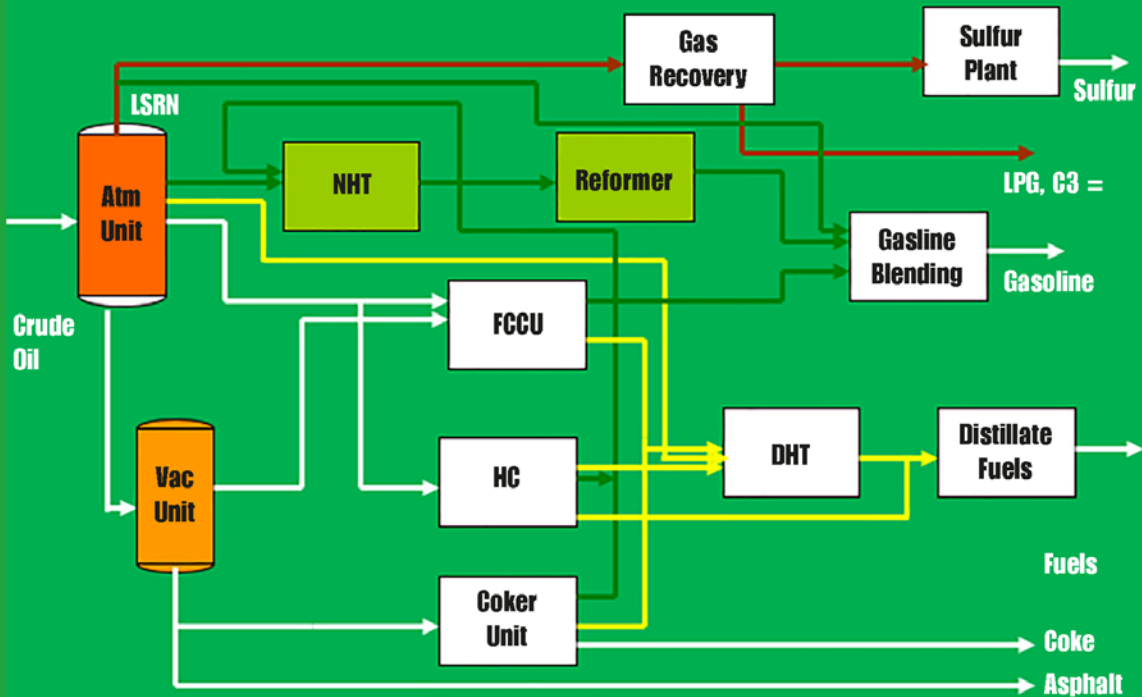


# Catalytic Naphtha Reforming Process

Soni O. Oyekan



# **Catalytic Naphtha Reforming Process**



# Taylor & Francis

Taylor & Francis Group

<http://taylorandfrancis.com>

# Catalytic Naphtha Reforming Process

Soni O. Oyekan



**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

© 2019 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: 978-1-138-03430-3 (Hardback)  
978-1-3152-7031-9 (eBook)

This book contains information obtained from authentic and highly regarded sources. Reasonable efforts have been made to publish reliable data and information, but the author 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) (<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>

---

# Contents

Preface.....	x1
Acknowledgments.....	xv
Author .....	xvii
<b>Chapter 1</b> Introduction to Catalytic Reforming and the Oil Business.....	1
1.0 Introduction .....	1
1.1 Early History of Crude Oil Business.....	2
1.2 Post-1900 History of Crude Oil Business.....	3
1.3 Source of Crude Oil.....	4
1.4 Crude Oil Reserves.....	5
1.5 Introduction to Opportunity Oils and Unconventional Oils.....	7
1.6 Global Oil Production .....	8
1.7 Oil Consumption .....	12
1.8 Crude Oil and Other Hydrocarbon Liquid Qualities.....	13
References .....	17
<b>Chapter 2</b> Basics of Crude Oil Refining .....	19
2.0 Introduction to Basics of Oil Refining.....	19
2.1 Crude Oil Composition.....	19
2.1.1 Paraffins .....	21
2.1.2 Naphthenes .....	22
2.1.3 Aromatics .....	23
2.1.4 Olefins .....	23
2.1.5 Heteroatom Compounds in Oils.....	24
2.1.6 Sulfur Compounds in Oils .....	25
2.1.7 Nitrogen Compounds in Oils.....	27
2.1.8 Asphaltenes .....	28
2.1.9 Porphyrins .....	30
2.2 Oil refining Economics.....	31
2.2.1 Oil Refining Profitability.....	31
2.3 Refinery Configurations .....	34
2.3.1 Topping Refineries .....	38
2.3.2 Hydroskimming Refineries .....	40
2.3.3 Cracking Refineries.....	42
2.3.4 Coking Refineries.....	43
2.4 Oil Refineries, Fuels, and Global Warming .....	51
2.4.1 Overview of Global Transportation Fuels.....	54
2.4.2 Diesel Fuels .....	55
2.4.3 Gasoline Fuels.....	56
References .....	60

<b>Chapter 3</b>	Overview of Oil Refining Process Units .....	63
3.0	Introduction .....	63
3.1	Crude Distillation Unit .....	63
3.2	Vacuum Distillation Unit.....	67
3.3	Butane Isomerization Unit.....	70
3.4	Light Naphtha Isomerization Unit.....	72
3.5	Hydrotreating Units .....	75
3.5.1	Hydrotreating Reactions.....	76
3.5.2	Hydrotreating Process Feedstocks and Catalysts .....	76
3.5.3	A Generalized Hydrotreating Process Unit .....	80
3.5.4	Light Naphtha Hydrotreating .....	81
3.5.5	Heavy Naphtha Hydrotreating.....	82
3.5.6	Gasoline Desulfurization .....	86
3.5.7	Distillate Hydrotreating.....	87
3.5.8	Vacuum Gas Oil Hydrotreating.....	90
3.5.9	Residual Oil Hydrotreating .....	94
3.6	Fluid Catalytic Cracking Units.....	95
3.7	Coking Process Units .....	98
3.8	Hydrocracking Processes .....	100
3.9	Alkylation Processes .....	102
3.10	Other Processes and Auxiliary Systems .....	104
3.10.1	Increased Hydrogen Demand.....	104
3.10.2	Sulfur Recovery Processes.....	105
	References .....	107
<b>Chapter 4</b>	Basic Principles of Catalytic Reforming Processes .....	111
4.0	Introduction to Basic Principles .....	111
4.1	A Brief History of Pre-1950 Catalytic Reforming Processes .....	112
4.2	Reforming Process Fundamentals.....	113
4.2.1	Octane Numbers.....	114
4.2.2	Process Objectives and Naphtha Feedstocks .....	117
4.2.2.1	Naphtha Composition .....	117
4.2.2.2	Heavy Naphtha Boiling Range .....	121
4.3	Key Catalytic Reforming Reactions.....	123
4.3.1	Naphthene Dehydrogenation .....	123
4.3.2	Isomerization of Naphthenes and Paraffins .....	124
4.3.3	Paraffin Dehydrocyclization.....	125
4.3.4	Paraffin Hydrocracking.....	127
4.3.5	Hydrodealkylation of Alkyl Aromatics.....	127
4.4	Process Variables of Catalytic Reformers .....	129
4.4.1	Reactor Temperature .....	130
4.4.2	Reactor Pressure .....	131

4.4.3	Recycle Gas Hydrogen to Hydrocarbon Molar Ratio .....	133
4.4.4	Reformate Octane.....	133
4.5	General Catalytic Reforming Operations.....	134
4.6	Catalytic Reforming Process Equipment .....	135
4.6.1	Reactors.....	136
4.6.1.1	Downflow Reactor .....	136
4.6.1.2	Spherical Reactor.....	137
4.6.1.3	Radial Downflow Reactor.....	138
4.6.1.4	Advances in Continuous Catalyst Regeneration Radial Reactor Design.....	138
4.6.2	Process Heaters .....	141
4.6.3	Heat Exchangers.....	145
4.6.3.1	Shell and Tube Heat Exchangers .....	145
4.6.3.2	Plate Heat Exchangers .....	148
4.6.4	Process Gas Compressors .....	149
	References .....	152
<b>Chapter 5</b>	<b>Catalytic Reforming Catalysts .....</b>	<b>155</b>
5.0	Introduction to Catalytic Reforming Catalysts .....	155
5.1	Reforming Catalyst Nomenclatures .....	156
5.2	Dehydrogenation/Hydrogenation Functionality of Reforming Catalysts .....	157
5.3	Acidic Isomerization Functionality .....	157
5.4	Platinum Catalytic Reforming Catalysts.....	159
5.5	Multimetallic Catalytic Reforming Catalysts .....	160
5.6	Catalyst Manufacturing Process.....	161
5.7	Catalyst Properties.....	162
5.7.1	Physical Properties .....	163
5.7.1.1	Bulk Density .....	163
5.7.1.2	Crush Strength .....	164
5.7.1.3	Catalyst Porosity .....	164
5.7.1.4	Surface Area .....	165
5.7.1.5	Attrition Resistance .....	168
5.7.2	Chemical Properties .....	170
5.7.2.1	Catalytic Reforming Catalyst Metals .....	170
5.7.2.2	Catalyst Chloride .....	171
5.8	Catalyst Evaluation Program .....	172
5.8.1	Catalyst Testing .....	173
5.8.1.1	Model Feed Test Program.....	173
5.8.1.2	Naphtha Feed Test Program .....	174
5.8.1.3	Catalyst Activation.....	175
5.8.1.4	Yield/Octane Test .....	176
5.8.1.5	Constant Octane Stability Test .....	177

5.9	Alumina Hydrothermal Stability Test .....	184
	References .....	187
<b>Chapter 6</b>	<b>Catalytic Reforming Technologies.....</b>	<b>191</b>
6.0	Introduction to Reforming Technologies.....	191
6.1	Semiregenerative Catalytic Reforming .....	192
6.1.1	Reformer Naphtha Feed .....	196
6.1.1.1	Heavy Naphtha Contaminants.....	198
6.1.1.2	Sulfur in Naphtha Feeds .....	198
6.1.1.3	Nitrogen in Naphtha.....	200
6.1.1.4	Naphtha Metal Contaminants.....	201
6.1.2	Process Variables .....	205
6.1.3	Water/Chloride Management .....	206
6.1.4	Catalyst Regeneration.....	208
6.1.4.1	Catalyst Coke Burn Principles.....	210
6.1.4.2	Catalyst Rejuvenation .....	212
6.1.4.3	Catalyst Metal Oxide Reduction.....	213
6.1.4.4	Catalyst Sulfiding .....	215
6.1.4.5	Sulfate Removal Procedure .....	216
6.2	Cyclic Catalyst Regenerative Reformers .....	218
6.2.1	Special Features of Cyclic Reforming Catalysts and Regenerations .....	221
6.2.2	Reliability Enhancement Programs .....	222
6.3	Continuous Catalyst Regenerative Reformers .....	222
6.3.1	Catalyst Circulation Systems.....	228
6.3.2	Catalyst Regeneration in Continuous Catalyst Regenerative Process Units .....	230
6.3.2.1	Primary and Secondary Coke Burns.....	232
6.3.2.2	Oxy-Chlorination Process .....	234
6.3.2.3	Drying and Cooling.....	235
6.3.2.4	Catalyst Reduction.....	236
6.4	Hybrid Catalyst Regenerative Reformers .....	237
	References .....	240
<b>Chapter 7</b>	<b>Catalyst and Process Management Challenges.....</b>	<b>245</b>
7.0	Introduction to Catalyst and Process Challenges .....	245
7.1	Physical and Chemical Characteristics of Catalysts .....	245
7.2	Catalyst Handling and Management .....	249
7.2.1	Catalyst Unloading Principles.....	249
7.2.2	Catalyst Loading Principles .....	251
7.3	Catalyst Management in Catalytic Reforming Operations ...	252
7.3.1	Key Performance Indicators and Unit Monitoring ..	254
7.4	Troubleshooting for Process Profitability.....	257

7.4.1	High Pressure Drop in Continuous Catalyst Regenerative Reformer Reactors.....	258
7.4.2	Managing Low Coke Naphtha Reforming in Continuous Catalyst Regenerative Process Units.....	260
7.4.3	Catalyst Regeneration Challenges.....	264
7.4.3.1	Flow Distribution Challenges in a Fixed-Bed Regenerative Reformer .....	265
7.4.3.2	Eliminate Delays after the Catalyst Oxy-Chlorination.....	266
7.4.3.3	Transition Smoothly between Black and White Burns in Continuous Catalyst Regenerative Regenerators .....	266
	References .....	270
<b>Chapter 8</b>	<b>Special Catalytic Reforming Topics.....</b>	<b>273</b>
8.0	Introduction to Special Catalytic Reforming Topics.....	273
8.1	Brief Review of Opportunity Oils and Reforming Operations .....	274
8.1.1	Initial Experiences with the Processing of Shale Oil.....	274
8.1.2	Challenges in the Processing of Opportunity Bitumen .....	276
8.1.3	Guidelines for Refining Opportunity Oils Can Minimize Losses .....	279
8.2	Strategies for Meeting Gasoline Benzene Regulations .....	282
8.2.1	Process Technologies for Meeting Gasoline Benzene Regulations .....	291
8.3	Chloride Management and Refinery Reliability.....	296
8.3.1	Management of Total Chlorides in Crude Unit Operations .....	296
8.3.2	Management of Chlorides in Oil Refining Processes .....	300
8.3.2.1	Chloride Management for Optimizing Reforming Operations .....	302
8.3.2.2	Mitigating HCl-Induced Fouling in Catalytic Reformers .....	303
8.3.2.3	Eliminating HCl in Net Hydrogen Gas from Catalytic Reformers .....	306
8.4	Catalytic Reformer Operations and Reliability Challenges with Refinery Maximum Achievable Control Technology II.....	309
8.5	Summary .....	314
	References .....	315

<b>Chapter 9</b>	Special Topics—Turnaround and Platinum Management.....	319
9.0	Introduction to Turnaround and Platinum Management .....	319
9.1	Turnaround Planning and Maintenance .....	319
9.1.1	Turnaround Planning for Catalytic Reforming Units .....	321
9.2	Overview of Platinum Supply and Management.....	326
9.2.1	Platinum Acquisition Cost.....	327
9.2.2	Fresh Catalyst Purchase .....	329
9.2.3	Catalyst Platinum Agreements.....	330
9.2.4	Catalyst Selection and Platinum Management.....	331
9.2.5	Overview of Platinum Management and Recovery .....	332
9.2.6	Platinum Recovery Processes .....	334
9.2.7	Catalyst Sampling and Settlement.....	335
	References .....	337
<b>Glossary</b>	.....	339
<b>Index</b>	.....	353

---

# Preface

It is with great pleasure that I offer this book as a product of my goal of conveying relevant information on key concepts, operations, and practices of catalytic naphtha reforming technologies and associated oil refining processes. This book will most likely be of use to those in academia and oil refining, petrochemicals, and allied businesses. I was motivated by several factors to write a book on the catalytic naphtha reforming process and technologies. Foremost is the need to review the collective technical and operational advancements with respect to efficient use of catalysts and catalytic reformers in oil refining.

The book on catalytic reforming by Donald Little published in 1985 and useful chapters in several other books provide fundamental and some practical aspects of catalytic reforming and light naphtha isomerization processes. Some of the chapters in separate books by James Gary and Glenn Handwerk; James Speight; and Bruce Gates, James Katzer, and G. C. A. Schuit provide relevant sections on catalytic reforming technologies. Books on catalytic naphtha reforming by George Antos, Abdullah Aitani, and Jose Parera provide comprehensive works with key basic and practical concepts of the catalytic reforming process and related sciences. The listed books were foundational for writing this book.

A second factor has been the need to incorporate key advancements from recent developments in catalytic reforming technologies and processes. Most of the recent innovations have been in continuous catalyst regenerative processes, and some of the enhancements are covered in this book. Some of the advancements in catalytic reforming have been driven by the need to provide high-octane reformate gasoline blendstock in current markets for unleaded and regulated environmentally friendly gasoline products. It is expected that this trend will continue as US and relevant global markets position to meet the projected Tier 3 Corporate Average Fuel Economy (CAFÉ) standard of 54.5 miles per gallon of gasoline for automobiles by 2025. In addition, as important as reformate production is, the higher demand for hydrogen production from catalytic reformers has re-emphasized interests in achieving reliable and efficient operations of the process units. Higher hydrogen demand is due to the increased requirements of oil refiners to produce ultralow-sulfur gasoline and diesel products. Furthermore, high-severity processing operations of catalytic reformers have led to increased organic chloride usage. Higher usage of organic chloride has exacerbated reliability challenges and heightened the need to establish cost-effective maintenance programs for piping and equipment, and for the other process units in oil refineries. Higher production of net hydrogen gas in catalytic reforming operations leads to increased use of chloride management strategies to protect oil refining equipment and process units from fouling and corrosion. The US Environmental Protection Agency (EPA) established stringent environmental regulations for the reduction of hydrogen chloride and toxic organic compounds (TOCs) in catalyst regeneration vent gases. Three major technologies are used for meeting the lower levels of hydrogen chloride and TOCs in regeneration vent gases. The caustic wash vent gas tower system, adsorbents, and Honeywell UOP's Chlorsorb are the available

technologies for reducing hydrogen chloride and volatile organic compounds in regenerator vent gas. The challenges associated with use of these technologies are discussed.

Third, with the shift to more abundant, high-contaminant conventional crude oils and unconventional bitumen and shale oils, catalytic reforming process units have now developed another critical role in conjunction with crude distillation units as “gatekeepers” in the optimization of the crude slates that are processed in oil refineries. The highly sensitive platinum-containing catalysts used in catalytic reforming units are very susceptible to metal contaminant poisoning in naphtha feeds at fractional parts per million levels. Oil refiners with good analytical and continuous monitoring programs can use their assets beneficially by applying them for monitoring the quality of the naphtha feed to catalytic reformers. These resources could enable oil refiners to detect changes in naphtha feed qualities, especially with respect to catalyst contaminants. Oil refiners can then develop timely responses to naphtha feed quality changes in catalytic reformers. These contaminants could be due to contaminant contributions from one of the oils that is being processed in the crude slate. Appropriate adjustments can then be made to optimize the percentages of oil constituents in the crude slates in order to minimize or eliminate catalytic reformer and refinery reliability and productivity challenges associated with the constituent oils in the crude slate. Meticulous and continuous monitoring of key performance indicators of the crude distillation and catalytic reforming process units are required, and the benefits of timely, effective unit monitoring are covered in this book.

The factors listed motivated me to write this book to incorporate many of the current key challenges, process developments, effective operations, and monitoring of catalytic reformers in order to achieve optimized oil refining operations and desired refinery reliability and profitability. In addition, since I could have benefited from a brief introduction to the history of the oil and oil refining business at the start of my career in oil refining about four decades ago, I devoted the first chapter of this book to a brief history of the oil business and emphasized the pioneering business leadership of John D. Rockefeller in growing Standard Oil at the turn of the twentieth century. Standard Oil became the dominant global oil production, refining, and marketing company at the beginning of the twentieth century. The history of oil production can enhance our understanding of current geopolitical developments that have led to changes in crude oil production and supply, crude oil quality, crude oil prices, and their impacts on oil refinery operations, profitability, and the fiscal health of national and global economies. The basics of oil refining are covered in the second chapter, and several oil refinery processes and transportation fuel specifications are covered in the third chapter. Brief reviews of oil refining process units are also provided in the third chapter. The reviews help to emphasize the pivotal position of the catalytic reforming process unit in oil refineries for the processing of straight run naphtha and unsaturated naphthas from other downstream thermal and catalytic conversion units in oil refineries. Catalytic reforming technologies, catalysts, and processes are covered in detail in the six chapters that follow. The eighth chapter is devoted to coverage of key specially selected topics of vital interest to enable successful, reliable, and optimal operations of catalytic reforming process units and oil refineries. Due to several challenges that can arise due to inadequate turnaround planning, subpar

execution of turnarounds, and safety problems during catalytic reformer startups, some best-practice concepts for turnaround maintenance are offered in [Chapter 9](#). An overview of cost-effective management programs for precious metals is provided with great emphasis on platinum management. Platinum management principles discussed can also be extended to managing other platinum group metals, as well as silver, rhenium, and palladium.

One of the goals of writing this book is to encourage a more proactive approach in the planning, operations and maintenance of catalytic reforming units and oil refineries. A number of recommendations are provided in this book for enhancing the operations, reliability, and productivity of catalytic reformers and oil refineries. These recommendations can lead to cost-effective, safer, and optimal process unit operations and maximization of the profitability of oil refiners.



# Taylor & Francis

Taylor & Francis Group

<http://taylorandfrancis.com>

---

# Acknowledgments

The contents, technical knowledge, and practical experiences covered in a book of this nature are developed via grounding in the principles of chemical engineering, catalysis, and oil refining processes. As a result, it is appropriate for me to start by acknowledging the training that I received from Professor Anthony Dent during my doctoral studies on reactor engineering and catalysis at Carnegie Mellon University. I am also grateful to Professors Csaba Horvath and Harding Bliss for the positive influences they had on me in my studies of reaction kinetics and thermodynamics, respectively, when I was at Yale University.

In the writing of a book of this scope, I have had to draw from course notes, technical presentations, and relevant data from my patents on the catalytic naphtha reforming process and other sources. The information that I share comes from about 40 years of technology development and training course notes that I shared with oil refining engineers and operators. Some of the older introductory information comes from the Petroleum Refining course that I taught at the New Jersey Institute of Technology, Newark, in 1983. Over the past 25 years, I taught courses on catalytic reforming, naphtha hydrotreating, paraffin isomerization, fluid catalytic cracking, aromatics isomerization, and sulfur guard bed systems to oil refining process technology personnel who worked with me at Sunoco, Amoco, and Marathon Petroleum Corporation.

My lecture notes were updated and used as part of a course that was offered in collaboration with Peter Kokayeff of Unocal and Dr. Stuart S. Shih of Mobil Oil for the American Institute of Chemical Engineers (AIChE) Continuing Education program between 1992 and 1998. The title of the course was Catalytic Processes in Petroleum Refining. Dr. Shih taught the hydrotreating processes section, the hydrocracking processing was taught by Kokayeff, and I taught the sections on catalytic reforming and fluid catalytic cracking processes.

A number of companies contributed to my development and experiences in research and development of oil refining technologies and operations of oil refining, and I gratefully acknowledge them. The companies are Exxon (now ExxonMobil), Engelhard (now BASF), DuPont, Sunoco, Amoco, and Marathon Petroleum Corporation.

For the continuous catalyst regenerative (CCR) process units and technologies, I acknowledge with special gratitude Axens and Honeywell UOP, for the opportunities to collaborate on several technical, revamp, and grassroots catalytic reforming projects with many of their personnel on CCR process-related challenges. In a number of sections, figures of process units from technical papers by Axens and Honeywell UOP have been used to enhance the quality of the description of the CCR processes. I thank the companies for granting me copyright permissions to use relevant images.

Lastly and foremost, I thank my wife, Priscilla Ann, for her love, support, and encouragement always, and especially during the time that I spent in writing this book. In addition, I am indebted to her for encouraging me to write with greater

clarity and make the content of the book of higher value for a wide spectrum of persons such as business executives, financial analysts and planners, environmental engineers, oil refining technical personnel and operators, chemical plant operators, and persons in academic communities. I thank my wife also for the many useful suggestions that she offered with respect to the chapters in the book.

---

# Author

**Soni O. Oyekan, PhD**, is president and CEO of Prafis Energy Solutions. He is a globally renowned expert in oil, gas, and oil refining. Dr. Oyekan was the corporate process technologist for Marathon Petroleum Corporation, BP/Amoco, and Sunoco separately, with responsibilities for naphtha processing, oil refining processes, and technology support over a span of 20 years. Prior to 1993, Dr. Oyekan conducted R&D studies at Exxon, Engelhard, and DuPont for 16 years, which resulted in his inventions for catalytic naphtha reforming. His key inventions are used globally to enhance the production of transportation fuels. Dr. Oyekan is the 2008 recipient of the AIChE William M. Grimes award for excellence in chemical engineering. He was awarded the NOBCCChE Percy Julian award in 2009 for his outstanding contributions in oil refining.

The author, a resident of Richmond, Texas, is a Fellow of the American Institute of Chemical Engineers and a member of the AIChE Foundation Board of Trustees and of NOBCCChE. He is a member of the Nigerian Society of Chemical Engineers, Sigma Xi, and Phi Kappa Phi societies.

Dr. Oyekan earned his BS degree (1970) in Engineering and Applied Sciences from Yale University, New Haven, Connecticut, and his MS (1972) and PhD (1977) degrees in Chemical Engineering from Carnegie Mellon University, Pittsburgh, Pennsylvania.



# Taylor & Francis

Taylor & Francis Group

<http://taylorandfrancis.com>

---

# 1 Introduction to Catalytic Reforming and the Oil Business

## 1.0 INTRODUCTION

Catalytic reforming is the process used in oil refineries for converting the low-value heavy naphtha fraction of crude oil to premium reformate, benzene, toluene and xylene (BTX), and hydrogen. As will be reviewed in detail, reformate constitutes about 30% of the gasoline that is produced. Hydrogen from catalytic reformers is used as coreactant in several hydroprocessing units in oil refineries. In some oil refineries, the catalytic reformer is the sole provider of a refinery's hydrogen. Additionally, benzene, toluene, and xylenes are used in the petrochemical industry in the production of other chemicals and solvents. Numerous technological advances have been made to improve catalytic reforming processes so as to provide increased productivity over much longer times between turnaround maintenance periods. Starting with a thermal naphtha cracking process, reforming technologies have evolved through fixed-bed semiregenerative catalytic reforming and fixed-bed cyclic regenerative reformers to the current high-performance, high-productivity continuous catalytic regenerative technologies. In the catalytic reforming process, as is the case for other catalytic processes, the catalyst during hydrocarbon processing loses activity with time and has to be regenerated. With the exception of continuous catalyst regenerative reforming processes, a reformer or a reactor shutdown is required to effect necessary catalyst regeneration and catalytic activity recovery for fixed-bed regenerative catalytic reformers.

In this book, some of the regulated gasoline quality requirements such as lower benzene concentrations and oxygenate blending that have some impact on catalytic reforming process operations are reviewed in appropriate chapters. Some of the expected regulated reductions of aromatics may further impact catalytic reforming units' utilization. The demand for BTX in the petrochemical industry and hydrogen for increased upgrading of heavy sour crude oil and unconventional bitumen-derived oils in oil refineries will continue to drive the need for more efficient and smart operations of catalytic reformers. Additionally, I have dubbed catalytic reformers "gate keepers" of oil refineries, as they are the first major catalytic conversion units after the crude distillation units. Catalytic reformers, with their highly sensitive platinum-containing catalysts, exhibit catalytic performance declines with the introduction of low concentrations of contaminants from the crude unit that are present in hydrotreated naphtha feeds. In the current era of the processing of a variety of crude oils and unconventional oils with highly variable qualities, changes

in catalytic reforming operations are often relatable to changes in either one of the crude oils or crude slate that the oil refiner is processing.

## 1.1 EARLY HISTORY OF CRUDE OIL BUSINESS

There is a long history of the use of oil by people. Historians suggest that crude oil was used over 5000 years ago and that Noah applied heavy crude oil or tar to his ark to maintain the ark and protect it from water damage. Noah, the ark, and the flood are discussed in the book of Genesis of the Bible. It has also been reported that China used oil in laboratories as early as 200 BCE. There are some historical reports of the use of crude oil in China and Japan in the seventh century. Historians indicate that by 1100 CE, Christian crusaders were “setting petroleum alight” and frightening and overcoming their enemies in battles. We are also informed that early immigrants in North America gathered the “black goo” or oil and used it for medicinal purposes. The “black goo” was used as ointment and medicine for toothache, fever, burns, open sores, and rheumatism and for caulking canoes by the Seneca Indians.<sup>(1)</sup>

The vast global oil and gas businesses that we now participate in and enjoy owe some of their origins to a little-known Persian physician and chemist, Muhammad Ibn Zakariya Razi, who in the ninth century demonstrated that kerosene could be produced via distillation of oil to generate a clean product for lamps.<sup>(2)</sup> In the middle of the nineteenth century, a Polish chemist, Filip Neriusz Walter, and a Scottish chemist, James Young, were later credited as key contributors in improving the process for the production of kerosene from crude oil via distillation. By 1848, James Young had an operating oil refining company producing kerosene.<sup>(3)</sup> Ignacy Lukasiewicz is credited by some with building the world’s first oil refinery in 1856. His legendary achievements included the discovery of how to distill kerosene from crude oil, the invention of the modern kerosene lamp, the introduction of the first street lamp in Europe in 1853, and the construction of the world’s first modern oil well in 1854.<sup>(4)</sup> About this time, there was significant oil production in Baku, and Meerzoeff is reported to have built the first modern Russian refinery at Baku by 1861.<sup>(5)</sup>

Abraham Pineo Gesner is recognized as one of the founders of the oil business in North America and Canada based on his three initial US patents on the production of kerosene from crude oils, which spurred extensive exploration and production of oil within the United States and Canada.<sup>(6)</sup> Kerosene was found to burn cleaner and cheaper than whale oil, and interest in the production of kerosene for lighting led to the beginnings of businesses based on oil. Oil and gas businesses have now grown exponentially into the global oil and gas business that we know.

After the startup of a plant by Abraham Pineo Gesner in 1854 for the production of kerosene for lamps, kerosene production reached 5000 gallons per day in the United States. The lure of instant wealth from the production of kerosene from crude oil led to increased exploration and production of oil. George Bissell, Edmund L. Drake, and William Smith were early innovators in developing technologies for the exploration and production of oil. By 1859, there were 34 startup companies, and they were producing a staggering 5 million gallons of kerosene annually. At the famous Pithole City, Pennsylvania, oil production reached 6000 barrels per day by 1865, and

unfortunately, this was followed soon by diminishing oil production rates, which finally led to a deserted Pithole City by 1869.<sup>(1,7,8)</sup>

Major investors made their play for oil, and that group included the great entrepreneur, business genius, and oil magnate, John Davidson Rockefeller, who transformed the oil business through ownership of Standard Oil. By 1879, Standard Oil owned 90% of the oil refining capacity in the United States, and by 1891, it owned an overwhelming 25% of oil production, 90% of the oil refining capacity, and an extensive transportation system for moving oil and refined products in the United States and in the world. The most productive oil find known at that time occurred in 1901 in Spindletop, just outside of Beaumont, Texas, in the United States. The Spindletop oil production rate was estimated at 72,000 barrels per day, and money from Spindletop later fueled the growth of the Gulf Oil Company.<sup>(7)</sup>

## 1.2 POST-1900 HISTORY OF CRUDE OIL BUSINESS

As a result of the oil business boom in the United States, a number of companies such as Gulf Oil, Phillips, and Texaco Fuels Oil began to operate and compete with Standard Oil at the start of the twentieth century. With the invention of electricity by Thomas Edison, the kerosene business for lighting was severely challenged, and rescue came from Ford and the automobile industry. The automobile's internal combustion engine had to be powered with gasoline or petrol. New demand for gasoline led to the installation of more oil refining capacities, which led to an increased need for oil exploration and production. This was followed by expansion of infrastructure for storage, capital for pipelines, and railroads for movement of crude oil and distribution and marketing of finished products.<sup>(8-10)</sup>

John D. Rockefeller continued to lead and grow Standard Oil and the United States economy by his exceptional business acumen and practices. However, some of his business practices were unacceptable for his competitors. Essentially, Rockefeller's business strategies eliminated inefficient businesses as Rockefeller focused on acquisition of smaller competing companies. Rockefeller understood the benefits of vertical and horizontal integration and the economy of scale, as his leadership strategies for Standard Oil positioned his company as the leader in oil exploration and production, oil refining, petrochemicals, transportation and distribution, and retail marketing in the United States and worldwide.<sup>(11)</sup>

To compete effectively with Standard Oil, Royal Dutch Oil and Shell Transportation and Trading Company (Shell) amalgamated to form the Royal Dutch Shell Company in 1907. As the application of mechanization increased in the early 1900s, the demand for gasoline increased, as gasoline was used as fuel by automobiles and airplanes. Increased demand for gasoline was met with greater expansion of every aspect of the oil business from exploration and production to distribution and marketing of refined transportation fuels. Standard Oil continued to encounter increased distrust of its business practices, which in part had its origin in Standard Oil's business relationships with the railroad companies and its effort to eliminate competition in the business segments that Standard Oil was engaged in. Due to the highly aggressive business practices of Standard Oil and concerns about a possible oil business monopoly, the United States Supreme Court ruled in 1911 that Standard Trust or Standard

Oil Company had operated to monopolize and restrain trade and ordered that the company be dissolved into 34 smaller competing companies, significantly degrading the size and business clout of Standard Oil.<sup>(11,12)</sup>

A major global oil and energy-impacting event occurred in September 1960 in Baghdad, Iraq, with the formation of the Organization of the Petroleum Exporting Countries (OPEC) by five countries, namely Iran, Iraq, Kuwait, Saudi Arabia, and Venezuela. The OPEC group was later expanded to include Qatar (1961), Indonesia (1962), Libya (1962), the United Arab Emirates (1967), Algeria (1969), Nigeria (1971), Ecuador (1973), Gabon (1975), and Angola (2007). Gabon and Ecuador later terminated their memberships, while Indonesia suspended its membership in 2009 and reactivated it in 2016. The OPEC countries currently produce about 40% of global oil and have about 75% of the proved oil reserves.<sup>(11,12)</sup>

The 1973 oil embargo and subsequent events in the oil and gas industry continue to show the clout of OPEC in crude oil pricing and the politico-economic decisions of non-OPEC countries. Impacts of a number of OPEC decisions and drastic cyclical economic downturns for the oil and gas industry led to consolidations of oil and gas companies through mergers and acquisitions after 1995. Merger and acquisition activities led to the formation of super major oil companies such as ExxonMobil, British Petroleum, Royal Dutch Shell, Total S.A., and Chevron. Other major global companies based on assets and revenues include Saudi Aramco of Saudi Arabia, Sinopec, Chinese National Petroleum Corporation (CNPC) and PetroChina of China, Kuwait Petroleum Corporation of Kuwait, ENI of Italy, and Lukoil of Russia. There are other national oil-exporting companies that also feature prominently with respect to crude oil source and oil qualities and in disruption of crude oil supplies and pricing. National oil-exporting companies such as National Iranian Oil Company (NIOC), Petroleos de Venezuela, (PDVSA), Nigerian National Petroleum Corporation (NNPC), and Petroleos Mexicanos (PEMEX) are expected to continue to impact crude oil supply and pricing for a variety of factors. Some of the factors include the size of proved oil reserves for Iran and Venezuela and periodic oil production challenges in some of the countries such as Nigeria and Venezuela.

### 1.3 SOURCE OF CRUDE OIL

Crude or petroleum oil is a complex mixture of thousands of hydrocarbon compounds with broad ranges of molecular weights and boiling points. In addition to compounds that contain only carbon and hydrogen, there are also a variety of organic compounds containing separately sulfur, nitrogen, nickel, and vanadium, as well as other contaminant metals. Inorganic contaminant metals such as sulfur, nitrogen, nickel, vanadium, calcium, magnesium, and copper are referred to as heteroatoms, as they are different from the carbon and hydrogen atoms in hydrocarbons. The wide variety of thousands of hydrocarbon compounds provides the bases for the use of various fractions, components, and compounds of oil in energy generation and in the manufacture of products for transportation, heating, lubrication, chemicals, pharmaceuticals, plastics, automotive industries, agriculture, clothing, and packaging. As a result of the use of oil and oil products as feedstocks in so many chemically based manufacturing industries, oil is most essential for sustaining our manufacturing plants and driving national economies.

Oils are usually found in various reservoirs where they have accumulated over the past millions of years. During that time, conversion of dead organisms, zooplanktons and algae, have occurred to form complex hydrocarbon mixtures through intense compression and heating in geologic formations.<sup>(14,15)</sup> Crude oils are found in onshore and offshore deposits in many regions of the world. As per the 2015 ranking of countries with major proved oil reserves, Venezuela, Saudi Arabia, Canada, Iran, and Iraq are the top five with proved oil reserves for each country of at least 140 billion barrels.

Petroleum fossil oil is not a renewable resource and there have expectedly been some concerns with the rate of consumption of oil relative to the rate of frequent discoveries of sizeable oil finds for oil replacements. Oil reserves, oil daily production rates, and some technological advancements for producing unconventional oils such as shale and bitumen from oil sands are reviewed in some detail later in this chapter.

## 1.4 CRUDE OIL RESERVES

An estimate of proved oil reserves is a moving target, as major oil discoveries made in the last 15 years via application of innovative technologies for oil exploration and production have significantly changed the ranking of countries. In addition, advances in deepwater oil-production technologies have also greatly increased oil discoveries and production. A conservative estimate is that total global proved oil reserves are about 1.6 trillion barrels, with about 70% of that estimate in the OPEC countries as of the first quarter of 2016. OPEC countries such as Venezuela, Saudi Arabia, Iran, Iraq, and Kuwait dominate, with at least 100 billion barrels each in oil reserve, as shown in [Table 1.1](#).<sup>(12,13)</sup>

As shown in [Table 1.1](#), OPEC countries Venezuela, Iran, Iraq, Libya, and Qatar now own huge amounts of proved oil reserves due to major oil discoveries in the last 20 years. Data in [Table 1.1](#) and [Figure 1.1](#) show that Venezuela, which had 64.4 billion barrels of proved oil reserves in 1993 and substantially lower than the 261 billion barrels of Saudi Arabia, now owns 298 billion barrels of oil and ranks as the country with the highest proved oil reserve in the world. Saudi Arabia's huge oil reserves are centered in the giant Ghawar field, whose oil reserves are estimated to be in excess of 75 billion barrels. Venezuela owns huge extra-heavy oil reserves that are roughly estimated to be greater than 500 billion barrels in the country's Orinoco belt region. It is estimated that 220 billion barrels of those have been credited as part of the 298 billion barrels of proved oil reserve for Venezuela at this time. Due to capital and financial constraints, political issues, and the quality of the extra-heavy oil in the Orinoco Belt region, oil production has not been as high as it could be. Based on its massive proved oil reserves, Venezuela has the potential to achieve much higher production rates in future.

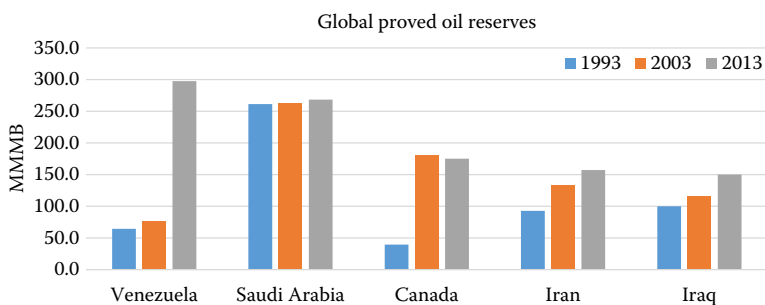
Non-OPEC countries such as Canada, Brazil, the United States, and Russia have also discovered huge reserves of unconventional oil and mostly bitumen from oil sands in Canada and shale oil in the United States. As shown in [Table 1.1](#), Canada's proved oil reserve grew from 39.5 billion barrels in 1993 to 175.4 billion barrels in 2013. The United States has benefited from applications of advanced oil geophysical technologies for unlocking a number of discoveries of shale oil deposits, and that has boosted the US oil reserves from 30.2 billion barrels in 1993 to 44 billion barrels in 2013.<sup>(12,13)</sup>

**TABLE 1.1**  
**Countries with High Proved Oil Reserves,**  
**MMMB 1993 to 2013**

Country	1993	2003	2013
Venezuela	64.4	77.2	297.7
Saudi Arabia	261.4	262.7	268.4
Canada	39.5	180.4	175.2
Iran	92.9	133.3	157.3
Iraq	100.0	116.0	150.0
Kuwait	96.5	99.0	101.5
UAE	98.1	97.6	97.8
Russia	n/a	79.0	93.0
Libya	22.8	39.1	48.5
Nigeria	21.0	35.3	37.3
USA	30.2	29.4	44.0
Kazakhstan	n/a	9.0	30.0
China	16.4	15.5	18.1
Qatar	3.2	27.0	25.2
Brazil	5.0	10.6	15.6

*Source:* Data taken from United States Energy Information Administration Reports. Giddens, P. H., *The Birth of the Oil Industry*, Porcupine Press, The Macmillan Company, New York, 1938; Williamson, H. F., Daum, A., Andreano, R., *The American Petroleum Industry, 1899–1959, The Age of Energy*, Northwestern University Press, Evanston, Illinois, p. 16.<sup>(10,11)</sup>

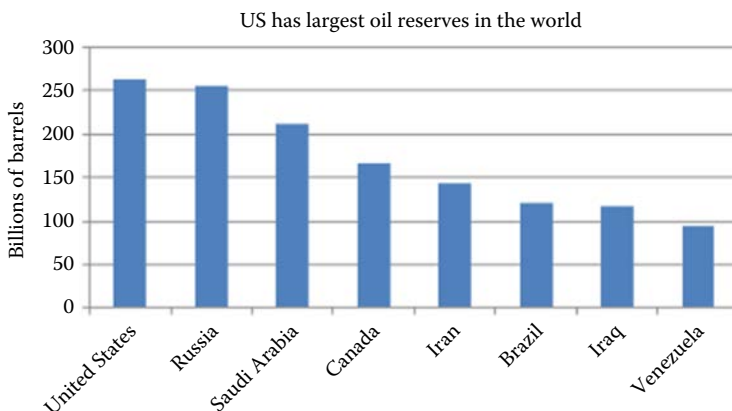
*Note:* MMMB is billions of barrels.



**FIGURE 1.1** Top five countries' proved oil reserves for 1993 to 2013.

*Note:* MMMB is billions of barrels.

It is necessary to emphasize the ever-changing landscape and leaderboard of proved oil reserves with time. A recent independent assessment report of proven oil reserves as of 2016 by Rystad Energy, a Norwegian consulting company, using data not provided by oil-producing countries, now shows that the United States has moved ahead of Saudi Arabia, Russia, and Venezuela as the global leader in oil reserves, with



**FIGURE 1.2** Proved oil reserves July 2016 by Rystad.

From Cunningham, N., US Has World's Largest Oil Reserve. Oil Price, 2016, <http://oilprice.com/Energy/General/US-Has-Worlds-Largest-Oil-Reserves.html>.<sup>(28)</sup>

over 260 billion barrels. Rystad Energy oil reserves data are as shown in Figure 1.2.<sup>(28)</sup> Rystad argued that there are no uniform ways to measure oil reserves and, as a result, oil reserves assessments differ grossly. It was suggested by Rystad that the United States holds over 260 billion barrels of oil reserves and more than 50% of that was located in shale formations.

## 1.5 INTRODUCTION TO OPPORTUNITY OILS AND UNCONVENTIONAL OILS

The goal of the review of the history of oil in this book is to share the author's appreciation of the rapid development of the oil business in the last 170 years. Additionally, items covered in this introductory section should provide appropriate background for a good understanding of the sources of crude oil, crude oil and liquid production, crude oil consumption rate, conventional and unconventional oil qualities, and oil prices. Opportunity oils are crude or unconventional oils and oil fractions that become available at "opportune" times and at favorable discounted prices. For opportunity crude oils, their prices are usually highly discounted relative to Western Texas Intermediate (WTI) and Brent crude oils. However, opportunity oils may vary widely with respect to the composition of their naphtha, distillate, gas oil, and residual oil fractions and heteroatom contaminant concentrations. Furthermore, the properties of naphtha, distillate, gas oil, and residual oil fractions from a crude distillation unit depend on the percentages of the constituent crude and unconventional oils in the crude slate. Since the ultimate properties of naphtha, distillate, gas oil, and residual oil feeds to downstream processing units are highly dependent on the oils in the crude slate, it is important to fully characterize the crude oils before purchasing and definitely before processing the oils in refineries. *Unconventional oils* in this book refers to bitumen-derived oils and tight or shale oils produced via nontraditional technologies such as surface mining, steam-assisted gravity drainage (SAGD) and hydraulic fracking.

Where applicable, unconventional oils should be reviewed in detail, as the properties of unconventional oils vary widely and are significantly different from the oils produced via conventional extraction technologies. Factors that can cause variability in the properties of unconventional oils are covered in some detail in a subsequent chapter in this book. Factors that are relevant in the ranking of countries with respect to oil reserves, daily oil production, and global oil consumption rates are provided.

## 1.6 GLOBAL OIL PRODUCTION

Crude oil production rates vary over time due to a multitude of factors. Contributory factors include production and supply disruptions as a result of vandalism of oil production assets, direct attacks and kidnappings of oil production personnel, regional conflicts, political factors, and OPEC-imposed production constraints on its members. OPEC-imposed constraints could impact the oil production rates of OPEC and non-OPEC countries as well as prices of crude oils. The oil glut of 2015 led to the collapse of oil prices, with negative consequences for the development and production of unconventional oils, as their costs of production are typically higher than those of conventional crude oils. The top-ranked daily oil-producing country has been Saudi Arabia and, as shown in [Table 1.2](#), Saudi Arabia maintained its position between 2003 and 2013. Saudi Arabia's production rate has been a dominant factor with respect to some of the oil production decisions made by OPEC. The daily production rates of petroleum oil for the top 15 countries are listed in [Table 1.2](#). Daily crude oil production rates of the top five countries for the years of 2003, 2008, and 2013 are as shown in [Figure 1.3](#).<sup>(12,13)</sup>

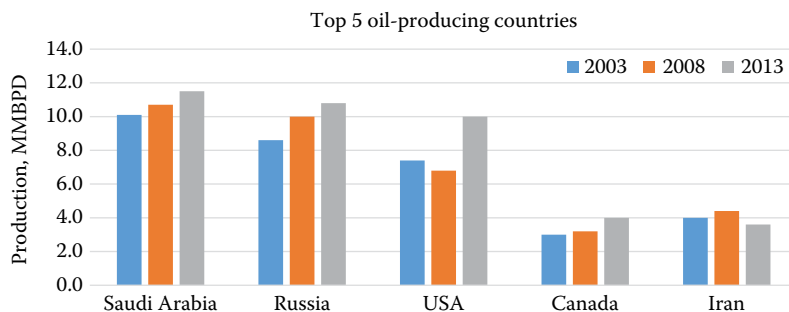
Oil production ranking for countries differs considerably, however, when it is based on total petroleum and other hydrocarbon liquids, as shown in [Table 1.3](#). Total

---

**TABLE 1.2**  
**Daily Crude Oil Production of Countries in**  
**MMBPD**

Country	2003	2008	2013
Saudi Arabia	10.1	10.7	11.5
Russia Federation	8.6	10.0	10.8
USA	7.4	6.8	10.0
Canada	3.0	3.2	4.0
Iran	4.0	4.4	3.6
Iraq	1.3	2.4	3.1
Venezuela	2.9	3.2	2.6
Kuwait	2.4	2.8	3.1
Nigeria	2.2	2.2	2.3
Mexico	3.8	3.2	2.9
Kazakhstan	1.1	1.5	1.8
Norway	3.3	2.5	1.8
Libya	1.5	1.7	1.0
Angola	0.9	1.8	1.8
Algeria	1.8	1.8	1.7

---



**FIGURE 1.3** Daily oil production rates in millions of barrels of oil per day (MMBPD) of top five countries.

petroleum and other hydrocarbon liquids as defined consist of crude oils, condensates, tight oil, extra-heavy crude oil, and bitumen produced by a country. Tight oil refers to oils that are produced from shale formations. Special unconventional technology referred to as hydraulic fracking is required for successful production of shale or tight oil. Bitumen is oil derived from oil sands and produced via surface mining and steam-assisted gravity drainage technologies. Bitumen as used in Table 1.3 represents the sum of all bitumen-derived oils, including diluted bitumen (Dilbit) and upgraded bitumen, and is referred to as a syncrude oil.

Diluted bitumen is bitumen that has a diluent such as water, condensate, naphtha, or crude oil added to permit facile transportation of the bitumen. An upgraded

**TABLE 1.3**  
**Total Petroleum and Other Liquids Production**  
**MMBPD**

Country	2006	2010	2014
USA	8.3	9.7	14.1
Saudi Arabia	11.1	10.9	11.6
Russia	9.7	10.3	10.9
China	3.9	4.4	4.6
Canada	3.3	3.4	4.4
UAE	3.0	2.8	3.5
Iran	4.2	4.2	3.5
Iraq	2.0	2.4	3.4
Brazil	2.2	2.7	3.0
Mexico	3.7	3.0	2.8
Kuwait	2.7	2.5	2.8
Venezuela	2.8	2.6	2.7
Nigeria	2.4	2.5	2.4
Qatar	1.3	1.8	2.1
Norway	2.8	2.1	1.9

*Note:* MMBPD is millions of barrels of oil per day.

bitumen oil is bitumen that has been upgraded via thermal and catalytic processes in order to improve the qualities of the resultant oil and render it suitable for processing in oil refineries. Synthetic crude oils are usually higher priced relative to the diluted bitumen oil or Dilbit, which is an oil sands–derived oil that has not been subjected to significant thermal and/or catalytic upgrading.<sup>(16,17)</sup> Details of unconventional oil production technologies are covered later in this section. Other liquids included in the data in Table 1.3 are natural gas plant liquid (NGPL), biofuels, gas-to-liquids (GTL), and coal-to-liquid (CTL) products.<sup>(12)</sup>

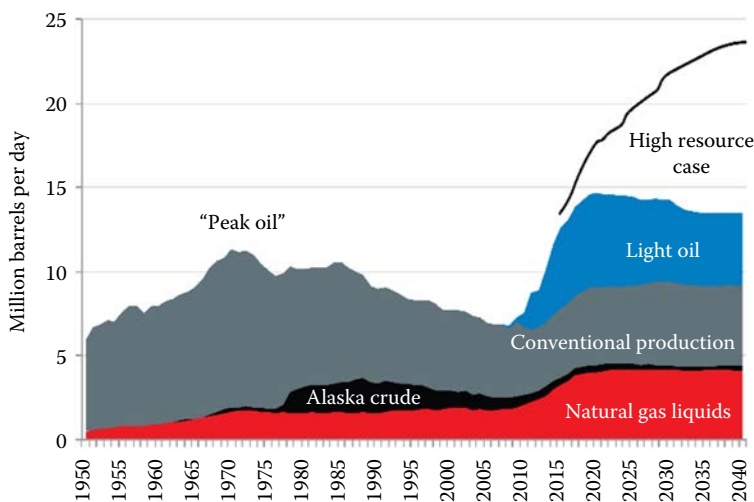
Projected increases in the production of natural gas liquids and light tight oil would most likely maintain the position of the United States as the top producer of total petroleum and other liquids in the world through 2040, as shown in Figure 1.4.<sup>(12)</sup>

Total oil liquid production for the United States shows that light tight oil and natural gas liquid production would increase significantly after 2015 and would be much higher than conventional oil rates.

2015 total liquid and gas production for the United States, Russia, and Saudi Arabia in Figure 1.5 shows that the United States maintained its position as the top producer of total liquids and gas.

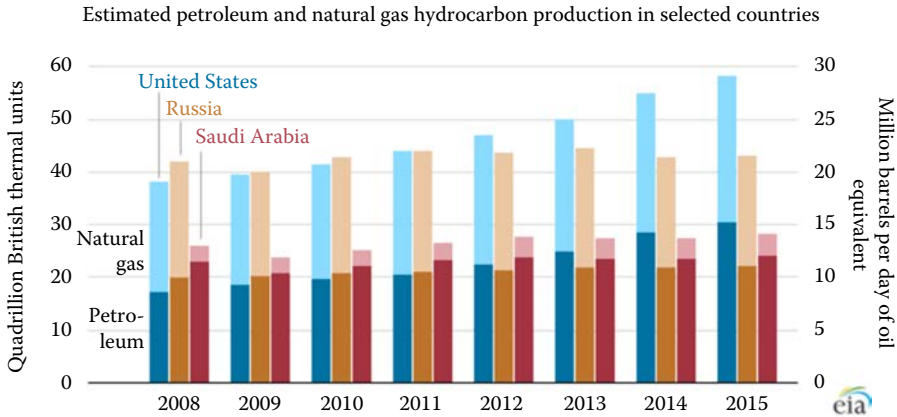
Unconventional oils represent a growing segment of oils from oil sands, shale rock, and deepwater that have to be extracted via the application of innovative, nontraditional drilling and extraction technologies. There are a variety of technologies used, and the major ones are surface mining and steam-assisted gravity drainage for oil sands and fracking for light tight oil from shale rock formations, as indicated previously.

Steam-assisted gravity drainage extraction is applied in addition to the extensively used surface mining for extracting bitumen from oil sands. Current extractive production of bitumen via surface mining is energy intensive, as only 10% of the



**FIGURE 1.4** US total liquids through 2040.

From US Energy Information Administration [EIA] Reports; Lance, R., The Benefits of US Crude Exports, IPAA Annual Meeting, November 13, 2014. [www.conocophillips.com/files/resource](http://www.conocophillips.com/files/resource).<sup>(12,27)</sup>



**FIGURE 1.5** Total liquids and gas production 2008–2015.  
*Note:* Lower bar represents total hydrocarbon liquids and upper bar total gas. Units are in million barrels per day of equivalent oil and quadrillion British thermal units. (From US Energy Information Administration [EIA] Reports.<sup>(12)</sup>)

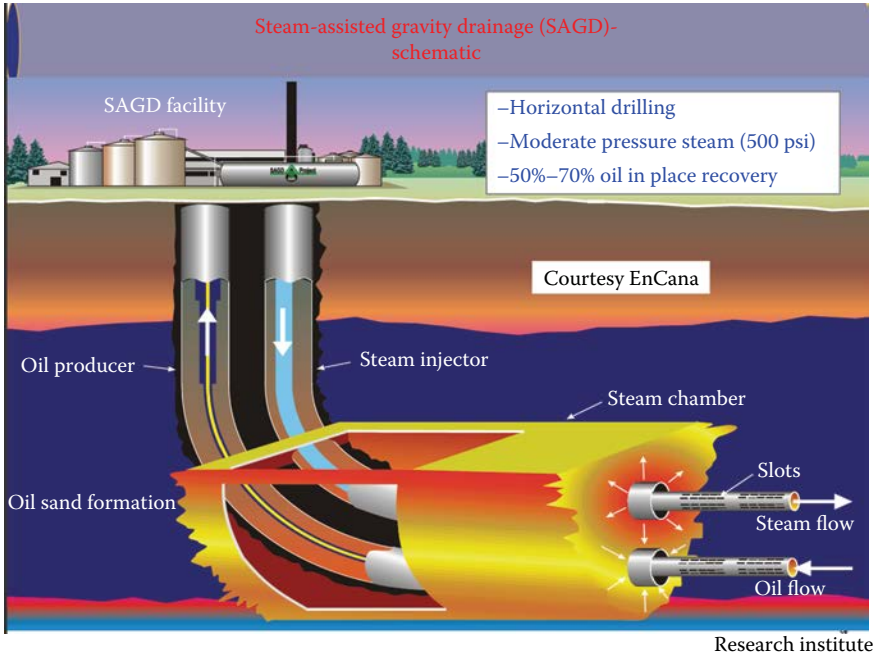


**FIGURE 1.6** Surface mining for recovery of bitumen.

sand, clay, and water is bitumen. A surface mining site is as shown in [Figure 1.6](#), and a schematic of the steam-assisted gravity drainage technology is shown in [Figure 1.7](#). In both SAGD and surface mining extractive processes, significant amounts of energy from natural gas use and for separation of oil from sands are required to produce a barrel of bitumen from oil sands.<sup>(17)</sup>

The need for innovative energy-efficient technology for extracting bitumen directly from oil sands is great. Surface mining extraction is currently in use in Canada and Mexico for the production of bitumen.

Light oils consist of tight and shale oils that are produced essentially from impermeable shale rock type formations. Shale is fine-grained sedimentary rock that is easily broken into parallel layers. Shale rock formations can contain large amounts of oil and/or natural gas. A major extraction challenge is that the hydrocarbons in the shale formation do not flow easily and must be dislodged for accessibility and recovery. In order to extract the oil efficiently and profitably, two production



**FIGURE 1.7** Steam-assisted gravity drainage recovery of bitumen from oil sands.

technologies are used. The technologies are referred to as horizontal drilling and hydraulic fracturing. Instead of the typical vertical drilling with possibly a J-type bend used for conventional oils, horizontal drilling involves an initial drilling in the vertical direction for a short distance, followed by drilling horizontally and possibly for a few miles to access oil deposits. To loosen oil deposits spread over a wide area of sedimentary rock, water and chemicals are added at high pressure during oil production to free the oil in the deposits. The application of hydraulic fracturing has led to record production of shale or light tight oil and shale gas in the United States. Unfortunately, the 2015 collapse of global oil prices moderated the rate of production of light tight oil. Similarly, applications of improved technologies for exploration and production have led to oil finds in deepwater off the coasts of West Africa and South America and in the Gulf of Mexico.

## 1.7 OIL CONSUMPTION

The US economy required the use of 20 million barrels per day in 1993, and this has gradually been reduced to 18.9 million barrels per day by 2013 due to energy conservation, automotive fuel efficiency, and environmental regulatory programs. Energy conservation programs include increased use of renewable transportation fuels, natural gas, and renewable fuels for power generation. There have been similar modest declines in oil consumption rates for the Organization for Economic Cooperation and Development (OECD) countries, notably for Germany, the United

**TABLE 1.4**  
**Daily Oil Consumption Rates in MMBPD**

Country	2003	2008	2013
USA	20.0	19.5	18.9
China	5.8	8.3	10.8
Japan	5.5	4.4	4.6
India	2.5	3.2	3.7
Russian Federation	2.7	2.9	3.3
Saudi Arabia	1.7	2.4	3.2
Brazil	2.0	2.4	3.0
Canada	2.2	2.3	2.3
Germany	2.7	2.5	2.4
UK	1.7	1.6	1.5
France	2.0	1.9	1.7
Italy	1.9	1.7	1.3
Spain	1.9	1.7	1.3
Mexico	1.9	2.1	2.0

*Note:* The oil consumption rates are in millions of barrels per day or MMBPD.

Kingdom, Italy, France, and Spain, as these countries have implemented energy conservation programs. Daily oil consumption rates for selected years, 2003, 2008, and 2013, are provided in [Table 1.4](#). Oil demand growth for non-OECD countries such as China and India is on the rise, though tempered slightly by slower economic growth rates in the past two decades.<sup>(13)</sup>

Oil demand declines for the United States and other OECD countries were partially offset by drastic demand increases of over 80% for China and over 45% for India between 2003 and 2013 due to increased oil refining for the production of transportation fuels and other refined products.

## 1.8 CRUDE OIL AND OTHER HYDROCARBON LIQUID QUALITIES

There are many types of crude oils, and they are classified broadly as sweet light, heavy sour, extra-heavy sour, and heavy blended synthetic crude oils. Sweet and sour are descriptive terms for crude oils that are based on the amount of organic sulfur in the crude oils. Sweet crude oils are those with sulfur concentrations that are less than 0.5 wt. %. Crude oils that contain greater than 0.5 wt. % sulfur are referred to as sour oils. Heavy sour crude oils are oils with American Petroleum Institute (API) gravity of less than 20 and concentrations of sulfur compounds that are greater than 0.5 wt. %. Extra-heavy oils are typically those with API gravities that are less than 10 API. More specifically, the World Energy Council (WEC) defined extra-heavy oil as crude oil having a gravity of less than 10° API and a reservoir viscosity of no more than 10,000 centipoises. When reservoir viscosity measurements are not available, extra-heavy oil is considered by the WEC to have a lower limit of 4 API.

**Note:**

Gravity of oils is determined and reported as degrees API.

Specific gravity is defined as the density of an oil relative to the density of water, where density of water is defined approximately as 1 gram/cubic centimeter.

Degrees API =  $(141.5/\text{Specific gravity}) - 131.5$ .

Based on the definitions, Louisiana Light Sweet (LLS), West Texas intermediate, and Brent are light sweet crude oils; Arabian Light is a sour crude oil; and both Maya and Tia Juana heavy are heavy sour crude oils. The profitability of refining a crude oil should be fully assessed, and the assessment should incorporate expected costs associated with processing the crude oil and relevant related asset maintenance costs. Due to the broad properties of crude oils, a current crude oil assay database is highly recommended. Pertinent crude oil properties such as sulfur, API gravity, total acid neutralization number (TAN), concentrations of contaminant metals, and concentrations of oil fractions on distillation should also be considered in estimating the value and price of a crude oil relative to the price of the benchmark crude oil used for setting its price. Typical benchmark crude oils include and are not limited to Brent, West Texas intermediate, and Dubai Fateh. Another benchmark for crude oil pricing that is favored by OPEC is what is referred to as the OPEC basket of oils. The OPEC basket of oils price is based on the prices of a collection of seven crude oils from Algeria, Saudi Arabia, Indonesia, Nigeria, Dubai, Venezuela, and the Mexican isthmus.

It is worth noting that oil refiners that have the necessary bottom-of-the-barrel upgrading processing assets in their refineries are in enviable positions to take advantage of lower-cost crude and synthetic oils, as they can reliably and profitably process a wide variety of purchased crude and synthetic oils. Selected oil quality data for a small number of crude oils used in oil refineries are provided in [Table 1.5](#).

General crude oil qualities should be taken as merely representative of analyzed samples of the crude oils, and it should be understood that oil qualities at the time of purchase could vary depending on the specific areas from which the oils are produced, the degree of upgrading of the oils, chemicals used during production, and flow enhancers for oil transportation. As indicated previously, it could be beneficial and profitable for the oil refiner to update its database for crude oil assays as often as feasible so as to fully take advantage of possible discounts for gross variations in crude oil qualities when the oils are available.

Bitumen from oil sands is extra-heavy oil and usually has gravity that is less than 10 API. As discussed, a variety of extraction technologies are applied for extracting bitumen, and two of the most favored ones are surface mining and steam-assisted gravity drainage.<sup>(16,18)</sup> Two of the largest deposits of oil sands are in the Orinoco Belt of Venezuela and Alberta, Canada. Bitumen is a highly viscous liquid that does not flow easily and can be transported in pipelines only after the addition of condensate diluent to produce Dilbit or the addition of a synthetic oil to produce Synbit. Since bitumen usually contains high amounts of contaminants, it has to be upgraded and blended with other oils so as to reduce its sulfur, nitrogen, nickel, vanadium, and acidic contents and render it suitable for profitable oil refining (see [Figure 1.8](#)). The qualities of the Hamaca from Venezuela and Athabasca bitumen from Canada, as

**TABLE 1.5**  
**Selected Properties for Crude Oils**

Crude Oil	LLS	WTI	WTS	AL	BR	TIA/H	MAYA
Gravity, API	36.1	40.8	34.1	33.4	38.3	12.3	22.2
Sulfur, wt. %	0.45	0.34	1.64	1.77	0.40	2.80	3.30
Pour point, C	-37.0	-29.0	-46.0	-54.0	-42.0	-16.0	-36.0
Viscosity @100F	4.3	4.9	4.6	8.4	3.9	8.6	102.0
V, wppm	1.2	1.6	6.4	13.5	6.0	386	314.0
Ni, wppm	7.1	1.6	3.7	3.3	1.0	38.5	52.0
CCR, wt. %	1.1	1.1	3.3	3.6	2.1	11.2	12.0
TAN, mgKOH/g	0.58	0.10	0.1	0.00	0.10	3.90	0.28

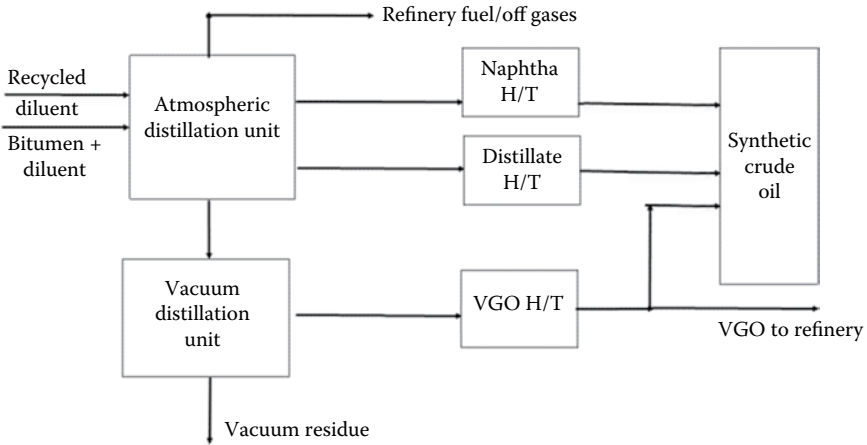
*Notes:*

1. LLS is Light Louisiana Sweet; WTI is West Texas Intermediate; WTS is West Texas Sour; AL is Arab Light; BR is Brent; TIA/H is Tia Juana Heavy. Maya is from Mexico.
2. Kinematic viscosity is at 100 F and the units are centistokes.
3. The crude oil characteristics are taken from a variety of sources. US Energy Information Administration (EIA) Reports; BP Statistical Review of World Energy, June 2014; Oyekan, S. O., Torrisi, S., Opportunities and Challenges in Transportation Fuels Production, Paper Presented at the AIChE Regional Process Technology Conference, Galveston, TX, October 2, 2009.<sup>(12-16)</sup>
4. CCR is Conradson Carbon and is a measure of the concentration of asphaltenes and how the heavy the oil is.
5. TAN is total acid neutralization number and the units are in mg of KOH per gram of the oil, where KOH is potassium hydroxide.
6. Viscosity is kinematic viscosity at 100°F.
7. Pour point is in degrees centigrade.

well as the upgraded Hamaca oil and Western Canadian Select (WCS), are given in [Table 1.6](#).<sup>(16,19,20)</sup> Western Canadian Select is a heavy blended crude oil comprised of sweet synthetic (upgraded) oils, other crude oils, and condensate.

It is beneficial for oil refiners to have good and current knowledge of the qualities of the crude oils that they are purchasing and available for processing in their refineries so as to anticipate potential operational and reliability challenges while taking advantage of opportunities to maximize refinery profitability. Also, since upgraded bitumen is usually sold in synthetic mixtures containing other crude oils and condensate, the quality of a given bitumen-derived oil is likely to vary substantially, and an up-to-date assay database program should be utilized for profitable processing of such oils in combination with the other crude oils in refineries.

A discussion of crude oil would be grossly incomplete without discussing the impact of the significant increase in the production of shale or light tight oil in the United States on crude oil prices. It is important to discuss tight oils with respect to the challenges that should be expected in processing significant percentages of shale oil in crude slates. Though organic sulfur, contaminant metals, and acid concentrations of tight oils are usually similar to those of sweet crude oils, the high paraffinic content and percentages of their oil fractions make processing of light



**FIGURE 1.8** A typical bitumen upgrader showing use of diluent and generation of synthetic crude oil.

*Note:* Recycled diluent could be a naphtha or light oil. Naphtha H/T is the naphtha hydrotreater. VGO is vacuum gas oil. (From Gray, M. R., *Tutorial on Upgrading of Sands Bitumen*, University of Alberta, Canada.<sup>(17)</sup>)

**TABLE 1.6**  
**Bitumens and Their Upgraded and Blended Oils**

Crude Oils	Hamaca Bitumen	Hamaca	Athabasca Bitumen	WCS
Gravity, API	8.4	26	7.7–9.0	19–22
Sulfur, wt. %	3.8	1.55	4.4–5.1	2.8–3.5
Ni, wppm	115	42	69–85	46–59
V, wppm	388	152	81–218	115–140
TAN, mg KOH/g	2.8	0.7	>5.4	<1.0

tight oils more challenging than the processing of conventional oils. However, due to favorable prices relative to WTI and Brent and reliable supply, tight oils are highly desirable, cost-efficient oils for some United States oil refiners. A number of US oil refiners are installing additional crude distillation units for efficient and profitable refining of higher percentages of light tight oils in their refineries' crude slates. The properties of tight oils are quite different from those of other crude oils, as shown by the properties of the Bakken and Eagle Ford oils in [Table 1.7](#).<sup>(21,22)</sup> Bakken and Eagle Ford oils are cost-effective replacements for imported light sweet crude oils. Tight oils had effectively replaced most of the imported light crude oils, especially Bonny Light from Nigeria, in oil refineries in the United States by 2016.

Since light tight oils are usually priced lower relative to benchmark WTI and Brent, they are desirable cost-effective feedstocks for refineries. However, challenges that have been identified in processing light tight oils include the negative impact of its high paraffinic contents, as this causes significant precipitation of some

**TABLE 1.7**  
**Tight Oils Compared to Conventional Crude Oils**

Crude Oil	Eagle Ford	Bakken	LLS	WTI	AL	Brent	Bonny
Gravity, API	45.7	40	36.1	40.8	33.4	38.3	32.9
Sulfur, wt. %	0.04	0.2	0.45	0.34	1.77	0.40	0.2
Pour Point, C	-27.4	N/a	-37.0	-29.0	-54.0	-42.0	-14.4
V, wppm	0.1	0.1	1.2	1.6	13.5	6.0	0.4
Ni, wppm	0.1	0.4	7.1	1.6	3.3	1.0	4.3
CCR, wt. %	0.2	0.8	1.1	1.1	3.6	2.1	1.4
TAN, mgKOH/g	0.1	0.1	0.58	0.10	0.00	0.10	0.3

of the asphaltenes of heavier crude oils in the crude unit. Significant asphaltene precipitation leads to increased reliability issues in atmospheric crude units and associated equipment. Furthermore, refiners who had upgraded their refining assets to process heavy crude oils may find that their bottom-of-the-barrel conversion units are underutilized. A number of oil refining technologies and catalyst providers suggest that installation of additional atmospheric distillation units, reconfiguring of refinery oil processing schemes, and use of the fluid catalytic cracker (FCC) for processing could be beneficial for maximizing profitability from processing high percentages of shale oil in refineries.<sup>(22–26)</sup>

Another major factor worth emphasizing with respect to crude oil qualities are the chemicals that are used during crude oil extraction, production, and transportation, as the chemicals could produce metals and chlorides that are either contaminants or corrosion agents in downstream processing of the crude oil fractions after the atmospheric and vacuum distillation units. Examples include the use of antifoaming agents containing silicon and condensate and naphtha used as flow improvers for crude oils and unconventional oils. Chemicals added during production and for transportation could undergo thermal and catalytic reactions to generate contaminant metals that can poison precious and base metals containing catalysts in oil refining processes. Poisoning by added contaminant metals other than the sulfur, nitrogen, iron, nickel, and vanadium typically inherent in crude oil could lead to poor catalytic performances of process units and underutilization of oil refining assets due to process units' reliability challenges.

Another class of seemingly cost-effective oil feedstocks for oil refiners are those typically characterized as opportunity crude oils and oil fractions. Detailed characterization of the oils should be conducted and is recommended before they are processed in high percentages in crude slates for crude units and process units in oil refineries. Documented cases of silicon and other poisoning events of the naphtha hydrotreater and catalytic reforming units are discussed in subsequent chapters.

## REFERENCES

1. My Channel Evolution of the Oil Industry, Documentary on the History of American Oil and Petroleum, October 2013, <http://youtube/TheBestFilmArchives>.

2. Bilkadi, Z., The Oil Weapons. *Saudi Aramco World*, 46(1), 20–27, 1995.
3. Russell, L. S., *A Heritage of Light Lamps and Lighting in the Early Canadian Home*, University of Toronto Press, Toronto, Canada, 2003.
4. Frank, A. F., *Oil Empire and Visions of Prosperity in Austrian Galicia*, Harvard University Press, Cambridge, 2005.
5. Matveichuk, A. A., *Intersection of Oil Parallels Historical Essays*, Russian Oil and Gas Institute, Moscow, 2004.
6. Murray, T. J., Dr. Abraham Gesner: The Father of the Petroleum Industry, *J. R. Soc. Med.*, 86(1), 43–44, 1993.
7. Owen, E. W., *Trek of the Oil Finders*, American Association of Petroleum Geologists, Tulsa, Oklahoma, p. 12, 1975.
8. McKain, D. L., Bernard, A. L., *Where It All Began, The Story of the People and Places Where the Oil Industry Began, West Virginia and Southeastern Ohio*, D. L. McKain, Parkersburg, West Virginia, 1994.
9. Gordon, J. S., *10 Moments That Made American Business*, American Heritage, February/March 2007.
10. Giddens, P. H., *The Birth of the Oil Industry*, Porcupine Press, The Macmillan Company, New York, 1938.
11. Williamson, H. F., Daum, A., Andreano, R., *The American Petroleum Industry, 1899–1959, The Age of Energy*, Northwestern University Press, Evanston, Illinois, p. 16.
12. U.S. Energy Information Administration (EIA) Reports, <https://www.eia.gov/>.
13. BP Statistical Review of World Energy World Petroleum Congress, Moscow, June 2014.
14. Leverett, F., Lecture # 2, “The Global Energy Industry, Geopolitical and Geo-Economics of Global Energy”, 2007, MIT Open Courseware, <http://www.ocw.mit.edu>
15. Speight, J. G., *The Chemistry and Technology of Petroleum*, 2nd edition, Marcel Decker, New York, 1991.
16. Oyekan, S. O., Torrisi, S., Opportunities and Challenges in Transportation Fuels Production, *Paper Presented at the AIChE Regional Process Technology Conference*, Galveston, TX, October 2, 2009.
17. Gray, M. R., *Tutorial on Upgrading of Sands Bitumen*, University of Alberta, Canada, 2015.
18. Stratiev, D., Dinkov, R., Petkov, K., Stanulov, K., Evaluation of Crude Oil Quality, *Petroleum & Coal*, 52(1), 35–43, 2010.
19. Mai, A., Bryan, J., Goodarzi, N., Kantas A., Insights into Non-Thermal Recovery of Heavy Oil, *Paper Presented at World Heavy Oil Conference*, Calgary, Alberta, Canada, 2006.
20. Dusseault, M. B., Comparing Venezuelan and Canadian Heavy Oil and Tar Sands, *Paper presented at the Petroleum Society’s Canadian International Petroleum Conference*, Calgary, Alberta, Canada, June 12–14, 2001.
21. Hill, D., North Dakota Refining Capacity Study, Final Technical Report, DOE Award No. DE-FE000516, 2011.
22. Bryden, K., Federspiel, M., Habib, E. T., Schiller, R., Processing Tight Oils in FCC: Issues, Opportunities and Flexible Catalytic Systems. W. R. Grace Catalogram No. 114, 2014.
23. US. Energy Information Administration, Technical Options for Processing Additional Light Tight Oil Volumes within the United States, 2015.
24. Benoit, B., Zurlo, J., *Overcoming the Challenges of Tight/Shale Oil Refining*, GE Water & Process Technologies, Processing Shale Feed, 2014, [www.eptq.com](http://www.eptq.com).
25. Olsen, T., Working with Tight Oil, *AIChE CEP*, 35–39, April 2015.
26. Jeff Koebel, AFPM Q&A Technology Conference 2013 Answer Book, Dallas, October 7–9, 2013.
27. Lance, R., The Benefits of US Crude Exports, IPAA Annual Meeting, November 13, 2014. [www.conocophillips.com/files/resource](http://www.conocophillips.com/files/resource)
28. Cunningham, N., US Has World’s Largest Oil Reserve. Oil Price, July 2016, <http://oilprice.com/Energy/General/US-Has-Worlds-Largest-Oil-Reserves.html>

---

# 2 Basics of Crude Oil Refining

## 2.0 INTRODUCTION TO BASICS OF OIL REFINING

A good working knowledge of the basic chemistry and operations of crude oil refining should enable engineers, chemists, technologists, and oil refining executives to better manage their oil refining assets. The basic chemical composition, chemicals, and some of the key contaminants in crude oils that could negatively impact oil refining processes and equipment are covered in this chapter. Most of the capital expansion projects in oil refineries usually have as a primary goal additional bottom-of-the-barrel upgrading technology assets for enhancing the profitability of oil refining companies. In recent years, some of the asset upgrading has been in response to ensuring that refining companies can produce transportation fuels such as gasoline, diesel, and bunker fuels from heavy sour crude and unconventional oils.

A simplified configuration of a refinery is given in [Figure 2.1](#). Crude oil is processed to produce refined oil products such as liquefied petroleum gas (LPG), propylene, gasoline, kerosene, diesel, heating oil, sulfur, asphalt, and coke. Oil refineries also produce feedstocks such as naphtha, propylene, benzene, and xylenes for the petrochemical industry. The major operating cost for oil refiners is that required for acquiring crude oils, and that cost can represent 75% to 80% of a refinery's operating budget. As a consequence, bottom-of-the-barrel upgrading technologies such as delayed coking units are usually key processing units in grassroots oil refineries. Many refineries have also been revamped to add coking process units to expand the oil refiner's capabilities to process cheaper heavy sour-type crude oils and reduce crude oil cost. Since most of the crude oils available are more of the medium-sour to heavy-sour types, oil refiners with adequate bottom-of-the-barrel processing technologies have significant competitive advantages.<sup>(1)</sup> The chemistry of crude oils, oil refining economics, refinery configurations, and process units are covered in this chapter. A simplified refinery configuration is provided in [Figure 2.1](#) in order to familiarize the reader with terms that are used in this book.

## 2.1 CRUDE OIL COMPOSITION

Crude oil consists of a variety of complex hydrocarbons and some small amounts of hydrocarbon compounds containing elements such as sulfur, nitrogen, nickel, vanadium, iron, copper, and so on. Though the crude oils are different, as discussed in [Chapter 1](#), carbon and hydrogen are the predominant elements, which typically vary within fairly narrow limits for the oils, as shown in [Table 2.1](#).<sup>(2,3)</sup> Due to the variety of complex hydrocarbons in crude oils, the boiling ranges for the compounds are quite broad, and this property enables the application of fractional distillation to separate