the least desirable underground storage method for seven reasons (Natural Gas Suppliers Association, 2013):

1. Geologic characteristics of a specific aquifer are generally not well known, which is usually not the case with a depleted gas or oil field. Thus, an initial investment is required to determine if the aquifer is suitable for gas storage.
2. Infrastructure (wells, pipelines, dehydration facilities, compression equipment, etc.) is unavailable at the aquifer site, whereas a depleted gas reservoir would have most of the required infrastructure in place.
3. Aquifer formations generally require a much higher level of cushion or base gas (up to 80% of the total gas volume) than do depleted fields or salt caverns, and, thus, less of the reservoir volume is working gas.
4. Considerable injection pressure may be required to displace the water with gas.
5. Withdrawn gas requires dehydration.
6. Aquifer formations are not tightly sealed, and "collector" wells are required to collect escaped gas.
7. Environmental regulations govern the use of aquifers for gas storage.

All of the above factors increase both the capital cost and the time necessary for the development of aquifer storage. The last five also increase operating costs.

A common and relatively inexpensive technique for creating large storage facilities is solution mining of underground salt beds. After the salt bed has been located and the appropriate well or wells drilled, a coaxial pipe is inserted in the well bore. Water is then pumped down the annulus of the pipe, and the dissolved brine is withdrawn through the inner pipe (Figure 17.10). The cavern formed tends to be free from fractures that would permit gas leaks and is well suited for pressurized gas storage. Beckman and Determeyer (1997) present additional information on this subject.

Underground storage is prevalent throughout the world, with two exceptions. Japan and Korea use LNG as the primary means of gas storage. Although LNG peakshaving facilities exist in the United States, in 2017 LNG provided 42.8 Bcf (1.15×10^9 Nm^3) storage (Energy Information Administration, 2018a) which is slightly less than 1% of the underground working gas storage.

More detailed information on gas storage in depleted reservoirs and aquifers is available in Katz and Lee (1990).

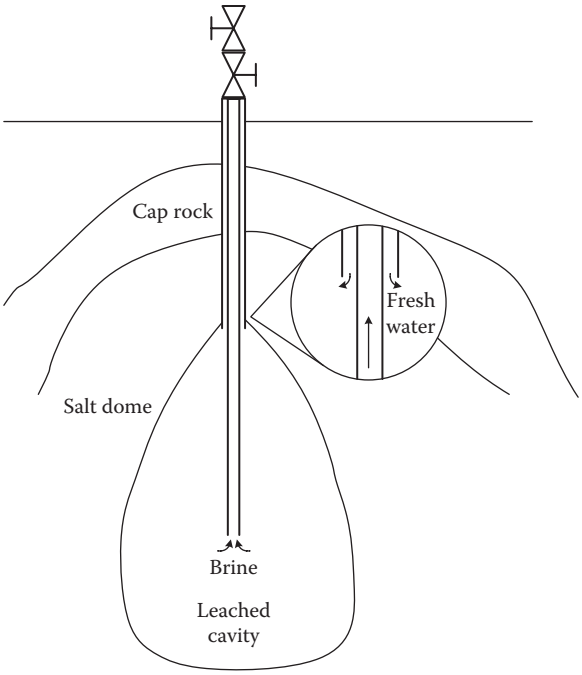


FIGURE 17.10 Generating underground-storage salt caverns by leaching with fresh water (Beckman and Determeyer, 1997).

17.3 LIQUIDS

17.3.1 Transportation

Like other petroleum products, liquid products from gas plants are transported by dedicated pipeline, by batching with other liquids in a petroleum pipeline, and by rail, truck, and marine transport. The most feasible and economical means of transport depends upon many factors, including:

- Product specifications, especially with respect to water and sulfur requirements
- Existing infrastructure
- Volatility
- Rate of product produced
- Distance between plant and customer
- Geographic location

Product specifications dictate the limitations of pipeline and storage container usage. Bulk containers and pipelines can have different contamination problems.

Contamination can occur because of a residual "heel" when one fluid is replaced with another. Surface adsorption of water and sulfur compounds can also contaminate product.

In pipelining a fluid, contamination between different products transported in the same line is impossible to avoid. An interfacial zone exists between the two fluids, where mixing occurs because of convection. Pipeline operators offload the mixture, called transmix, into storage tanks at pipeline terminals. The transmix then is fractionated to regain the two products. To reduce the amount of transmix by up to 50%, some pipeline operators use batching pigs (Webb, 1978).

Whereas pipeline operators know how much transmix to remove from the shipment, they have no idea of how much product can be contaminated by surface adsorption. Even worse, some fluids

are shipped saturated with water. If the fluid temperature drops, water may condense and collect in line depressions. Large quantities of water-dry product can be contaminated this way. Therefore, pipeline operators monitor product quality when contamination can occur. When it happens, the pipeline goes out of service and "chasing fluids" are run through the line to remove contaminates. This process is costly to both the pipeline operator and those who use the pipeline.

Because of the diverse nature of the liquid products from a gas plant, we address transporting each of the products separately.

17.3.1.1 Natural Gas Liquids

Mixed NGL is usually the major liquid product from gas plants. Most plants do not fractionate demethanizer bottoms on-site but ship raw mixed NGL product to a fractionation center. Some plants fractionate only seasonally. The quantity is usually large enough to dedicate a pipeline to a central NGL fractionation and storage hub. Specifications exist on methane content, water content, and sulfur content, but the need for continuous flow is the major reason for the dedicated line. This arrangement allows minimal storage at gas processing plants. The following sections discuss individual products if fractionation occurs at the gas plant.

17.3.1.2 Ethane–Propane Mixtures

The high vapor pressure of ethane–propane mixtures (E–P mix) and water-content specification make dedicated pipelines the common transport means for this liquid. Common carriers in Texas provide dedicated pipelines to transport E–P mixes to the major customers: refineries and chemical plants. This also applies to high purity ethane.

17.3.1.3 Liquefied Petroleum Gas

Because it is a widely used fuel with strict specifications on water and sulfur, liquefied petroleum gas, or LPG (more specifically, HD-5 propane) often uses dedicated transport. During the early years of the evolving LPG transportation system, the principal method was the railroad tank car, with pipelines playing a minor role; but by 1962, more than 40% of LPG was transported by pipeline, and today it is the preferred method. A major reason for this shift was the construction of the Mid-America Pipeline in the early 1960s, a line added to serve the upper Midwest. This 2,200 mile (3,500 km) pipeline starts in eastern New Mexico and runs up to Wisconsin and Minnesota. Since then, additional LPG pipelines have been added to service most of the eastern United States.

17.3.1.4 Butanes

No strong preference exists for how butanes are shipped from gas plants, because the quantities produced usually do not justify the cost of a pipeline. If available, railroad tank cars are desirable. Butane can be stored on-site for batch loading into tank cars or trucking to a hub. For distribution of the product to long distances from the hub, it can be put into pipelines that transport gasoline and diesel.

17.3.1.5 Natural Gasoline

Natural gasoline production is typically so small that it can be stored and then loaded into a tank car or truck. There is little contamination issue because the customer is often a refinery.

17.3.1.6 Odorization

In the United States, Department of Transportation regulations (Title 49 CFR Part 173, Section 173.315(b)(1)) apply to the LPG leaving the plant via rail or truck destined for a fuels market. However, because they are transported as liquids, ethyl mercaptan is typically the odorant (Roberts, 2004). Typically, 20%–25% of the ethyl mercaptan vaporizes with propane to provide a warning. Tank cars, trucks, and cylinders are commonly used for shipping. The tank car or truck must be labeled as to whether the contents have been odorized or not. The DOT code provides what is

sufficient to be safe odorant concentrations. For ethyl mercaptan, there needs to be 1.0 lb_m/10,000 gal (12 g/m^3) of LPG.

Like gas systems, odorant fade can occur in storage tanks. Adsorption followed by oxidation is the primary cause. Roberts and Jacobus (1997) note that any propane tank filled to only 5% capacity and put into service has the potential for extensive odorant loss. Most tank manufacturers require that their tanks be filled to 80% prior to inception of service at a customer location (Roberts, J.S., Private Communication, 2018). Odorant fade may become a major safety problem if the liquid is left in a new tank for extended periods. However, for a tank in continual use, three refills usually are sufficient to eliminate fade problems. There have been many explosions, and subsequent lawsuits, arising from odorant fade in LPG tanks.

17.3.2 Storage

Light gas plant product liquids can be stored aboveground in pressurized vessels or below ground in large caverns. Figure 17.11 shows a typical row of cylindrical storage vessels, and Figure 17.12 is an example of a spherical vessel for butane storage. Figure 17.13 shows an underground cavern being prepared for NGL storage (Cannon, 1993). Additional information on cavern storage is available in the book by Katz and Lee (1990).

FIGURE 17.11 Aboveground storage vessels for LPG and NGL.

FIGURE 17.12 Spherical storage tanks. (Courtesy of DCP Midstream.)

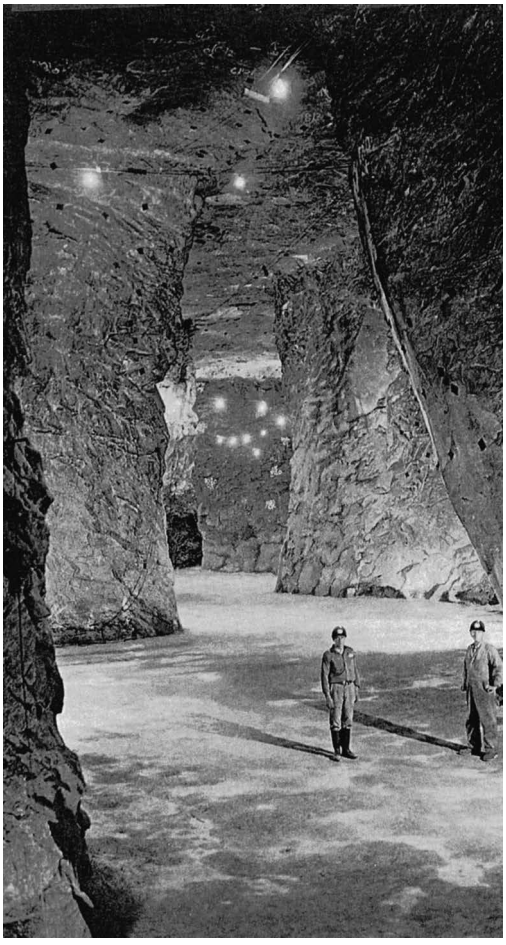


FIGURE 17.13 Underground storage cavern being prepared for NGL service (Cannon, 1993). (Courtesy of Gas Processors Association.)

DISCUSSION QUESTIONS

1. What products from a gas plant are commonly transported via pipeline?
2. What is the purpose of adding an odorant to natural gas and must it always be added?
3. What are some possible reasons for differences in the distribution of planned pipeline milage between the United States and other parts of the world?
4. What are the principle causes of odorant fade in gases and liquids?
5. What are some of the functions of market hubs?
6. Explain the cyclic behavior of natural gas demand and the ways used to compensate for this behavior.
7. What are the relative advantages and disadvantages of common types of baseload and peakshaving gas storage?
8. What are the advantages and disadvantages in having high pressures in underground storage?
9. What is transmix and how is it minimized?
10. Which liquids from a gas plant are commonly transported by pipeline, tank car, and truck? What factors dictate the mode of transport?

EXERCISES

17.1 Natural gas (molar mass = 17.0) is flowing in a 19.44 in ID (0.493 m) pipeline. The gas flows at a rate of 300 MMscfd (13,950 Nm3/day). The first section of the pipeline is 100 km (62.15 mi) in length and is approximately level for the entire length. At the pipe inlet, the pressure is 1,200 psia (83 bara) and the temperature is 80°F (27°C). Assume the gas temperature is constant along the length of the line. What is the pressure drop in the line?

Additional information

As a reasonable approximation, pressure drop and flow rate in gas pipelines can be related by the Panhandle B equation (*Engineering Data Book*, 2016):

$$Q = C\left(\frac{T_b}{P_b}\right)^{1.02} E\left[\frac{P_1^2 - P_2^2}{SpGr^{0.961} L_m T_{avg} z_{avg}}\right]^{0.51} d^{2.53}$$

where

C = 737 in USES and 0.01 in SI
Q is the gas flow rate, scfd (m^3/day at base conditions)
d is the internal pipe diameter, in (mm)
T_b and P_b are base pressures and temperature, 14.73 psia, 520°R (1.0156 bara, 288.9 K)
E is an efficiency factor, normally between 0.88–0.92
P_1 and P_2 are the inlet and outlet pressures, psia (kPa (abs))
$SpGr$ is gas relative density
L_m length of line in mi (m)
T_{avg} average temperature of the gas °R (K)
z_{avg} average compressibility factor (see Appendix B[4])

17.2 At the exit of the pipeline segment in Exercise 17.1, the gas enters a compressor station and is recompressed to its original pressure, 1,200 psia (83 bara). What compressor horsepower (*bhp* [MW]) is required for the recompression? Assume a compressor efficiency of 70%. The heat capacity ratio is 1.29.

17.3 The Bobcat gas storage facility in Louisiana consists of two salt caverns with a net storage capacity of 15.6 bcf (billion cubic feet). Storage conditions are 80°F (27°C), 1,000 psia (69 bara), and the gas has a molar mass of 17.0. What is the available storage capacity in MMscf (Nm^3)?

REFERENCES

Alaska Gasline Development Corporation, The Pipeline, undated. https://agdc.us/alaskas-lng-project/project-overview/the-pipeline/ (Retrieved April 2019).

Anonymous, Nord Stream 2 completes Swedish permitting, *Oil Gas J., June 11*, 2018. www.ogj.com/articles/2018/06/nord-stream-2-completes-swedish-permitting.html (Retrieved April 2019).

Beckman, K.L., and Determeyer, P.L., Natural gas storage: Historical development and expected evolution, *Gas TIPS, 3*(2), 13, 1997.

Cannon, R.E., *The Gas Processing Industry, Origins and Evolution,* Gas Processors Association, Tulsa, OK, 1993.

Cates, H.C., Storage functions evolve to match changes in U.S. natural gas industry, *Oil Gas J., 99.41*, 48, 2001.

Energy Information Administration, *The basics of underground natural gas storage*, U.S. Department of Energy, 2015. www.eia.gov/naturalgas/storage/basics/ (Retrieved April 2019).

Energy Information Administration, Natural gas, Data, Liquefied natural gas additions to and withdrawals from storage, 2018a. www.eia.gov/dnav/ng/ng_stor_lng_dcu_nus_a.htm (Retrieved April 2019).

[4] See Appendix B on publisher website: www.crcpress.com/Fundamentals-of-Natural-Gas-Processing-Third-Edition/Kidnay-Parrish-McCartney/p/book/9781138612792

Energy Information Administration, Natural gas, Data, Underground natural gas storage by all operators 2018b. www.eia.gov/dnav/ng/ng_stor_sum_dcu_nus_m.htm (Retrieved April 2019).

Energy Information Administration, Natural gas, Data, Underground natural gas storage capacity, 2018c. www.eia.gov/dnav/ng/ng_stor_cap_dcu_NUS_a.htm (Retrieved April 2019).

Energy Information Administration, Pipeline Projects [Data file], 2018d. U.S. Department of Energy, www.eia.gov/naturalgas/pipelines/EIA-NaturalGasPipelineProjects.xlsx (Retrieved April 2019).

Energy Information Administration, Table 1.1. Net Generation by Energy Source: Total (All Sectors), 2008–July 2018, 2018e. U.S. Department of Energy, www.eia.gov/electricity/monthly/epm_table_grapher.php?t=epmt_1_01 (Retrieved April 2019).

Energy Information Administration, About U.S. Natural Gas Pipelines - Transporting Natural Gas, U.S. Department of Energy, undated-a. www.eia.gov/naturalgas/archive/analysis_publications/ngpipeline/index.html (Retrieved April 2019).

Energy Information Administration, About U.S. Natural Gas Pipelines - Transporting Natural Gas, Natural gas market centers and hubs in relation to major natural gas transportation corridors, U.S. Department of Energy, undated-b. www.eia.gov/naturalgas/archive/analysis_publications/ngpipeline/MarketCenterHubsMap.html (Retrieved April 2019).

Energy Information Administration, About U.S. Natural Gas Pipelines - Transporting Natural Gas, Natural gas transmission path, U.S. Department of Energy, undated-c. www.eia.gov/naturalgas/archive/analysis_publications/ngpipeline/transpath_fig.html (Retrieved April 2019).

Engineering Data Book, Section 17, Fluid flow and piping, GPSA Midstream Suppliers, Tulsa, OK, 2016.

Federal Energy Regulatory Commission, Natural gas markets: National overview, 2018. U.S. Department of Energy, www.ferc.gov/market-oversight/mkt-gas/overview.asp?csrt=16741591176509423783 (Retrieved April 2019).

Jacobus, J., and Roberts, J.S., Relationship between gas composition and odor intensity, *Gas Technology Institute Odorization Symposium*, Chicago, IL, 1996.

Katz, D.L., and Lee, R.L., *Natural Gas Engineering, Production and Storage,* McGraw-Hill, New York, 1990.

Manning, F.S., and Thompson, R.E., *Oilfield Processing of Petroleum,* Pennwell Publishing, Tulsa, OK, 1991.

McAllister, E.W., *Pipeline Rules of Thumb Handbook,* 8th edn. Gulf Professional Publishing, Oxford, 2013.

Mohitpour, M., et al., Pipeline Design and Construction, A Practical Approach, 3rd edn. ASME Press, New York, 2007.

Natural Gas Suppliers Association, Storage of natural gas, 2013. http://naturalgas.org/naturalgas/storage/ (Retrieved April 2019).

Roberts, J.S., The effect of ozone generation on odorants, *Gas Technology Institute Odorization Symposium*, Chicago, IL, 2001.

Roberts, J.S., Natural gas and LP odorants: A review of the basic science, *Gas Technology Institute Odorization Symposium*, Gas Technology Institute, Chicago, IL, 2004.

Roberts, J.S., and Jacobus, J., Case study: The effect of propane tanks on odorants, *Gas Technology Institute Odorization Symposium*, Chicago, IL, 1997.

Smith, C.E., Near-term pipeline projects nearly double, future slows, *Oil Gas J., 116.2*, 72, 2018a.

Smith, C.E., Pipeline operators' net income rise sharply, *Oil Gas J., 116.10*, 56, 2018b.

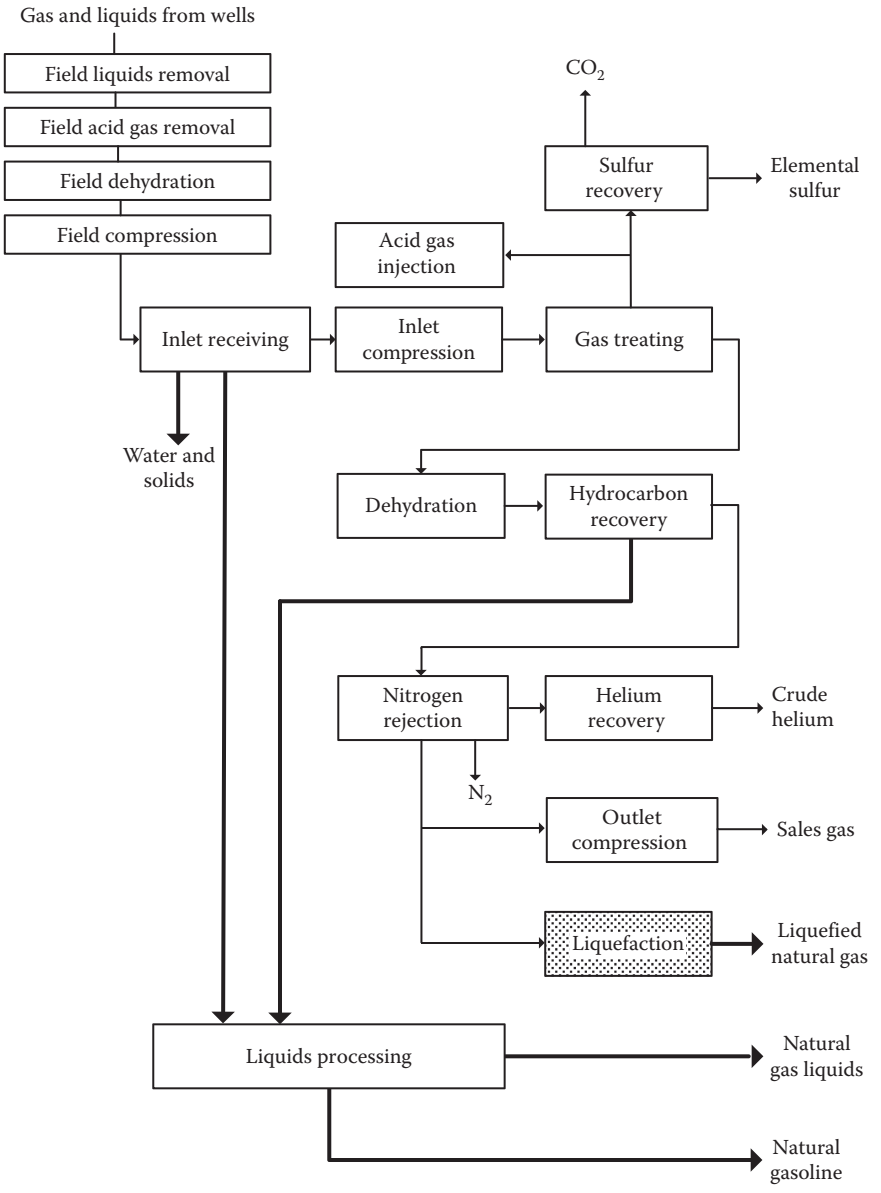
Smith, J.M., et al., *Introduction to Chemical Engineering Thermodynamics,* 8th edn. McGraw-Hill Higher Education, New York, 2018.

Tobin, J., Natural gas market centers and hubs: a 2008 update, Energy Information Administration, Office of Oil and Gas, U.S. Department of Energy, p. 14, 2009. www.eia.gov/naturalgas/archive/ngmarketcenter.pdf (Retrieved April 2019).

Webb, B.C., Guidelines set out for pipeline pigging, *Oil Gas J., 76*(46), 196, 1978.

Taylor & Francis
Taylor & Francis Group
http://taylorandfrancis.com

18 Liquefied Natural Gas



18.1 INTRODUCTION

The rationale for liquefying natural gas is simple: at atmospheric pressure, the liquid density at the normal boiling point of methane is approximately 610 times greater than that of the gas at ambient temperature and pressure. Consequently, a given volume of liquid contains over 600 times the heating value as the same volume of ambient gas. This density increase at ambient pressure makes

it attractive to liquefy, transport, and store natural gas in large quantities and makes technically feasible the transport of the equivalent of several Bcf (PJ) of gas per ship from the gas resource to the markets. Liquefaction and transport become economically feasible when the size of the reserves justify the capital investment of a liquefied natural gas (LNG) plant. Large-capacity, transoceanic LNG carriers permit the natural gas market to be international in scope. Gas is transported from areas with a surplus of production and reserves to areas without adequate local supply.

Storage applications include storage at LNG terminals and, just as important, storage for gas utility peakshaving operations. LNG also provides a source of gas supply in parts of the world where the gas pipeline infrastructure is difficult to construct or not well developed. This is particularly true in China where mid-scale LNG facilities are commissioned for trucking to end-use customers in remote areas like Inner Mongolia. LNG also is used as a clean-burning transportation fuel where it is economically attractive.

Like conventional gas processing, there is an energy cost for gas treating and compression to make LNG. For liquefaction, there is a more stringent gas treating requirement and significantly more compression required to provide refrigeration for liquefaction. The gas consumption required for liquefaction depends upon how much treating is required as well as inlet pressures. Peakshaving liquefaction plants consume the energy equivalent of 1%–3% of the incoming gas as fuel. A baseload plant has an overall energy consumption, including gas treating and compression, of about 10%–15% of the incoming gas.

Regasification consumes about 4% of the energy delivered to the receiving location. Facilities using seawater for regasification consume less fuel but some of the energy difference is expended in pumping water. As will be discussed in Section 18.6, it is possible to lower the overall regasification energy cost if natural gas liquid (NGL) is recovered from the LNG.

After a general discussion of peakshaving and baseload plants, this chapter focuses on seven topics:

1. Gas treating before liquefaction
2. Liquefaction cycles
3. Storage
4. Transport
5. Regasification and cold utilization
6. Economics
7. Safety and environmental considerations

While the LNG technology is relatively established, the LNG business is dynamic. Announced new projects often are delayed or dropped for economic, social, or political reasons. Even purchasing contracts can be dynamic with in-transit LNG cargos being diverted from one customer to another. This chapter provides a snapshot of the LNG industry in 2019. The various statistics presented here will be different in the future.

Note that because the LNG industry is international, metric units are used. The most common units are millions of metric tonnes (Mt) and millions of metric tonnes per annum (Mtpa). One Mt equals approximately 50,000 MMscf (1.4×10^9 Nm^3) and a metric tonne per annum (tpa) corresponds to about 140 MMscfd (3.8×10^6 Nm^3/d).

18.1.1 Peakshaving Plants and Satellite Facilities

In the previous chapter on transportation and storage, Figures 17.7 and 17.9 clearly show the large seasonal shifts in gas demand that result in the need for gas storage facilities. Natural gas fields are often located far from residential and industrial consumers. Therefore, storing large quantities of gas near the point of consumption to supplement the normal pipeline supply of gas during periods of peak demand (peakshaving) is essential. Chapter 17 discussed gas storage techniques, the most common of which are underground storage in depleted oil or gas fields, salt caverns, or aquifers.

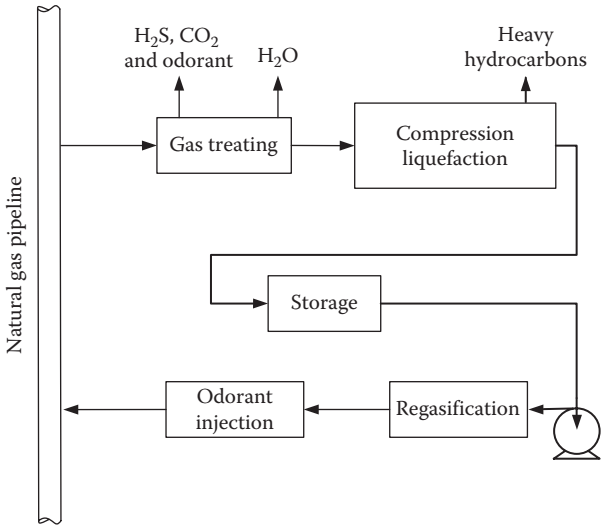


FIGURE 18.1 Schematic of peakshaving facility.

Where underground storage is unavailable, aboveground storage of natural gas as LNG becomes attractive, and utilities use relatively small liquefaction, storage, and regasification plants to meet the demand. Plants that liquefy, store, and regasify are referred to as peakshaving plants.

"Stranded" utilities, those not connected to a national pipeline grid, rely upon LNG received by truck to support their customers. LNG facilities like these, which contain only storage and regasification units, are called "satellite facilities."

Figure 18.1 shows a block diagram of the common steps involved in a peakshaving facility. Gas treating and compression are discussed in earlier chapters. This chapter discusses liquefaction, liquid storage, and regasification. Odorant injection may or may not be required at the peakshaving plant.

The first peakshaving plant built in the United States was in Cleveland, OH, in 1941 (Miller and Clark, 1941). The plant performed successfully, but in October 1943, a metallurgical failure of a storage tank resulted in a fire and explosion that destroyed the plant, with a heavy loss of life.[1] Although this disaster was a major setback to the industry, in 2018, the United States had over 100 peakshaving plants and satellite facilities with world totals over 300 facilities. In addition, the United States had 12 LNG marine-import terminals and three LNG marine-export terminals. As of early 2019, an additional five marine-export terminals are in the final stages of commissioning and startup. Mexico has three operable marine-import terminals.

18.1.2 Baseload Plants and Stranded Reserves

Initially, baseload LNG plants existed to provide the world with gas from remote reserves far from consumer demand. Stranded gas reserves are located where no economic use for the natural gas exists at the point of origin and where transportation of the gas by pipeline to a point of end use is not feasible. Romanow (2001) estimates that approximately 60% of the world's gas reserves are considered stranded. When gas pipelines are impractical or impossible, a limited number of conventional options are open (Taylor et al., 2001), such as compression and transport of the gas in specially built

[1] The U.S. Federal Energy Regulatory Commission document, *A guide to LNG - What all citizens should know* states that "Modern LNG tanks are constructed with materials proven capable of safely containing LNG at cryogenic (supercold) temperatures. Modern day spill containment/dike requirements for LNG facilities ensure that in the unlikely event of an LNG spill, none would leave the plant site."

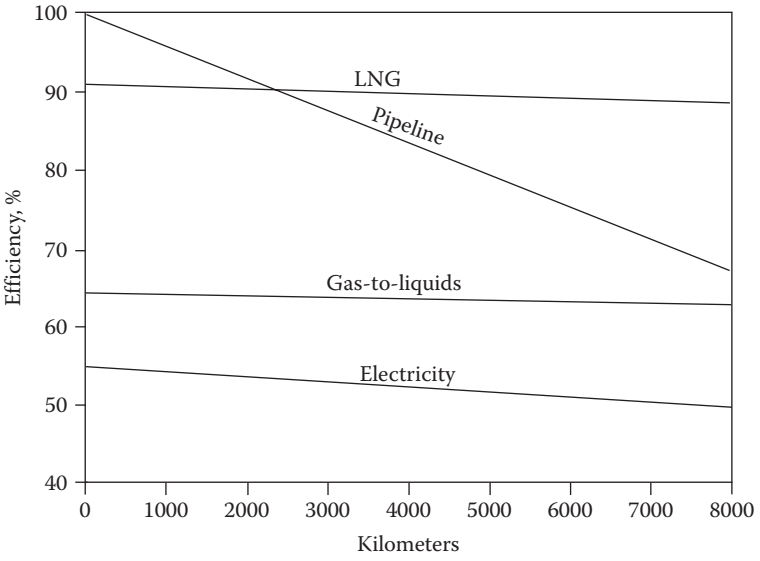


FIGURE 18.2 Energy transmission efficiency for transporting energy over long distances. (Adapted from Avidan, 2000.)

ships (Wagner, 2002), conversion of the natural gas into a liquid fuel through gas-to-liquid (GTL) technology, and liquefaction and shipment of the gas in specially built LNG carriers. Leibon et al. (1986) as well as Taylor et al. (2001) evaluate the status of several of the technologies. Hidayati et al. (1998) compare the cost of a compressed gas pipeline to LNG carriers for a large Indonesian project. Some unconventional methods that have been considered include the conversion of natural gas to hydrates for shipping (Gudmundsson and Mork, 2001) and even use of a train of airships that contain natural gas.

Not all baseload plants are built to liquefy truly stranded reserves. For example, the advent of shale gas reserves in North America resulted in a significant surplus of gas. This resulted in development of baseload LNG plants to export the surplus to areas lacking adequate supply to meet local demand.

Figure 18.2 compares the energy efficiency of transporting gas in various forms including GTL (Avidan, 2000). Included are energy losses if the natural gas is converted to other energy forms. Ignoring the technical feasibility of extremely long pipelines and power lines, the figure clearly shows that LNG offers the most efficient means of transporting energy over long distances if it is to be used as a fuel. The curves ignore losses at the point of distribution, which are higher for electricity than others.

LNG is often the most viable option in almost all situations involving surplus reserves, if the gas can be pipelined to a seaport. However, to economically justify a traditional baseload LNG plant requires reserves of approximately 3 Tcf (90×10^9 m^3). Newer designs reduced the reserve volumes down to around 1 Tcf (30×10^9m^3) (Price et al., 2000).

As Figure 18.3 shows, bringing the gas from the field to the customer involves multiple steps, which include:

1. Gas production, gathering, and processing
2. LNG production, including gas treating, liquefaction, NGL and heavy hydrocarbon removal, and LNG storage and loading
3. LNG shipping
4. LNG receiving facilities, which include unloading, storage, regasification, and distribution

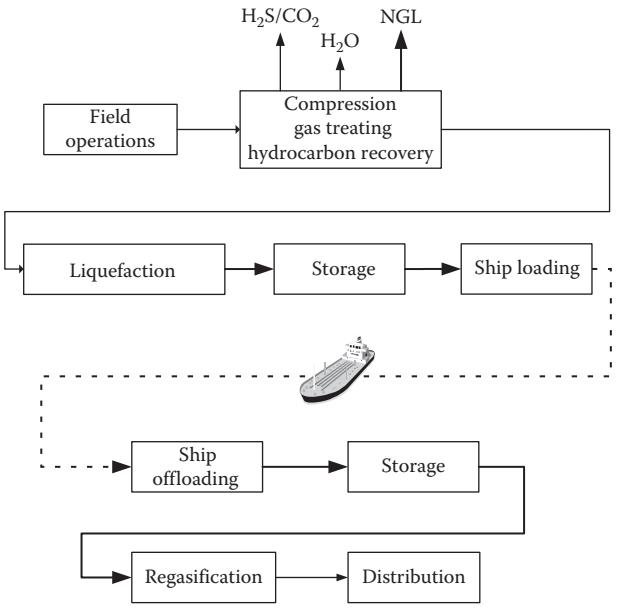


FIGURE 18.3 Schematic of a baseload plant combined with transporting, receiving, and regasification facilities.

Depending on the specific situation, not all plants will have all the processes shown, some plants may have additional processes. Note that nitrogen rejection is not included. Nitrogen is the most volatile LNG component. If present in high concentrations, it is removed by flashing the LNG. This gas typically becomes fuel gas for the plant. If in sufficiently high concentrations a nitrogen rejection unit (see Chapter 13) is used. As noted in Chapter 14, the off-gas can become a feedstock for helium recovery if the helium content is greater than 0.3 vol%. The large volumes of off-gas from baseload plants make helium recovery economically feasible even at lower concentrations. LNG facilities in Qatar and Australia recover helium from the liquefaction flash gas stream.

Figures 18.4 and 18.5 show the worldwide movements of LNG. In 2017, five countries, Qatar, Australia, Malaysia, Nigeria, and Indonesia, accounted for over 68% of the world's exports. Asia,

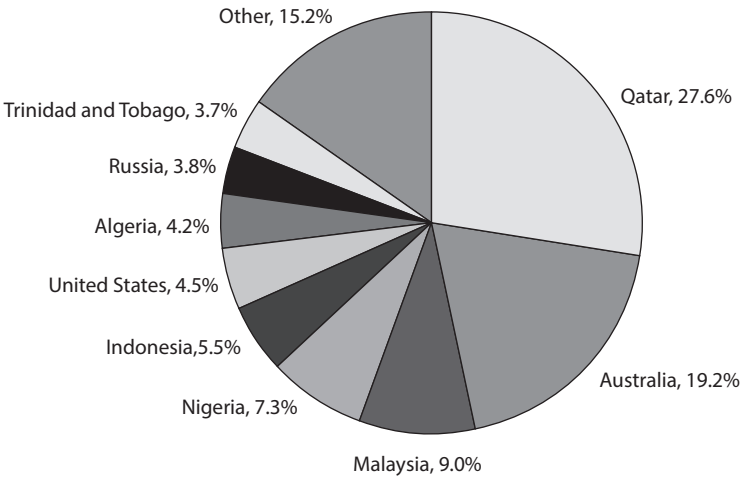


FIGURE 18.4 Worldwide LNG exports in 2017. Total exports were equivalent to 14.98 Tcf (17.0 PJ) of natural gas (International Gas Union, 2018).

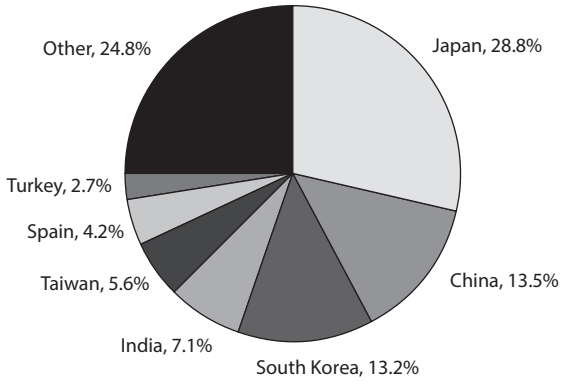


FIGURE 18.5 Worldwide LNG imports in 2017 (International Gas Union, 2018).

led by Japan, China, South Korea, India, and Taiwan accounted for 68% of the world's imports. Figure 18.4 does not include the 2.7 Mt which were re-exported in 2017. The distributions will continue to change as new, large production facilities add to the world's supply of LNG and new marine-import terminals are completed in consuming nations. For example, within six months after the report, Australia added about 70 Mtpa and the United States added over 20 Mtpa.

The liquefaction and storage facilities for baseload plants are necessarily quite large, complex, and expensive. Table 18.1 lists plants in operation in early 2019 compiled from various sources.

The worldwide future of the LNG industry's utilization of natural gas reserves appears bright. Table 18.2 lists some projects that were in planning, engineering, or under construction in early 2019.

TABLE 18.1
Operational Baseload LNG Plants in Early 2019

Country	Capacity, Million tpa[a]	Number of Plants
Abu Dhabi (UAE)	5.7	1
Algeria	29.1	2
Angola	5.2	1
Australia	84.8	10
Brunei	7.2	1
Cameroon	1.2	1
Egypt	12.2	2
Equatorial Guinea	3.4	1
Indonesia	31.4	3
Malaysia	27.5	2
Nigeria	21.9	1
Norway	4.2	1
Oman	10.8	1
Papua New Guinea	6.9	1
Peru	4.4	1
Qatar	77.0	2
Russia	26.1	2
Trinidad and Tobago	14.8	1
United States	32.3	3
Yemen	6.7	1

[a] Metric tonnes per annum (tpa), 1×10^6 tpa ≈ 140 MMscfd (≈3.8×10^6 Nm^3/d)

TABLE 18.2
LNG Baseload Liquefaction Facilities in Planning, Engineering, and Construction Phases in Early 2019

Country	Capacity, Million tpa[a]	Comments
Australia	8.6	Planning
Canada	28.0	Planning and engineering
Indonesia	2.0	Planning
Mozambique	20.0	Planning and engineering
Nigeria	7.0	Planning
Papua New Guinea	8.1	Engineering
Qatar	33.0	Engineering
Russia	29.4	Planning
United States	151.0	Planning, engineering, and construction

[a] Metric tonnes per annum (tpa), 1×10^6 tpa ≈ 140 MMscfd (≈3.8×10^6 Nm^3/d)

If these projects are built, the new capacity represents a 70% increase in capacity available since 2017. Expansions being developed will allow Qatar to remain the largest exporter of LNG, at least for the time being. In 2018, Australia surpassed Qatar as the leading exporter of LNG during one month but gas reserve and supply limitations in Australia limit actual production and export (Wilkinson, 2019).

Stranded gas exists offshore as well and can be either associated gas, with oil production, or nonassociated gas. A number of papers, including Finn et al. (2000) and Wagner and Cone (2004) look at possible LNG liquefaction cycles for offshore applications (FLNG). Wagner and Cone (2004) conclude that if the gas is nonassociated, reserve sizes comparable to those for onshore baseload plants will be needed. Associated gas is more economical at lower reserve volumes when the value of the combined gas-oil project is considered. As of early 2019, three offshore floating liquefaction facilities were in operation with a total capacity of 5.9 Mtpa, including the Hilli Episeyo facility offshore Cameroon shown in Figure 18.6. The facility was constructed using a refurbished LNG carrier and employs a mixed refrigerant process. Although many of the papers discount mixed refrigerant cycles for this application, the three operational FLNG facilities in 2019 used mixed refrigerant processes.

FIGURE 18.6 Golar Hilli Episeyo FLNG facility offshore Cameroon.

TABLE 18.3
Typical Composition Specifications of LNG Plant Feed and Pipeline Gas

Impurity	LNG Plant Feed[a]	Pipeline Gas[b]
Water	<0.1 ppmv	150 ppmv (7.0 lb_m/MMscf, 110 kg/Nm^3)
Hydrogen sulfide	<0.25 grain/100 scf (6 mg/Nm^3)	0.25 grain/100 scf (6 mg/Nm^3)
Carbon dioxide	<50 ppmv	2–3 mol%
Total sulfur (H_2S, COS, elemental sulfur, etc.)	<20 ppmv	5–20 grains/100 scf (110–430 mg/Nm^3)
Nitrogen	<1 mol%	<3 mol%
Mercury	<0.01 μg/Nm^3	N/A
Butanes	2 mol% max	N/A[c]
Pentanes+	0.1 mol% max	N/A[c]
Aromatics	<2 ppmv	

[a] Foglietta (2002).
[b] Engineering Data Book (2016a).
[c] Hydrocarbon dew point is often specified.

Implemented floating LNG facilities are both retrofits of old LNG carriers and new ships. The scale of the new ships is large and can be up to 1,600 ft (488 m) long and 243 ft (70 m) wide. The floating approach allows the costly LNG facility to be relocated once the initial reserves are depleted.

18.2 GAS TREATING BEFORE LIQUEFACTION

The production of LNG requires temperatures as low as –260°F (–160°C) and consequently, the allowable impurity levels in a gas to be liquefied are much lower than that of a pipeline-quality gas. For example, gas to be pipelined and sold to residential or industrial customers may contain a maximum of 2–3 mol% carbon dioxide, but gas for liquefaction must have a carbon dioxide content of less than 50 ppmv. Table 18.3 compares compositional specifications for the two cases.

Gas processed to make LNG must have much less water and carbon dioxide than gas delivered to pipelines. The tight specifications on all the listed components, except for nitrogen and mercury, are needed to avoid solids deposition that will plug the heat exchangers. Nitrogen is a volatile diluent, which, at higher concentrations, can raise the potential for stratification and rollover (discussed in Section 18.4.3). Elemental mercury presents serious problems in cryogenic operations. As noted in Chapter 14, trace quantities of mercury condense in aluminum cryogenic heat exchangers and can lead to exchanger failure. Consequently, mercury must be removed to a level of 0.01 μg/Nm^3. Techniques for achieving the desired levels for all of the above-mentioned impurities are discussed in the previous chapters. Heavy hydrocarbons can also cause plugging at LNG temperatures. Techniques to prevent this problem are discussed in Section 18.3.3.2.

Table 18.4 shows the range of compositions and properties for numerous LNG samples. These compositions are for the produced LNG and not the feed gas to the plant. There is a variation in both the heating value and the Wobbe number specifications for LNG produced around the world.

Two geographical markets for LNG exist—Asia and the Atlantic Basin. In the Asian market, there was little, if any, indigenous gas produced. Therefore, no infrastructure existed for using gas in an energy market until LNG became available. The LNG destined for that market contains higher quantities of propane and butanes and typically no heating value limits are set. However, LNG going to the Atlantic Basin (North America and Europe) must be blended into an existing gas grid and be compatible with existing supply. This severely limits the amount of ethane, propane, and butane, which can be delivered in LNG for these markets. As a result of these requirements,

TABLE 18.4
LNG Composition Ranges

Component	Composition Range (mol%)
Nitrogen	0.00–3.91
Methane	84.18–99.80
Ethane	0.06–13.64
Propane	0.00–3.82
Isobutane	0.00–0.89
n-Butane	0.00–1.70
Isopentane	0.00–0.10
n-Pentane	0.00–0.12
HHV gas, Btu/scf (MJ/Nm^3)	1,006–1,173 (39.62–46.20)
Wobbe number, Btu/scf (MJ/Nm^3)	1,345–1,448 (52.97–57.02)
C_2^+ GPM (m^3 liquid/1,000 Nm^3 gas)	0.02–4.23 (0.0–0.563)

LNG producers must tailor specifications to the appropriate market. This limits the amount of LNG that can be delivered across the market boundaries except for LNG from the Middle East. Based upon its geographic location and the ability of some large plants to store and market NGL, LNG from the Middle East may be produced to meet either specification. This made that region the swing supply to balance demand between the two markets. Additional information on NGL content in LNG delivered into Atlantic Basin markets can be found in Section 18.6.1.

18.3 LIQUEFACTION CYCLES

An LNG liquefaction cycle is a refrigeration process to turn a fluid that is a gas at ambient temperatures into a liquid at cryogenic temperatures. All cycles require expanding a high-pressure gas (working gas) to obtain the refrigeration. The two means of expansion are Joule–Thomson (J–T) and isentropic expansion in an engine doing external work. (Chapter 1 discusses the merits and thermodynamics of these expansions.)

To maximize liquefaction cycle efficiency (i.e., minimize compression work and maximize liquid production), cycles make extensive use of heat exchange of warm and cold fluids. Cycles using the feed gas as a working gas are called "open" cycles; those using a continuously recycled fluid are "closed" cycles. Most simple refrigeration cycles, e.g., propane refrigeration as discussed in Chapter 12, are closed cycles. If two or more working fluids are used in progressively lower temperature cycles, then the process becomes a "cascade" cycle. Traditionally, the working fluids were pure components, but many cascade cycles use mixed refrigerants. Ultimately, the size of a liquefaction train is limited by the power available from the prime movers used to drive compressors for each of the cycles utilized.

There are many ways to combine expansion methods, heat exchange, and working fluids to obtain an LNG cycle process. This section discusses the more commonly used LNG cycles and thermodynamically analyzes two of the cycles.

18.3.1 J–T Cycles

As discussed in Chapter 1, the J–T effect is the change in temperature that results when a gas is expanded adiabatically from one pressure to another in such a way that no external work is done and no net conversion of internal energy to kinetic energy occurs. Thermodynamically, it is an irreversible process that wastes the potential for doing useful work with the pressure drop. However, J–T expanders are as simple as a valve or orifice and find wide use in refrigeration cycles (see Chapter 12). The following discussion illustrates the simple J-T cycle which is not used commercially.

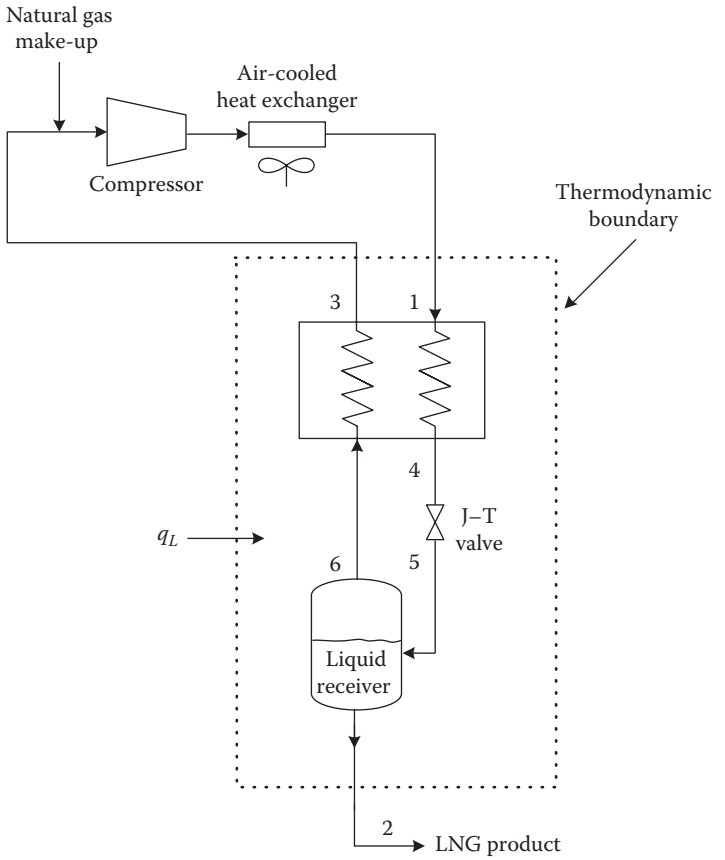


FIGURE 18.7 Simple J–T liquefaction cycle.

Because methane, the principal constituent of natural gas, must be cooled to –258°F (–161°C) before it becomes a liquid at atmospheric pressure, a liquefier that uses only a J–T expansion requires more than a compressor and an expansion valve if it is to function at reasonable initial pressures. A counterflow heat exchanger needs to be added to make a complete system.

Figure 18.7 shows a simple J–T system suitable for natural gas liquefaction. The liquefaction cycle begins with natural gas being compressed to 1,500 psia (103 bara), cooled by 80°F (44°C), and sent through the heat exchanger and expansion valve. Upon expansion, the gas cools by approximately 84°F (47°C) but none liquefies because a temperature drop of approximately 338°F (188°C) is required to form a liquid. Thus, all of the chilled, low-pressure gas going into the empty Liquid receiver is recycled through the heat exchanger for recompression. This cold low-pressure gas lowers the temperature of the high-pressure gas stream to the expansion valve, which results in a lower temperature upon expansion.

As long as all of the gas being expanded is recycled through the counterflow heat exchanger to cool the high-pressure gas stream, temperatures will be progressively lower upon expansion. The start-up continues until liquid is formed during the expansion from high to low pressure. The liquid formed is separated from the low-pressure gas stream in the liquid receiver and is ultimately withdrawn as the product. The amount of low-pressure gas recycled to the compressor is now reduced, which cuts back on the cooling effect in the heat exchanger. By adding makeup gas to the low-pressure side of the compressor to compensate for the liquid product being withdrawn, a steady state is reached in the liquefaction system and no further cooling can be achieved.

Applying the first law of thermodynamics (ignoring kinetic and potential energy effects) for a steady-state flow system (Equation 1.19) to the components inside the thermodynamic system boundary of Figure 18.6 (heat exchanger, J–T valve, and liquid receiver) gives the relation

$$\Delta h = q_L \tag{18.1}$$

where the overall enthalpy change of the gas, Δh, on a mass basis equals the heat leak, q_L, per unit mass of gas. On a per unit of mass flow of entering gas, and defining $f = \dot{m}_2 / \dot{m}_1$, the fraction of entering gas (1) withdrawn as a liquid (2), the equation becomes:

$$fh_2 + (1 - f)h_3 - h_1 = q_L \tag{18.2}$$

or

$$f = \frac{h_3 - h_1 - q_L}{h_3 - h_2} \tag{18.3}$$

For a given system, h_2, h_3, and q_L are essentially fixed, so the only way to increase liquefaction is to decrease the inlet gas enthalpy, h_1, which is done by increasing the inlet pressure, assuming that the compressor outlet gas temperature remains constant. Thus, more compressor work should lead to more liquid production.

Example 18.1

Methane is to be liquefied in a J–T cycle, as shown in Figure 18.6. The methane enters the heat exchanger at 80°F (26.7°C) and 1,500 psia (103 bara) and expands to 14.7 psia (1 bara).

1. Calculate the fraction of methane entering the system that is liquefied using an ideal heat exchanger (no warm end ΔT and no pressure drop) and assuming no heat leak ($q_L = 0$).
2. Estimate the percent decrease in production if a heat leak q_L of 15 Btu/lb$_m$ (38 kJ/kg) of methane entering is present and if a temperature approach of 5°F (2.8°C) is obtained at the warm end of the exchanger.
3. Calculate the fraction liquefied if the pressure is 2,000 psia (138 bara).

Solution

1. Calculate the fraction liquefied: From the methane PH diagram (Appendix B[2]) the following values are obtained:

$$h_1 = 380\,\text{Btu / lb}_m\,(80°\text{F}, 1500\,\text{psia})$$
$$h_3 = 420\,\text{Btu / lb}_m\,(80°\text{F}, 14.7\,\text{psia})$$
$$h_2 = 31\,\text{Btu / lb}_m\,(-259°\text{F}, 14.7\,\text{psia}, \text{liquid})$$

   Then by use of Equation 18.3

$$f = \frac{h_3 - h_1 - q_L}{h_3 - h_2} = \frac{420 - 380 - 0}{420 - 31} = 0.103 \text{ or } \sim 10\% \text{ liquefied}$$

2. *Effect of heat leak on production*: Use the same cycle but now have a 5°F temperature difference at the warm end of the heat exchanger (t_1, t_3) and a heat leak, q_L = 15 Btu/lb$_m$. This change lowers the recycle gas outlet temperature to 75°F (change in h_3 will be C_P Δt = 0.5 Btu/lb$_m$-°F × (75–80) = –2 Btu/lb$_m$ and h_3 = 418 Btu/lb$_m$).

[2] See Appendix B on publisher website: www.crcpress.com/Fundamentals-of-Natural-Gas-Processing-Third-Edition/Kidnay-Parrish-McCartney/p/book/9781138612792

The liquid fraction generated now becomes

$$f = \frac{h_3 - h_1 - q_L}{h_3 - h_2} = \frac{418 - 380 - 15}{418 - 31} = 0.059 \text{ or} \sim 6\% \text{ liquefied}$$

3. *Effect of pressure on production*: Determine how liquid production is affected by increasing the pressure on the inlet gas to 2,000 psia from 1,500 psia.

$$h_1 = 370 \text{ Btu / lb}_m \left(80°\text{F}, 2{,}000 \text{ psia}\right)$$

$$f = \frac{h_3 - h_1 - q_L}{h_3 - h_2} = \frac{420 - 370 - 0}{420 - 31} = 0.129 \text{ or} \sim 13\% \text{ liquefied}$$

This example illustrates the effect of pressure and heat exchanger performance on liquid yield.

Considerable improvement can be achieved in this simple J–T cycle, but at the expense of added equipment and complexity of operation. The addition of an external source of refrigeration markedly improves efficiencies, as does the use of multiple expansions of the high-pressure gas instead of a single expansion. Both of these techniques are extensively used in LNG processing.

Figure 18.8 shows the schematic of a commercial facility that used the J–T cycle in a Richmond, BC plant, near Vancouver, BC. This plant served a stranded utility and all LNG was transported overland by truck. It was designed and built to allow easy movement to a new location.

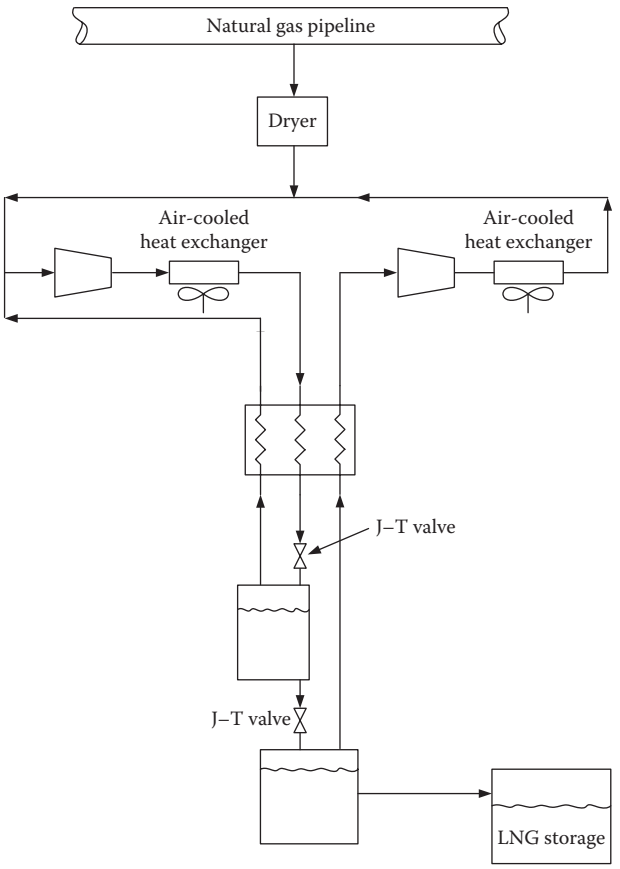


FIGURE 18.8 J–T liquefaction plant. (Adapted from Blakely, 1968.)

Feed to the plant was obtained from a natural gas pipeline at 40°F (4°C) and pressures in excess of 300 psig (20 barg). The inlet gas pressure was reduced to 300 psig (20 barg) and passed through a molecular sieve to remove both water vapor and carbon dioxide. The gas was then compressed to 3,000 psig (200 barg) in an electrically driven, two-stage reciprocating compressor. After passing through the three-stream heat exchanger, the gas underwent a double J–T expansion, first to ~300 psig (20 barg), and then to 10 psig (0.7 barg) to liquefy the stream. The LNG was transferred to one of the two storage tanks at the facility, either a 25,000 gal (95 m^3) horizontal cylindrical tank that uses vacuum perlite insulation, or a 42,000 gal (160 m^3) aluminum tank embedded in the ground (see Section 18.4 for storage tank details). The LNG was shipped to Squamish, BC, by truck in a 6,000 gal (Imperial) (27 m^3) trailer. At Squamish, the LNG is transferred to a 25,000 gal (95 m^3) storage tank before regasification and distribution in the town's natural gas system.

No specific details are available regarding the composition of the natural gas or the specific economics of the facility. Truck transport was more economical than pipelining the gas between the two locations, a distance of about 40 mi (65 km) of mountainous terrain. In a very small installation such as the Richmond facility, with a liquefaction capacity of 140 Mscfd (150 Nm^3/h), the low capital cost and simplicity of the J–T cycle counterbalanced the inherent thermodynamic inefficiency and, thus, made this cycle a good choice. For larger installations, however, the increase in thermodynamic efficiency available in both the expander and the more complex cycles becomes the determining factor in their selection.

18.3.2 Expander Cycles

The point was made during the discussion of the J–T expansion that it was a thermodynamically irreversible process. The expansion of high-pressure gas to a lower pressure in a reversible or nearly reversible manner provides two distinct improvements over the J–T expansion. First, in the reversible expansion, a large fraction of the work required to compress the gas can be recovered and used elsewhere in the cycle thus increasing cycle efficiency. Second, the reversible process will result in a much larger cooling effect. Section 1.5.5 illustrates the significant advantage in cooling using isentropic expansion and notes that it provides the most cooling possible over a given pressure range.

Like pumps and compressors, expanders can be either positive displacement or dynamic. While the first expanders were reciprocating, they are never used in LNG cycles. For more information of reciprocating expanders, see Collins (1947) and Barron (1966).

Turboexpanders have isentropic efficiencies on the order of 80% (Swearingen, 1970). Turboexpanders are high-speed machines, generally designed to operate from 10,000 to 100,000 rpm, depending on the throughput and wheel size. Chapter 12 provides more details.

For design purposes, several techniques may be used to compute the expected enthalpy change, but for a pure fluid, the simplest method is to use a value from a PH diagram or from a table of enthalpy values and correct this value with the anticipated turboexpander efficiency (Swearingen, 1970; Williams, 1970). To obtain enthalpy values for mixtures, a process simulator is used. The work generated in the expander must be utilized within the cycle to maximize the thermodynamic efficiency.

As mentioned previously, several options are available in the type of expander cycle. All expander cycles fall into two groups: closed cycles and open cycles. Note that most expander cycles bypass the turboexpander with a J–T valve for use in startup.

18.3.2.1 Closed Cycles

In a closed turboexpander cycle, the fluid being expanded is not the fluid to be liquefied; the expander simply acts as an external source of refrigeration, similar to the propane refrigeration discussed in Chapter 12. For example, in LNG production, nitrogen may be used in a closed expander system to liquefy natural gas. A very simple schematic of a closed cycle is shown in Figure 18.9. The compressed fluid is expanded, and the cold gas is then used to cool and liquefy the natural gas

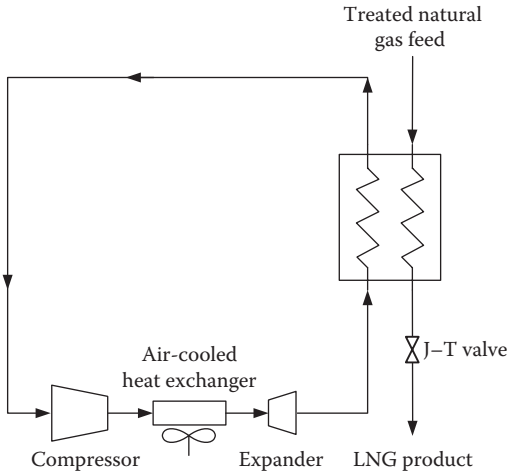


FIGURE 18.9 Simple closed-cycle liquefaction process.

stream. Actual cycles for producing LNG are more complex. Hathaway and Lofredo (1971) provide a complete process flow sheet for a plant that has four warm heat exchangers, one large nitrogen compressor, and three turboexpander/compressor combinations.

The closed cycle has several advantages over the open cycle, in which the natural gas itself is expanded. First, if nitrogen is used, safety is enhanced because the closed cycle reduces the number of processing steps in which flammable fluid is used. Second, the closed nitrogen cycle has been reported (Anonymous, 1970) to require simpler shutdown procedures than its open-cycle counterpart and appears to be an economical process under some conditions. Finally, because natural gas is not passing through the expander, the process purification system is not so critical. Gas passing through the expander must be free of any components that solidify at the expander exhaust temperature. Because the nitrogen in the loop never undergoes a phase change, distribution of the vapor within the heat exchangers is simpler. Nitrogen is by far the most common working fluid for closed expander cycles but other gases can be used provided they achieve the temperature level needed for LNG production.

A disadvantage of the cycle shown in Figure 18.9 is that it is relatively inefficient and requires a much larger compressor energy input for a given quantity of LNG produced. In addition, the volume of nitrogen circulated tends to be higher than a natural gas cycle, which results in larger equipment.

18.3.2.2 Open Cycles

An open expander cycle uses the gas being liquefied as the working fluid. A basic expander cycle is shown in Figure 18.10. In this example, the cold exhaust stream from the expander is simply used as a source of refrigeration, and the high-pressure gas is liquefied as it expands through the J–T valve. The first law of thermodynamics for a steady-state flow system applied to the two heat exchangers, the expander, and the liquid receiver gives the following equation:

$$f = \frac{h_3 - h_1 - q_L}{h_3 - h_2} + \frac{e(h_4 - h_6)}{h_3 - h_2} \tag{18.4}$$

where

e is the fraction of the gas going to the expander
$(h_4 - h_6)$ is the work done by the expander

The quantities $\dot{m}$, $\dot{m}_f$, and $\dot{m}_e$ in Figure 18.10 represent the mass flow rate into the liquefier, the mass flow rate of liquefied product, and the mass flow rate to the expander, respectively. A more

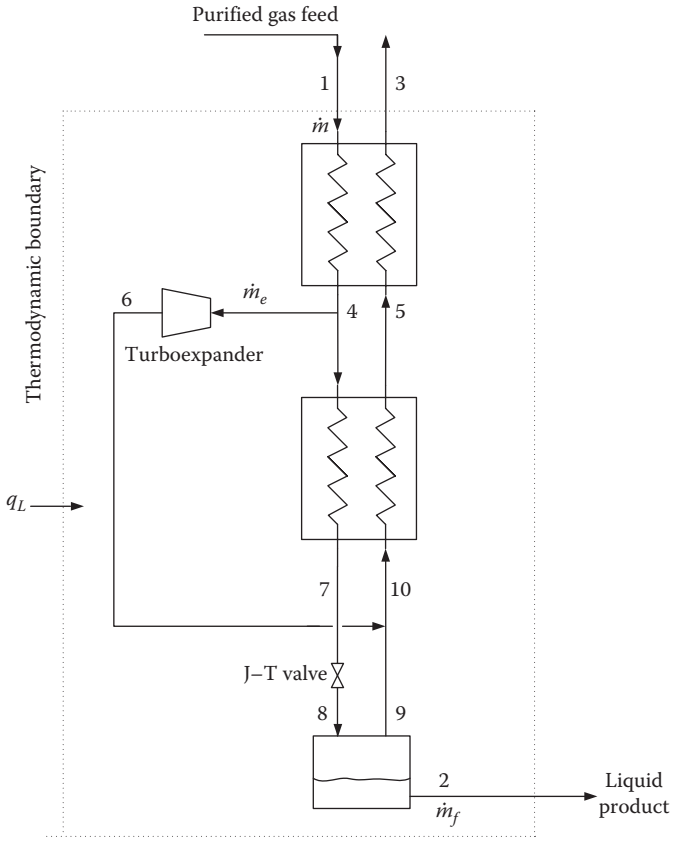


FIGURE 18.10 Open-cycle expander plant.

detailed analysis of the overall system is available (Dodge, 1944). The cycle shown is only one of many possible process arrangements.

A peakshaving LNG facility that uses an open expander cycle (Figure 18.11) is the Chula Vista plant of San Diego Gas and Electric Company (Hale, 1966). The plant receives 25 MMscfd (28,000 Nm^3/h) from a natural gas pipeline at 300 psia (21 bara) and 90°F (32°C). Prior to liquefaction, CO_2, H_2S, and water are removed by physical adsorption on a molecular sieve. The stream then splits, with about 21 MMscfd (23,000 Nm^3/h) going to the expander to provide refrigeration. This stream is cooled in the first heat exchanger before going to a separator. Liquid from the separator expands through a J–T valve. It recombines with the vapor from the separator, which has been through a turboexpander where the pressure drops to 60 psia (4 bara) and the temperature drops to –175°F (–115°C), and through the second heat exchanger. This stream provides cooling to both the incoming refrigerant stream and the fraction to be liquefied in the first exchanger. The gas then is compressed to 82 psia (5.6 bara), odorized and sent to a local power plant. Compression energy comes from work done by the turboexpander.

The remaining 4 MMscfd (4,500 Nm^3/h) of feed gas passes through all three heat exchangers and a J–T expansion valve. Liquid and vapor are then separated; the vapor stream passes through the heat exchangers and then goes to fuel for the power plant. About 8% of the gas that enters the plant becomes LNG. The vapor from the J–T expansion is exchanged to provide cooling and then goes to the power plant.

The LNG is stored in a single 175,000-barrel (27,800 m^3) aboveground storage tank. When desired, the LNG is gasified by pumping the liquid to 460 psia (32 bara) and vaporizing it in a hot

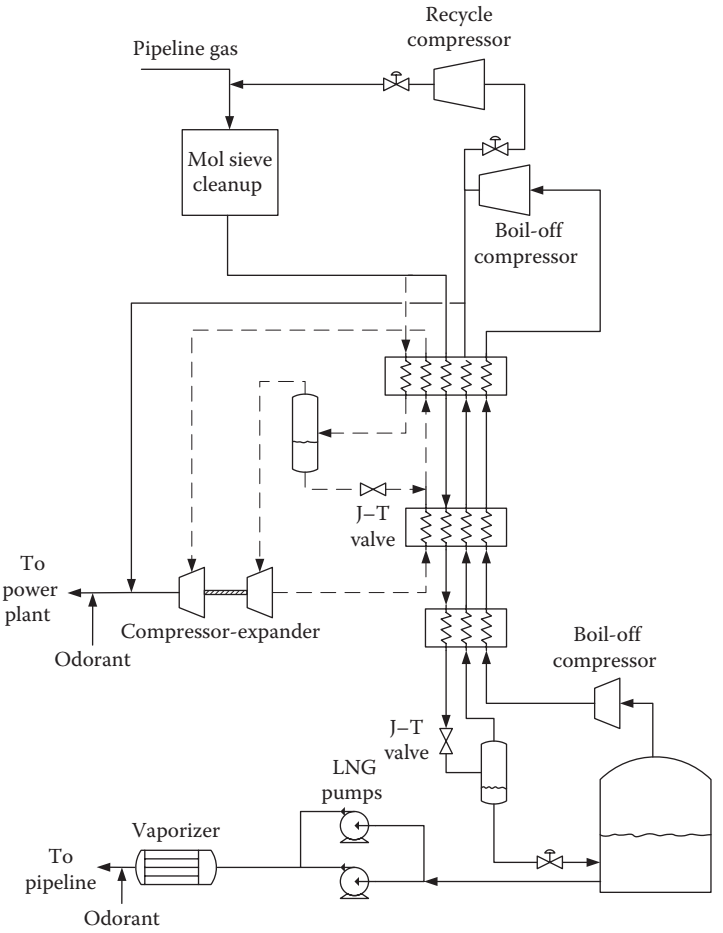


FIGURE 18.11 Peakshaving plant with open cycle.

water heat exchanger. The gas, at 400 psia (28 bara) and 60°F (16°C), is then ready for distribution. The vaporizer capacity is 60 MMscfd (67,000 Nm^3/h).

Boil-off from the storage tank provides some refrigeration and is compressed and combined with the vapor from the separator before going to the power plant. With a net liquefaction rate of 2 MMscfd (2 200 Nm^3/h), 315 days are required to fill the storage tank, but only 10 days are required to empty the tank at maximum vaporization rate. This matches the gas demand, as the company typically has surplus gas available about 300 days a year. During this period, the storage tank is filled. During the short periods of peak demand, LNG is vaporized and placed in the distribution system.

18.3.3 Cascade Cycles

One source of thermodynamic inefficiency is the finite temperature difference that must be present for heat transfer. The maximum thermodynamic efficiency in a liquefaction cycle is realized when the heating curve of the refrigerant corresponds to the cooling curve of the natural gas being liquefied. This relation means that ΔT (and thus ΔS) is zero for the heat transfer process (Dodge, 1944). Figure 18.12 is a schematic of a cooling curve for a natural gas system and heating curves for a mixed refrigerant system and a three-fluid classical cascade system. The natural gas and mixed

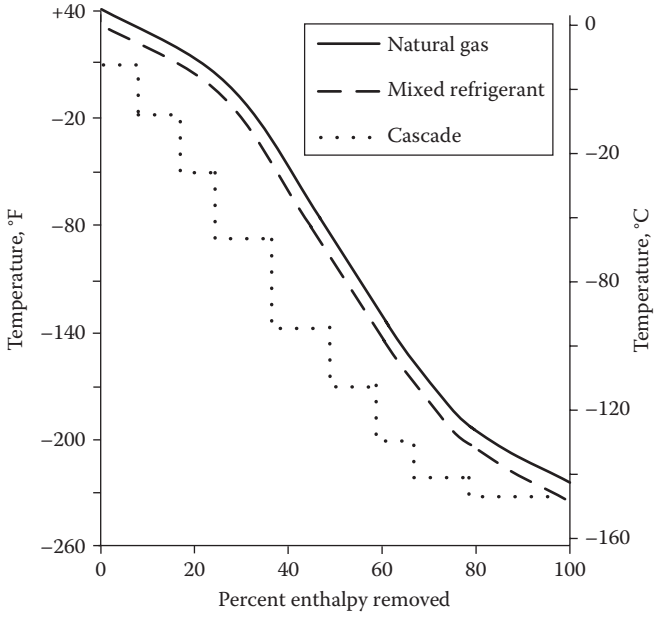


FIGURE 18.12 Cooling curve for natural gas and the warming curves for the mixed refrigerant and classical cascade cycles.

refrigerant curves show marked curvature because the fluids are mixtures. Thermodynamically, the mixed refrigerant comes closest to a reversible process because it minimizes the temperature difference between the two fluids.

The classical cascade is a closed cycle and attempts to approximate the cooling curve by use of a series of refrigerants (usually three) in separate loops. Use of more than three refrigerants allows a closer approximation to the cooling curve but with the penalty of extra equipment and added cycle complexity. Both mixed refrigerant and classical cascades will be discussed in more detail in subsequent sections.

The classical cascade is attractive because it can be relatively efficient thermodynamically. Most LNG baseload plants employ some version of the cascade cycle using pure fluids, mixed refrigerants, or combinations of refrigerants. In addition, there are both closed and open cascade cycles. For large, baseload plants, the higher efficiency justifies the added complexity. The classical cascade is discussed first because it is the simplest. This is followed by descriptions of more complex mixed refrigerant cycles.

18.3.3.1 Classical Cascade

The classical cascade was one of the earliest cycles developed and used in the liquefaction of the so-called permanent gases, helium and hydrogen, and was used both by Pictet in 1877 and by Kamerlingh-Onnes in 1892–1894 for the liquefaction of air. The method was also used in the first LNG plant built in the United States at Cleveland, OH, in the 1940s.

The classical cascade process starts with a working fluid, which is a vapor that can be liquefied at ambient temperature by the application of pressure only. The liquid formed by pressurization is then expanded to a lower pressure, which results in a partial vaporization and cooling of the remaining liquid. This cold liquid bath is then used to cool a second gas so that it may also be liquefied by the application of moderate pressure and then expanded to a lower pressure. (This is comparable to propane refrigeration discussed in Chapter 12. In cascade cycles, the propane condenses another refrigerant instead of the gas being processed.) The temperature reached in the expansion of the second

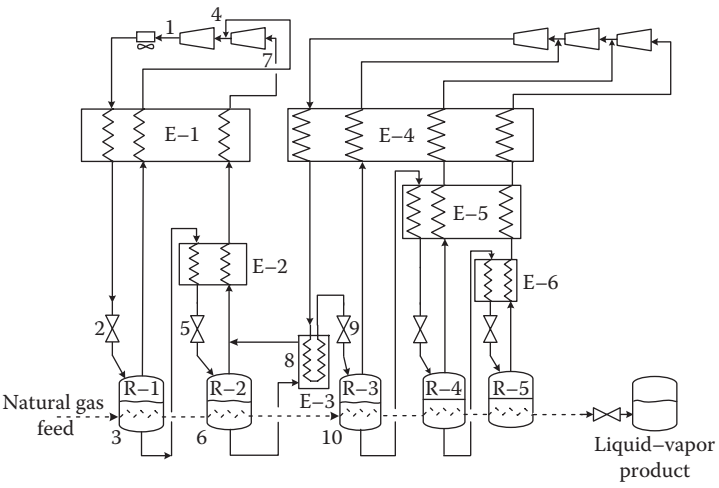


FIGURE 18.13 Schematic of a hypothetical two-fluid cascade cycle.

liquid will be substantially lower than that achieved by the expansion of the first liquid. In principle, any number of different fluids may be used and any desired temperature level can be reached by use of the appropriate number of expansion stages. In practice, however, three fluids and three levels of expansion are typical. The additional efficiency gained from using four or more levels of expansion cannot justify the additional heat exchangers and process complexity. In natural gas liquefaction, the custom now is to use a propane–ethylene (or ethane)–methane cascade, although the first LNG plant at Cleveland, OH, used an ammonia–ethylene–methane cascade (Miller and Clark, 1941).

A simplified process flow diagram for the first stage in a cascade cycle is shown in Figure 12.4 and the operation of a refrigeration system is discussed in Chapter 12. The cascade process differs from the previously described liquefaction techniques, in that the cooling is obtained principally from closed-cycle refrigeration circuits.

Figure 18.13 is a simplified schematic of a hypothetical two-fluid cascade designed to produce a low temperature liquid product. The process shown uses variations of a two-stage and three-stage refrigeration system (see Chapter 12), with two different working fluids. As noted above, plants that use this cycle normally use three fluids, but only a two-fluid cycle is discussed here to keep the schematic simple.

Following the flow from the compressor discharge (1) for the high-temperature working fluid, the fluid is condensed and then flows through heat exchanger E-1, expanded through a J–T valve (2), and goes to liquid-vapor receiver R-1 (3). The liquid in the receiver cools the gas feed, and exiting vapor flows back through heat exchanger E-1 to the second-stage compressor suction (4). In addition to cooling the gas feed, part of the liquid from the receiver (3) flows through heat exchanger E-2, where it is subcooled before expansion through a J–T valve (5), which creates a liquid–vapor mixture in the receiver R-2 (6). Both the temperature and the pressure of the liquid–vapor mixture in receiver R-2 are lower than in receiver R-1. The liquid in receiver R-2 further cools the gas feed. The vapor passes through heat exchangers E-2 and E-1, and goes to the compressor suction (7). Liquid from receiver R-2 goes to heat exchanger E-3 (8) to condense the fluid in the second cascade. This liquid is then expanded through a J–T valve (9) to create a liquid–vapor mixture in receiver R-3 (10). Essentially, the same process is repeated for the second working fluid, which goes through three stages of refrigeration. The feed gas progressively cools and is condensed until it leaves receiver R-5. It then passes through the final J–T valve, and becomes a liquid–vapor mixture at the final desired temperature and pressure. The liquid goes to storage, while the cold vapor is used for heat exchange before being recycled or used for fuel. For simplicity, this loop is not shown.

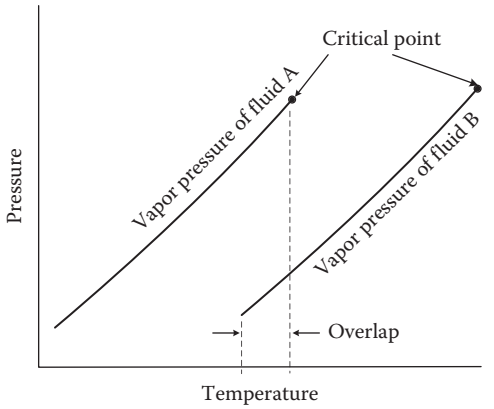


FIGURE 18.14 Qualitative plot of vapor pressure for two pure refrigerant fluids that shows the overlapping region needed for cascade cycles.

Although the figure and its discussion are simplified, they do illustrate the fundamental features of a classical cascade. Industrial cascades for LNG production use three fluids with two or three stages of refrigeration for each fluid. Andress (1996) discusses an industrial application of the classical cascade. Note that for the classical cascade system to function, the vapor pressure curves of the fluids must overlap, as shown in Figure 18.14.

Ransbarger (2007) provides a comparison of the commercially used ConocoPhillips Optimized Cascade® to the classical cascade described here. Since 1999, this cycle has been selected for a number of baseload plants around the world. It traces its roots to the Kenai LNG plant in Alaska, which began operation in 1969 and benefits from improvements developed in the 1990s. Figure 18.15 shows the cooling curve for this process. Note how the cooling curve is improved as compared to the classical cascade shown in Figure 18.12. Figure 18.16 shows the 14.8 Mtpa capacity baseload plant in Trinidad.

18.3.3.2 Mixed Refrigerant Cycles

As mentioned earlier, the maximum thermodynamic efficiency in a liquefaction cycle is realized when the heating curve of the refrigerant corresponds to the cooling curve of the natural gas being liquefied. The classical cascade attempts to approximate the cooling curve by use of three refrigerants in separate loops. However, Figure 18.12 shows that replacing several refrigerants in separate cycles with a single refrigerant composed of many components condensing at various temperatures

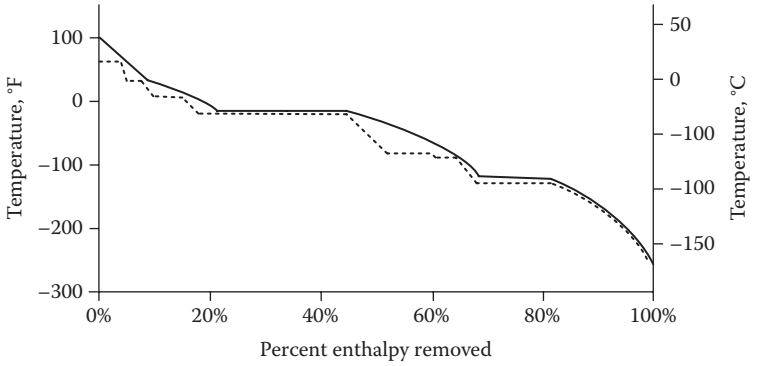


FIGURE 18.15 ConocoPhillips Optimized Cascade® cooling curve (Ransbarger, 2007).

FIGURE 18.16 The ConocoPhillips Optimized Cascade® cycle is used at the pictured Atlantic LNG facility in Trinidad. (Photo Courtesy of ConocoPhillips.)

in one cycle makes it possible to more closely match a natural gas cooling curve. In addition, only a single compressor is required for the refrigerant.

The technical feasibility of mixed refrigerant cycles was apparently first proven experimentally by Kleemenko (Forg and Etzbach, 1970) in 1959. Actual cycles using mixed refrigerants appear in a variety of configurations, but they can be loosely grouped into two basic categories: closed cycles and open cycles.

18.3.3.2.1 Closed Cycles

Figure 18.17 shows a schematic of a simple closed cycle (single-flow, mixed refrigerant). The refrigerant would probably be a mixture of nitrogen, methane, ethane, propane, butane, and perhaps pentane; the exact composition depends upon the composition of the natural gas being liquefied. The refrigerant mixture is compressed and then partially condensed in a water or air-cooled exchanger. The refrigerant then undergoes a series of pressure reductions and liquid–vapor separations to provide the cold fluid needed to liquefy the natural gas. The temperatures attained in the various heat exchangers depend on the composition of the refrigerant and the compressor discharge pressure. These operating parameters are selected to approximate the cooling curve of the natural gas being liquefied. In this cycle, the natural gas passes through four heat exchangers in series and is then expanded into a separator, where the liquid and vapor fractions are separated.

For smaller baseload, midscale, and peakshaving applications, the PRICO® process has been employed. It is similar to the cycle presented in Figure 18.17, but has been improved by rejecting heat from the loop at two pressure levels. Its wide range of applicability is due to the simple flow diagram (Figure 18.18) and relatively smaller equipment count. Figure 18.19 shows a typical PRICO® peakshaving plant.

Figure 18.20 is a schematic of a popular closed cycle, mixed refrigerant system, the propane precooled mixed refrigerant system. It is the most commonly used cycle for LNG baseload plants, and until 1999 was almost exclusively the process of choice for new baseload plant installations. The process uses both propane refrigeration and refrigeration from expanding a mixed refrigerant. A three-stage propane refrigeration cycle (see *Engineering Data Book* (2016b) for propane refrigeration systems) provides the initial cooling for the natural gas and partially condenses the mixed refrigerant in exchangers HX1, HX2, and HX3 as well. Compressor C1 provides the work for the propane refrigeration. Further cooling is supplied by the expansion of the mixed refrigerant liquid and vapor leaving the cold separator S1. Both of these streams and the process gas are chilled by the expanded mixed refrigerant in HX4 and HX5. The low-pressure mixed refrigerant is recompressed by use of

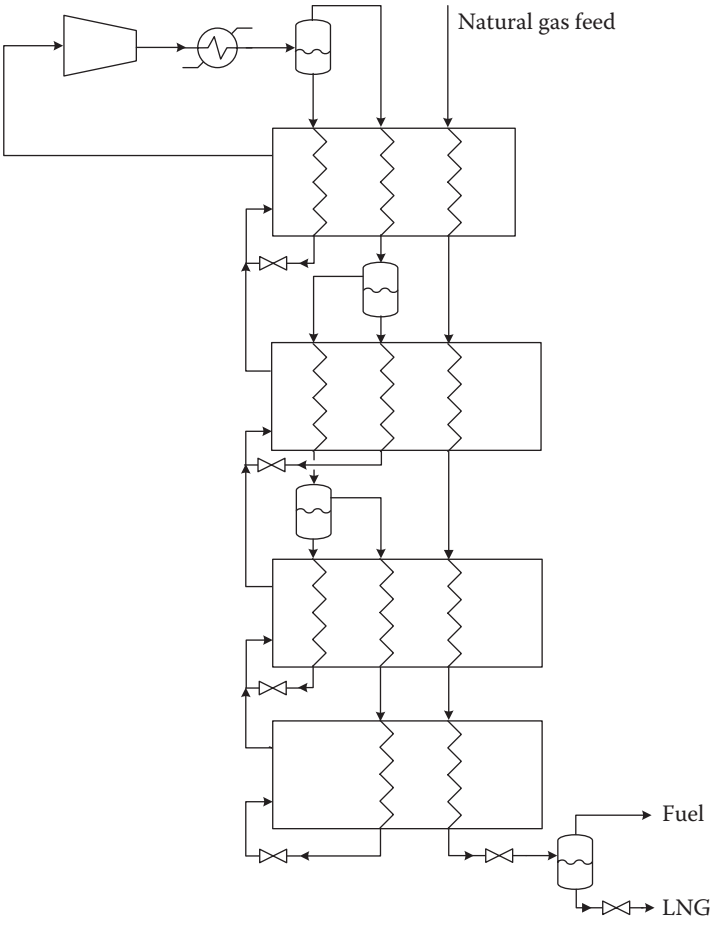


FIGURE 18.17 Schematic of simple closed cycle, single-flow mixed refrigerant (Forg and Etzbach, 1970).

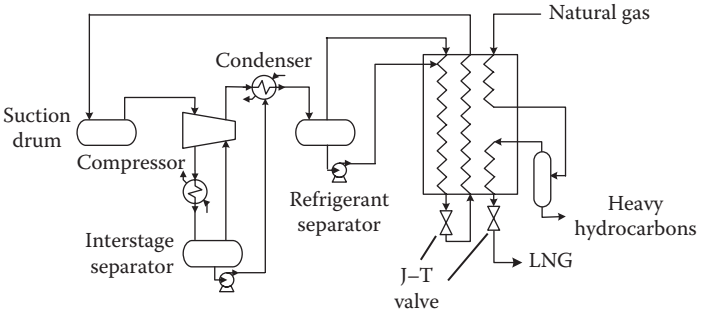


FIGURE 18.18 Schematic of commercial closed-cycle PRICO® system (Price et al., 2000.)

the two-stage mixed refrigerant compressor C2. Perez et al. (1998) provide a complete description of a large propane precooled, mixed refrigerant system. Improvements to this popular cycle include the use of a mixed refrigerant in lieu of the propane loop and the use of a nitrogen cycle (condensed by the cold mixed refrigerant) to provide refrigeration at the cold end of the cycle.

FIGURE 18.19 PRICO® peakshaving plant in the southern United States. (Courtesy of Black & Veatch.)

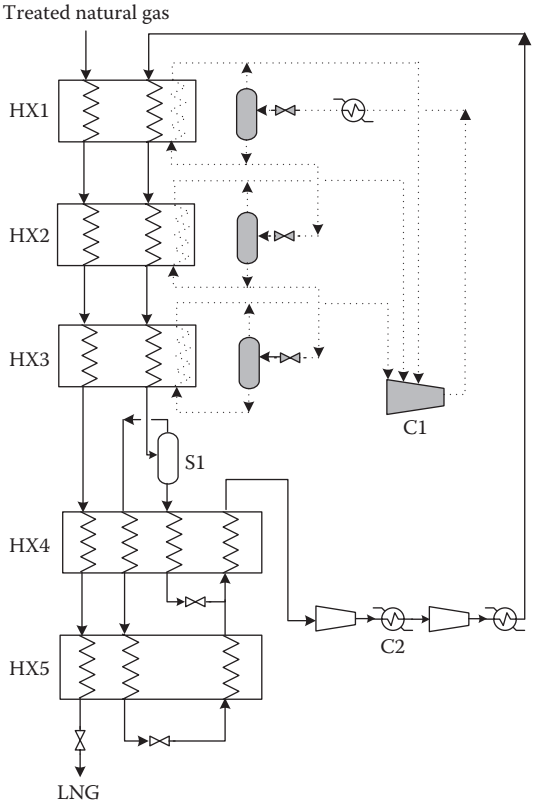


FIGURE 18.20 Schematic of a closed-cycle propane precooled mixed refrigerant system. Shaded areas and dotted lines represent propane cooling system.) (Adapted from Foerg et al., 1998.)

18.3.3.2.2 Open Cycle

In the open-cycle system shown in simplified form in Figure 18.21, the natural gas stream to be liquefied is the working fluid. The mixing of the gas to be liquefied into the refrigerant loop can take place before, during, or after feed compression, depending upon the pressure at which the natural gas feed is available. After compression, the gas stream is partially condensed in a water- or air-cooled

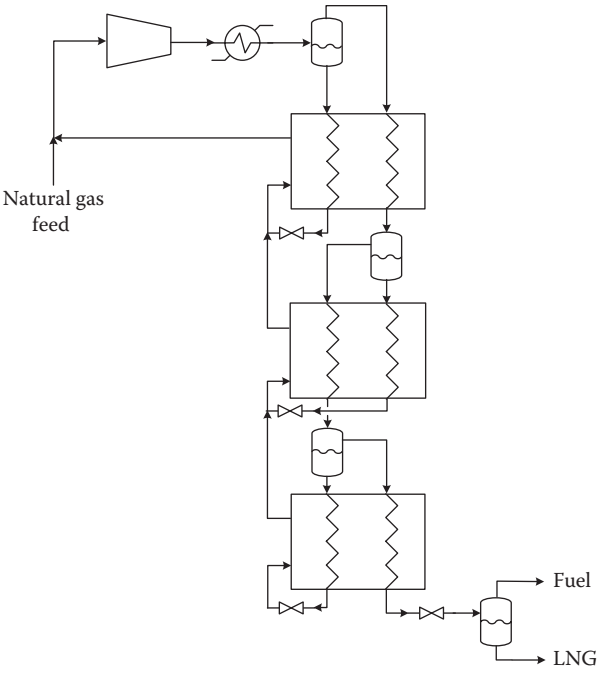


FIGURE 18.21 Open-cycle schematic. Refrigerant and process stream are mixed (Forg and Etzbach, 1970).

heat exchanger, and then separated into liquid and vapor fractions in a separator. After this point, the process is similar to the closed-cycle system. That is, the liquid fractions are expanded, which results in vaporization and cooling, and these cold streams are used as the coolant in the heat exchangers. The vapor from the last separator is condensed in the final heat exchanger and then expanded and separated into an LNG product and a flash gas used for plant fuel.

18.3.3.2.3 Summary

The mixed refrigerant cycles discussed above possess several advantages over the classical cascade system. The principal advantage is the use of fewer refrigerant compressors in place of the three refrigerant compressors and cycles of the classical cascade. This configuration provides simplification in instrumentation and piping and a better use of compression power. Further advantages include the ability to readily change the composition of the refrigerant for cycle optimization, should the composition of the feed gas change, and the ability to extract cycle refrigerants directly from the feed gas. The disadvantage when compared with the standard cascade is the necessity for having facilities to store and blend the components in the refrigerant cycle.

A number of studies compare the various cycles for a particular application. These studies include Vink and Nagelvoort (1998), Foerg et al. (1998), Linnett and Smith (1970), Finn et al. (2000), Foglietta (2002), and Kotzot (2003).

Regardless of cycle, an important step in the liquefaction of natural gas is the separation of heavy hydrocarbons, which are solids at LNG temperature. For example, benzene solubility in LNG is typically limited to a few ppm. Figure 18.18 shows a typical means of removing these hydrocarbons by illustrating a separator with heavy hydrocarbons being withdrawn from the gas to be liquefied. This separation can frequently be difficult and require one or more fractionation columns in place of this separator. For example, if the gas to be liquefied contains a significant concentration of benzene, a fractionation column is often required. The recovered hydrocarbons are typically marketed as a liquid product or burned as fuel in the liquefaction plant. A careful examination of Figure 18.11 illustrates the heavy hydrocarbons being removed, blended with a gas stream, vaporized by exchange

and compressed and sent to power plant fuel. The GPA Midstream Association endorsed a program called ThermoFAST for use in predicting solid formation in LNG systems (May, 2018).

As shown in Figure 18.21, a common part of most liquefaction systems is the final flash of the LNG from refrigeration. Because nitrogen is much more volatile than methane at low pressure, it provides separation of nitrogen (and helium, if present) from the LNG product. The vapor from this flash is typically used as facility fuel.

18.4 STORAGE OF LNG

Discussions of LNG storage facilities are normally divided into two major categories: aboveground and in-ground. Each has three natural subcategories, and each is discussed below. Also, LNG storage involves a feature peculiar to the storage of cryogenic liquid mixtures, stratification. This section includes a discussion of this important phenomenon.

18.4.1 Cryogenic Aboveground Storage

Storage of LNG in aboveground metal tanks is a widely accepted method for both baseload and peakshaving uses. Nine percent nickel steel is the most widely used metal for large LNG tanks but it may be used in combination with prestressed concrete. Because of its relatively higher cost, stainless steel is generally used only for small vessels, LNG plant piping, and heat exchangers. A few older tanks use aluminum. The tragedy experienced in Cleveland in 1944 was caused by using of a lower nickel material due to wartime material shortages.

Three basic types of aboveground storage vessels are in use:

- Single-containment tanks
- Double-containment tanks
- Full-containment tanks

Each type of construction will be discussed briefly.

18.4.1.1 Single-Containment Tanks

Figure 18.22 shows the typical configuration for single-containment steel tank. The conventional configuration is a double-walled, flat-bottomed tank, with the annular space between the walls filled

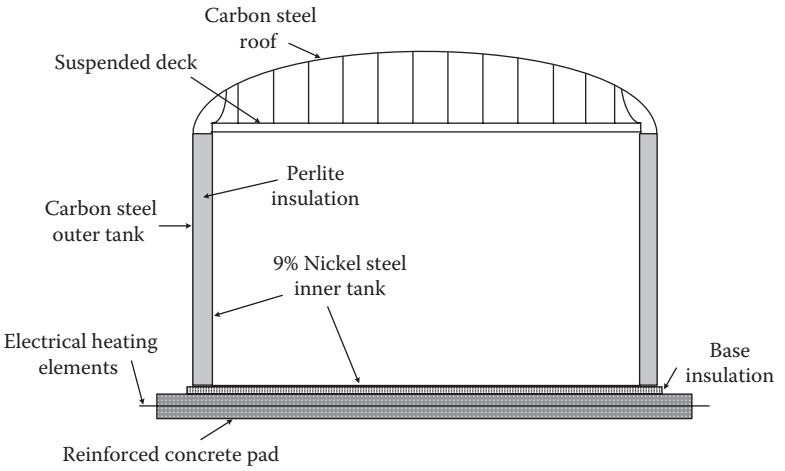


FIGURE 18.22 Single-containment tank. (Adapted from Long (1998), and Kotzot, 2003.)

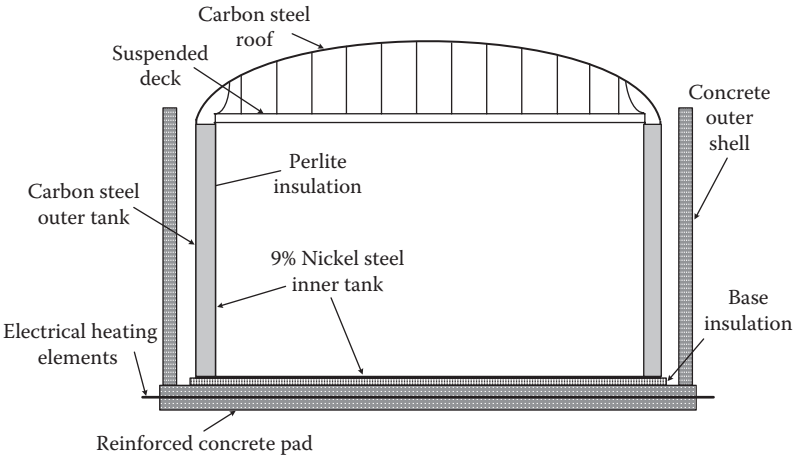


FIGURE 18.23 Double-containment tank. (Adapted from Long, 1998 and Kotzot, 2003.)

with an insulating material. The electrical heating elements shown in the figure are to prevent frost heave of the soil under the tank. Single-containment tanks are not frequently used in new construction except where large areas are available for earthen dikes to contain LNG in the unlikely event of the primary tank failure. The earthen dike is typically designed to hold 110% of the capacity of the largest tank within the berm but obviously cannot contain flammable vapors from a spill.

18.4.1.2 Double-Containment Tanks

Figure 18.23 shows the configuration of a double-containment tank. Long (1998) discusses single-containment and double-containment tanks using 9% nickel steel construction. The single-containment tank is less expensive to build but has the disadvantage of only one containment wall that is compatible with LNG. Double-containment tanks can be installed on a smaller plot than a single-containment tank because the tank is surrounded by a prestressed concrete outer shell to act as secondary containment in lieu of a large diked area. An economic study by Long (1998) indicated that double-containment tanks are 12%–17% less expensive that full-containment tanks. Like single-containment tanks, they do not contain the flammable gas vapor, which would evolve from a spill. Rapallini and Bertha (1998) discuss the conversion of two single-containment 9% nickel steel tanks into double-containment tanks by the addition of an outer concrete tank. The only double-containment tank in the United States is in Puerto Rico. Because double-containment tank construction is relatively difficult, many tank fabricators offer full-containment tanks at the same price as double-containment tanks.

18.4.1.3 Full-Containment Tanks

A full-containment tank is designed to completely contain a rupture of the inner metal tank, except for some vapor from the tank relief valves.

Figure 18.24 shows the configuration of a full-containment tank containing a metal liner. The roof is constructed of concrete with a metal liner. Nishizaki et al. (2001) discuss the construction of a 180,000 m^3 (1.2 MMBbl) LNG storage tank that is one of the world's largest aboveground tanks. The structure consists of an inner tank of 9% nickel steel, an outer prestressed concrete tank, with a cryogenic insulation between the two tanks.

Concrete tanks may be constructed where the concrete is protected from direct contact with the LNG by a membrane[3] or where the LNG directly contacts the concrete. The Portland Cement Association (Monfore and Lentz, 1962) showed that concrete cured at ordinary temperatures can

[3] Membranes here denote sheets of impervious material, typically metal, that prevent the LNG and gas vapors from contacting the tank walls, not membranes for separation as discussed in Chapters 10–12.

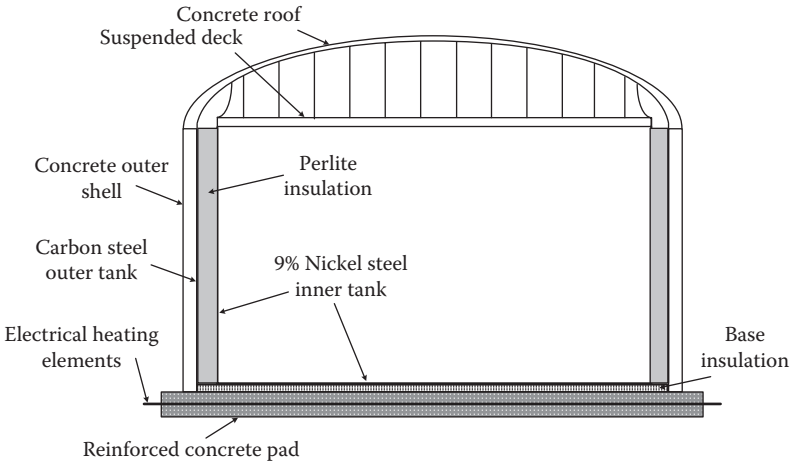


FIGURE 18.24 Full-containment tank. (Adapted from Long, 1998 and Kotzot, 2003.)

be used to form tanks for holding cryogenic fluids. The mechanical properties of concrete are not significantly impaired at low temperatures. In fact, the compressive strength of concrete at –250°F to –150°F (–155°C to –100°C) is almost triple that of concrete at room temperature. Legatos et al. (1995) and Jackson and Powell (2001) provide details on the construction and economics of full-containment prestressed concrete tanks. Jackson and Powell (2001) include data on the rate of LNG permeation of the concrete.

Prestressed concrete tanks may be constructed at grade, below ground, or partially below ground, depending on site conditions or other factors. Giribone and Claude (1995) describe a novel concept for an aboveground tank that features a 1.2-mm thick stainless steel membrane combined with a prestressed concrete outer wall. In this configuration, the membrane acts to contain the LNG, but all the hydrostatic load is taken by the concrete.

Figure 18.25 shows one installation of a prestressed concrete storage tank. The tank was constructed with its base at grade but was completely surrounded by an earthen berm. The tank had a capacity of approximately 2 billion cubic feet of gas (approximately 600,000 barrels [95,000 m^3]) and was built for a peakshaving facility on Staten Island, New York. Prater (1970) provides details of the tank construction. The reinforced concrete walls were insulated on the inside of the tank with polyurethane. The LNG was isolated from the insulation with a thin laminate film that had additional protective insulation.

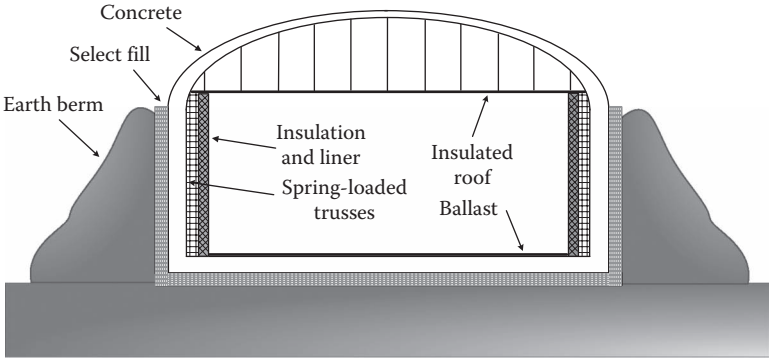


FIGURE 18.25 Prestressed concrete storage tank for LNG (Duffy et al., 1967).

The tank was destroyed in an unfortunate maintenance construction accident in 1973. During repairs to the inside of the storage tank, a fire unrelated to the storage of LNG started. The increase in pressure that resulted was rapid and lifted the concrete roof, which then collapsed and killed 37 workers inside the tank (McFadden, 1973).

Some LNG codes have been updated to include the use of prefabricated storage tanks to provide potential cost and schedule savings but they have had only limited acceptance.

18.4.2 Cryogenic In-Ground Storage

Three basic types of in-ground storage have been used:

- Conventional concrete or steel tanks in an underground configuration
- Tanks formed around a frozen-earth cavity
- Mined caverns

All three types will be discussed briefly.

18.4.2.1 Conventional Tankage

Aboveground tank storage requires that the walls supply all of the mechanical strength. In-ground tanks may use either the surrounding earth to provide mechanical support or an in-pit construction in which the tank is built as a separate unit and the pit provides containment in case of leakage or rupture.

Two of the world's largest LNG tanks use earth as a mechanical support. These each hold 200,000 m^3 (1.3 MMBbl), and are installed at the Ohgishima LNG terminal of the Tokyo Gas Company (Umemura et al., 1998). The tanks are unique not only because of their size but also because the entire tank, including the domed roof, is buried. Each of the cylindrical tanks is constructed entirely of reinforced concrete and has 2.2 m-(7.2 ft) thick sidewalls, with a 9.8 m-(32 ft) thick bottom slab, 78 m (255 ft) in diameter, all designed to withstand ground water uplift. The domed roofs are also made of reinforced concrete (1 m thickness at center and 2.5 m at circumference). Because the tanks are totally buried, each roof supports its own weight (15,000 metric tons) plus the weight of the soil covering it (40,000 metric tons). The inside of the tanks, including the domes, are lined with cryogenic insulation and 2 mm stainless steel membranes for liquid and gas tightness. Heating systems surround the sides and bottoms to control ground freezing.

Okamoto and Tamura (1995) discuss the first in-pit storage unit built in Japan, an 85,000 m^3 (0.53 MMBbl) unit. In their design, they chose a storage tank identical to an aboveground, cylindrical and vertical, metallic double-shell, flat-bottom tank, and installed the tank inside an in-ground reinforced concrete pit. Dragatakis and Bomard (1992) discuss in some detail the problem of tank construction in areas prone to severe earthquakes, and they describe in-pit units at the Revythousa Island LNG facility, located 30 km from Athens, Greece. In their in-pit approach, the tank is free-standing in the pit and functions like an aboveground tank during a seismic event.

18.4.2.2 Other Storage Types

To take advantage of the low thermal conductivity of earth two other storage concepts have been considered: frozen earth and mined caverns. Four early LNG plants incorporated frozen-earth cavities for storage. In 1983, only two were in service (Boulanger and Luyten, 1983) and none are in use today. Reasons for abandoning the cavities are unknown.

Mined caverns are similar to underground gas storage discussed in Chapter 17 in that a subterranean cavity is created to hold the LNG. In this case, the cavity walls are either in direct contact with the liquid or separated by an insulating wall. Boulanger and Luyten (1983) describe test results in a frozen-clay cavern at Schelle, Belgium.

Ahlin and Lindblom (1992) discuss a cavern model in which the LNG is stored in vertical rock caverns, with the LNG separated from the cavern by a layer of concrete cast against the wall and an inner wall of Invar steel on insulating panels. Neither of these techniques has been applied commercially.

18.4.3 Rollover

In 1971, at the LNG terminal in La Spezia, Italy, a sudden increase in pressure occurred, with subsequent substantial venting of an LNG tank that had received delivery some 18 h earlier. Fortunately, no damage or injuries occurred. This incident was the first well-documented instance of a large, sudden vapor releases that became known as "rollover" (Acton and Van Meerbeke, 1986). This section provides a short overview of the cause of the releases and how they are prevented.

18.4.3.1 Cause of Rollover

Storage of cryogenic liquids is unique in that the heat leak continually warms the liquid, whereas fluids stored at ambient temperature experience both heating and cooling. To dissipate the heat influx, the cryogenic liquid boils off. For pure liquids, such as liquid nitrogen, this process causes no problems because the liquid is pure and no composition change takes place.

As Table 18.4 shows, LNG contains many components with normal boiling points differing by hundreds of degrees. Of these liquids, only nitrogen and methane vaporize at LNG temperatures because they are the only components with a significant vapor pressure.

First, consider a tank that contains LNG that is well mixed, with no nitrogen present. As methane boils off, the LNG "weathers" off methane. This increases the concentration of the heavier components and, thus, increases the boiling point of the liquid. An increase in density occurs because of the loss of methane, which offsets the density decrease caused by the temperature increase. Heat leak from the bottom and sides of the tank causes continual mixing through natural convection. Over time, this mixture slowly warms and increases in density.

Figure 18.26 shows a tank after the addition of a fresh batch of LNG on top of the existing liquid, which creates two stratified layers. Initially, the top layer is both lighter and cooler than the bottom layer. However, the top layer increases in density as methane vaporizes. At the same time, the bottom layer continues warming due to heat leak, but it cannot vaporize because of the hydrostatic head of the top layer. The temperature increase from heating lowers the bottom-layer density. Although some mixing occurs between the layers at the interface, it is minimal, considering the typically large volumes of liquid in each layer.

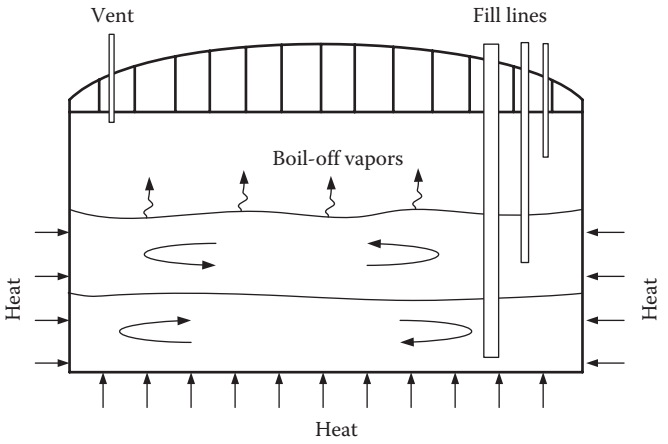


FIGURE 18.26 Schematic of tank that contains two stratified layers of LNG. Heat flux into tank promotes mixing in each layer by natural convection.

Continual weathering in the top phase, which increases its density and, concurrently, continual warming of bottom phase caused by heat leak, which lowers its density, can lead to the bottom phase becoming the lighter phase. If the density inversion becomes large enough to overcome the hydrostatic head, the potential exists for the phases to flip, or rollover, which brings the warm liquid to the top, with a sudden evolution of gas, because the hydrostatic head on the lighter phase is gone. Tank size and type (aboveground, in-ground, concrete, or metal) apparently have no significant effect on the occurrence of rollover (Acton and Van Meerbeke, 1986). The slight changes in liquid composition, along with density difference caused by temperature, are the important variables.

Nitrogen at concentrations above 1 mol% in LNG is believed by some investigators to increase the potential for rollover.

18.4.3.2 Prevention of Rollover

Rollover prevention requires knowledge of the temperature and density pattern throughout the tank when adding a new quantity of LNG. If the new LNG is lighter than the existing liquid, it should enter at the bottom of the tank. This action forces immediate turnover of the liquids and provides the mixing required, avoiding stratification. Conversely, heavier LNG is filled at the top. Modern tanks are instrumented with level devices, which also measure density and temperature to monitor for potential signs of stratification and the potential for rollover.

To ensure that no danger is present, safety codes (NFPA 59A, 2009) require that storage tanks have vent capacities many times larger than the normal boil-off rate. European Standards (BS EN 1473:2007, 2007) require tank vents to handle as much as 100 times the normal boil-off rate to ensure that tanks will not be overpressured.

18.5 TRANSPORTATION

As noted in Section 18.1, for transporting large quantities of gas, often the only alternative to pipelines is shipping by LNG. Three options are possible for transporting LNG:

- Truck transport
- LNG pipelines
- Marine carriers

Each method will be discussed, with the emphasis on marine carriers because they are the most important, especially internationally.

18.5.1 Truck Transport

Cryogenic liquids, including liquid helium, liquid hydrogen, liquid nitrogen, and liquid oxygen, are routinely moved by transport truck. Thus, over-the-road movement of LNG is a relatively simple, straightforward process that requires no new technology. The major consumers of trucked LNG are vehicle fueling stations and "stranded utilities (distribution companies not connected to the national pipeline grid)" (Energy Information Administration, 2018). Additionally, some LNG has been used to fuel truck fleets although that is a specialized market.

18.5.2 Pipelines

The concept of long-distance LNG pipelines was studied by Hoover (1970), Katz and Hashemi (1971), and Dimentberg (1971). Pumping liquid instead of compressing gas makes the concept seem attractive. Hoover's (1970) detailed study of LNG pipeline concluded that en route refrigeration, primarily for removing heat generated by friction losses, make pipelining economically feasible only in certain situations, at distances less than 200 mi (320 km).

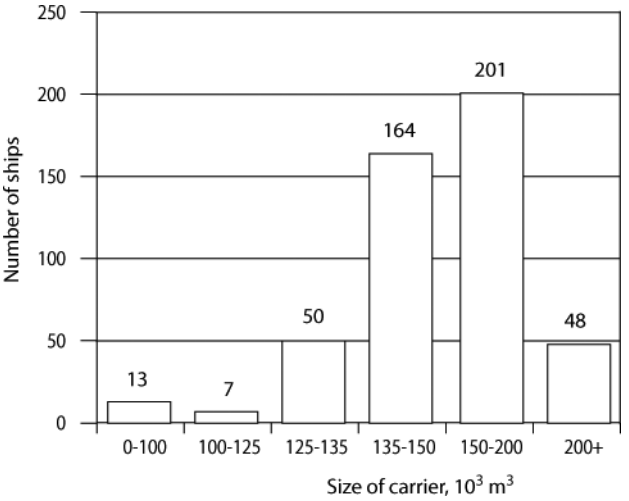


FIGURE 18.27 Size distribution of world's LNG carrier fleet in 2017 (LNG Journal, 2018).

18.5.3 Marine Transport

The first ship, Methane Pioneer, sailed from Lake Charles, Louisiana, to the United Kingdom with 32,000 barrels (Bbl) (5,100 m^3) of LNG on January 28, 1959. Figure 18.27 shows that at the beginning of 2018, the LNG fleet had 500 carriers. The largest carriers in use or under construction hold 266,000 m^3 (1.7 MMBbl). With savings due to economy of scale, reduced transportation costs are the prime motivation for the larger capacities. Ships with a capacity of less than about 20,000 m^3 (125,000 Bbl) are typically used for delivering fuel on inland rivers. Those with a capacity of about 75,000 m^3 (475,000 Bbl) are commonly used for shorter distances such as North Africa to southern Europe.

There are two basic types of LNG containment for carriers, classified as:

- Independent (freestanding) tanks
- Membrane tanks

We briefly discuss several of the more important design considerations of each carrier type, and then show details of some typical LNG carriers. Ffooks and Montagu (1967) present a detailed discussion of the evolution of LNG ship design, and they list several basic design criteria:

1. The low density of LNG and the requirement for separate water ballast containment require a large hull, with low draft and high freeboard.[4]
2. The low temperature of LNG requires the use of special and expensive alloys in tank construction. For freestanding tanks, only aluminum or 9% nickel steel are suitable, whereas for membrane tanks, stainless steel or Invar is used.
3. The large thermal cycling possible in the storage tanks demands special supporting arrangements for freestanding tanks and membrane flexibility in membrane designs.
4. The hull of the vessel is carbon steel, so good thermal insulation is required between the tanks and the hull. In addition, for membrane tanks, the insulation must be capable of supporting the full weight of the cargo.
5. The cargo-handling equipment must be carefully designed to account for thermal expansion and contraction.

[4] Draft is the depth of water necessary to float a ship, and freeboard is that part of the ship's side between the waterline and the main deck.

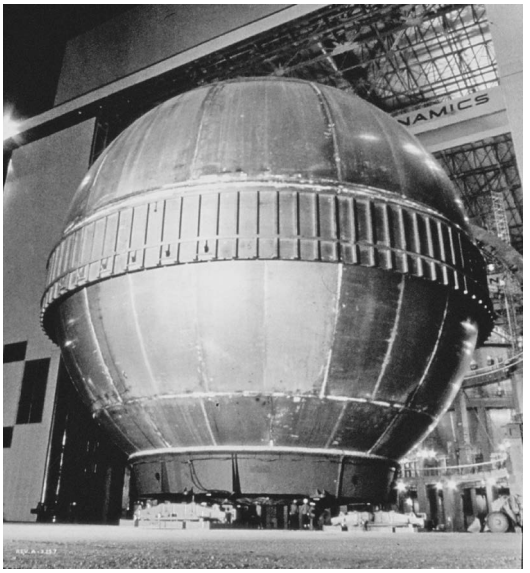


FIGURE 18.28 Spherical LNG storage tank before installation on carrier hull.

The application of these principles in the design of LNG carriers resulted in a number of different containment concepts; but today, only two systems are in general use: independent tank and membrane designs. At one time, independent tanks dominated the market but new construction heavily favors membrane tanks. As of early 2017 about 75% of the fleet is membrane-type ships (International Gas Union, 2018).

All LNG carriers are double hulled. Many use steam turbines for propulsion but newer ships often use dual-fueled engines burning both diesel and natural gas. Their efficiencies are about 25% higher than straight natural gas engines and are gaining market share. Boil-off gas is used for fuel in dual-fuel engines.

18.5.3.1 Independent Tanks

Independent tanks are self-supporting, do not form part of the ship's hull, and are not essential to the hull strength (Marshall, 2002). The principal system in use is the Moss system, originally designed by Moss Rosenberg Verft (see discussions in Marshall (2002) and Harper (2002)). This system uses spherical aluminum tanks. Figures 18.28 and 18.29 show a tank ready to be placed in the ship's hull and a view of the vessel with three of the four tanks installed. Kato et al. (1995) describe a typical design for vessels and tanks used on two ships for the Indonesia–Japan route. The four aluminum-alloy tanks on each vessel are of the Moss spherical design and can hold a total of 125,000 m^3 (0.8 MMBbl) of LNG, filled to 98.5% of capacity. The tanks are insulated on the external surface with insulation composed of phenol resin and polyurethane foam and are designed for a boil-off rate of 0.15% per day. A typical Moss carrier is shown in Figure 18.30.

18.5.3.2 Membrane Tanks

The capacity of Moss carriers is limited by the size of the independent tanks. Larger carriers typically use membrane tanks. Membrane tanks are non-self-supporting and consist of a thin metal membrane, stainless steel, or Invar (36% nickel steel), supported by the ship's hull through the thermal insulation. Invar is widely used because it has a very small coefficient of thermal expansion in the operating ranges of the tanks, which are approximately ambient to –260°F (–160°C). Figure 18.31 shows some details of the often used containment system, the Gaztransport Technigaz containment systems (Harper, 2002). The Invar membrane (Gaztransport) design is equal in popularity with the stainless steel (Technigaz) membrane. Figure 18.32 shows an example of a membrane tank carrier.

FIGURE 18.29 Ship with three of four storage tanks installed.

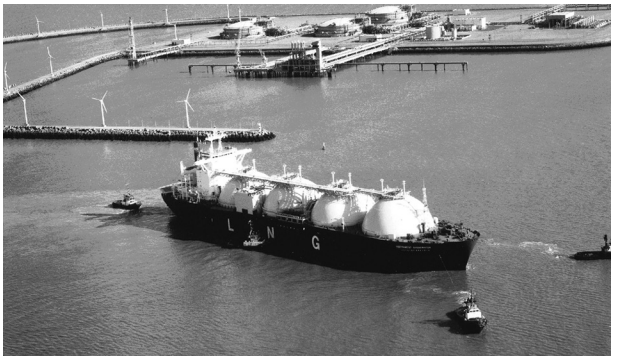


FIGURE 18.30 Photo of Moss-type (independent tank) carrier being escorted by tugs. (Courtesy of B.P, © p.l.c.)

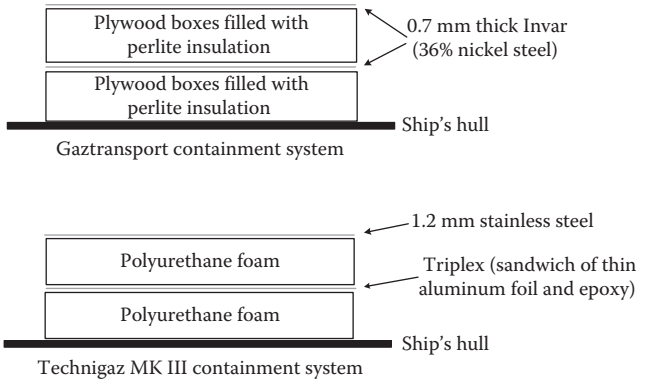


FIGURE 18.31 Gaztransport and Technigaz containment systems (Harper, 2002).

FIGURE 18.32 Photo of membrane carrier. (Courtesy of B.P, © p.l.c.)

18.6 REGASIFICATION AND COLD UTILIZATION OF LNG

18.6.1 Regasification

Regasification of the stored LNG is the final step in the operation of LNG peakshaving and off-load terminal storage facilities. The regasification, or vaporization, is accomplished by addition of heat from ambient air, ambient water, or fired vaporizers. The cost of the regasification system generally represents only a small fraction of the cost of the storage plant; however, the availability of the system is critical because failure or breakdown would defeat the purpose of the facility.

The regasification section of a peakshaving plant is designed for only a few days of operation each year to meet the extreme peak loads. To obtain adequate availability, total send-out capacity is divided into independent parallel systems, each capable of handling all or a substantial fraction of the total demand. Designs for the regasification section at the offload terminal are similar to those for a peakshaving plant, but the capacities of these facilities are much higher, and more equipment may be required to achieve the required delivery rates.

Figure 18.33 is a simplified flow diagram of a typical LNG regasification system. Liquid is pumped from the storage container to the vaporizer. The pump discharge pressure must be high enough to provide the desired gas pressure for entry into the transmission or distribution system. Heat is added to vaporize the high-pressure LNG and to superheat the gas. Gas leaving the vaporizer may have to be odorized (see Chapter 17).

One marine terminal in the United States includes a facility to separate ethane, propane, and butane from imported LNG using refrigeration provided in the LNG itself (True, 2010). This is discussed more in the next section.

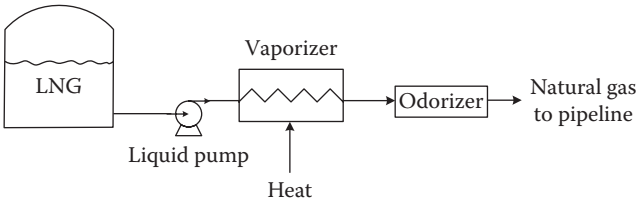


FIGURE 18.33 Typical LNG regasification system.

18.6.2 Cold Utilization

A striking characteristic of the LNG industry is the waste of the vast amount of potential refrigeration available. The utilization of the refrigeration from LNG vaporization has been examined for years but making economically viable use of the resource has been difficult. This is probably because in many locations, the need for vaporization is intermittent. Two general approaches have been advanced for utilization of the cold in LNG vaporization:

- Extraction of work from a power cycle that uses the LNG cold as a heat sink
- Use of the LNG as a source of refrigeration

Very few of the more than 100 large LNG receiving facilities in the world use the cold in LNG, and none are in the United States. Some commercial facilities are:

- An LNG receiving facility in Barcelona, Spain, which uses an LNG cryogenic process to recover heavy hydrocarbons from Libyan LNG (Rigola, 1970).
- An LNG receiving facility at La Spezia, Italy (Picutti, 1970).
- A Japanese facility that produces liquid oxygen and liquid nitrogen and provides warehouse refrigeration for frozen food as well (Kataoka et al., 1970); the plant received a 38% reduction in power requirement by use of the cold LNG.
- An LNG-assisted air-separation plant in France (Grenier, 1971).

With the expected increase in LNG production, there will be greater incentive to utilize the available refrigeration.

As noted earlier, LNG imported into the Atlantic basin must meet specified heating values and Wobbe numbers. To lower heating value for LNG containing too much C_2^+, which can also present a potential dropout in pipelines, it may be possible to dilute the gas with nitrogen. However, this requires a nearby nitrogen source. Because of pipeline limits on total inerts and the fact that dilution does not significantly lower the hydrocarbon dew point, the use of nitrogen must be considered carefully.

Another option is to remove the C_2^+ fraction using a demethanizer. There are numerous processes that employ a cold separator and a demethanizer (see Chapter 12) to remove the heavy components (Huang et al., 2004). To make this concept feasible, there must be a readily available market for the large volume of NGLs produced.

18.7 ECONOMICS

Reports by the Energy Information Administration provide information on global LNG costs and are the source of much of the data in this section. Because these data are very volatile and change frequently, no values are available which are representative of prices in 2019. The four steps for bringing gas to the consumer are:

- *Gas production*: Developing the reserves and transporting gas from the reservoir to the LNG plant (including any field processing) are 15%–20% of the total cost.
- *Liquefaction*: Treating, liquefaction, NGL recovery, storage, and LNG loading are 30%–45% of the total cost.
- *Shipping*: Maritime shipping is 10%–30% of the total cost.
- *Receiving*: Unloading, storage, regasification, and distribution are 15%–25% of the total cost.

This section briefly looks at some of the component costs of the last three items and other items impacting the cost to produce and market prices for LNG.

TABLE 18.5
LNG NETBACKS $/MMBtu[a] in 2009

	Liquefaction Plant					
Receiving Terminal	**Algeria**	**Malaysia**	**Nigeria**	**Australia NW Shelf**	**Qatar**	**Trinidad**
Barcelona	$7.71	$5.53	$6.84	$6.10	$6.14	$6.76
Everett	$3.49	$1.47	$3.13	$1.56	$2.01	$3.78
Isle of Grain	$3.09	$0.96	$2.45	$0.86	$1.51	$2.48
Lake Charles	$1.63	–$0.20	$1.42	–$0.03	$0.19	$2.21
Sodegaura	$5.86	$8.00	$6.12	$7.69	$6.94	$5.16
Zeebrugge	$6.91	$4.73	$6.26	$4.61	$5.34	$6.32

[a] To convert $/MMBtu to $/GJ multiply by 0.948.

Some markets such as India and Pakistan are very price sensitive and the LNG price must be competitive with alternate fuels such as coal or locally produced natural gas. Imported LNG is generally more expensive than produced gas in North America and little LNG comes to marine terminals in the United States except during periods of extreme cold weather when pipeline deliveries are curtailed.

The LNG trading business in the 1970s was characterized by firm, long-term contracts where a given volume of LNG from a given production site was transported to a fixed market location at a known price. This arrangement allowed market stability and a fixed return on capital for the relatively expensive plants. Over time, the market has become more dynamic. Fixed volume sales are common but with flexibility on delivered location and shipping arrangement. In 2017, LNG represented about 10% of world gas utilization and short-term sales represented 30% of the total LNG transported. These figures are up significantly from earlier years. In addition, companies involved in the LNG trade have opted to own more of the value chain from gas production to gas market. Examples of this trend are the common ownership of the production facilities, the ships capable of transporting large cargoes, and the receiving terminals.

With the expansion of the LNG markets, competition for cargoes made it possible to shift supply to higher priced areas. Netback is the price received at the destination terminal less the transportation cost from the shipping location. To illustrate the principle, the values in Table 18.5 show that value received depends on liquefaction plant and destination locations. The market is dynamic and real-time shipping and cargo information such as given in Table 18.5 are used by most LNG trading companies. For example, using Table 18.5, if a cargo from Trinidad destined for Everett on the United States East Coast ($3.78) can bring a higher price in Barcelona, Spain ($6.76), it can be re-routed to get the better price. More information on netbacks can be found in Holmes (2007).

Table 18.6 lists an approximate breakdown of costs (wellhead gas price through liquefaction, marine transportation, and regasification in 2001) for three existing LNG operations. In all three situations, the price of the wellhead gas is less than 40% of the total cost of marketing the reserve. Transportation costs vary significantly and are illustrated by Table 18.7. To develop the current LNG economics one has to consider all aspects of the value chain including both the highly volatile transportation costs and market prices in the destination market.

18.7.1 Liquefaction Costs

Liquefaction is the largest cost component of the LNG value chain and is typically high relative to other energy projects, for reasons such as:

- Remote locations
- Strict design and safety standards

TABLE 18.6
Cost Breakdown in $/MMBtu[a] for LNG Plants

	Qatar	Australia	Indonesia
Wellhead gas	0.50–0.75	0.65–0.95	0.60–0.80
Liquefaction	0.40–0.60	0.40–0.60	0.45–0.65
Transportation	1.10–1.20	0.75–0.95	0.55–0.75
Regasification	0.40–0.60	0.35–0.55	0.30–0.60

Source: Troner (2001).
[a] To convert $/MMBtu to $/GJ multiply by 0.948.

TABLE 18.7
Representative LNG Shipping Rates in $/MMBtu ($/GJ) to LNG Terminals in the United States (to Convert to $/GJ Multiply by 0.948)

Exporter	Everett	Cove Point	Elba Island	Lake Charles
Algeria	0.52	0.57	0.60	0.72
Nigeria	0.80	0.83	0.84	0.93
Norway	0.56	0.61	0.64	0.77
Venezuela	0.34	0.33	0.30	0.35
Trinidad and Tobago	0.35	0.35	0.32	0.38
Qatar	1.37	1.43	1.46	1.58
Australia	1.76	1.82	1.84	1.84

Source: Energy Information Administration (2003).
Prices are based on a 138,000 m^3 carrier at a charter rate of $65,000 per day. See text for information on variability of charter rates over time.

- Large amounts of material in cryogenic service required
- Tendency to overdesign to ensure supply security

Major savings have been obtained by increasing the size of liquefaction trains, which requires fewer trains for a given output. In the early days of the industry, trains were 1.0–2.0 Mtpa, but 7.8 Mtpa trains were built in Qatar in the early 21st century.

In 2003, a generic liquefaction plant was estimated to cost $1.09 /MMBtu ($1.03/GJ) (based on fuel value) for a two-train, 8 Mtpa greenfield[5] project and $0.97 /MMBtu ($0.92/GJ) for an expansion train (Office of Fossil Energy, 2005). Historically, costs are stated on the basis of $/Mtpa of capacity with larger plants at the lower end of the range. In 2019 capital cost estimates were difficult to quantify because of significant non-standard costs of plants. Examples included:

- A Russian arctic plant built in and for extremely cold weather
- Australian projects with unusually high construction labor costs
- United States plants built using existing, expensive LNG storage tanks at an import terminal.

Publically available data in early 2019 for North America shows capital costs from about $400/Mtpa to $1000/Mtpa with some projects significantly above this range.

[5] A greenfield project is one built in an area without supporting infrastructure.

18.7.2 Shipping Costs

Shipping costs are determined by the daily charter rate, which has varied from as low as $27,000 to as high as $200,000 over the decade ending in 2018. The average rate in 2010 for long-term charters was $55,000–$65,000 per day. Table 18.7 lists some shipping rates. Prices are based on a 138,000 m^3 (0.87 MMBbl) carrier at a charter rate of $65,000 per day. In 2018 spot charter rates ranged from approximately $40,000/day to $200,000/day.

Purchase prices for LNG carriers vary significantly, but for a 138,000 m^3 carrier in the mid-1980s, the price was approximately $280 million (nominal), whereas in November 2003, it had dropped to approximately $170 million. The main factor driving down the price was competition among the shipyards that were qualified to build the vessels.

In addition to the charter rate and fuel cost, a major factor in the cost of operating an LNG ship is the distance traveled. Trading patterns continue to change and were altered by the opening of the Panama Canal to LNG carriers.

18.7.3 Regasification Terminal Costs

Terminal costs vary widely and naturally are site specific. A small terminal might cost as little as $100 million, whereas a state-of-the-art Japanese facility can be $2 billion or more. In the United States, 2019 capital investment costs are in the range of $400 million to $500 million for capacities of 183–365 Bcf ($5.2–10.3 \times 10^9$ m^3). The 2015 price of regasification is generally assumed to add about $0.30/MMBtu ($0.28/GJ) to the cost of imported LNG.

18.8 SAFETY AND ENVIRONMENTAL CONSIDERATIONS

The major difference in safety of LNG facilities compared with that of normal gas plants is the larger equivalent amount of gas present on ships and in storage facilities. As noted earlier, large LNG carriers hold the equivalent of 5.5 Bcf (155×10^6 m^3). This section first discusses two aspects relating to ships, and then touches on the issues that surround the siting of proposed new LNG terminals.

An aspect of LNG marine transport that has received much attention is safety. In addition to the usual problems in handling large quantities of flammable material, two safety problems are unique to LNG, and both are functions of the low temperature of the product.

The first problem involves materials of construction. Material for tanks and cargo-handling equipment must be chosen with care because of thermal expansion and contraction problems during the normal thermal cycling of the equipment. Many materials, notably carbon steel, become dangerously brittle at low temperatures and are unsatisfactory for normal use. This problem has been addressed as newer LNG carriers have been brought into service. According to the Federal Energy Regulatory Commission (2009b) more than 33,000 LNG carrier voyages have taken place in the past 40 years, with no significant accidents. To address the concerns of citizens regarding movements of LNG on the water, a number of studies and procedures have been implemented in the United States. The FERC commissioned a study (Sandia National Laboratories, 2004) that used state-of-the-art modeling of LNG spills on water and in marine import terminals. In addition, the United States Coast Guard instituted a Waterway Suitability Analysis (United States Coast Guard, 2005) as part of their review process for proposed LNG marine terminals. The original report was updated to address the larger carriers now in LNG service (Sandia National Laboratories, 2008).

The second problem is that the so-called rapid phase transition induced pressure wave that may occur when large quantities of LNG are rapidly dumped on the ocean, as could be the case in a maritime accident. This phenomenon received much attention (Burgess et al., 1970; Nakanishi and Reid, 1971) because of its unique character. Nakanishi and Reid (1971) give an excellent summary of the problem and suggest an explanation based on the rapid, often violent boiling caused by the extreme

large temperature difference between the LNG and the water. In later work, Cleaver et al. (1998) summarize the results of a collaborative industrial research program on the rapid phase transitions of LNG, and Conrado and Vesovic (1998) present the results of a study on the effect of composition on the vaporization rate of LNG on water.

In 2009, there were proposals to establish at least 12 new LNG receiving facilities in North America (Federal Energy Regulatory Commission, 2009a). The most desirable locations are in areas of high population density (e.g., the northeast), so that pipeline distances to market are minimized. However, the combination of the perceived threat from terrorists and officials not wanting any new facilities in local areas slowed the implementation of new receiving facilities.

An alternative is to locate the receiving facilities offshore. In 2010, the United States had three terminals which use a floating storage and regasification unit (FSRU). In addition, there were five potential offshore LNG facilities with a combined capacity of 6.6 Bcf (185×10^6 m^3) (Federal Energy Regulatory Commission, 2009a). In the highly politically charged atmosphere surrounding proposed LNG terminals and difficult market conditions, it will be interesting to see if any of the many announced facilities are permitted and constructed.

In the ensuing years, there has been little demand for LNG import terminals in North America. A FERC map (Federal Energy Regulatory Commission, 2019) showed no active applications for import facilities in January of 2019. This is in sharp contrast to the large number of proposed export facilities listed in Table 18.2 above.

DISCUSSION QUESTIONS

1. What makes LNG an attractive means of storing and transporting energy?
2. What are differences between peakshaving and baseload LNG facilities in terms of purpose, size, and storage?
3. What are possible differences in gas processing when producing LNG instead of a pipeline gas?
4. What is the major difference between LNG sold to the United States and to Japan and why does the difference exist?
5. What are relative advantages of open and closed liquefaction cycles?
6. Why can mixed refrigerant cycles be more thermodynamically efficient than pure fluid refrigerants?
7. What are the differences between "single-containment," "double-containment," and "full-containment" storage facilities in terms of containing an LNG leak?
8. What causes "rollover" and how is it prevented?
9. What are the major differences between the two major types of LNG carriers?
10. What are the four major cost components of moving natural gas in the form of LNG from the wellhead to the customer's gas pipeline?

EXERCISES

18.1 How much HHV energy (in Btu or PJ) is contained in the cargo aboard a 145,000 m^3 LNG carrier? Assume the LNG has a relative density of 0.45, a molar mass of 18, and a heating value of 1,000 Btu/scf (39.4 MJ/Nm^3).

18.2 What is the value of the cargo in Exercise 18.1 if the fuel is priced at $5.00 per MMBtu ($4.75/GJ)?

18.3 What is the equivalent volume of gas (in scf [Nm^3]) of the cargo in Exercise 18.1?

18.4 An LNG receiving terminal sends gas to the pipeline at 1,000 psig (70 barg). The LNG is essentially pure methane and is stored in a tank at 2 psig. What is the pump energy (hp, kW) required to send out 400 MMscfd (10.7×10^6 Nm^3/day) of gas to the pipeline at 40°F (4.4°C)? Assume a pressure drop through the vaporizer of 20 psi (1.4 bar) and a pump

efficiency of 70% and a methane liquid density ≈ 26.2 lb_m/ft^3 (444 kg/Nm^3) (see Chapter 2 for pumps).

18.5 The LNG terminal in Exercise 18.4 uses seawater to heat LNG from storage temperature for send out. For a gas send-out rate of 400 MMscfd (10.7×10^6 Nm^3/day) and using fresh water properties:
   a. What water flow rate (lb_m/h, kg/h) is required to heat the LNG, assuming an inlet water temperature of 50°F (10°C) and an outlet water temperature of 40°F (4°C)?
   b. What is the hp (kW) required to lift the water 50 ft (15 m) above sea level to the vaporizer assuming a pump efficiency of 80%?

18.6 The LNG terminal operator in Exercises 18.4 and 18.5 decides to explore vaporizing LNG at low pressure, then compressing for send out. The LNG is first pumped to 30 psig (2.1 barg), then passed through the vaporizer exiting as a gas at −200°F (−129°C) and 25 psig. The gas then goes to a compressor for compression to the pipeline pressure of 1,000 psig. How does the pump and compressor energy compare with that required using seawater heating (Exercises 18.4 and 18.5)? Assume the pump and compressor are both 70% efficient.

18.7 The LNG terminal in Exercise 18.5 has a standby gas-fired submerged combustion vaporizer. What portion of the vaporized LNG must be consumed as fuel to heat LNG to 40°F (4.4°C) and 1,000 psig (70 barg) if seawater is not used? Assume the vaporizer is 100% efficient (HHV basis).

18.8 A classic cascade LNG design cools the inlet gas with cooling water, propane, ethane, and methane refrigerants. The gas being converted to LNG has been processed to remove NGL and is essentially methane. Gas enters the liquefaction section at 104°F (40°C), 1,000 psig (70 barg), and a rate of 400 MMscfd (10.7×10^6 Nm^3/day). Plant cooling is accomplished with water from a cooling tower, which supplies water at 80°F (27°C). All heat exchangers have a pressure drop of 10 psi (0.7 bar) and an approach of 10°F (5.6°C). The suction pressure for the refrigeration compressors is atmospheric pressure (14.7 psia, 1.01 bara). The final LNG flash is at 10 psig (0.7 barg) and the vapors are sent to a fuel compressor.
   a. Draw a diagram of the inlet gas (only) flow through the liquefaction system showing the gas temperatures leaving each refrigerant step. The fuel gas compressor need not be shown.
   b. What is the duty of each of the gas cooling steps?
   c. What fraction of the inlet gas is sent to storage as LNG?

18.9 Most LNG import terminals are designed to receive LNG at a maximum rate of 12,000 m^3/h.
   a. How long will it take to unload an LNG carrier with a capacity of 138,000 m^3 at such a terminal?
   b. What is the time for a 266,000 m^3 ship?

REFERENCES

Acton, A., and Van Meerbeke, R.C., Rollover in LNG storage - an industry perspective, *Eighth International Conference on Liquefied Natural Gas*, Gas Technology Institute, Chicago, IL, 1986.

Ahlin, L., and Lindblom, U., A new Swedish concept for storing LNG underground, *Tenth International Conference on Liquefied Natural Gas*, 1992.

Andress, D.L., The Phillips optimized cascade LNG process, a quarter century of improvements, ConocoPhillips Petroleum Company, 1996. http://static.conocophillips.com/files/resources/smid_016_the_phillips_optimized_cascade_lng_proces.pdf (Retrieved April 2019).

Anonymous, LNG liquefaction cycles, *Cryo. Ind. Gases, 5*(5), 33, 1970.

Avidan, A., Drive to lower transportation costs key for many gas projects, *Oil Gas J., 98*(20), 62-X, 2000.

Barron, R., *Cryogenic Systems*, McGraw-Hill, New York, 1966.

Blakely, R., Remote areas of Canada can now be served by trucked LNG, *Oil Gas J., 66*(1), 60, 1968.

Boulanger, A., and Luyten, W., Test cryogenic storage at Schelle, results and conclusions, *Seventh International Conference on Liquefied Natural Gas*, Gas Technology Institute, Chicago, IL, 1983.

BS EN 1473:2007, Installation and equipment for liquefied natural gas — Design of onshore installations, British Standards Institute, 2007.

Burgess, D.S., et al., Hazards associated with the spillage of liquefied natural gas on water, Report of Investigations 7448, U.S. Bureau of Mines, 1970.

Cleaver, P., et al., Rapid phase transition of LNG, *Twelfth International Conference on Liquefied Natural Gas*, Gas Technology Institute, Chicago, IL, 1998.

Collins, S.C., A helium cryostat, *Rev. Sci. Instr., 18*, 157, 1947.

Conrado, C., and Vesovic, V., Vaporization of LNG on unconfined water surfaces, *Proceedings of the Twelfth International Conference on Liquified Natural Gas*, Gas Technology Institute, Chicago, IL, 1998.

Dimentberg, M., Development of LNG pipeline technology, *Cryo. Ind. Gases, 6*(5), 29, 1971.

Dodge, B.F., *Chemical Engineering Thermodynamics*, McGraw-Hill, New York, 1944.

Dragatakis, L., and Bomard, H., Revythousa Island LNG facility - LNG storage tanks for seismically highly affected areas, *Tenth International Conference on Liquefied Natural Gas*, Institute of Gas Technology, 1992.

Duffy, A.R., et al., Heat transfer characteristics of belowground storage, *Chem. Eng. Progr., 63*, 55, 1967.

Energy Information Administration, The global liquefied natural gas market: status and outlook*, DOE/EIA-0637* Office of Oil and Gas, U.S. Department of Energy, 2003. http://large.stanford.edu/courses/2012/ph240/mao1/docs/eia_0637.pdf (Retrieved April 2019).

Energy Information Administration, Natural gas, Natural gas annual, U,S, Department of Energy, 2018. www.eia.gov/naturalgas/annual/ (Retrieved April 2019).

Engineering Data Book, Section 2, Product specifications, GPSA Midstream Suppliers, Tulsa, OK, 2016a.

Engineering Data Book, Section 13, Compressors and expanders, GPSA Midstream Suppliers, Tulsa, OK, 2016b.

Federal Energy Regulatory Commission, A guide to LNG - What all citizens should know, Federal Energy Regulatory Commission, U.S. Department of Energy, 2005. www.mudomaha.com/sites/default/files/lng.pdf (Retrieved April 2019).

Federal Energy Regulatory Commission, North American LNG import terminals, Federal Energy Regulatory Commission, U.S. Department of Energy, 2009a.

Federal Energy Regulatory Commission, Safety record, U.S. Department of Energy, 2009b. https://ferc.gov/industries/gas/indus-act/lng/cons-model.asp (Retrieved April 2019).

Federal Energy Regulatory Commission, North American LNG import terminals proposed, U.S. Department of Energy, 2019. https://ferc.gov/industries/gas/indus-act/lng/lng-proposed-import.pdf (Retrieved April 2019).

Ffooks, R.C., and Montagu, H.E., LNG ocean transportation: experience and prospects, *Cryogenics, 7*(6), 324, 1967.

Finn, A.J., et al., LNG technology for offshore and mid-scale plants, *Proceedings of the Seventy-Ninth Annual Convention Gas Processors Association*, Tulsa, OK, 2000.

Foerg, W., et al., A new LNG baseload process and the manufacturing of the main heat exchangers, *Twelfth International Conference on Liquefied Natural Gas*, Institute of Gas Technology, Chicago, IL, 1998.

Foglietta, J.H., Production of LNG using dual independent expander refrigeration cycles, *Eighty-First Annual Gas Processors Association Convention*, Tulsa, OK, 2002.

Forg, W., and Etzbach, V., Linde Report on Science and Technology, 15, 27, 1970.

Giribone, R., and Claude, J., Comparative safety assessment of large LNG storage tanks, *Eleventh International Conference on Liquefied Natural Gas*, Gas Technology Institute, Chicago, IL, 1995.

Grenier, M.R., La Centrale d'Oxygene de Fos-sur-Mer, *XIII Congress of the International Institute of Refrigeration*, Washington, DC, 1971.

Gudmundsson, J.S., and Mork, M., Stranded gas to hydrate for storage and transport, *2001 International Gas Research Conference*, Amsterdam, 2001.

Hale, D., San Diego LNG plant puts "pressure energy" to work, *Am. Gas J. (now Pipeline and Gas Journal), 193*(1), 30, 1966.

Harper, I., Future development options for LNG marine transportation, *Second Topical Conference on Natural Gas Utilization Conference*, AIChE Spring National Meeting, New Orleans, LA, 2002.

Hathaway, P., and Lofredo, A., Experience pays off for this peakshaving pioneer, *Cryo. Ind. Gases, 6*(5), 25, 1971.

Hidayati, L., et al., Comparison of LNG transportation to JAWA Island: tanker or gas pipeline, *Twelfth International Conference on Liquefied Natural Gas*, Gas Technology Institute, Chicago, IL, 1998.

Holmes, C., World LNG netback series begins in this issue, *Oil Gas J., 105*(14), 57–61, 2007.

Hoover, T.E., Technical feasibility and cost of LNG pipelines, *Proceedings of the 2nd International Conference and Exhibition on LNG*, Paris, 1970.

Huang, S., et al., Select the optimum extraction method for LNG regasification, *Hydroc. Proc., 83*(7), 57, 2004.

International Gas Union, IGU World Gas LNG Report – 2018 Edition, 2018. www.igu.org/research/igu-world-lng-report-2018-edition (Retrieved April 2019).

Jackson, G., and Powell, J., A novel concept for offshore LNG storage based on primary containment in concrete, *Thirteenth International Conference on Liquefied Natural Gas*, Gas Technology Institute, Chicago, IL, 2001.

Kataoka, H., et al., Utilization of LNG cold for the production of liquid oxygen and liquid nitrogen, *Second International Conference and Exhibition on LNG*, Paris, 1970.

Kato, M., et al., Flora Vesta LNG carrier construction, *Eleventh International Conference on Liquefied Natural Gas*, Gas Technology Institute, Chicago, IL, 1995.

Katz, D.L., and Hashemi, H.T., Pipeline LNG in the dense phase, *Oil Gas J., 69*(23), 55, 1971.

Kotzot, H., Gas treatment, liquefaction storage, LNG seminar, *Eighty-Second Annual Gas Processors Association Convention*, Tulsa, OK, 2003.

Legatos, N.A., et al., Very large prestressed concrete LNG tanks, *Eleventh International Conference on Liquefied Natural Gas*, Gas Technology Institute, Chicago, IL, 1995.

Leibon, I., et al., Comparison of natural gas transportation using LNG pipelines, and other methods, *Eighth International Conference on Liquefied Natural Gas*, Gas Technology Institute, Chicago, IL, 1986.

Linnett, D.T., and Smith, K.C., Mixed refrigerant cascade liquefiers for natural gas, design and optimization, *Advances in Cryogenic Engineering*, Timmerhaus, K.D. (ed.), Plenum Press, New York, 1970. p. 18.

LNG Journal, World LNG carrier fleet, (November/December), 29, 2018.

Long, B., Bigger and cheaper LNG tanks? Overcoming the obstacles confronting freestanding 9% nickel steel tanks up to and beyond 200,000 m3, *Twelfth International Conference on Liquefied Natural Gas*, Gas Technology Institute, Chicago, IL, 1998.

Marshall, G., LNG ships - an important link in the chain, *Second Topical Conference on Natural Gas Utilization*, AIChE Spring National Meeting, March 10–14, 2002.

May, E., ThermoFAST: A new tool for predicting solids formation risk in cryogenic gas processing, GPA Midstream Convention, 2018. https://gpamidstream.org/committees/research (Retrieved April 2019).

McFadden, R.D., 43 Workers buried in huge gas tank in explosion and fire on Staten Island, *New York Times*, 1973, www.nytimes.com/1973/02/11/archives/43-workers-buried-in-huge-gas-tank-in-explosion-and-fire-on-staten.html (Retrieved April 2019).

Miller, R.W., and Clark, J.A., Liquefying natural gas for peak load supply, *Chem. Metallurg. Eng., 48*(1), 74, 1941.

Monfore, G.E., and Lentz, A.E., Physical properties of concrete at very low temperatures, Research Bulletin No.145, Portland Cement Association, Chicago, IL, 1962.

Nakanishi, E., and Reid, R.C., Liquid natural gas-water reaction, *Chem. Eng. Progr., 67*(12), 36, 1971.

NFPA 59A, Standard for the production, storage, and handling of liquefied natural gas (LNG) National Fire Protection Association, 2009.

Nishizaki, T., et al., Largest aboveground PC LNG storage tank in the world, incorporating the latest technology, *Thirteenth International Conference on Liquefied Natural Gas*, Gas Technology Institute, Chicago, IL, 2001.

Office of Fossil Energy, Liquefied natural gas: Understanding the basic facts, Office of Fossil Energy, U.S. Department of Energy, 2005. www.energy.gov/sites/prod/files/2013/04/f0/LNG_primerupd.pdf (Retrieved April 2019).

Okamoto, H., and Tamura, K., Hatsukaichi LNG receiving terminal construction-LNG in-pit storage tank construction, *Eleventh International Conference on Liquefied Natural Gas*, Gas Technology Institute, Chicago, IL, 1995.

Perez, V., et al., The 4.5 MMTPA LNG train – a cost effective design, *Twelfth International Conference on Liquefied Natural Gas*, 1998.

Picutti, E., The LNG terminal at La Spezia, *Second International Conference and Exhibition on LNG*, Paris, 1970.

Prater, P.B., Design considerations of an LNG peak shaving facility, *Cryo. Ind. Gases, 5*(3), 15, 1970.

Price, B.C., et al., Developments in the design of compact LNG facilities, *Proceedings of the Seventy-Ninth Annual Convention Gas Processors Association*, Tulsa, OK, 2000, p. 407.

Ransbarger, W., A fresh look at LNG process efficiency, *LNG Industry, a supplement to Hydrocarbon Engineering, Spring*, 2007.

Rapallini, R., and Bertha, G.J., Conversion of the LNG storage tanks at Panigaglia, Italy, to double containment storage systems, *Twelfth International Conference on Liquefied Natural Gas*, Gas Technology Institute, Chicago, IL, 1998.

Rigola, M., Recovery of cold in a heavy LNG, *Second International Conference and Exhibition on LNG*, Paris, 1970.

Romanow, S., Got gas!!, *Hydroc. Proc., 80*(11), 11, 2001.
Sandia National Laboratories, Guidance on risk analysis and safety implications of a large liquefied natural gas (LNG) spill over water, Report SAND20046258, 2004.
Sandia National Laboratories, Breach and safety analysis of spills over water from large liquefied natural gas carriers, Report SAND2008–3153, 2008.
Swearingen, J.S., Engineers guide to turboexpanders, *Hydroc. Proc., 49*(4), 97, 1970.
Taylor, M., et al., LNG is king - but what are the alternatives? *Thirteenth International Conference on Liquefied Natural Gas*, Gas Technology Institute, Chicago, IL, 2001.
Troner, A., Russian Far East natural gas searches for a home, *Oil Gas J., 99*(10), 68, 2001.
True, W.R., Trunkline LNG approved to start vaporization, NGL recovery, *Oil Gas J., 108*(10), 2010.
Umemura, J., et al., Technological challenges for the construction of the Ohgishima LNG terminal, *Twelfth International Conference on Liquefied Natural Gas*, 1998.
United States Coast Guard, Navigation and vessel inspection circular (NVIC) 05-05, Guidance on assessing the suitability of a waterway for liqueified natural gas (LNG) marine traffic, 2005.
Vink, K.J., and Nagelvoort, R.K., Comparison of baseload liquefaction processes, *Twelfth International Conference on Liquefied Natural Gas*, Gas Technology Institute, Chicago, IL, 1998.
Wagner, J.V., Marine transportation of compressed natural gas, *Second Topical Conference on Natural Gas Utilization*, 2002.
Wagner, J.V., and Cone, R.S., Floating LNG concepts, *Eighty-Third Annual Gas Processors Association Convention*, Tulsa, OK, 2004.
Wilkinson, R., Queensland's CSG-LNG plants unlikely to reach full capacity, *Oil Gas J., 117*(3), 27, 2019.
Williams, V.C., Cryogenics, *Chem. Eng., 77*(25), 92, 1970.

WEB SITES

The Center for LNG, www.lngfacts.org/: Home site for organization that provides information on issues relating to LNG. It has many links to other related sites.
California Energy Commission, www.energy.ca.gov/lng/index.html: Home page for LNG at the state energy commission. Provides an overview of LNG beyond California and contains many links.
LNG Journal home page, www.lngjournal.com/: Page contains news stories related to LNG on worldwide basis.

19 Capital Costs of Gas Processing Facilities

19.1 INTRODUCTION

Completely objective capital cost data for any kind of major plant facilities, for obvious reasons, are rarely available in the open literature. However, a report by Tannehill and Chandra (2018) provides estimated capital costs for grass-root facilities. These data are unique in that they represent consensus values based on input from numerous engineering firms and operating companies, representing actual plant cost data. With the authors' permission, the data are presented here.

Numerous assumptions and qualifications to the costs are outlined below. These cost data should be used only as a quick guide to a first estimate of capital costs. An added contingency of 20%–40% that covers other project costs and costs unique to each facility is realistic (see Table 19.1).

After a discussion on the basic premises that apply to all cost data, this chapter presents cost data along with the premises for the costs of the major components in a gas plant. Note that the total capital cost of a plant can be obtained by adding the various plant component costs. The advantage is that the cost can be based on variables such as inlet concentrations of H_2S, CO_2, and C_2^+ liquids. An example of a plant estimation is provided at the end of the chapter.

The project may require inlet or outlet compression. Installed capital cost for compression can be estimated at between $2,000 and $3,000 per horsepower. (Note that outlet compression for cryogenic plants is included in the cryogenic plant component cost.)

19.2 BASIC PREMISES FOR ALL PLANT COMPONENT COST DATA

Table 19.1 presents the basic premises that apply to all of the cost data presented in this chapter for plant components. These data apply only to new, grass-root facilities, and are not applicable to retrofits or used equipment. Tannehill and Chandra (2018) estimate that costs excluded in Table 19.1, plus other contingencies, constitute an additional 25%–40% to the total costs. All costs are on a total installed basis using 2017 U.S. dollars and assuming a U.S. Gulf Coast basis.

TABLE 19.1
Premises and Assumptions for All Capital Cost Data

Costs Include	Costs Exclude[a]
2017 U.S. Gulf Coast location	Miscellaneous equipment associated with grassroots plant
Those directly associated with process	Costs not directly associated with process
Two month startup operating expense	Site and site preparation
Initial supplies and minimum spare parts	Owner home office costs
Sales taxes	Interest on investment during construction
Contingency of 10%	Construction insurance and bond costs
New facilities only	

Source: Tannehill and Chandra (2018).

[a] Excluded costs range from 25% to 40% of total plant costs.

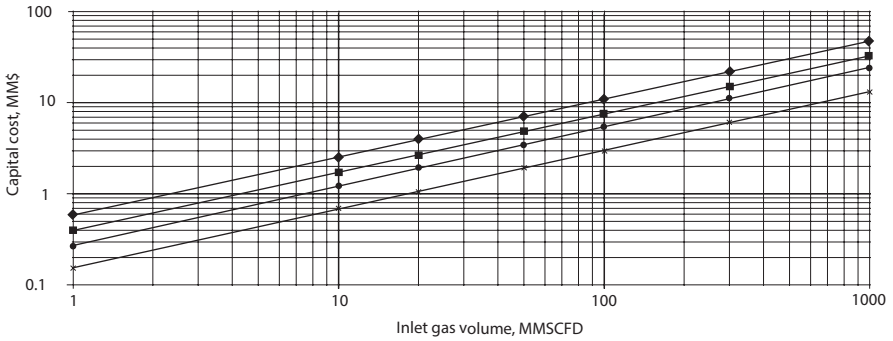


FIGURE 19.1 Capital cost of gas treating by use of DEA as a function of plant capacity in 2017. The lines denoted by x, ●, ■, ◆ denote 2%, 5%, 10%, and 20% acid gas removal, respectively. See Table 19.1 and text for premises (Tannehill and Chandra, 2018).

19.3 AMINE TREATING

Figure 19.1 shows the capital cost for new facilities that remove various amounts of acid gases (CO_2 and H_2S) as a function of plant capacity. The costs assume the following:

- Use of DEA (see Chapter 10) as solvent
- Operating pressure of 600–800 psig (40–55 barg)

Although this figure is specifically for DEA based treating, capital costs of MDEA units are comparable.

Costs exclude the dehydration of gas after treating. Operating and capital costs increase with acid gas volume to be removed because both absorber and regenerator capacities must increase to handle increased amine circulation rates.

The majority of new gas plants being built in the United States in 2018 process shale gas which contains little or no H_2S. When sulfur rates are approximately 400 lb_m/d (180 kg/d) or less scavengers are attractive (see Section 10.7 for details). Capital costs are minimal for scavenger processes (Chandra, A., Private Communication, 2018). Echt et al. (2017) provide process configurations and some economics for scavengers.

19.4 GLYCOL DEHYDRATION

Figure 19.2 gives the capital cost of new glycol dehydration facilities (see Chapter 11). These costs are based on the following:

- Using TEG as the absorbent
- Having BTEX containment equipment
- Operating at pressures of 600–800 psig (40–55 barg)

The cost is for a standard glycol unit and does not include enhancements to yield lean glycol concentrations of greater than about 98.6 wt%. Adding the capital costs for both amine and glycol processes gives the overall cost for gas treating and dehydration.

19.5 NGL RECOVERY WITH STRAIGHT REFRIGERATION (LOW ETHANE RECOVERY)

Figure 19.3 provides costs for a straight refrigeration process (see Chapter 12) to produce a single mixed NGL product stream. The figure shows how an increase in the liquids content (on C_3^+ basis)

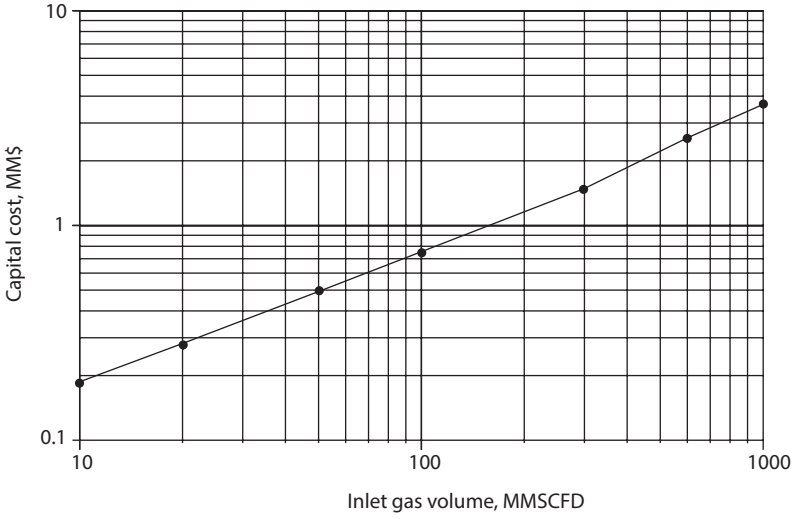


FIGURE 19.2 Capital cost of TEG dehydration in 2017. See Table 19.1 and text for premises (Tannehill and Chandra, 2018).

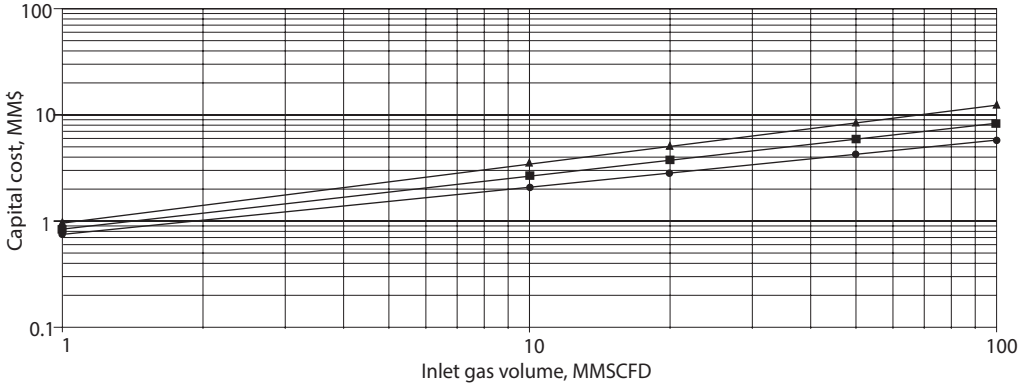


FIGURE 19.3 Capital cost of NGL recovery with straight refrigeration in 2017. See Table 19.1 and text for premises. The lines denoted by ●, ■, ▲ represent 1.5, 3, and 6 GPM (0.2, 0.4 and 0.8 m^3 liquid/1,000 m^3gas) on a C_3^+ basis, respectively (Tannehill and Chandra, 2018).

affects the cost. Costs include limited storage and use of ethylene glycol injection for hydrate inhibition. Glycol regeneration costs are included. However, the costs exclude any cost of upstream compression or treating. Costs also exclude any fractionation of the liquid product. It excludes any outlet gas compression because the pressure drop is small through the unit.

Going from a lean gas (1.5 GPM (gal/Mscf), 0.2 m^3 liquid/1,000 Nm^3 gas) to a rich gas (6 GPM, 0.8 m^3 liquid/1,000 Nm^3 gas) doubles the capital cost for large plants, primarily because of the increased refrigeration load required. Refrigeration plants are rarely larger than 30 MMscfd (0.8×10^6 Nm^3).

19.6 NGL RECOVERY WITH CRYOGENIC PROCESSING (HIGH ETHANE RECOVERY)

Figure 19.4 shows capital costs for recovering C_2^+ by use of cryogenic processing (see Chapter 12). Table 19.2 gives the premises used for the cost in 2017.

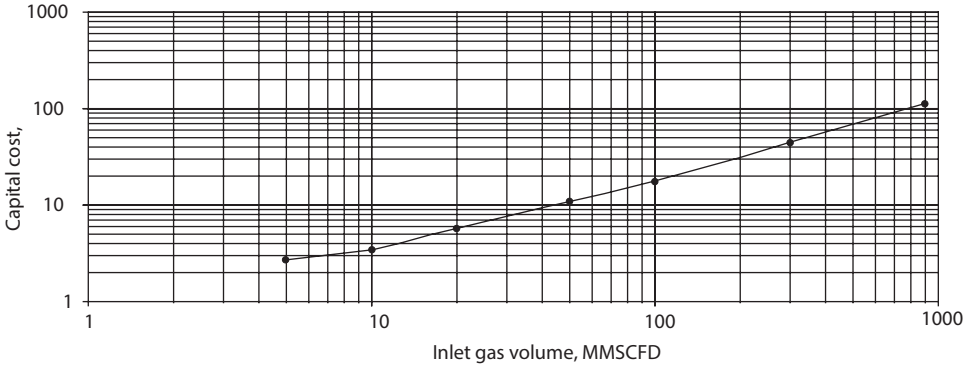


FIGURE 19.4 Capital cost of NGL recovery with cryogenic processing with no nitrogen rejection (Tannehill and Chandra, 2018).

TABLE 19.2
Premises for Cryogenic Processing Capital Costs

Costs Include	Costs Exclude
Molecular sieve dehydration	Feed gas treating
Limited storage	Compression of feed gas
Recompression of residue gas to plant inlet pressure	Additional fractionation of demethanizer bottoms product
	Nitrogen rejection

Source: Tannehill and Chandra (2018).

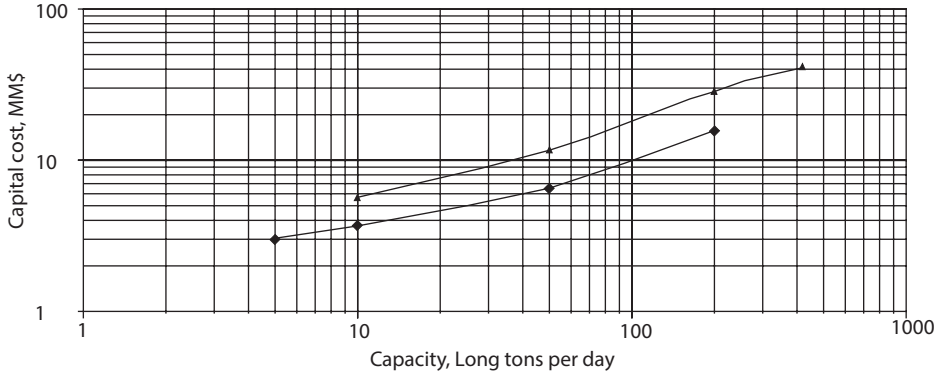


FIGURE 19.5 Capital cost of modified Claus sulfur recovery processes with tail gas cleanup, in 2017. The symbol ♦ denotes processes using an incinerator and ▲ denotes Claus with SCOT® tail gas cleanup. See Tables 19.1, 19.3, and 19.4 for premises (Tannehill and Chandra, 2018). (One long ton = 2,240 lb = 1,018 kg)

19.7 SULFUR RECOVERY AND TAIL GAS CLEANUP

19.7.1 Sulfur Recovery at High Capacities

For processing gas that produces more than about 50 long tons per day (50 metric tons per day) of elemental sulfur, modified Claus units with tail gas cleanup are the most economical processes to meet sulfur emissions requirements. Figure 19.5 shows capital costs for a Claus sulfur recovery

TABLE 19.3
Premises for Capital Costs of Claus Unit Sulfur Recovery Process

Costs Include	Costs Exclude
Claus unit with three reactor beds and indirect reheat	Treating natural gas to obtain H_2S
Feed gas H_2S content of >80% with sulfur recovery rates of 94%–97%	Process for enriching feed gas with high CO_2 content
Only boiler and condenser waste heat recovery	
Incinerator and limited storage	

Source: Tannehill and Chandra (2018).

TABLE 19.4
Premises for Capital Costs of SCOT® Tail Gas Cleanup Unit

Costs Include	Costs Exclude
Amine-based cleanup by use of selective solvent (e.g., MDEA)	Heat recovery by steam generation
Direct-fired heater	Off-site disposal of purge water
Reducing gas generator	
Maximum use of air-cooled heat exchangers	

Source: Tannehill and Chandra (2018).

unit having a SCOT® tail gas cleanup process (see Chapter 16) as a function of sulfur production. Table 19.3 gives the premises used for generating cost of the Claus unit; Table 19.4 lists the premises for the SCOT® tail gas unit.

19.7.2 Sulfur Recovery at Low Capacities

For production of less than about 50 long tons per day of elemental sulfur, a number of processes that make a direct conversion of H_2S into elemental sulfur are economically viable. Amine treating may or may not be used. One commonly used technology is liquid redox (see Chapter 16). Figure 19.6 shows the capital costs for one process, the AutoCirc LO-CAT® process for sulfur production rates up to 20 long tons per day. The costs assume the feed is a concentrated H_2S stream coming from a conventional amine treater. Table 19.5 lists the premises for the costs. Incinerator costs could not be included because of the wide variation in the CO_2 and other inerts in the feed gas.

For sulfur production rates of 1 LTD or less, the stream can be treated with a liquid-filled absorber and round oxidizer. The produced sulfur is disposed of in a landfill. Higher sulfur rates require a sulfur melter to produce a sulfur cake that can be marketed.

Example 19.1

A plant is to be designed to process 100 MMscfd (2.7×10^6 Nm^3/d) of natural gas containing 5% CO_2 and a small amount of H_2S. Inlet gas pressure is 400 psig and sales gas pressure is 1,000 psig. Estimate the plant capital cost based on the following premises:

The gas is treated at 400 psig with amine to remove the CO_2 and H_2S.

Conventional glycol provides initial dehydration.

Gas is compressed from 350 to 1,000 psig to provide refrigeration for cryogenic NGL recovery and requires 7,000 hp. (Use average compressor cost.)

Stripped H_2S is converted to 5 long ton/d (LT/d) of solid sulfur using the liquid-redox process. Plant produces sales gas, a raw NGL stream and elemental sulfur.

Solution

Each of the component costs are tabulated below:

Amine treating cost for 5% acid gas removal (Figure 19.1)	$5.0 MM
Glycol dehydration cost (Figure 19.2)	$6.3 MM
Compression cost (7,000 hp × $1,400/hp)	$9.8 MM
Cryogenic NGL recovery cost (Figure 19.4)	$18.0 MM
Liquid-redox sulfur recovery at 5 LT/d (Figure 19.6)	$6.5 MM
Total cost of components	$42.6 MM
Other costs and contingency at 30%	$12.8 MM
Total estimated plant cost	$55.4 MM

Note that configuration used glycol dehydrator to reduce water content. Molecular sieve dehydration is required but the cost is included in the total cost for cryogenic hydrocarbon recovery.

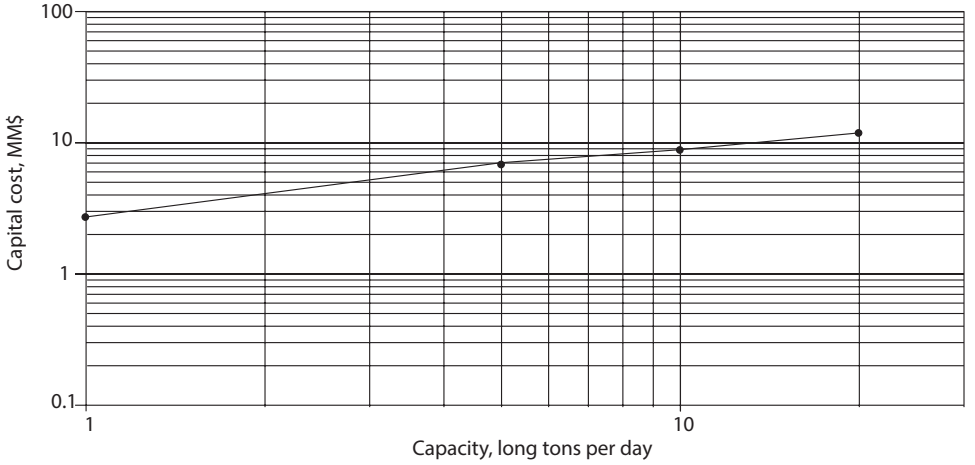


FIGURE 19.6 Capital cost of liquid-redox sulfur recovery process. See Tables 19.1 and 19.5 for premises (Tannehill and Chandra, 2018).

TABLE 19.5
Premises for Liquid-Redox Sulfur Recovery Process Capital Costs

Costs Include	Costs Exclude
Sulfur melter if >1 TPD of sulfur	Preconditioning or filtering of feed gas
Initial supplies and minimal spare parts	Treating natural gas to obtain acid gas stream
Limited storage	Incinerator

Source: Tannehill and Chandra (2018).

TABLE 19.6
Approximate Distribution of Cost Components for Gas Processing Facilities

	Percent of Total Installed Cost	
Cost Component	**NGL Recovery (%)**	**Amine Treating, Dehydration, Sulfur Recovery (%)**
Pumps, compressors, etc.	10	20
Electrical machinery	5	5
Internal combustion engines	25	0
Instruments	5	5
Heat exchangers	15	20
Miscellaneous equipment (average)	5	5
Materials	15	25
Labor	20	20

Source: Chandra, A., Private Communication (2018).

19.8 CORRECTIONS TO COST DATA

A number of corrections are required for use of the above cost data for the preparation of preliminary cost estimates. The three major factors are time of construction, location, and inflation. Providing these data is beyond the scope of this book.

Estimated time for construction is important for planning but also affects economics in terms of tied up capital, interest cost, and when the plant will produce revenue. Beginning around 2015, large construction companies began offering modular plants sized at 60 MMscfd (1.7×10^6 Nm^3/d) and 200 MMscfd (5.4×10^6 Nm^3/d). Plant sizes could be set by selecting the proper combinations of number of trains. Construction times of 18 months are typical in the Gulf Coast region. Building in colder climates may extend construction times (Chandra, A., Private Communication, 2018).

Initial estimates of inflation can be made using cost index data available in trade journals. Table 19.6 lists the approximate breakdown of costs for the various processes discussed above. Any cost index can be used if values for 2017 are known. For example, the CE Plant Cost indices in Chemical Engineering can be used to update the cost curve data by using the percentages given in Table 19.6.

DISCUSSION QUESTIONS

1. Figure 19.1 shows that the capital costs increase with increasing volumes of acid gas removed. What factors account for this increase in capital cost?
2. How are plant operating costs affected by the amount of acid gas removed?
3. Figure 19.3 shows that capital costs increase with increasing liquids content of inlet gas whereas Figure 19.4 does not. Why is liquids volume content more of a cost factor for low ethane recovery than for high ethane recovery?
4. What justification is there for Table 19.2 to exclude additional demethanizer bottoms product fractionation?
5. What are the advantages and disadvantages of using modular plants for high ethane recovery unit?

REFERENCES

Echt, B., et al., Fundamentals of low-tonnage sulfur removal and recovery, *Laurance Reid Gas Conditioning Conference*, Norman, OK, 2017.

Tannehill, C.C., and Chandra, A., Budget estimate capital cost curves for gas conditioning and processing – Updated 2018, CCCP-18, GPA Midstream Association, 2018. https://gpamidstream.org/publications/category/?id=3 (Retrieved April 2019).

Taylor & Francis
Taylor & Francis Group
http://taylorandfrancis.com

20 Natural Gas Processing Plants

20.1 INTRODUCTION

The objective of this chapter is to show how the processes discussed in Chapters 8–16 are blended together to form a complete processing plant. This chapter discusses three modern plants with significantly different feed and product slates:

- A 500 MMscfd (13×10^6 Nm^3/d) plant with sweet gas feed and 98% ethane recovery.
- A 279 MMscfd (7.5×10^6 Nm^3/d) plant with sour gas feed and both NGL and sulfur recovery.
- A 7.1×10^6 Nm^3/d (265 MMscfd) plant with sour gas feed, NGL recovery, and nitrogen rejection.

Block schematics for each plant provide an overview of processing schemes. Details come from the open literature. Feed and product slates change with time, and plant modifications are common. Therefore, current plant configuration and operating conditions may differ from those discussed here.

20.2 PLANT WITH SWEET GAS FEED AND 98% ETHANE RECOVERY

Mallett (1988) provides an excellent description of the San Juan gas plant located in New Mexico. Figure 20.1 shows a block schematic of the plant, which is capable of processing 500 MMscfd (13×10^6 Nm^3/d) of low-sulfur gas, with the emphasis on obtaining extremely high ethane recovery. To accommodate limitations on equipment sizes and to minimize the loss of productivity during equipment downtime, gas is processed in two identical 250 MMscfd (6.7×10^6 Nm^3/d) streams. The streams split after the heat exchange section. There are parallel dehydration units, propane chillers, and cold boxes containing a demethanizer. Liquids recombine after the demethanizers while the sales gas recombines after outlet compression. It generates its own power by use of gas turbines and relies heavily upon centrifugal compressors.

20.2.1 Overview of Plant Feed and Product Slate

The San Juan plant feed is sweet, that is, it contains less than the maximum allowable limit of both sulfur compounds and carbon dioxide (refer to Chapter 6 for pipeline gas specifications). Table 20.1 lists the compositions of both the inlet gas and the products.

The feed gas is rich in liquids, which are removed to produce a marketable sales gas. At the same time, the plant generates a profit from the extracted liquids. While recovering 98% of the ethane, the plant also recovers 100% of the C_3^+ for a total liquids production of 42,000 bpd (6,700 m^3/d). The plant is designed to produce ethane–propane–butane–condensate (EPBC) liquid or propane–butane–condensate (PBC) liquid products. Relative gas and liquid prices (frac spreads) dictate the optimum distribution of ethane between the liquid product and residue sales gas streams. Liquids leave the plant via pipeline.

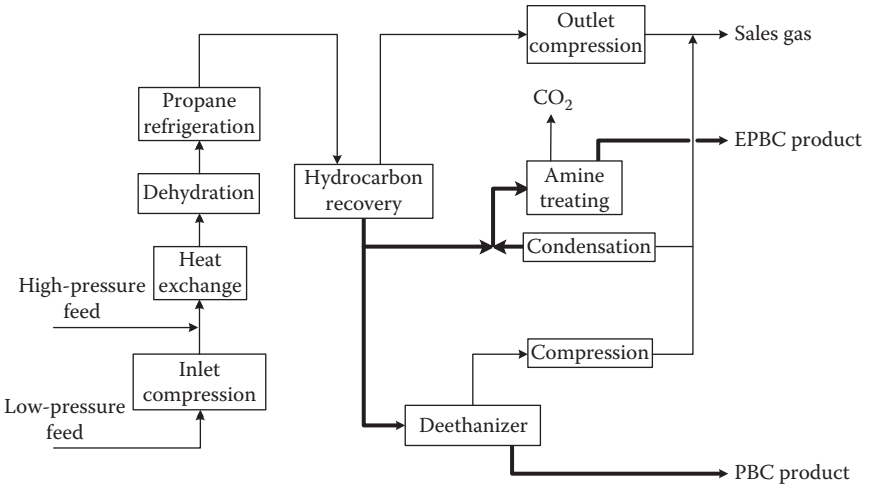


FIGURE 20.1 Simplified block schematic of the San Juan gas plant. The light and heavy lines denote gas and liquid streams, respectively (Mallett, 1988). See text for details.

TABLE 20.1
Feed and Product Compositions for the San Juan Plant

	Gas Compositions (mol%)	
Component	**Feed Gas**	**Sales Gas**
N_2	0.55	0.64
CO_2	1.13	0.54
C_1	85.57	98.67
C_2	7.60	0.15
C_3	3.03	0
iC_4	0.53	0
nC_4	0.78	0
C_{5+}	0.81	0
Gallons/Mscf (m^3 [liq]/1000 Nm^3 [gas])	3.59 (0.507)	0.04 (0.006)
Btu/scf (MJ/Nm^3)	1154.9 (45.48)	978.9 (38.55)
Volume, MMscfd (10^6 Nm^3/d)	500 (13)	420 (11)
	Product Liquids (mol%)	
Component	**EPBC[a]**	**PBC[b]**
N_2	0	0
CO_2	0	0
C_1	0.9	0
C_2	58.6	0.7
C_3	23.8	54.2
iC_4	4.2	11.2
nC_4	6.1	16.6
C_{5+}	6.4	17.3

Source: Mallett (1988).

[a] Liquid mixture of ethane, propane, butane, and condensate.

[b] Liquid mixture of propane, butane, and condensate.

20.2.2 Inlet Compression

The plant receives both high-pressure (320 MMscfd [8.6×10^6 Nm^3/d], 850 psig [59 barg]) and low-pressure (120 MMscfd [3.2×10^6 Nm^3/d], 350 psig [24 barg]) inlet gas feed. The low-pressure feed is compressed to 850 psig (59 barg) using 1,100 hp (0.82 MW) of centrifugal compression and then enters the heat exchange block with the high-pressure gas.

20.2.3 Heat Exchange

The combined gas stream is cooled to 80°F (30°C) in a water-cooled heat exchanger to condense as much water as possible before the stream splits and enters the two parallel trains. (The gas that enters the plant contains water, but the water is not reported as a component in the inlet feed composition (Table 20.1). Most gases that enter a gas plant contain water vapor, but standard practice is not to include water as a component when reporting the composition.)

20.2.4 Dehydration

Recovery of more than 60% of the ethane requires cryogenic processing and, consequently, water must be removed to a dew point of –150°F (–100°C). Dehydration in each train is accomplished by use of three molecular sieve adsorption beds. Two beds are always adsorbing on 16 h cycles, while one bed is undergoing regeneration using 14 MMscfd (0.38×10^6 Nm^3/d) of dehydrated gas.

20.2.5 Propane Refrigeration

As is common practice for cryogenic gas plants propane refrigeration provides much of the initial cooling. Propane refrigeration supplies 64% of the plant cooling requirements. The centralized system uses three electric motor driven centrifugal compressors and has an economizer.

20.2.6 Hydrocarbon Recovery

This section of the plant is a proprietary design that uses cold reflux in the demethanizer but is similar to other residue recycle processes. The turboexpander provides the remaining 36% of the required refrigeration. The turboexpander drops the gas pressure from 850 psig (59 barg) to 350 psig (24 barg) to provide the –150°F (–100°C) feed to the top of the demethanizer. The turboexpander operates at 14,000 rpm and provides 4,800 hp (3.6 MW) of residue gas compression.

The demethanizer in each train has 28 valve trays and operates at 350 psig (24 barg) and temperatures of –150°F (–100°C) at the top to 63°F (17°C) at the bottom. Four reboilers (upper side, lower side, bottom, and trim) are used. (The "trim" reboiler is a second reboiler in series with the bottom reboiler to provide control of the bottoms temperature.) By use of cold reflux in the top of the tower, the overhead residue gas product can be up to 98.7% methane. The bottoms product is the EPBC stream that feeds the deethanizer or can be used as a product stream. Although the CO_2 content of the inlet gas to the plant is only 1.13%, the CO_2 concentrates in the demethanizer bottoms, and the EPBC liquid stream contains 5% CO_2. Consequently, additional purification is required for the liquid stream.

20.2.7 Amine Treating

The EPBC stream from the demethanizers split with one branch feeding the deethanizer and the other flowing to the amine treating unit. The amine treater operates at 655 psig (45 barg) and 85°F (30°C) and uses a 30 wt% diethanolamine solution to remove the CO_2. Activated alumina beds are

used to remove water and amine in the liquid EPBC before it goes to storage. Rich amine passes through a hydrocarbon coalescer, flash vessel, and sock filter to remove hydrocarbons and impurities before being regenerated. This stream must have minimal hydrocarbons in it to avoid foaming in the regenerator.

20.2.8 Deethanizer

The tower contains 35 valve trays and operates at 400 psig (28 barg), with overhead and bottoms temperatures of 58°F (14°C) and 220°F (104°C), respectively. The PBC bottoms product goes to storage, whereas the overhead stream is partially condensed by use of propane refrigeration to provide reflux to the column. The vapor from a reflux accumulator is compressed and joins the sales gas stream or is condensed and sent to the amine treater.

20.2.9 Outlet Residue Sales Gas Compression

Each demethanizer overhead is first compressed by the compressor coupled to the turboexpanders, which generate 4,800 hp (3.6 MW) each. The final sales gas stream pressure of 850 psig (59 barg) is obtained by using two parallel 15,000 hp (11 MW) gas turbine-driven centrifugal compressors.

20.3 PLANT WITH SOUR GAS FEED, NGL, AND SULFUR RECOVERY

The Whitney Canyon plant, located in Wyoming, is an excellent example of a large plant that processes a sour gas, extracts NGL, and recovers large quantities of sulfur. Figure 20.2 is a block diagram that shows only the major processes at Whitney Canyon. The discussion in this section focuses on those processes emphasized in this book and is consequently very limited. Webber et al. (1984) present a very detailed discussion of the entire project, and the material presented here is taken from their paper. This section discusses some of the changes in processing required when relatively high H_2S concentrations are present.

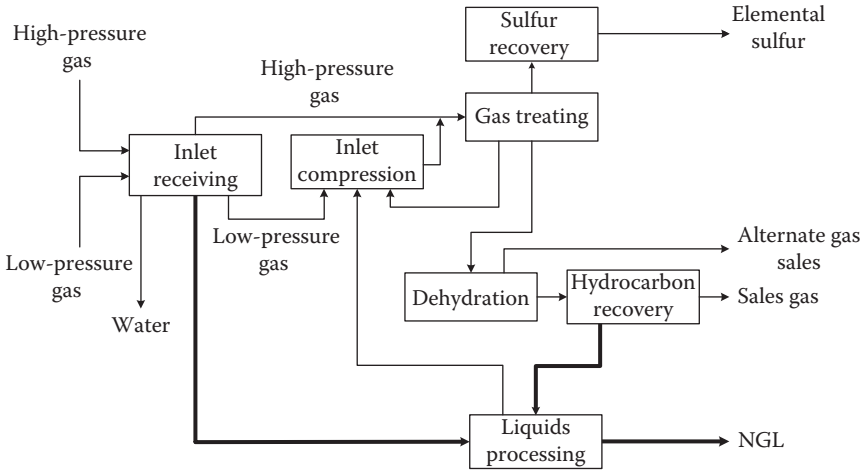


FIGURE 20.2 Simplified block schematic of the Whitney Canyon plant (Webber et al., 1984). See text for details.

20.3.1 Overview of Plant Feed and Product Slate

The plant was dedicated in late 1982 and lies near the producing field. The field contains 17 wells that produce from four different formations that range in depth from 9,000 ft (2,700 m) to 16,500 ft (5,000 m). The H_2S concentration in the gas varies from 1% to 19%, depending on the well and producing formation. Because of the large variability of the feed gas, no feed or product stream compositions were reported. The plant can handle 270 MMscfd (7.2×10^6 Nm^3/d) of feed and produce 200 MMscfd (5.4×10^6 Nm^3/d) of sales gas, 13 Mbbl/d (2,100 m^3/d) of NGL, 6 Mbbl/d (950 m^3/d) of condensate, and 1,200 long ton/d (1,220 t/d) of elemental sulfur. Sulfur is trucked to rail cars. All other products are pipelined from the plant.

20.3.2 Inlet Receiving

Both low-pressure and high-pressure gas from the gathering system enter inlet receiving, where water and condensate are separated from the gas. After removal of dissolved H_2S, the water is sent to disposal wells. The condensate and gas enter the plant in separate lines that operate at approximately 1,000 psig (70 barg) and 250 psig (17 barg), respectively. All inlet receiving facilities are located in a valley 800 ft (240 m) lower in elevation than the rest of plant to avoid slug flow into the gas going to inlet compression and gas treating.

An important feature of the inlet facility is control of the temperature of gas and condensate to manage hydrocarbon dew point and prevent hydrate formation. The paper does not provide details of these processes or the stripping of H_2S from the water.

20.3.3 Inlet Compression

The high-pressure gas from inlet receiving goes directly to gas treating, whereas the low-pressure gas is compressed by two 1,500 hp (1.1 MW) compressors before it joins the high-pressure stream at gas treating. Another pair of compressors process gas from condensate stabilization and from the amine treating flash tank, so that the gas can be blended with the high pressure gas. Both streams are discussed in the following paragraphs.

20.3.4 Gas Treating

Gas sweetening is accomplished in two identical parallel trains. Each consists of an amine unit that uses a 35 wt% solution of diethanolamine to remove the H_2S to less than one-quarter grain H_2S/100scf (6 mg/Nm^3) and the CO_2 to a level sufficiently low to prevent freezing in the hydrocarbon recovery process. The amine circulation rate for each train is 2,700 gpm (610 m^3/h), with a rich-amine loading of 0.75 mol acid gas per mole of amine. This treating system differs from many in that both high-pressure and low-pressure contactors are used.

Lean amine goes to both the high-pressure and low-pressure contactors. In the high-pressure contactor, sour gas contacts the amine at 95°F (35°C) and 1,000 psig (69 barg) and uses both lean and semi-lean amine from the regenerator. The lean amine enters at the top of the high-pressure contactor. The semi-lean amine is a partially regenerated stream from a side draw on the regenerator. It enters about midway on the contactor. The high-pressure rich amine is expanded through a power-recovery turbine to 250 psig (17 barg) and goes to a low-pressure flash tank for removal of dissolved hydrocarbons.

The gas from the flash tank also contains H_2S. This gas joins the condensate stabilizer overhead gas and goes to a low-pressure contactor (250 psig, 17 barg), where it contacts lean amine. The sweet gas then returns to inlet compression.

20.3.5 Sulfur Recovery

The acid gas from gas treating goes to a two-train, straight-through Claus process for primary (95%) sulfur recovery. The waste-heat boiler from the Claus process provides much of the plant steam. Each train has two Claus reactors and sulfur condensers.

Final recovery of the sulfur is accomplished using the cold-bed adsorption (CBA) process, with two CBA reactors per train. The overall recovery of sulfur is greater than 99%. Effluent from the CBA reactors goes to an incinerator for conversion of all remaining sulfur compounds to SO_2, which is then vented into the atmosphere through a stack.

The molten sulfur is trucked 32 mi (51 km), in specially designed, oversized trailers using a private road from the plant to a rail terminal.

20.3.6 Dehydration

After acid gas removal in the gas treating section, the two gas streams recombine and go to dehydration. Glycol dehydrator and molecular sieve adsorption beds are used in series. The triethylene glycol dehydrator removes the bulk of the water, but it cannot achieve the necessary removal (to less than 0.1 ppm water) for cryogenic processing, so the second dehydrator, a four-bed molecular sieve unit, is used for final purification. Two beds are in adsorption while one undergoes regeneration. The four bed configuration permits changing adsorbants in one bed without a plant shutdown. When NGL recovery is not required (no cryogenic units needed), the molecular sieve beds can be bypassed with the gas going to alternate gas sales.

20.3.7 Hydrocarbon Recovery

The dehydrated gas stream goes to a cryogenic hydrocarbon recovery where up to 88% of the ethane in the gas is removed. The plant design allows operation in either an ethane recovery or ethane rejection mode, depending on the current economic situation. Refrigeration is obtained from heat exchange and gas expansion using a turboexpander before the cold fluids go to a demethanizer. When rejecting ethane, the propane recovery rate is still 97%.

20.3.8 Liquids Processing

This section of the plant has two separate units: condensate stabilization and NGL treating. Condensate stabilization consists of taking the liquids from inlet receiving, water washing them to remove salt, and then processing them in a stabilizer. The stabilizer uses a sweet stripping gas, combined with a direct-fired reboiler to reduce the condensate H_2S level to less than 10 ppm and strip light hydrocarbons. The overhead from the stabilizer combines with treater flash tank gas and goes to a low-pressure amine gas treating column before returning to inlet compression.

The natural gas liquids are amine treated with a 30 wt% diethanolamine solution to remove acid gases, and then dehydrated, refrigerated, and transferred to storage. To perform satisfactorily, the amine used for treating liquids must have lower residual acid gas content than required for gas treating to meet liquid sulfur specifications.

20.4 PLANT WITH SOUR GAS FEED, NGL RECOVERY, AND NITROGEN REJECTION

The Hannibal plant, located in Sfax, Tunisia, processes gas recombined with condensate received from a platform 70 mi (110 km) offshore over the Miskar field. In full operation since 1996, it provides 80% of the gas used in Tunisia. Jones et al. (1999) and Howard (1998) give complete discussions of the plant. Figure 20.3 is a block diagram of the major processing steps. The primary

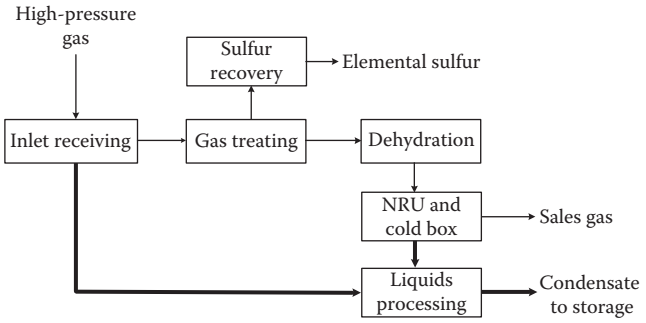


FIGURE 20.3 Block schematic of the Hannibal gas plant (Howard, 1998; Jones et al., 1999).

functions of the plant are to recover the liquids, reduce the acid gas content, and to greatly reduce the nitrogen content to provide a sales gas.

20.4.1 Overview of Plant Feed and Product Slate

Inlet pressure is approximately 1,200 psig (83 barg) and delivery pressure is up to 1,100 psig (75 barg). The design feed gas composition is shown in Table 20.2. The plant processes 7.1×10^6 Nm^3/d (265 MMscfd) of gas and produces 4.9×10^6 Nm^3/d (180 MMscfd) of sales gas. The sales gas specifications include:

- No H_2S present (no concentration specification given)
- N_2 not to exceed 6.5 mol%
- H_2O less than 80 ppmw
- Hydrocarbon dew point less than −5°C (25°F)

TABLE 20.2
Design Feed Gas Composition for the Hannibal Plant

Component	mol%
N_2	16.903
CO_2	13.588
H_2S	0.092
C_1	63.901
C_2	3.349
C_3	0.960
iC_4	0.258
nC_4	0.286
iC_5	0.142
nC_5	0.147
C_6	0.138
BTEX	0.121
C_7 fraction	0.057
C_8 fraction	0.019
C_9 fraction	0.005
C_{10}^+	0.001

Source: Jones et al. (1999).

Reduction of the N_2 to the specified level requires cryogenic processing in the nitrogen rejection unit (NRU) (see Chapter 13). Consequently, the CO_2, H_2O, and BTEX must be removed to levels low enough to prevent freezing and plugging in the gas–gas exchangers.

20.4.2 Inlet Receiving

The feed from the Miskar field that enters inlet receiving contains both the gas and the associated wet condensate. A slug catcher separates the liquid from the gas. The liquid goes to liquids processing and the gas goes to gas treating. The slug catcher consists of six 48 in. (1,200 mm) diameter pipes that are 182 m (600 ft) long.

20.4.3 Gas Treating

An amine unit that uses 50 wt% activated-MDEA solution removes both the H_2S and the CO_2. The H_2S is removed to sales gas specifications and the CO_2 to 200 ppmv. Some BTEX is also removed by the amine; however, not enough to prevent solid deposition in the cryogenic unit. Additional removal is required and is accomplished in the dehydration section.

20.4.4 Sulfur Recovery

The acid gases from the amine unit are treated for sulfur removal by use of the liquid-redox LO-CAT™ process. A Claus unit was not utilized because the sulfur production rate is only approximately 10 t/d (9.8 LTD).

20.4.5 Dehydration

Water removal is accomplished by use of two dehydrators, a triethylene glycol unit followed by molecular sieve adsorption beds. Although the glycol dehydrator reduces the load on the adsorption beds, it was designed for removing the bulk of the BTEX to prevent freezing in the cryogenic NRU. That turned what is often considered an environmental issue into an asset. The glycol regenerator operates at around 190°C (375°F). The overhead reflux drum runs at 0.2 barg (3 psig) and 28°C (80°F), where the water and BTEX are separated, and the BTEX goes to condensate storage.

20.4.6 NRU and Cold Box

The cold box contains a series of heat exchangers to condense the heavier hydrocarbons along with both warm and cold vapor–liquid separators. Only Joule–Thomson (J–T) expansion is used for cooling. After heat exchange using aluminum plate-fin heat exchangers, the liquid from the warm separator (−42°C, −44°F) goes to liquids processing; the gas is chilled, partially condensed, and sent to the cold separator (−67°C, −89°F). The liquid from the cold separator ultimately combines with the liquid from the NRU to become part of the sales gas. The vapor from the cold separator is chilled, condensed, and expanded through a J–T valve into the NRU. In the NRU, dual-column cryogenic distillation is used to separate the N_2 from the hydrocarbons. The N_2 is vented, and the sales gas stream contains less than 6.5% N_2, to meet specifications.

20.4.7 Liquids Processing

In this plant, liquids processing consists of sending the condensate from inlet receiving and the liquids from the cold box to a distillation system, where the lighter components are removed to adjust the vapor pressure of the remaining liquid to a specific value (condensate stabilization).

The stabilized condensate (Reid vapor pressure of 12 psi [0.8 bar]) is then sent to storage. The paper provides no details on the fate of the gas from the stripper or on the treating and disposition of the NGL stream.

DISCUSSION QUESTIONS

1. The San Juan plant uses cogeneration for power generation. Which kinds of contracts with producers make cogeneration attractive and why?
2. The San Juan plant can recover up to 98% of the ethane and can profit by selling the liquids. When, if ever, would it be more profitable not to maximize ethane recovery?
3. It is noted that water is not included in the gas analysis. Why is this customary practice?
4. The San Juan plant uses parallel trains for portions of the plant. Why use parallel trains instead of one large train?
5. Some of the plants use propane refrigeration while others do not. What are the major factors in deciding when propane refrigeration is required?
6. List two or three processing features in the Whitney Canyon plant that are the result of the very high sulfur content feeds being processed.
7. Whitney Canyon plant uses a stripping gas to remove H_2S from condensate, which is then sent to inlet compression. What are the advantages and disadvantages of using a stripping gas?
8. The Hannibal plant uses a pipe design for the slug catcher. Why is this preferred to using just a large inlet receiver?

EXERCISES

20.1 Table 20.1 gives the liquids content of the feed. Is this on a C_2^+ or C_3^+ basis?

20.2 The San Juan gas plant (Section 20.2) generates 8.8 MW of electrical power to run the gas plant. Assuming that the gas turbine has a heat rate of 7,200 Btu/hp-h (10,000 kJ/kWh), what fraction of the inlet gas (assuming plant is at stated capacity) is consumed in power generation? Table 20.1 gives the sales gas composition. Assume sales gas is used for fuel and the efficiency of the generator is 100% for these calculations.

20.3 Section 20.2.4 states that 14 MMscfd (0.4×10^6 Nm^3/d) of dehydrated gas is used to regenerate the molecular sieve beds. Assume that sales gas (see Table 20.1 for composition) fires the regeneration furnace. Using the assumptions below

a. Estimate how much sales gas (Mscf, Nm^3) would be consumed in one bed regeneration.
b. Estimate energy consumed (Btu, MJ) by furnace and regeneration compressor in one bed regeneration.

Assumptions:

1. The furnace is 80% efficient (LHV basis), runs for 6 h in regeneration, and heats gas from 80°F (27°C) to 500°F (260°C). The average C_P is 0.66 Btu/lb$_m$-°F (2.76 kJ/kg-°C) for the gas in the regeneration furnace.
2. Cool regeneration gas runs through the bed for 2 h.
3. Regeneration gas leaves bed at 800 psig (55.2 barg) during heating and cooling steps. The gas enters the recycle compressor at 80°F (27°C) and the discharge pressure is 850 psig (58.6 barg). Use $\gamma = 1.25$ for compressor calculations. Overall adiabatic compressor efficiency is 76% (includes driver and compressor).

20.4 Section 20.3.4 describes the acid gas treating section of the Whitney Canyon Plant where high and low pressure contactors are used. The plant also uses partially regenerated amine in the gas treater. Based on information given, sketch the process flow diagram for the treating and regeneration system of one of the two parallel trains. Show only the components and lines mentioned in section.

REFERENCES

Howard, I., Hannibal's experiences, *Proceedings of the Laurance Reid Gas Conditioning Conference*, Norman, OK, 1998, p. 194.

Jones, S., et al., Simultaneous removal of water and BTEX from feed gas for a cryogenic plant, *Proceedings of the Seventy-Eighth Annual Convention Gas Processors Association*, Tulsa, OK, 1999, p. 108.

Mallett, M.W., Conoco/Tenneco gas plant meeting the challenges, *Proceedings of the Sixty-Seventh Annual Convention Gas Processors Association*, Tulsa, OK, 1988, p. 150.

Webber, W.W., et al., Whitney Canyon project, *Proceedings of the Sixty-Third Annual Convention Gas Processors Association*, Tulsa OK, 1984, p. 10.

Appendix A: Glossary of Gas Process Terminology

Most terms in this glossary were obtained from the Gas Processors Association (GPA Publication 1167–77, *GPA, Glossary, Definitions of Words and Terms Used in the Gas Processing Industry*, (Gas Processors Association, Tulsa, OK, 1977) and *Engineering Data Book*, Section 1, General information, GPSA Midstream Suppliers, Tulsa, OK, 2016) and the Energy Information Administration Annual Energy Review, 2019 [www.eia.gov/outlooks/aeo/pdf/aeo2019.pdf]. The remaining terms were added by the authors. The references cited are periodically updated and readers should consult the original sources for the latest updates.

Acid gas: The hydrogen sulfide and/or carbon dioxide contained in or extracted from gas or other streams.

AGI: Acid Gas Injection. See Chapter 16.

Allowable: The maximum rate of production from an oil or gas well or group of wells that is allowed by a state or governing body. The rate is set by rules that vary among the different governing bodies.

Amine: Any of several nitrogen-based compounds employed in treating natural gas. See Section 10.2.1 for details.

APC: Advanced Process Control system. A control system trained to optimize plant operations. It can supervise the basic process control system.

API Gravity: An arbitrary scale expressing the relative density (SpGr) of petroleum liquids. The measuring scale is calibrated in degrees API, which is calculated by the following formula: °API = 141.5/(SpGr. 60°F/60°F)−131.5.

Associated gas: Natural gas which is produced with crude oil or condensate.

Availability: The probability of equipment being available for service.

Azeotrope: A mixture of two or more liquid components that cannot be separated by distillation because the liquid and vapor compositions are equal.

BACT: Best Available Control Technology. Sometimes required for emissions from a new or modified emission source, such as a plant or combustion device.

Baseload plant: A large-scale natural gas liquefaction facility designed to convert from gas to LNG for transit.

Barrel: A unit of liquid volume measurement, which equals 42 U.S. gallons for petroleum or natural gas liquid products measured at 60°F and at equilibrium vapor pressure.

Baumé Gravity: An arbitrary scale expressing the relative density (SpGr) of petroleum liquids. For liquids lighter than water, the gravity Baumé can be calculated from the following equation: degrees Baumé = [140/SpGr]−130. For liquids heavier than water, the formula is: degrees Baumé = 145−[145/SpGr].

bcf: billion cubic feet (28.32×10^6 Nm^3)

Blanket gas: A gas phase in a vessel above a liquid phase. The purpose may be for protecting the liquid from air contamination, for reducing the hazard of detonation, or for pressuring the liquid. The source of the gas is external to the vessel.

Blow case: A small tank in which liquids are accumulated and drained by applying gas or air pressure above the liquid level. Such a vessel is usually located below a pipeline or other equipment, at a location where an outside power source is not convenient for removing the drained liquids. In a gathering system this is sometimes referred to as a drip.

Blowdown: The act of emptying or depressuring a vessel. This may also refer to the material such as water drained from a boiler or cooling tower.

Bottom hole pressure (temperature): The pressure (temperature) measured in a well at a depth which is at the mid-point of the thickness of the producing zone.

B–P mix: A liquefied hydrocarbon product composed chiefly of butanes and propane. If it originates from a refinery, it may also contain butylenes and/or propylene. More specifically, it conforms to the GPA specifications for commercial B–P mixes, as defined in GPA Standard 2140.

Breathing: The movement of vapor in or out of a storage tank because of the change of level of the storage liquid, a change in the temperature of the vapor space above the liquid, or change of atmospheric pressure.

BS&W: Bottom sediment and water that collects in the bottom of storage tanks. Also called tank bottoms.

BTEX: Benzene, toluene, ethyl benzene, and xylene.

Butane, commercial: A liquefied hydrocarbon consisting predominately of butane and/or butylenes, and which conforms to the GPA specification for commercial butane defined in GPA Standard 2140.

Butane, field grade: A product consisting predominately of normal and isobutane that is produced at a gas processing plant. Also called "mixed butane." It is defined in GPA Standard 2140.

Butane, normal: In commercial transactions, a product meeting the GPA specification for commercial butane and, in addition, containing a minimum of 95 liquid volume percent normal butane. It is defined in GPA Standards 2108 and 2140.

Calorific value: See Heating value.

Casinghead gas: The natural gas that is produced from a reservoir containing oil and is sometimes produced from the casing on a well.

Casinghead gasoline: An obsolete term for natural gasoline.

CFD: Computational Fluid Dynamics

Charcoal test: A test standardized by the American Gas Association (AGA) and the Gas Processors Association to determine the natural gasoline content of a given natural gas. The gasoline is absorbed from the gas on activated charcoal and then recovered by distillation. The test is described in Testing Code 101-43, a joint AGA and GPA publication.

Chromatography: A technique for separating a mixture into individual components by repeated adsorption and desorption on a confined solid bed. It is used for analysis of natural gas and NGL.

CIF: Carriage, insurance, and freight.

City-gate: A point or measuring station at which a local distribution gas utility company (LDC) receives gas from a natural gas pipeline company or transmission system.

Claus process: A process to convert hydrogen sulfide into elemental sulfur by selective oxidation.

CBM: Coal-bed methane.

Color test: A visual test made against fixed standards often specified for products to determine the color of a liquid.

Compression ratio: The ratio of the absolute discharge pressure from a compressor to the absolute intake pressure. Applies to one cylinder of a reciprocating compressor and one or more stages of a rotating compressor.

Compression tests: See Charcoal Test.

Condensate: The liquid formed by the condensation of a gas; specifically, the hydrocarbon liquid separated from natural gas because of changes in temperature and pressure when the gas from the reservoir is delivered to the surface separators. Such condensate remains liquid at atmospheric temperature and pressure.

It is also be the liquid water formed by condensation of water vapor or steam.

Condensate gas reservoir: A hydrocarbon reservoir with natural gas that will yield condensate.

Condensate well: A gas well producing from a condensate reservoir.

Connate water: Water which settled with the deposition of solid sediments and which has not existed as surface water at atmospheric pressure. Also, water in a particular formation that fills a portion of the pore space.

Copper strip test: A test using a small strip of copper to qualitatively determine the corrosivity of a fluid per ASTM D130 or D1838.

Cricondenbar: Maximum pressure at which a mixture containing both supercritical and subcritical components can form two phases.

Cricondentherm: Maximum temperature at which a mixture containing both supercritical and subcritical components can form two phases.

Critical point: For a pure component, it is the temperature and pressure where liquid and vapor densities become equal. For mixtures containing at least one component above its critical point temperature, it is the temperature and pressure where the composition of the liquid and vapor are equal.

Cryogenic plant: A gas processing plant that is capable of producing natural gas liquids which operates at very low temperatures, usually below –50°F (–45°C).

Cushion gas: Volume of gas intended as a permanent inventory in a storage reservoir to maintain adequate pressure and deliverability rates throughout the withdrawal season.

Cycle gas: Gas that is compressed and returned to the gas reservoir to minimize the decline of reservoir pressure.

Cycling: The process whereby gas from a gas reservoir is passed through a gas processing plant or separation system and the remaining residue gas returned to the reservoir.

DCS: Distributed control system. Basic process control system used to manipulate control valves and other devices to maintain a desired process value.

DEA (diethanolamine): See amine.

DEA unit: A treating system using DEA for removal of hydrogen sulfide, carbon dioxide, carbonyl sulfide, and other acid gases from process streams.

Debutanizer: A distillation column for separating butane, with or without lighter components from a mixture of hydrocarbons and leaving a bottoms product which is essentially butane free.

Deethanizer: A distillation column for separating ethane with or without lighter components from a mixture of hydrocarbons and leaving a bottoms product which is essentially ethane free.

Degree-day: A unit of temperature and time, showing the difference between a 65°F (18.3°C) base and a daily mean temperature when the latter is less than 65°F. This temperature difference is the number of degree-days for a particular day.

Deisobutanizer: A distillation column for separating a mixture of butanes into isobutane from normal butane.

Demethanizer: A distillation column for separating methane and more volatile components from a mixture of hydrocarbons and leaving a bottoms product which is essentially methane free.

Depropanizer: A distillation column for separating propane, with or without lighter components from a mixture of hydrocarbons and leaving a bottoms product which is essentially propane free.

Disulfides: Chemical compounds containing an –S–S– linkage. They are colorless liquids completely miscible with hydrocarbons, insoluble in water, and sweet to the Doctor test. Disulfides are formed by oxidation of mercaptans.

Doctor test: A qualitative method for detecting hydrogen sulfide and/or mercaptans in petroleum distillates. The test distinguishes between "sour" and "sweet" products using ASTM D4952.

Drip: See blow case.

Drip gasoline: Hydrocarbon liquid that separates in a pipeline transporting gas from the well casing, lease separation, or other facilities.

Dry gas: (1) Gas whose water content has been reduced by a dehydration process. (2) Gas containing little or no hydrocarbons commercially recoverable as liquid product. Gas in the second definition preferably should be called lean gas.

Equation of State (EOS): A mathematical expression relating pressure, temperature, and volume of a fluid. Equations are used to calculate physical properties of pure fluids and fluid mixtures. Equations commonly used in gas processing include Peng-Robinson (PR) and Soave Redlich Kwong (SRK).

EOR: Enhanced Oil Recovery. See Chapters 13 and 16.

EPC: Engineering, procurement, and construction.

EP-mix (ethane–propane mix): A product consisting of a mixture of essentially ethane and propane as defined in GPA Standard 2108

Extraction loss: The reduction in volume of natural gas due to the removal of natural gas liquid constituents such as ethane, propane, butane, and natural gasoline at natural gas processing plants.

Fast-cycle unit (quick or short cycle unit): An adsorption process that has adsorption cycles of relatively short duration.

Field condensate: See condensate.

Field processing unit: A unit through which a well stream passes before the gas reaches a processing plant or sales point. Field processing units may be separator systems, dehydration units, etc.

Field separator: A vessel in an oil or gas field for separating gas, hydrocarbon liquid, and water from each other.

Formation gas: Gas initially produced from an underground reservoir.

FPSO: Floating production, storage, and offloading vessel used in offshore operations.

Frac spread: Difference in value of natural gas liquid products as a liquid and as fuel value in natural gas. These are used to determine optimum recoveries in a gas plant.

Freeze valve: A specially constructed and calibrated valve designed and used solely to determine the water content in an LPG product. See ASTM D2713.

Full well stream: The total flow stream or effluent from a producing well containing all the constituents of the reservoir fluids.

Gas cap: The natural gas zone located above an oil zone in a common reservoir.

Gas condensate: See condensate.

Gas condensate reservoir: A reservoir which produces gas and gas condensate.

Gas condensate well: A gas well that produces from a gas reservoir containing considerable quantities of liquid hydrocarbons generally described as "condensate."

Gas drive: A manner of producing crude oil or other liquids from the reservoir wherein the required energy is provided by gas pressure.

Gas hydrate: A clathrate solid formed by the combination of natural gas components and water. Hydrate formation conditions depend upon gas composition, temperature, and pressure and may be formed above 32°F (0°C).

Gas injection: The injection of natural gas into a reservoir to maintain or increase the reservoir pressure or reduce the rate of decline of the reservoir pressure.

Gas lift: A method for bringing crude oil or water to the surface by using gas pressure to lift the fluid using a gas-driven pump in the producing well bore.

Gas–oil ratio (GOR): The ratio of gas to liquid hydrocarbon produced from a well. This may be expressed as standard cubic feet per barrel of stock tank liquid.

Gasoline: A product that, by its composition, is suitable for use as a fuel in internal combustion engines.

Gasoline plant: An obsolete term for a natural gas processing plant.

Gas reservoir: A geological formation containing a single gaseous phase. When produced, the surface equipment may or may not contain condensed liquid, depending on the temperature, pressure, and composition of the single reservoir phase.

Gas-well gas: The gas produced or separated at surface conditions from the full well stream produced from a gas reservoir.

Gas-well liquids: The liquid separated at surface conditions from the full well stream produced from a gas reservoir.

Glycol: A group of compounds used to dehydrate gaseous or liquid hydrocarbons or to inhibit the formation of hydrates. Commonly used glycols are ethylene glycol (EG), diethylene glycol (DEG), and triethylene glycol (TEG).

gpm: Gallons per minute. The term is lower case and used to describe a flow rate in gallons per minute for a liquid.

GPM (preferably Gal/Mcf): Gallons per thousand cubic feet. This upper-case term refers to the content in theoretically recoverable natural gas of components which can be recovered as liquid products. The preferred form of the term prevents confusion with "gallons per minute."

In legal contracts the term "potential hydrocarbon content" may be used.

GTL: Gas to liquid. Refers to process or plants designed to convert natural gas to hydrocarbon liquids.

Heating value (heat of combustion): The amount of heat developed by the complete combustion of a material. For natural gas, the heating value is usually expressed as the gross or higher heating value in British thermal units (Btu) per cu. ft. of gas at designated conditions, and either on a dry or water saturated basis. The gross or higher heating value is that measured in a calorimeter or computed from gas composition, when the heat of condensation of the water produced by a combustion process is included in the total measured heat. The net or lower heating value is that obtained when the water produced by a combustion process is not condensed. This is the usual circumstance in equipment burning fuel gas. The net value is the maximum portion of the heating value that can be utilized in usual equipment. The difference between the gross and net heating value is the heat that could be recovered if the water produced could be condensed.

Hot carbonate process: A process for removing acid gases from a gas stream by contacting with a water solution of potassium carbonate at a temperature in the range of 220°F–240°F (104°C–116°C).

Hydrate: See gas hydrate.

Hydrate off: Stoppage of the flow of fluid by formation of hydrate crystals.

Injection gas: Gas injected into the producing formation to maintain or increase the reservoir pressure or to reduce the rate of decline of the reservoir pressure.

Injection well: The well through which the injection fluid flows into an underground formation.

Iron sponge process: The method for removing small concentrations of hydrogen sulfide and mercaptans from natural gas by passing the gas over a bed of wood shavings which have been impregnated with a form of iron oxide. The impregnated wood shavings are called "iron sponge." The hydrogen sulfide reacts with the iron oxide, forming iron sulfide and water. Regeneration may be accomplished by exposing the depleted sponge bed to oxygen.

Jumbo tank cars: Tank cars having capacities of 30,000 gal (114 m^3) or more. Another group of cars known as "small jumbo" have capacities ranging from 18,000–22,000 gal (68–83 m^3). There are also various other sizes. "Standard" tank cars have a capacity of 10,000–11,000 gal (38–42 m^3).

Knockout (liquid): Any liquid condensed from a stream by a scrubber following cooling.

Lead acetate test: A method for detecting the presence of hydrogen sulfide in a fluid by discoloration of paper which has been moistened with lead acetate solution. See ASTM D2420.

Lean amine: Amine solution that has been stripped of absorbed acid gases, giving a solution suitable for recirculation to the contactor.

Local distribution company (LDC): A legal entity engaged primarily in the retail sale and/or delivery of natural gas through a distribution system that includes mainlines (i.e., pipelines designed to carry large volumes of gas, usually located under roads or other major right-of-ways) and laterals (i.e., pipelines of smaller diameter that connect the end user to the mainline).

LAER: Lowest Achievable Emission Rate. May be required on major new or modified emission sources in non-attainment areas.

Lean gas: (1) The residue gas remaining after the recovery of natural gas liquids in a gas processing plant. (2) Unprocessed gas containing little or no recoverable natural gas liquids.

Lean glycol: The glycol that has been stripped of absorbed water.

Lean oil: Absorption oil purchased or made by the plant or oil from which the absorbed constituents have been removed.

Lease condensate: A mixture primarily of pentanes and heavier hydrocarbons recovered at the wellhead.

Lease fuel: Natural gas used in well, field, and lease operations, such as gas used in drilling operations, heaters, dehydrators, and field compressors.

Lift gas: See "gas lift."

Looping: Installing a parallel pipeline alongside an existing line in order to increase capacity.

LNG (liquefied natural gas): The light hydrocarbon portion of natural gas, predominately methane, which has been liquefied.

LPG (liquefied petroleum gas): Product streams containing primarily propane and butane with minor amounts of ethane. See GPA Standard 2140.

LTS (low-temperature separation), or LTX unit (low temperature extraction unit): A process for limited NGL removal from raw natural gas. See Chapter 12.

Mainline plant: A plant that processes the gas which is being transported through a large volume pipeline. Also called "pipeline", "on line", or "straddle plant."

Make-up gas: (1) Gas that is taken in succeeding years, which has been paid for previously under a "take or pay" clause in a gas purchase contract. The contract will normally specify the number of years after payment in which the purchaser can take delivery of makeup gas without paying a second time. (2) Gas injected into a reservoir to maintain a constant reservoir pressure and thereby prevent retrograde condensation. (3) In gas processing, there is a reduction in gas volume due to plant loss fuel and shrinkage. Some agreements between gas transmission companies and plant owners require plant losses to be made up or paid for. The same may apply to Btu reduction as well.

MDEA (methyldiethanolamine): An amine for treating gas. See amine.

MEA (monoethanolamine): An amine for treating gas. See amine.

MER: Maximum efficient rate or most efficient rate. (1) "Maximum efficient rate" is the highest rate at which a well or reservoir may be produced without causing physical waste in the reservoir. (2) "Most efficient rate" is the highest rate at which a well or reservoir can be produced without either reservoir or surface physical waste. The first of these two meanings is more common.

As an example of the distinction between the two definitions, a reservoir may be produced at the "maximum efficient rate," but at such a rate gas production will be in excess of the capacity of facilities in the field to handle the gas; consequently, a lower or "most efficient rate" is set up for the reservoir to avoid surface waste of valuable hydrocarbons in the form of vented or flared gas.

MMscf: million cubic feet: A standard unit for measuring or expressing the volume of a million cubic feet of gas ($2.832 \times 10^4 m^3$). The pressure and temperature conditions for the standard measurement must be defined.

Mscf: thousand standard cubic feet: A unit for measuring or expressing the volume of a thousand cubic feet of gas ($28.32 m^3$). The pressure and temperature conditions for the standard measurement must be defined.

Natural gasoline: A mixture of hydrocarbons, mostly pentanes and heavier, extracted from natural gas, which meets vapor pressure, end point, and other specifications for natural gasoline as specified by the GPA. See GPA Standard 2108.

Natural gasoline plant: One of the terms, now obsolete, used to denote a natural gas processing plant. See "gas processing" and "gas processing plant."

Netback: The price received for the sale of a product after deducting transportation or associated costs (pipeline tariffs, waterborne freight, storage fees, line costs, etc.) in shipping the product from its point of origin.

NGL (natural gas liquids): Natural gas liquids are those hydrocarbons liquefied at the surface in field facilities or in gas processing plants. Natural gas liquids include ethane, propane, butanes, and natural gasoline. The raw product stream from a plant recovering C_2^+ is variously known as "Y-Grade, Demethanized Raw Mix and "raw product."

NRU: Nitrogen Rejection Unit. See Chapter 13.

Odorant: A highly odiferous fluid or gas, usually a light mercaptan or other sulfur compound added to a gas or LP-gas to impart a distinctive odor for safety reasons and to facilitate detection of leaks.

Oil well (casinghead) gas: Associated and dissolved gas produced along with crude oil from oil completions.

Operating factor: The percentage of time that a unit is performing the function for which it was designed.

Olefin(s): Hydrocarbons which contain a carbon to carbon double bond such as ethylene and propylene.

Outage: The difference between the full interior volume of a storage vessel or sample container and the volume of liquid therein. For NGL products, outage is provided in order to provide space for expansion of the liquid.

Peak day requirements: Maximum requirement of gas for a 24-h period. The quantity may be considerably greater than the daily average flow.

Peakshaving: The use of stored fuels to supplement the normal supply of pipeline gas during periods of high demand.

Peakshaving plant: A liquefaction facility designed to produce LNG for storage and re-vaporization during times of peak demand.

Pentane-plus: A hydrocarbon mixture consisting mostly of isopentane and heavier components with higher boiling points. See also, Natural Gasoline.

Pigging: A procedure of forcing a solid object through a pipeline for cleaning purposes, separating different products being transported in same line, or inspecting the line.

Pipeline gas: Gas that meets a transmission company's minimum specifications.

Processing upgrade: The difference between the value of the liquids extracted from the gas and sold and the value if sold as a gas component. See also Frac spread.

Propane, HD-5: A grade of propane consisting predominately of propane, and which conforms to the GPA specification for HD-5 propane in GPA Standard 2140.

Pulsation dampener: A vessel attached to the suction and/or outlet of reciprocating pumps and compressors to dampen pressure pulsations.

RACT: Reasonability Achievable Control Technology. This is sometimes required for emissions from a new or modified emission source, such as a plant or combustion engine.

Raw gas: Unprocessed gas or the inlet gas to a gas processing plant.

Raw mix liquid: A mixture of natural gas liquids prior to fractionation. Also called "raw make." See also, NGL.

Reclaimer: A system in which undesirable contaminants of a stream are separated from the desired materials using heat and/or chemical reaction.

Reliability: Reliability is the probability that a given component will not fail within a specified time period. Mean Time Between Failures (MTBF) is indicative of reliability.

Residue: The material that remains after a separation process. (1) Residue gas is that gas remaining after the recovery of liquid. (2) Residue may also be the liquid or solid remaining after laboratory separation or some reclaiming process.

Retrograde condensation: Condensation that occurs in a pressure region when the pressure on the gas is reduced. This is the reverse of the behavior at lower pressures; hence, the term "retrograde condensation" is used to describe this phenomenon.

Retrograde pressure region: The pressure region wherein the hydrocarbons exhibit increased volatility as the pressure increases.

Retrograde temperature region: The temperature region wherein the hydrocarbons exhibit increased volatility as the temperature increases.

Rich amine: The amine leaving the bottom of the contactor. It is the lean amine plus the acid gases removed from the gas or liquid by the lean amine.

Rich gas: A gas that is suitable as feed to a gas processing plant and from which products can be extracted.

Rich glycol: The glycol solution leaving the contacting device. It is the lean glycol plus water removed from the process stream by the lean glycol.

Rich oil: The oil leaving the bottom of an oil absorber. It is the lean oil plus all of the absorbed products.

RVP (Reid Vapor Pressure): A vapor pressure specification for the heavier liquid products as determined by the ASTM D323 test procedure. The vapor pressure is reported as pounds per sq. in. Reid. The pressure approximates, but is somewhat less than the absolute vapor pressure of the liquid. Also, sometimes used to describe LPG meeting ASTM D1267 or ASTM D6897.

SCADA: Supervisory Control and Data Acquisition. A computer system used to both monitor and control field and plant systems.

Scavenger: A nonregenerative solid or liquid used to remove trace amounts of a compound from a process stream. It is attractive when the total amount of impurity is too low to justify a continuous or regeneratable process.

Shrinkage: The reduction in volume and/or heating value of a gas stream due to the removal of some of its constituents.

SI: The international system of units. Refer to Chapter 1.

Slop or slop oil: A term rather loosely used to denote a mixture of oil produced at various places in the plant, which must be rerun or further processed to be suitable for use. Sometimes sold as crude oil.

Slug catcher: A separator that designed to separate intermittent large volumes of liquids from a gas stream. It may be a vessel or a manifolded pipe system.

Snubber: See "Pulsation dampener."

Solution gas: Gas that originates from the liquid phase in the oil reservoir.

Sour: Liquids and gases are said to be "sour" if they contain hydrogen sulfide and/or mercaptans over a specified level. See also "Doctor test."

Sour gas: Gas containing an appreciable quantity of hydrogen sulfide and/or other sulfur species.

Splitter: A name applied to fractionators, particularly those separating isomers (i.e., butane splitter refers to a deisobutanizer).

SPA: Sales and purchase agreement.

Stain tube: A glass tube filled with a material which changes appearance based on the concentration of a compound to which it is being exposed. Often used to quickly detect small amounts of a component such as hydrogen sulfide. Used in standards such as ASTM D4913.

SRU: Sulfur recovery unit.

Stabilized condensate: Condensate that has been stabilized to a definite vapor pressure in a distillation system.

Stabilizer: A name for a distillation system that stabilizes any liquid, i.e., reduces the concentration of more volatile components so that the resulting liquid is less volatile.

Standard cubic feet (scf): Refers to a gas volume measurement at a specified temperature and pressure. The temperature and pressure may be defined in the gas sales contract or by reference to other standards. The commonly used temperature and pressure is 60°F and 14.696 psia.

Straddle plant: See "mainline plant."

Stranded reserve: A gas reserve located where there is no economic use for the gas at the point of origin, and transportation of the gas by pipeline from the reserve to a point of end use is not economically feasible.

Strapping: A term applied to the process of calibrating liquid storage capacity of storage tanks by increments of depth.

Stripping gas: A noncondensing gas at operating conditions that is used to remove the more volatile components from a liquid.

Stream day: Refers to a basis for calculating plant production. A stream day is equivalent to 24 h of operation at 100% of design rate. This is different from a calendar day, which would be used to give average production for a full year.

Stripper: A column wherein absorbed constituents are stripped. The term is applicable to columns using stripping medium, such as steam or gas.

Substitute natural gas (SNG): See "synthetic gas."

Supercritical component: A component that is at a temperature above the critical temperature, i.e., above a temperature where the pure component can exist as a liquid and vapor.

Sweet: Refers to the near or absolute absence of sulfur compounds in either gas or liquid, as defined by a given specification standard.

Sweet gas: Gas that has no more than the maximum sulfur content defined by (1) the specifications for the sales gas from a plant; (2) the definition by a legal body such as the Railroad Commission of Texas.

Synthetic gas (SG): The term used to describe the salable gas product resulting from the gasification of coal and/or gas liquids or heavier hydrocarbons.

T&F (Transportation & Fractionation): The cost (or fee) of transporting an NGL mix to a fractionation center and separating into finished products.

Tail gas: The gas exiting a process or plant, e.g., the gas leaving a sulfur recovery unit.

Tailgate: The point within the gas processing plant wherein the residue gas is last metered. This is usually at the plant residue sales meter.

Take-or-pay clause: A clause that may be in a contract, which guarantees payment to the seller even though the particular volume is not taken during a specified time period. Some contracts may contain a time period for the buyer to later take delivery.

TGTU (Tail Gas Treating Unit): A process unit that takes tail gas from a SRU and removes additional sulfur components. Also sometimes referred to as a TGCU.

Therm: A unit of heating value equivalent to 100,000 Btu (1.055056×10^8 J).

Tonne: A unit of mass measurement commonly used in international petroleum commerce equal to 1,000 kg.

Turndown: The level to which the flow in a process unit may be reduced without significantly changing the unit's performance. The minimum flow, relative to design conditions, at which the equipment still operates properly.

USES: U.S. Engineering System and its variants. The U.S. Engineering System is in general use in the United States, but all other industrialized countries use a system based on SI. Refer to Chapter 1

Ullage: See "outage."

Vane pack: An insert in gas–liquid separators where gas goes through a torturous path to force mists to coalesce into droplets and drop out of the gas phase.

Vapor pressure gasoline: A descriptive phrase for natural gasoline meeting a specified vapor pressure.

Vapor pressure, GPA: Vapor pressure as specified by GPA standards.

Weathering: The evaporation of liquid by exposing it to the conditions of atmospheric temperature and pressure. Partial evaporation of liquid by use of heat may also be called weathering.

Weathering test: A standard GPA test for LP-gas for the determination of heavy components in a sample by evaporation of the sample.

Wet gas: (1) A gas containing water, or a gas that has not been dehydrated. (2) A term synonymous with rich gas, i.e., a gas from which the products have not been extracted. See also "rich gas."

Wild gasoline: An obsolete term for natural gas liquids before stabilization.

Wobbe number: A number proportional to the heat input to a burner at constant pressure. In USES practice, it is the higher heating value of a gas divided by the square root of its relative density (specific gravity). Widely used internationally, together with measured or calculated flame speed, to determine the interchangeability of gases.

Author Index

A

Abbott, J., 323, 324
Acton, A., 414, 415
Afzal, W., 261
Agahi, R., 290
Ahlin, L., 414
Alvarez, M.A., 312
Amiridis, M.D., 338
Anderson, L.E. 134
Anderson, S.T., 316, 317
Andress, D.L., 405
Areneault, G., 62
Ariyapadi, S., 362
Arshad, A., 232
Avidan, A., 390

B

Bacon, K.H., 335
Baker, R.W., 96, 97, 98, 100, 241, 296, 310
Barron, R., 399
Batzle, M.L., 127
Beckman, K.L., 375, 377, 379, 380
Benson, H.E., 232
Bergman, T.L., 53
Bertha, G.J., 411
Bertrand, T., 244
Betting, M., 294
Bhattacharya, C., 310
Bialek, R., 239
Bierlein, J.A., 240
Bikin, B., 273
Binci, F., 273
Bird, R.B., 34, 58
Blachman, M., 263
Blakely, R., 398
Bleizeffer, D., 130
Bomard, H., 413
Borsboom, H., 350
Boswell, R., 131
Boulanger, A., 413
Bourke, M.J., 325
Brouwer, J.M., 325
Brown, T.S., 240
Bruce, J.T., 201
Bryner, C., 128
Bucklin, R.W., 179, 235, 244
Bullin, J.A., 133, 139, 327
Burgess, D.S., 423
Burr, B., 233

C

Cannon, R.E., 127, 298, 382, 383
Carroll, J.J., 174, 362, 363
Carson, J.K., 227
Cates, H.C., 377
Cengal, Y.A., 53
Chandra, A., 429–435
Chi, C.W., 237, 238, 265
Choe, J.S., 317
Clare, R.T., 234
Clark, J.A., 389, 404
Clark, K.R., 272
Clark, P.D., 21, 338, 356
Claude, J., 412
Cleaver, P., 424
Cline, C., 244
Clinton, P., 257
Coleman, J.L., 127
Collett, T., 333
Collett, T.S., 131
Collie, J., 326
Collins, S.C., 399
Compton, A., 219
Cone, R.S., 393
Conrado, C., 424
Cooley, T.E., 242
Cooper, M.W., 166
Corvini, J., 325
Coulson, J.M., 50
Covington, K., 327
Crevier, P.P., 354, 357
Crum, F.S., 298
Cummings, W., 238, 265
Currence, K., 274

D

d'Haêne, P.E., 355
Dalrymple, D.A., 360
D'Amico, J., 310
Davis, P.M., 259
Davis, R.A., 313
de Bruijn, J.N.H., 92, 266
Deaton, W.M., 316, 317
Determeyer, P.L., 375, 377, 379, 380
Dimentberg, M., 415
Dittman, R.H., 22
Dodge, B.F., 401, 402
Dong, Z., 130
Dragatakis, L., 413
Drinkwine, P.M., 156, 164
Duda, J.R., 361
Duffy, A.R., 412

E

Eble, C., 134
Echterhoff, L.W., 221, 222,349, 354,356
Eckersley, N., 141, 325, 338
Edwards, T.W., 40
Eisenberg, B., 225

Engel, D.B., 232, 333
Epps, R., 235, 236
Epsom, H.D., 294
Ershaghi, B., 290
Etzbach, V., 406, 407, 409

F

Fabio, D.G., 117
Ffooks, R.C., 416
Finn, A.J., 393, 409
Fisher, K., 261
Fitz, C.W., 139
Foerg, W., 408, 409
Foglietta, J.H., 394, 409
Forg, W., 406, 407, 409

G

Gabelman, A., 91
Geankoplis, C.J., 75
Giacomin, S., 133, 219
Giribone, R., 412
Goar, B.G., 218, 233, 354
Godby, S., 169
Goddin, C.S., 356
Goethe, A., 313
Granger, L., 334
Gray, P.R., 134, 320
Grekel, H., 352
Grenier, M.R., 420
Grigson, S., 105, 108, 113, 114, 115
Guccione, E., 316, 317
Gudmundsson, J.S., 390

H

Hale, D., 401
Hale, P., 295, 296, 308
Hammerschmidt, E.G., 174, 178
Hardison, L.C., 358
Harper, I., 417, 418
Harris, R.A., 237
Harryman, J.M., 334
Hashemi, H.T., 415
Hatcher, N., 349
Hatcher, N.A., 361, 364, 365
Hathaway, P., 400
Haynes, B.S., 69
Haynes, B.S., 69
Haynes, R.D., 69, 316, 317
Heald, C.C., 33, 40, 41, 45, 46, 49
Hegarty, W.P., 233
Heguy, D.L., 358,359
Hegwar, A.M., 237
Hernandez-Valencia, V.N., 256
Herrin, J.P., 286
Hicks, T.G., 40
Hidayati, L., 390
Hildebrand, J.H., 80
Hilsenrath, J., 250
Hix, M., 334
Holden, B.S., 88, 89
Holman, J.P., 53
Holmes, A.S., 239
Holmes, C., 421
Holub, P.E., 230, 231, 244, 359
Hoover, T.E., 415
Horstmann, S., 261
Houghton, J.E., 244
Howard, I., 310, 442, 443
Huang, S., 420
Hudson, H., 302, 303
Huffmaster, M., 274
Humphrey, S.E., 257, 258

J

Jackson, G., 402
Jacobus, J., 374, 382
James, R., 232
Jandjel, D.G., 190
Johnson, A.M., 69
Johnson, D.J., 316, 317, 318
Johnson, J.E., 218, 237, 335, 361, 364, 365
Jones, S., 132, 310, 327, 442, 443
Jordan, T.J., 166
Jou, F.Y., 227
Judd, D.K., 237
Jumonville, J., 287, 289

K

Kane, J.A., 141, 338
Karacan, C.Ö., 129
Karassik, I.J., 33, 34, 36, 39, 40, 41, 48, 49
Kataoka, H., 420
Kato, M., 417
Katz, D.L., 415
Katz, D.L., 379, 382
Kay, W.B., 240
Keller, A.B., 159
Kent, R.L., 225
Khan, T.S., 136
Kim, A.G., 134
Kimmitt, R.P., 182, 183
Klinkenberg, A., 3
Klinkenbijl, J.M., 219
Klomp, U.C., 182
Koh, C.A. 174, 175
Kotzot, H., 409–412
Kruka, V.R., 255
Kuchinski, J., 158, 168, 332
Kumana, J.D., 45
Kuo, J.C., 311
Kuuskraa, V., 311, 361, 362

L

Lagas, J.A., 354, 355
Langston, L.V., 165
Lee, H., 237, 238, 265
Lee, R.L., 379, 382
Legatos, N.A., 412
Leibon, I., 390
Lentz, A.E., 411
Leppin, D., 244, 349
Lesage, K.L., 21, 338

Likins, W., 334
Lillard, J.K., 288
Lindblom, U., 414
Linnett, D.T., 409
Lofredo, A., 400
Lokhandwala, K., 98
Lokhandwala, K., 295, 296, 308
Lokhandwala, K., 97
Lokhandwala, K., 311
Long, B., 410, 411
Lorentzen, C., 112
Lukchis, G.M., 265
Lund, D.L., 325
Lunsford, K.M., 69
Lyddon, L., 233
Lyddon, L., 230

M

Maddox, R.N., 349
Malino, H.M., 265
Mallett, M.W., 437, 438
Maloney, J.J., 313
Mamrosh, D., 261
Mamrosh, D., 333, 335
Manning, F.S., 372
Markovs, J., 325
Marriott, R.A., 261
Marshall, G., 417
Masoudi, R., 255
Mawer, D.J., 313
May, E., 410
McAllister, E.W., 370, 372
McCabe, W., 34, 53, 58, 75
McCain, W.D., 17
McCallum, V., 115
McCartney, D.G., 323, 325
McFadden, R.D., 413
McGuire, T 33, 36, 39, 40, 41
McHenry, R.C., 323, 325
McHugh, T., 263
McIntush, K.E., 361
McJannett, J., 233, 234
McLeod, R.P., 312
McMichael, N., 320
McNeilly, A., 68
Mehta, A.P., 182
Meisen, A., 348
Meyer, B., 346, 348
Meyer, H.S., 219
Meyer, S.E., 346, 348, 354
Mick, M.B., 334, 335
Miller, R.W., 389, 404
Mitariten, M., 99, 296, 310
Mock., 325
Mohitpour, M., 370
Mokhatab, S., 99, 333, 335, 337
Monfore, G.E., 411
Montagu, H.E., 416
Morgan, D.J., 349
Moritis, G., 219, 311
Mork, M., 390
Mortko, R.A., 237
Müssig, S., 324

N

Nagelvoort, R.K., 409
Nagl, G.J., 358, 359
Nakanishi, E., 423
Nelson, D.R., 324
Nelson, P.H., 127, 128
Ng, H.-J., 253, 326
Nguyen, H., 230
Nicholas, J.W., 177
Nicol, G., 288
Nielsen, R.B., 335
Nishizaki, T., 411
Northrop, P.S., 232, 239

O

O'Brien, D., 327
Oberding, W., 237
Ohama, T., 201
Okamoto, H., 413
Okimoto, F.T., 294
Oppenshaw, P., 323, 324

P

Panter, J.L., 185
Parnell, D., 350, 352
Parrish, W.R., 255, 256
Pelletier, D., 320
Pennybaker, K., 303
Peranteaux, J., 287, 289
Perez, V., 407
Petty, L.E., 265
Picutti, E., 420
Pilling, M., 88, 89
Pitman, R., 303
Poling, B.E., 19, 297
Powell, J., 402
Prater, P.B., 412
Prausnitz, J.M., 9, 80, 85, 251
Price, B.C., 407
Pua, L.M., 69

R

Ramshaw, D.E., 358
Raney, D.R., 237
Ransbarger, W., 405
Rapallini, R., 411
Rastelli, H., 265
Reid, R.C., 423
Remirez, R., 317
Rhodes, Z., 323
Richardson, J.F., 50
Richman, P., 92, 272, 335
Rigola, M., 420
Rios, J.A., 323, 324, 325
Roberts, J.S., 374, 382
Roberts, J.S., 374, 375, 381, 382
Roberts, P., 333, 335
Robinson, D.B., 326
Rollenhagen, T., 244
Romanow, S., 389

Ruddy, T., 323, 324, 325
Rueter, C.O., 326
Rumbold, S.O., 69
Ruppel, C., 129, 131
Ruthven, D.M., 95
Rydjord, K., 316, 317, 318

S

Sambrook, R.M., 335
Sanders, J.E., 125, 128
Sargent, A., 335
Schaaf, R.P., 221
Schaak, J.P., 312
Schendel, R.L., 179, 272
Schimmoller, B., 159
Schinkelshoek, P., 294
Schulz, M., 244
Seagraves, J., 232, 335
Sell, K.T., 69
Shah, K., 292
Shah, V.A., 237
Sheilan, M., 230, 231, 244, 255, 256, 257, 258, 359
Sherik, A., 136
Shields, P., 68
Shirley, A., 310
Shuai, X., 348
Simmons, C.V., 230
Skiff, T., 274
Slavens, A., 353
Sloan, E.D., 173, 174, 175, 177, 182, 185
Smith, B., 334
Smith, C.E., 371, 372, 373
Smith, K.C., 409
Smith, R.S., 255, 256, 257, 258, 273, 274
Smith, W.A., 228, 230
Speight, J.G., 15
Spillman, R.W., 242
Stepanoff, A.J., 36
Sterner, A.J., 113, 227, 239
Stewart, E., 244, 245, 335
Stiltner, J., 323, 325
Stiltner-Shadden, J., 265
Strickland, J.F., 349
Stucky, B., 292
Suarez, M.R., 45
Swearingen, J.S., 290. 399,
Sweny, J.W., 234, 235

T

Tamura, K., 413
Tan, J., 320
Tannehill, C.C., 308, 429, 430, 431, 432, 433, 434
Taylor, M., 389, 390
Tennyson, R.N., 221
Thompson, R.E., 372
Tobin, J., 375, 376
Tonjes, M., 353
Traconis, B., 134, 325
Trahan, D.O., 323
Trent, R.E., 263, 265, 266, 272, 298
Trimble, H.M., 255
Troner, A., 422
True, W.R., 348, 349, 419
Tsochatzidis, N.A., 136
Tuller, W.N., 346, 348

U

Umemura, J., 413

V

Valdes, A.R., 352
Valentine, J.P., 234
Valentine, J.P., 234, 235
Vallee, S., 68
van Grinsven, P.F.A., 266
Van Meerbeke, R.C., 414, 415
Varnell, B., 169
Verachtert, T.A., 336
Veroba, R., 244, 245, 335
Vesovic, V., 424
Vines, H.L., 312
Vink, K.J., 409

W

W. Luyten, W., 413
Wagner, J.V., 390, 393
Wallace, C.B., 259, 311, 361, 362
Wallace, M., 311, 361, 362
Warren, G.L., 244
Webb, B.C., 168, 170, 380
Webber, W.W., 333, 440
West, J., 158
West, J.R., 346
Wichert, C.G., 259, 260
Wichert, E., 259, 260, 346, 362
Wieninger, P., 256, 261, 275
Wilhelm, S.M., 324
Wilkes, J.O., 34
Wilkinson, J., 302, 303
Wilkinson, R., 393
Williams, T., 143
Williams, V.C., 399
Willis, J., 310
Willman, T.J., 338
Wilson, J.L., 274, 294
Wines, T.H., 112
Winston, K., 115, 263

Y

Yang, R.T., 95
Yoon, S.H., 69
Young, S.M., 313
Yuvancic, J., 274, 294

Z

Zammerilli, T., 97
Zemansky, M.W., 22

Subject Index

A

Absorption
- basic concepts, 85
- chemical (*see* Absorption processes for acid gas removal; Amine treating)
- comparison to other separation processes, 102
- difference between physical and chemical absorption, 85
- good solvent attributes, 86
- physical (*see* Physical absorption for acid gas removal; Glycol dehydration processes; TEG dehydration process)

Absorption processes for acid gas removal, *see also* Amine treating; Physical absorption for acid gas removal
- using alkali salts, 232
- using amines, 222–232, 334–335
- using caustic, 335–337
- using hybrid solvents, 237
- using physical absorption, 233–237

Absorption processes for dehydration, *see* Glycol dehydration processes; TEG dehydration process

Acid gas, *see also* Hydrogen sulfide (H_2S); Carbon dioxide (CO_2)
- concentrations in liquid products (*see* Product specifications)
- concentrations in conventional natural gas, 132
- concentrations in shale gas,133
- concentrations in pipeline gas, 139
- corrosivity in aluminum heat exchangers, 68
- corrosivity with water present, 68, 218
- definition, 218
- dehydration, 259–261
- disposal, 219, 361–363
- solubility in TEG, 259–261
- specifications for LNG plant feed, 394

Acid gas injection (AGI), 362–363

Acid gas removal processes, 222, *see also* Hydrogen sulfide removal; Carbon dioxide removal
- by adsorption, 237–239
- using alkali salts, 232
- by amine treating, 228–232, 334–335
- commercial processes, 220
- comparison of processes for removal from gas, 220–222
- by cryogenic distillation, 239–240
- factors affecting process selection, 220–221
- using hybrid systems, 237
- using membranes, 240–243 (*see also* Membranes)
- using molecular sieve, 222, 237–239, 335 (*see also* Molecular sieve)
- by physical absorption, 233–237, 335 (*see also* Physical absorption for acid gas removal)
- Process flow diagram for MEA, 228

Activated alumina
- in adsorption processes, 91
- for dehydration, 262, 274
- for mercury removal, 325
- representative properties, 263
- for sweetening, 439

Activated charcoal, 115
- compared to other adsorbents, 115
- for helium purification, 317
- for mercury removal, 325

Activity coefficient
- calculation in immiscible systems, 80
- definition, 80

Adiabatic compression, *see* Isentropic compression

Adsorbent properties for dehydration, 263

Adsorbate
- definition, 91
- factors affecting selectivity of, 92

Adsorption, *see also* Adsorption processes; Molecular sieve; Molecular sieve dehydration process
- comparison between physical and chemical, 91
- definition, 91
- factors affecting selectivity in, 91
- of water on molecular sieve, 261

Adsorption processes, *see also* Adsorption; Molecular sieve; Molecular sieve dehydration process
- comparison to other separation processes, 102–103
- for carbon dioxide and hydrogen sulfide removal, 237–239, 335
- for dehydration, 263–265, 338
- for helium purification, 316–317
- for nitrogen rejection, 310
- fundamentals of process, 91–96

Affinity laws
- for centrifugal compressors, 212
- for centrifugal pumps, 46

Air, molar mass for relative density calculations, 12

Air–cooled exchanger, forced and induced draft, 64–65

Alkali salt processes, 232

Alkanolamines, *see* specific amine; Amine treating

Amine contactor, 90, 228–229

Amine reclaimers, 228, 230, 245

Amine stripper, 58, 228

Amine treating,
- capital cost, 430
- chemistry, 224–225
- contactor temperature profile, 229
- corrosion in, 231
- foaming, 231
- heat of reaction, 226, 227–228
- hybrid, for acid gas removal, 237
- operating parameters, 229
- in liquids, 334–335
- process flow diagram for MEA, 228
- reclaiming amines, 230
- slippage, 225

Amine, *see also* specific amine
reactions with carbon dioxide and hydrogen sulfide, 224–225
structures, 223
Antiagglomerates (AA) hydrate inhibitors, 182
Aquifers for storage, 379
Arsenic, 323
API gravity, definition,13
ASME pipeline standards, 168
ASTM D130, *see* Copper strip test
ASTM D1838, *see* Copper strip test
ASTM D2713, test for water content in LPG, 141
ASTM D323, *see* Reid vapor pressure
ASTM D4084, test for H_2S content in gas, 222
ASTM D–56, test for color of liquids, 332
ASTM D6897, *see* Reid vapor pressure
ASTM D–86, test for distillation of petroleum products, 332
Asymmetric membranes, 97
Availability, definition, 197
Axial flow compressors, 205

B

Bag filters, 117
Benzene, *see* BTEX (benzene, toluene, ethylbenzene, xylene)
Black powder, 136
Boiling heat transfer, 60–61
Boiling point,
definition, 9
versus molecular weight (molar mass), 9
Booster stations, 166–168
Brazed aluminum plate–fin heat exchangers, *see* Plate–fin heat exchanger
Brake power, definition, 38
BTEX (benzene, toluene, ethylbenzene, xylene)
absorption in amine processes for acid gas removal, 237, 245
absorption in TEG dehydration, 261
chemical structure, 7
emissions from purification processes, 326–327
in Claus process, 354
composition in LNG plant feed gas, 394
emissions from purification processes, 326–327
methods for minimizing emissions, 327
potential plugging by freezing, 327
Btu efficiency, 158–159
Bubble cap trays, 88
Common applications, 90
Bubble point, definition, 78
n–Butane (C_4H_{10})
dehydration, 340
fractionation, 340–341
product specifications, 140–141
storage, 382
transmission (*see* Transporting liquids)
uses 138
Butane splitter operating conditions, 341
Butanes
composition specifications in LNG plant feed gas, 394
product specifications, 140–141
storage, 382
transporting, 381

C

Calcium chloride ($CaCl_2$) as desiccant, 273, 338
Capital costs
of amine treating, 430
of glycol dehydration, 430
of NGL recovery with high ethane recovery, 431–432
of NGL recovery with low ethane recovery, 430–431
of pipeline compressor stations, 373
of sulfur recovery and tail gas cleanup, high sulfur rates, 432–433
of sulfur recovery and tail gas cleanup, low sulfur rates, 433–444
updating cost data, 435
Carbamate, 225
Carbon dioxide (CO_2)
chemical properties, 222
concentration limits for LNG, 222
concentrations in natural gas, 219
in Enhanced Oil Recovery (EOR), 149, 361
specifications for sales gas, 219
specifications for LNG plant feed, 394
Carbon dioxide removal, *see also* Acid gas removal processes
by physical absorption, 233–237, 335
by chemical adsorption, 222–232
by cryogenic distillation, 239–240
from liquids, 335–336
using membranes, 240–243
Carbon dioxide slippage, 225, 227
Carbon disulfide (CS_2)
in natural gas, 222
reaction with primary amines, 222, 225
removal from gas, 222, 227, 234
in SCOT process, 356
in selecting acid gas removal processes, 219–222
Carbon monoxide (CO)
emissions control on compressor drivers, 213
in SCOT process, 350, 356
Carbonyl sulfide (COS)
distribution between phases, 334
effect on Copper Strip test, 338
formation in adsorbent beds, 263, 272
in natural gas, 222
reaction with primary amines, 222, 225
removal from gas, 222, 227, 234, 237
removal from liquids, 334, 334–335, 335, 335–336
in SCOT process, 356
in selecting acid gas removal processes, 221–222
Cascade cycle, *see* LNG liquefaction cycles
Caustic treating processes, 232, 335–337
Cavitation
in centrifugal pumps, 40–41
in reciprocating pumps, 48
Centrifugal compressors, 203–205
flow rate calculations, 207–208, 211–212
maintenance costs, 213
power requirement calculations, 211–212 (*see also* Head)
stonewalling in, 205
surge in, 205
with turboexpanders, 287
Centrifugal Pumps

comparison between centrifugal and positive displacement pumps
definition, 36
power calculations, 38
relationship between discharge pressure and discharge head, 34–36
temperature rise in, 39
Chelated iron solutions for hydrogen sulfide removal, *see* LO–CAT II
Chemistry
of amine adsorption processes, 224–225
of caustic treating, 232, 335–336
of Claus sulfur recovery processes, 350
of hot potassium carbonate process, 232
of LO–CAT II process, 352–353 359
of SUPERCLAUS process, 354–355
Claus process, 349–350, *see also* Tail gas cleanup
acid gas enrichment of feed, 353
chemistry, 350
BTEX effect on catalyst, 354
effect of temperature on conversion, 351
feed concentration effect on flow configuration, 351
split–flow, 353–354
straight–through process, 352–353
Closed cycle, *see* LNG liquefaction cycles
Coal bed methane (CBM)
composition, 134
definition, 128
resource, 130
Coalescing filter separators, 105, 110–111
Coalescing filter, 105, 111
in membrane pretreatment, 99
in TEG dehydration, 261, 275
reverse flow, 112
Cocurrent and countercurrent heat exchange, 59
Columns, *see* specific process
Commercial propane, product specifications, 140–141
Composite membranes, definition, 97
Composition
of coal bed methane, 134
of conventional natural gas, 132
of LNG plant feed, 394
of shale gas, 133
units, for gas phase, 17
units, for liquid phase, 18
Compressibility factor (z)
definition, 11
in compressor calculations, 197, 207–208, 210
Compressor stations, 166–168
capital cost, 373
Compressors; *see also* Centrifugal compressors; Reciprocating compressors
axial, 205
capital cost, 429
centrifugal (*see* Centrifugal compressors)
drivers, 197
efficiencies, 195–197
estimation of discharge temperature, 192, 196
flow rates
calculation of, 207–208
ranges of, 198–199
multistaging, 194
pressure, ranges of, 198, 119
reciprocating (*see* Reciprocating compressors)
rotary screw, 200, 201
work, calculation of, 190–191
Condensate
dehydration, 333
specifications, 332
stabilization, 332
sweetening, 333
water wash, 332
Condensate stabilizer, 291, 293, 332, 341
Condensers
heat exchanger types, 69–70
partial, 83
total, 83
Conductive heat transfer, *see* Heat conduction
Contactor, 86–87; *see also* specific absorption process
Contactor operating conditions
for amine acid gas removal process, 90, 229
for glycol dehydration, 255
for hot potassium carbonate process, 232
Contractual agreements between producer and processor, 156–158
alternative provisions, 157
effect on capital expenditures, 157
Convection heat transfer, *see* Heat transfer coefficients
Conventional natural gas, 132–133
Cooling water, 61
Copper strip test, 21, 222
and carbonyl sulfide, 338
Corrosion
in aluminum heat exchangers, 323
in amine acid gas removal processes, 231
caused by acid gases, 136
oxygen, caused by, 319
sulfur compounds, caused by, 361, 362
Corrosion inhibitors, effect on processing, 17, 231
Cricondentherm, 280
Critical point
of mixtures, definition, 280
of pure fluid, definition, 13, 76
Cricondenbar, 280
Cryogenic fractionation, *see* Fractionators
CrystaSulf, 222, 360–361
Cyclones, for coalescing fine droplets, 112–113

D

DCS (digital control systems), 155
DEA (diethanolamine)
for acid gas removal, 222, 227
structure, 223
Debutanizer operating conditions, 340–341
Deethanizer operating conditions, 340–341, 440
DEG (diethylene glycol), structure of, 255
DEG (diethylene glycol), *see also* Glycols; Glycol dehydration processes
Degradation
of amine solutions, 221, 222
of glycols, 255
Dehydration of gas, *see* Gas dehydration; Liquid dehydration
Demethanizers, 291
Density, of gases and liquids, 10
Depleted reservoirs for gas storage, 379
Depropanizer operating conditions, 340–341

Desiccants, *see* Gas dehydration; Liquid dehydration
Dew point
  definition, 77
  effect on membranes (*see* Membranes)
  of hydrocarbon mixtures, effect of composition on, 280
  of water + gas mixtures (*see* Water)
Dew point control
  using adsorption, 296
  importance, 279
  using low temperature separators, 293–294
  using membranes, 295–296
  using Twister, 294
DGA (diglycolamine)
  in acid gas removal, 222, 226–227, 334–335
  structure, 223
Diffusion
  effect on selectivity in membranes, 97
  in mass transfer, 75
DIPA (Diisopropanolamine)
  in acid gas removal, 222, 237, 334–335
  in SCOT process, 357
  structure, 223
Distillation, *see* Fractionators
Disulfides
  in natural gas, 134
  in odorants, 374
  removal using caustic wash, 335–337
Doctor test (GPA 3132), test for reactive sulfur in liquids, 336
Drip system, 105, *see also* Gas–liquid separator in gathering system, 165
Drivers, *see* specific driver type
Drizo process in TEG dehydration, 257
Dry gas filter, 105, 115–116
  in adsorption dehydration, 263
Drying
  of gas (*see* Gas dehydration)
  of liquids (*see* Liquid dehydration)

E

Economizers in propane refrigeration, 285
Efficiency
  compressors, 195–197 (*see also* Reciprocating compressors)
  of gas turbines, thermal, 206
EG (ethylene glycol)
  for dehydration (*see* Glycol dehydration processes)
  gas dehydration in low temperature separators, 294
  as hydrate inhibitor, 179–180, 180
  structure, 255
Electric motors
  with compressors, 197
  with centrifugal pumps, 47
Elemental sulfur, *see* Sulfur, elemental
Energy
  definition of, 6
  forms of, 22–26
Energy efficiency of asset, 158–159
Enhanced oil recovery (EOR)
  acid gas flooding, 361
  carbon dioxide flooding, 149, 361
  nitrogen flooding, 151, 311–313
Enthalpy, definition of, 24
E–P mix (ethane–propane mix)
  product specifications, 140–141
  uses, 138
Entropy, definition of, 28
Ergun equation, for calculating packed bed pressure drop, 267
Ethane (C_2H_6)
  fractionation, 340–341
  product specifications, 140–141
  transporting, 381
  uses, 137
Ethane recovery
  gas composition, dependence on, 296
  in high ethane recovery processes, 302
  inerts concentration, dependence on, 300
  in low ethane recovery processes, 296–297
Ethanolamines, *see* specific amine; Amine; Amine treating
Ethylene glycol, *see* EG (ethylene glycol)
Expander cycle, *see* LNG liquefaction cycles
Expanders (turboexpanders), 286–290, *see also* Joule–Thomson expansion
  efficiency, 288
  in liquids recovery processes, 298, 301–303
  Operating parameters, example of, 290

F

Fee–based contracts, 156
Filter separators, 110–111
  in TEG dehydration, 261
Filters; *see also* specific type; specific application
  accumulation of NORM in, 320
Filtration
  in adsorption, 93, 263
  in amine systems, 231–232, 440
  in CrystaSulf process, 360
  in membrane pretreatment, 99
  overview, 115
  in TEG dehydration, 261
  in Twister pretreatment, 294
Firetube heaters
  definition, 63–64
  in wellhead operations, 165
Fixed efficiency contracts, 157
Flare systems, 155
Flash
  definition, 81
  in fractionation column, 83
Flash point
  definition, 62
  of molten sulfur, 364
  of Selexol solvent, 234
Flash tank, *see also* Gas–liquid separator
  in amine treating, 228, 229
  definition, 105
  function of, 88
  in glycol dehydration process, 256, 257
  in Selexol process, 236
Flash tank operating conditions
  in amine treating process, 230
  in TEG dehydration process, 257
Flow assurance, 172
Foaming

in amine acid gas processes, 231
in glycol dehydration processes, 259, 261
Forced draft air–cooled exchanger, 64–65
Frac spreads, 159
Fractionators
for acid gas removal, 239–240
advantages of trays vs. random packing, 90, 90
basic concepts, 81–83
column internals, 88–91
for condensate stabilization, 293–294, 332
for helium recovery, 317
for liquid products, 340–341
for liquids dehydration, 340
for nitrogen removal, 309–310
operating conditions for NGL streams, 341
types of columns, 83–84
Fuel conditioning, *see* Dew point control
Fuel gas system, 154–155

G

Gas dehydration
using absorption, 255–261 (*see also* Glycol dehydration process)
using adsorption, 261–273 (*see also* Adsorption; Molecular sieve; Molecular sieve dehydration process)
using membranes, 273–274
processes comparison, 274
using refrigerated methanol, 274
when required, 250
Gas distribution system, U.S., 369
Gas hydrates
comparison between methanol and glycol inhibitors, 180
effect of composition on formation, 174–175
formation, prediction of, 175–176
as gas resource, 129
inhibitors, 178–182
methods to prevent formation, 177–178
properties, 173–175
removal, 185
for shipping gas, 390
subcooling, 181, 182
Gas odorization, 374–375
Gas pipelines, *see* Gas transmission; Gathering systems
Gas processing plants
different purposes of, 149
overview of processes in, 150–153
Gas processing plant examples
for helium recovery, 317–318
for sour inlet gas, high nitrogen and carbon dioxide, 442–445
for sour inlet gas, NGL and sulfur recovery, 440–442
for sweet inlet gas, 437–440
Gas purity requirements for LNG, 394
Gas storage, *see* Storage, gas
Gas stripping
for drying liquids, 339–340
for enhancing glycol dehydration, 258
Gas subcooled process (GSP), 302
Gas transmission
comparison of methods for stranded gas, 390
comparison of methods for transmitting stranded gas, 390
compressor stations, 373
market centers (hubs), 375
pipeline installation costs, 370
pipeline operating pressures, 369, 370
pipelines, 370
Gas turbines, 205–206
exhaust emissions, 213
heat rate, calculation of, 206
Gas–fired engines, exhaust emissions, 213
Gas–liquid separator, *see also* Flash tank
common names for, 105
residence times, 114
separator principles, 105–110
Gas–oil separators, 164
Gathering systems, 165–166
Glycol dehydration process, 255–256, 340, *see also* Glycols; TEG dehydration process
contactor, 255
effect of liquid hydrocarbons, 261
effect of oxygen, 261
effect of pH, 261
effect of trace contaminants, 261
foaming, 261
maximum recommended regeneration temperatures, 255
process flow diagram, 256
selecting glycol based on properties, 255
Glycols
chemical formulas, 8, 255
decomposition temperatures, 255
effect of pH on glycol decomposition, 261
in offshore dehydration, 261
salt solubility in, 255
GPA 2172, calculation of nonideal gas behavior, 141
GPA Standard 2108, specifications of liquid product, 140
GPA Standard 2140, specifications for propane, 140
GPA Standard 3132, natural gasoline specifications and test methods, 336
GPM (gallons of liquids per Mscf), calculation of, 135–136

H

HD–5 propane
product specifications, 140–141
transporting, 381
odorization, 381
Head, hydrostatic, *see also* Centrifugal compressors; Pumps
definition, 24, 34
suction head, definition, 40–41
suction lift head, definition, 40
total discharge head, definition, 40
total head, definition, 40
Heat
of absorption of carbon dioxide in potassium carbonate, 232
of combustion (*see* Heating value)
definition, 23
of fusion, definition, 14
of reaction between amines and acid gases, 227
of regeneration in molecular sieve dehydration, 270
of vaporization, definition, 14

Heat capacity
definition, 15
of mixture, 20
Heat conduction
definition, 53
calculation equations for different geometries, 54
Heat exchanger, *see* specific type
Heat of combustion, *see* Heating value
Heat rate, of gas turbines, 206
Heat stable salts
formation in acid gas removal processes, 226, 231
removal from amine solutions, 230
Heat transfer coefficients
definition, for convection, 57–59
effect of phase change on, 60–61
ranges of, 58
using plant data to detect fouling, 59
Heating media, *see* Hot oil; Steam
Heating value
definition of higher and lower heating value, 15, 141–142
for mixtures, computation of, 140–141
Heavy hydrocarbons
limits in LNG plant feed gas, 394
in LNG liquefaction, 394, 409
in membrane pretreatment, 99
in physical absorption treating processes, 233
removal in dew point control and fuel conditioning, 293, 295–296
Helium
concentrations in natural gas, 132, 316
from LNG vent gas, 316
Grade–A definition, 316
recovery methods, 316–317
reserves and uses, 316
Henry Hub, 375
Henry's law, 235
Hindered amines, 222–223, 227
Hollow fiber membranes, 99–100
Horsepower calculations
for centrifugal pumps, 38
for centrifugal compressors, 211–212
for reciprocating compressors, 211
Hot oil, 61–62, 70, 256
comparison with steam, 61
Hot potassium carbonate process for acid gas removal, 222, 232
Hubs, for gas transmission, 375
Hybrid processes, for acid gas removal, 237
Hydrate inhibitor concentration, calculation of, 178–181
Hydrates, *see* Gas hydrates
Hydrocarbon recovery processes, *see* Dew point control; Liquids extraction, low ethane recovery; Liquids extraction, high ethane recovery
Hydrogen
in natural gas, 319
in SCOT process, 356
Hydrogen bonding, 9–10
Hydrogen sulfide (H_2S), *see also* Acid gas removal processes; Hydrogen sulfide removal
chemical properties, 218
concentration in natural gas, 218–219
conversion to sulfur (*see* Claus process)
disposal, 219, 361
effect on Copper strip test, 222
effect on molecular sieve regeneration, 263
in enhanced oil recovery (EOR), 361
safety and handling, 222, 364
specifications for levels in U.S. pipeline–quality gas, 139
specifications for levels in liquid products, 141
specifications for levels in LNG plant feed gas, 394
toxicity, 222
Hydrogen sulfide removal, *see also* Acid gas removal processes
by absorption in very sour gas stream, 441
by adsorption, 237–239, 335
by chemical absorption, 222–232, 334–335
by conversion to sulfur (*see* LO–Cat II, THIOLEX, Thiopaq)
from liquids, 333, 334–336
by physical absorption, 233
by scavengers, 243–244
Hydrostatic head, *see* Head
Hydraulic power, definition, 38

I

Ideal gas law, 10
Independent tank LNG carriers, 416, 417
Induced draft air–cooled heat exchangers, 64–65
Inlet receivers, 184
Inlet scrubber, *see also* Scrubbers
in TEG dehydration, 261, 275
Instrument air, 154
Insulation, thermal conductivities, 55
Interfacial tension, 17, 75
Internal combustion engines
with compressors, 197, 213, 213
exhaust emissions, 213
fraction of total installed costs, 434
Iron sponge, 244
Isenthalpic process, definition, 27
Isentropic compression, 191–192
Isentropic efficiency, 195, 282
Isentropic process, definition, 28
Isobutane (C_4H_{10})
fractionation, 340–341
product specifications, 140–141
storage, 382
transmission (*see* Transporting liquids)
uses, 138

J

Joule–Thomson coefficient, definition, 27
Joule–Thomson expansion
definition, 27
in propane refrigeration units, 282–284
compared to turboexpansion, 28
J–T cycle, *see* LNG liquefaction cycles
J–T expansion, *see* Joule–Thomson expansion

K

Keep–whole contracts, 157
Kettle heat exchanger
definition, 62
in propane refrigeration, 284
Kimray pump, 256

Kinetic hydrate inhibitors (KHI), 182
Knockout drums 105
in flare systems, 155
K–values for solutes in Selexol, 234

L

Lamda point of molten sulfur, 348
Lead acetate test, for sulfur detection, 218
Lean oil absorbers, 292
Lean solvent, definition, 86
Liquid dehydration
by absorption, 340
by adsorption, 338 (*see also* Adsorption; Molecular sieve)
using desiccants, 338
by distillation, 340
by gas stripping, 339–340
Liquid formation in turboexpanders, 288
Liquid sweetening, 334
by adsorption, 335
by amine treating, 334
by caustic treating, 335
Liquid–liquid separator principles, 113
Liquid–liquid separator, 105, 113
retention times, 114
Liquids content of natural gas, calculation, 135
Liquids extraction, high ethane recovery, 299
capital costs, 431
conventional expander process, 299
cryogenic fractionation, 299
Liquids extraction, low ethane recovery, 296
capital costs, 430
lean oil absorption, 298
using low temperature separators, 296
Liquids odorization, 381
Liquids recovery processes, *see* Liquids extraction, high ethane recovery; Liquids extraction, low ethane recovery
Liquids storage, *see* Storage, liquids
Liquids transport
E–P mix (ethane–propane mix), 381
factors for selecting transport method, 381
HD–5 propane, 381
natural gasoline, 381
NGL, 381
LNG baseload plant
composition specifications for feed gas, 394
gas reserves required for plant, 389
liquefaction processes (*see* LNG liquefaction cycles)
offshore facilities (FLNG), 393
plants in operation, 392
plants, possible future facilities, 393
plant processing steps, 388
LNG carriers
shipping costs, 423
types of LNG containment, 417
LNG composition ranges, 395
LNG economics, 420
cost of components, 422
liquefaction costs, 422
netback on LNG delivery, 421
regasification terminal costs, 423
shipping costs, 432
LNG export and import volumes, 391
LNG heating value, 395
LNG liquefaction
cost of liquefaction, 422
energy consumed in liquefaction, 388
energy consumed in regasification, 388
liquefaction processes (*see* LNG liquefaction cycles)
LNG liquefaction cycles
cascade
advantages of cycle, 402
classical, 403
mixed–refrigerant, 405
expander
comparison of open and closed cycles, 400
closed, 399
open, 400
Joule–Thomson, 395
LNG peakshaving facilities
number of facilities, 371
plant using closed cycle, mixed–refrigerant, 405
plant using open cycle, 400
regasification, 419
storage tanks in, 410, 412
LNG receiving facilities
cost, 423
siting limitations and offshore facilities, 423
floating storage and regasification units (FSRU), 424
LNG regasification, 419
cold utilization, 420
cost, 423
LNG storage
aboveground tanks
materials of construction, 410
single–containment tanks, 410
double–containment tanks, 411
full–containment tanks, 411
in–ground tanks
conventional tankage, 413
frozen–earth, 413
rock cavern, 413
rollover, 414
LNG transport
marine shipping cost, 423
by marine transport, 416
by pipeline, 415
safety of, 423
by truck, 415
LNG, feed gas quality requirements, 394
Local distribution companies (LDC), 370
LO–CAT II, 222, 358
capital costs, 433
Low dosage hydrate inhibitors, 178
Low temperature separators, 293
LPG *see* HD–5 propane; Butanes; NGL
LTS, *see* Low temperature separators
LTX, *see* Low temperature separators

M

Make–up water in amine process, 232
Market centers, for gas transmission, 375
Mass transfer zone (MTZ) in adsorption beds, 92
estimating length, 266
factors affecting length, 92, 266

MDEA (methylediethanolamine)
in acid gas removal, 222, 227,
in hybrid processes, 237
in mixed amines, 227
in SCOT process, 356
structure, 223
MEA (monoethanolamine)
in acid gas removal, 222, 225
structure, 223
MEG (monoethylene glycol) *see* EG (ethylene glycol)
Membrane tank LNG carriers, 417
Membranes
for carbon dioxide removal, 222, 240
comparison to other separation processes,102
for dehydration, 273
fundamentals of separation process, 96
for heavy hydrocarbon removal (gas conditioning), 295
for nitrogen removal, 310
operating variables, 100
potential contaminants, 98
preconditioning of feed gas, 96
relative permeabilities of glassy and rubbery membranes, 97
Mercaptan odorant
in gas, 375
in HD–5 propane, 381
Mercaptan removal
by adsorption, 335
by amines, 222
by caustic treating, 335
by Merox process, 336
by Selexol, 238
by THIOLEX process, 337
Mercaptans
chemical structure, 8
in natural gas, 218
Mercury
concentrations in gas, 133, 324
corrosion by, 323, 324
distribution in products, 323
environmental concerns, 324
maximum acceptable levels in LNG, 394
nonregenerative removal processes, 325
regenerative removal processes, 325
Merox process for mercaptan removal, 336
Mesh pads, for coalescing, 107
Metal oxides
for hydrogen sulfide removal from gas (*see* Hydrogen sulfide removal)
for sulfur removal from liquids, 338
Metering, gas, 171, 280
Methane, *see also* Natural gas; LNG
dehydration (*see* Gas dehydration)
storage (*see* Storage, gas)
sweetening (*see* Acid gas removal processes)
transmission (*see* Gas transmission)
uses, 137
Methanol
distribution between gas and aqueous phases, 179
as hydrate inhibitor, 177, 178
for liquids sweetening, in caustic wash, 335
removal, 327
reuse, 328
solubility in condensate, 179
Mist extraction, *see* Coalescing filter; Coalescing filter separator; Vane pack; Wire mesh
Mixed amines, 227
Molecular Gate for nitrogen removal, 310
Molecular sieve; *see also* Adsorption processes; Molecular sieve dehydration process
clay binder, 91
for dehydration, 263, 338
for sweetening, 237, 335
Molecular sieve dehydration process; *see also* Adsorption processes; Gas dehydration; Molecular sieve
calculation of bed pressure drop, 267
calculation of heat of regeneration, 270
effect of temperature and inlet water content on bed capacity, 267
effect of trace impurities on bed performance, 272
length of MTZ, 266
refluxing and caking during regeneration, 265
schematic of two–bed unit, 264
typical operating conditions, 265
Molecular sieve 3A
carbonyl sulfide formation, 263
carbonyl sulfide removal, 335
Molecular sieve 4A, *see also* Molecular sieve; Molecular sieve dehydration process
carbonyl sulfide formation, 263
representative properties, 263
water adsorption isotherm, 262
Molecular sieve 5A, sulfur compound removal from liquids, 335
Molecular sieve, 13X, sulfur compound removal from liquids, 335
Multistaging compressors, 194

N

Natural convection
definition, 53
in LNG rollover, 414
Natural gas
advantages as a fuel, 121
conventional gas reserves, 126, 130
important impurities, 134 (*see also* specific Impurity)
liquids content (GPM), 135
origins, 125
product specifications, 139
reserves, U.S., 122, 129
reserves, world, 122, 129
specifications for LNG plant feed, 394
unconventional reserves, 126, 129, 130
U.S. usage, 122, 124
Natural gas industry in United States
consumption, 123
pipeline statistics, 121
production, 124
Natural gas liquids *see* NGL
Natural gas, raw gas composition
coal bed methane (CBM), 134
conventional gas, 132
shale gas, 133
Natural gas, resources
coal bed methane (CBM), 128, 130
conventional, 126, 129, 132
gas hydrates, 129, 131

other sources, 129
shale gas, 128, 130
tight gas, 127, 130
Natural gasoline
definition, 138
product specifications, 140, 332
transport, 381
uses, 138
New York Mercantile Exchange (NYMEX), 375
NGL
amine treating, 334
caustic treating processes, 335
dehydration processes, 338
fractionation, 340, 341
Merox process for mercaptan removal, 336
sulfur removal processes, 334
THIOLEX process for mercaptan removal, 337
transport, 381
Y–grade, 340
Nitrogen
fractionation, 309
refrigerant in LNG cycles, 399, 406
Nitrogen concentration in natural gas, 132
Nitrogen rejection unit (NRU), *see* Nitrogen removal
Nitrogen removal
by cryogenic fractionation, 309
in LNG base load plants, 391
by membranes, 310
by pressure swing adsorption (PSA), 310
for EOR, 311
process comparison, 308
Nitrogen–rich gas, processing options, 308
NORM (naturally occurring radioactive material), 134, 323, *see also* Radon
NPSH (Net positive suction head), definition, 24, 40, 48
NPSHA (Net positive suction head available), definition, 41
NPSHR (Net positive suction head required), definition, 41

O

Odorant fade
in gas, 374
in LPG, 382
Odorant, *see* Mercaptan odorant
Oil–free screw compressors, 200
Oil–injected screw compressors, 201
Open cycle, *see* LNG liquefaction cycles
Operating costs
of gathering and processing gas, 164
sharing between producer and processor, 156, 213
Optimum ethane recovery, 159
Oxygen
allowable concentration, 139, 141, 319
compounds, 8
in caustic wash for mercaptan removal, 336
in Claus process, 350
control in SUPERCLAUS process, 355
effect on molecular sieve regeneration, 272
in gathering systems, 134, 166, 319
in LO–CAT II process, 358
reaction with amines in acid gas removal processes, 222, 226, 227, 230, 231
reaction with glycols in dehydration processes, 261
removal, 320
sources, 320

P

Partial Pressure, 18
Particles sizes in liquid–vapor streams, 107
Peakshaving, *see* LNG peakshaving facilities
Permeability in membranes, 97
PH (pressure–enthalpy) diagrams, 28
for compressor work calculations, 193
for propane refrigeration calculations, 282
Physical absorption for acid gas removal, 233, *see also* Selexol process
advantages and disadvantages, 233
comparison with amine processes, 233
Physical properties of mixtures, estimation of, 19, *see also* specific property
Physical property, *see* specific property or compound
Pig launchers, 168
Pig receivers, 168
Pigging operations, 168
Pigs, 168
Pipeline installation and maintenance, 168
Pipeline safety requirements, 168, 171
pipeline specifications, *see* Product specifications
Plant processes, overview, 150
Plate–fin heat exchanger
adsorbent dust contamination, 263
advantages and disadvantages, 67
in cryogenic service, 290
definition of, 67
and liquid slugging, 68
mercury corrosion, 324
in propane refrigeration, 290
Plate frame heat exchangers, 66
Polyethylene glycol, *see* Selexol process
Polytropic compression, 192
Polytropic efficiency, 195
POP (percentage of proceeds) contracts, 156
Pressure drop
in dehydration adsorption beds, 263, 265
in filter separators and coalescing filters, 111
in gas–liquid separators, 108, 110
in membrane processes, 100
in mist extracting devices, 108
in packed beds, calculation of, 267
in propane refrigeration units, 293
in TEG contactors, 257, 294
Pressure swing adsorption (PSA)
comparison to other separation processes, 103
comparison with temperature swing adsorption (TSA), 95
fundamentals of process, 93
for helium purification, 317
for nitrogen removal, 310
Printed circuit heat exchanger, 69
Process control systems, 155
Process flow diagram, *see* specific process
Processing condensate, 293, 332
Processing margins (Frac spreads), 159
Product specifications
liquid products, 139, 332
pipeline–quality gas, 139

Propane (C_3H_8)
dehydration, 338
fractionation, 340
product specifications, 139
sweetening, 333
transmission (*see* Transporting liquids)
uses, 137
Propane chiller in Selexol process, 236
Propane chiller, 283, *see also* Propane refrigeration
Propane extraction processes, *see* Ethane recovery
Propane recovery
as function of ethane recovery, 300
as function of separation temperature and gas composition, 296
in high ethane recovery processes, 300
in low ethane recovery processes, 296
Propane refrigeration, 282
compression work, 282
economizers, 285
effect of impurities on performance, 286
effect of operating conditions on performance, 286
multistaging, 286
typical operating conditions, 282
Pumps, *see also* specific pump type
comparison between centrifugal and positive displacement, 50
classifications, 33
flow and discharge pressure ranges, 34
flow control, 46, 49
temperature rise in, 38
power calculation, 38
priming, 50
work calculation, 38

Q

Quick cycle units for dew point control, 296

R

Radon, *see also* NORM
concentration in natural gas, 134, 320
decay rate and daughter products, 320
distribution in products, 320
Random packing, 89
common applications, 90
comparison with trays, 90
Raoult's Law
definition, 80
deviations from, 80
Reboilers
internal reboilers, 72
kettle reboiler, 70
once–through reboilers, 71
pump–through reboilers, 71
side reboilers, 70, 83, 292, 301
thermosyphon reboilers, 70
Reciprocating compressors, 199
flow control, 200
flow rate calculations, 209
maintenance costs, 213
power calculations, 210
volumetric efficiency of, 196
Reciprocating pumps, 47
flow control, 49
flow rate calculations, 48
Reclaimers, amine, 230, 245
Recycle split–vapor process (RSV), 302
Rectisol process, 222
Reduced pressure, definition, 207
Reduced temperature, definition, 207
Refrigeration process for low ethane recovery, 296
Regeneration of adsorbents, *see* Adsorption processes; Molecular sieve
Regenerators, *see* specific absorption process
for hot potassium carbonate process, 232
operating conditions in amine acid gas removal process, 230
operating conditions in TEG dehydration process, 256
Reid vapor pressure (RVP)
definition, 21
specifications for liquids, 140, 332
Relative density of gases and liquids, 12
Reliability, definition, 197
Residence time in separators, 114, 115
Retrograde condensation, 281
Rich oil demethanizer (ROD), 299
Rich Solvent, 87
Rollover, in LNG storage, 414
Rotary screw compressors, 200, 201
Rotary screw pumps, 49
R–value of materials, in relation to thermal conductivity, 54

S

Safety systems, 155
Salt cavern storage, 379
Satellite facilities, LNG, 389
SCADA (Supervisory control and data acquisition), 155
Scavengers for hydrogen sulfide removal, 243
SCOT process, 356, *see also* Tail gas cleanup
Screw compressors, 200, 201
Screw pumps, 49
Scrubbers, 105, *see also* Gas–liquid separator
Selective oxidation of hydrogen sulfide, 354
Selectivity in membranes, 97
in glassy and rubbery polymers, 97
Selectivity of amines for hydrogen sulfide removal, 222
Selexol process, 222, 233
Self–cleaning filters, 115
on gas turbines, 206
Shale gas
composition,133
definition, 128
resource, 130
Shell and tube heat exchanger
comparison with plate–frame exchanger, 66
definition, 62
Shrinkage, 158
Sieve trays, 89
in amine contactor, 335
common applications, 90
Silica gel
in adsorption processes, 91
for dehydration, 262, 274
for dew point control, 296
representative properties, 274

Slippage, of carbon dioxide in amine treaters, 225, 227
Slop oil, *see* Natural gasoline
Slug catchers, 105, 182, 184
Slugging, liquid, 169
Smart pig, 171
Solvent absorption, *see also* Amine treating; Glycol dehydration processes; Physical absorption for acid gas removal
  for acid gas removal from gas, 222
  advantages and disadvantages for acid gas removal, 222
  basic concepts, 85
  comparison to other separation processes, 102
  for dehydration of gas, 255
  for dehydration of liquid, 340
Solvent regenerator, *see* specific process; Regenerators
Specific gravity of gases and liquids, 10
Specific volume, *see* Density
Spiral wound membranes, 100
Stabilized condensate, 332
Stabilizer, *see* Condensate stabilizer
Standard conditions, 6
Static mixers, for increasing throughput to acid gas removal process, 230
Steam
  comparison with hot oil, 61
  in flare systems, 155
  in heat recovery, 205, 352, 442
  as heating medium, 61, 153, 230, 255
  make–up water, 61, 232
  turbines (*see* Steam turbines)
Steam turbines
  with compressors, 203
  with pumps, 47
Sterically hindered amines, 222
Storage, gas
  baseload, 375
  as LNG, 379 (*see also* LNG peakshaving facilities; LNG storage)
  necessity of, 369, 375
  types of, 372
  underground storage capacity in U.S., 378
  underground storage terminology, 377
Storage, liquids
  LNG (*see* LNG storage)
  LPG, 382
  NGL, 382
  in slug catchers, 184
  types of storage facilities, 382
Stranded gas reserves, 389
Stranded utilities, 389
Stretford process, 222
Strippers, *see* Fractionators; specific absorption process
Stripping gas
  for acid gas removal from liquids, 333, 442
  in fractionators, 83
  in glycol regeneration, 258
Structured packing, 89
  common applications, 90
  in TEG contactors, 256
Subcooling, related to gas hydrate formation, *see* Gas hydrates
Subquality gas, 219, 308
Sulfides
  in natural gas, 134
  removal from liquid, 334
Sulfinol process for gas treating, 222, 237
Sulfur compounds, *see* Hydrogen sulfide (H_2S); Sulfur, elemental; Carbonyl sulfide (COS); Mercaptans; Carbon disulfide (CS_2); Sulfur dioxide (SO_2)
Sulfur dioxide (SO_2)
  in Claus process, 350
  safety in sulfur handling and storage, 364
Sulfur emission regulations, 354
Sulfur recovery processes
  large capacity (*see* Claus process)
  small to medium capacity, 357
Sulfur recovery, *see* Claus process; Tail gas cleanup
Sulfur removal processes for liquids, *see* Liquid sweetening
Sulfur, elemental
  degassing, 361
  distribution of species in vapor phase, 348
  economic value of, 349
  generation in molecular sieve beds, 263, 272
  in mercury removal processes, 325
  molecular species in the vapor, 348
  in natural gas, 218
  physical properties of liquid, 348
  physical properties of solid, 347
  physical properties of vapor, 348
  production (*see* Claus process; Tail gas cleanup)
  safety and handling, 364
  storage, 361
  uses, 138
SUPERCLAUS, 355, *see also* Tail gas cleanup
Surface tension, definition, 17
Sweetening, *see* Acid gas removal processes
Synthetic zeolites, *see* Molecular sieve
System Curve, 45

T

Tail gas cleanup
  capital costs, 432
  cold bed adsorption (CBA), 355
  need for, 354
  SCOT process, 356
  SUPERCLAUS, 355
Transport, liquids, *see* Liquids transport
TEA (triethanolamine), structure, 223
TEG (triethylene glycol), *see also* Glycols; Glycol dehydration processes; TEG dehydration process
  capital costs, 430
  structure, 255
TEG dehydration process, *see also* Glycols; Glycol dehydration process
  BTEX emissions, 326
  capital cost, 430
  equilibrium water dew point as function of temperature and TEG purity, 258
  methods for increasing lean glycol purity, 257
  representative operating conditions, 257
  solubility of hydrogen sulfide and carbon dioxide in TEG, 259
  TEG losses in dehydration process, 259

Temperature profile in amine contactor, 229
TENORM, *see* NORM; Radon
Tetraethylene glycol, *see also* Glycols; Glycol dehydration processes, structure, 255
TGCU, *see* Tail gas cleanup
TGTU, *see* Tail gas cleanup
Thermal conductivity
  definition, 54
  of insulating materials, 55
THIOLEX process for mercaptan removal, 337
Thiopaq, 244
Tight gas, definition, 127
Total sulfur
  detecting, 218
  limits in hydrocarbon liquids, 139
  limits in LNG plant feed, 394
  limits in pipeline quality gas, 134
Transmix, 380
Transportation and Fractionation (T&F), 159
Transporting liquids
  LNG (*see* LNG transport)
  other than LNG, 380
Triazine, 244
Trim reboiler, 439
Turboexpanders, *see* Expanders (turboexpanders)
Turboexpansion compared to J–T expansion, 28, 298
Twister
  for dehydration, 274
  for dew point control, 294

U

Unconventional gas, *see* Natural gas; Coal bed methane (CBM); Gas hydrates; Shale gas; Tight gas
Units of measure, 3
Utilities, overview, 153, *see also* specific utility

V

Valve trays, 89
  common applications, 90
Vane pack, for coalescing, 107
Vapor pressure
  definition, 13
  of mixtures, 76
  Reid (*see* Reid vapor pressure)
  true, 78
Vapor recovery systems, 154
Variable speed drives (VSD), 197
Viscosity
  definition, 16
  of molten sulfur, 348
Volume, standard, *see* Standard conditions
Volumetric efficiency, of reciprocating compressors, 196

W

Waste heat boiler in Claus process, 352
Water
  concentration units, 250
  removal processes (*see* Gas dehydration; Liquid dehydration)
  solubility in gas as a function of temperature, pressure and composition, 251
  solubility in liquid hydrocarbons, 339
Water content
  in gas as a function of temperature, pressure and composition, 251
  for hydrate prevention, 177
  in liquid hydrocarbons, 337
  in products (*see* Product specifications)
  requirements in cryogenic processing, 250
Wellhead operations, 151, 164
Wellhead purchase contracts, 157
Wire mesh, for coalescing, 107
  Estimating mesh area required, 107
Wet surface air coolers, 65
Wobbe number
  definition, 143
  of LNG, 395, 420

Z

Zeolites, 91, *see also* Molecular sieve
Zinc oxide (ZnO) for hydrogen sulfide removal, 244