




HAROLD H. SCHOBERT



# Chemistry of Fossil Fuels and Biofuels

CAMBRIDGE

# Chemistry of Fossil Fuels and Biofuels

HAROLD SCHOBERT

The Pennsylvania State University  
and  
North-West University



CAMBRIDGE  
UNIVERSITY PRESS

CAMBRIDGE UNIVERSITY PRESS

Cambridge, New York, Melbourne, Madrid, Cape Town,  
Singapore, São Paulo, Delhi, Mexico City

Cambridge University Press

The Edinburgh Building, Cambridge CB2 8RU, UK

Published in the United States of America by

Cambridge University Press, New York

[www.cambridge.org](http://www.cambridge.org)

Information on this title: [www.cambridge.org/9780521114004](http://www.cambridge.org/9780521114004)

© H. Schobert 2013

This publication is in copyright. Subject to statutory exception  
and to the provisions of relevant collective licensing agreements,  
no reproduction of any part may take place without  
the written permission of Cambridge University Press.

First published 2013

Printed and bound in the United Kingdom by the MPG Books Group

*A catalog record for this publication is available from the British Library*

*Library of Congress Cataloging-in-Publication Data*

Schobert, Harold H., 1943–

Chemistry of fossil fuels and biofuels / Harold Schobert.

p. cm. — (Cambridge series in chemical engineering)

ISBN 978-0-521-11400-4 (Hardback)

1. Fossil fuels—Analysis. 2. Biomass energy. 3. Energy crops—Composition.  
4. Fuelwood crops—Composition. I. Title.

TP318.S368 2012

553.2—dc23

2012020435

ISBN 978-0-521-11400-4 Hardback

Cambridge University Press has no responsibility for the persistence or  
accuracy of URLs for external or third-party internet websites referred to  
in this publication, and does not guarantee that any content on such  
websites is, or will remain, accurate or appropriate.

## **Chemistry of Fossil Fuels and Biofuels**

Focusing on today's major fuel resources – ethanol, biodiesel, wood, natural gas, petroleum products, and coal – this book discusses the formation, composition and properties of the fuels, and the ways in which they are processed for commercial use. The book examines the origin of fuels through natural processes such as photosynthesis and the geological transformation of ancient plant material; the relationships between their composition, molecular structures, and physical properties; and the various processes by which they are converted or refined into the fuel products appearing on today's market. Fundamental chemical aspects such as catalysis and the behaviour of reactive intermediates are presented, and global warming and anthropogenic carbon dioxide emissions are also discussed. The book is suitable for graduate students in energy engineering, chemical engineering, mechanical engineering, and chemistry, as well as for professional scientists and engineers.

**Harold H. Schobert** is Professor Emeritus of Fuel Science, The Pennsylvania State University, and Extra-ordinary Professor, Coal Research Group, North-West University. A recognized leading authority on energy technology, he has over 30 years' experience in teaching and research on fuel chemistry.

## Cambridge Series in Chemical Engineering

### Series Editor

Arvind Varma, *Purdue University*

### Editorial Board

Christopher Bowman, *University of Colorado*

Edward Cussler, *University of Minnesota*

Chaitan Khosla, *Stanford University*

Athanassios Z. Panagiotopoulos, *Princeton University*

Gregory Stephanopoulos, *Massachusetts Institute of Technology*

Jackie Ying, *Institute of Bioengineering and Nanotechnology, Singapore*

### Books in Series

Baldea and Daoutidis, *Dynamics and Nonlinear Control of Integrated Process Systems*

Chau, *Process Control: A First Course with MATLAB*

Cussler, *Diffusion: Mass Transfer in Fluid Systems, Third Edition*

Cussler and Moggridge, *Chemical Product Design, Second Edition*

Denn, *Chemical Engineering: An Introduction*

Denn, *Polymer Melt Processing: Foundations in Fluid Mechanics and Heat Transfer*

Duncan and Reimer, *Chemical Engineering Design and Analysis: An Introduction*

Fan and Zhu, *Principles of Gas-Solid Flows*

Fox, *Computational Models for Turbulent Reacting Flows*

Leal, *Advanced Transport Phenomena: Fluid Mechanics and Convective Transport*

Mewis and Wagner, *Colloidal Suspension Rheology*

Morbidelli, Gavriilidis, and Varma, *Catalyst Design: Optimal Distribution of Catalyst in Pellets, Reactors, and Membranes*

Noble and Terry, *Principles of Chemical Separations with Environmental Applications*

Orbey and Sandler, *Modeling Vapor-Liquid Equilibria: Cubic Equations of State and their Mixing Rules*

Petyluk, *Distillation Theory and its Applications to Optimal Design of Separation Units*

Rao and Nott, *An Introduction to Granular Flow*

Russell, Robinson and Wagner, *Mass and Heat Transfer: Analysis of Mass Contactors and Heat Exchangers*

Schobert, *Chemistry of Fossil Fuels and Biofuels*

Slattery, *Advanced Transport Phenomena*

Varma, Morbidelli, and Wu, *Parametric Sensitivity in Chemical Systems*

“The book is a welcome modern update to the available literature regarding the genesis, characteristics, processing and conversion of fossil and bio-derived fuels. Its comprehensive coverage of the chemistry involved with each of these aspects makes it an important source for upper-level undergraduates, graduate students, and professionals who need a strong understanding of the field. It is an interesting read for anyone who really wants to understand the nature of fuels.”

*Robert G. Jenkins, University of Vermont*

“There is no other book like this in field of energy science. It is the perfect introduction to the topic; but Professor Schobert has packed so much in, that it is just as much a valuable reference for more experienced professionals. It touches on all aspects of fuel formation, transformation and use as well as strategies for managing the end product, carbon dioxide. I will be using it as a text in my own teaching to both senior undergraduate and graduate students.”

*Alan L. Chaffee, Monash University, Australia*

“This is an excellent reference for the student of modern fuel science or the practitioner wishing to sharpen their ‘big-picture’ understanding of the field. The book offers a seasoned balance between technical rigor and readability, providing many helpful references for the reader interested in further study. I found the text engaging and enlightening, with the end-of-chapter notes a particularly thought-provoking and entertaining bonus.”

*Charles J. Mueller, Sandia National Laboratories*

## Preface

About twenty years ago I wrote a short book, *The Chemistry of Hydrocarbon Fuels\**, that was based on lectures I had been giving at Penn State University for a course on Chemistry of Fuels. In the years since, that book has long been out of print, and the energy community has seen a significant increase in interest in biofuels, and concern for carbon dioxide emissions from fuel utilization. It seemed time, therefore, for a new book in the area. While this present book owes much to the earlier one, the changes are so extensive that it is not simply a second edition of its predecessor, but merits a new title and new organization of chapters.

The life cycle of any fuel begins with its formation in nature, followed by its harvesting or extraction. Many fuels then undergo one or more processes of refining, upgrading, or conversion to improve their properties or to remove undesirable impurities. Finally, the fuel is put to use, usually in a combustion process, but sometimes by further conversion to useful materials such as carbon products or polymers. *Chemistry of Fossil Fuels and Biofuels* focuses primarily on the origins of fuels, their chemical constitution and physical properties, and the chemical reactions involved in their refining or conversion. Most fuels are complex mixtures of compounds or have macromolecular structures that are, in some cases, ill-defined. But that does not mean that we throw away the laws of chemistry and physics in studying these materials. The composition, molecular structures, and properties of fuels are not some curious, random outcome of nature, but result from straightforward chemical processes. Any use of the fuels necessarily involves breaking and forming chemical bonds.

This book has been written for several potential audiences: those who are new to the field of fuel and energy science, especially students, who seek an introduction to fuel chemistry; practicing scientists or engineers in any field who feel that some knowledge of fuel chemistry would be of use in their activities; and fuel scientists who have been specializing in one type of fuel but who would like to learn about other fuels. I have presumed that the reader of this book will have had an introductory course in organic chemistry, so is familiar with the basic principles of structure, nomenclature, and reactivity of functional groups. I have also presumed that the reader is familiar with aspects of the descriptive inorganic chemistry of the major elements of importance in fuels, and with some of the basic principles of physical chemistry. As a textbook, this book would therefore be suitable for third- or fourth-year undergraduates or first-year graduate students in the physical sciences or engineering. However, anyone with some elementary knowledge of chemistry and who is willing to refer to other appropriate texts as needed could certainly derive much from this book.

Our civilization once relied almost entirely on biomass fuel (wood) for its energy needs. Then, for about two centuries, the fossil fuels – coal, oil, and natural gas – have dominated the energy scene. In recent decades biomass has experienced increasing interest – a revival of interest in wood, as well as ethanol and biodiesel. Anything that we do in daily life requires use of energy, and, in most parts of the world, much of that energy derives from using fossil or biofuels. Despite the critical importance of fuels, few, if any, texts in introductory chemistry or organic chemistry give more than passing mention to these resources. So, I hope that this book might also be of use to chemists or chemical engineers curious to learn about new areas.

This book does not intend, nor pretend, to provide encyclopedic coverage of fuel formation or of refining and conversion processes. At the end of each chapter I have provided a number of suggested sources for those wishing to probe further. The material in the book is the distillation of having taught Chemistry of Fuels at least twenty times to students in fuel science, energy engineering, and chemical engineering. The course has changed somewhat each year, incorporating student feedback as appropriate. The person using this book, either as a textbook or for self-study, should become equipped with enough knowledge then to follow his or her interests with confidence in the professional journals or monographs in the field.

*\*The Chemistry of Hydrocarbon Fuels*, London, Butterworths, 1990.



# Acknowledgments

I could not have done this without the help and support of my dear wife Nita, who assisted in many, many ways. This book has been developed from more than twenty years' worth of notes for a course, Chemistry of Fuels, that I taught at Penn State University. Every year I started over again making entirely new notes for the lectures. My good friend and colleague, Omer Gül, provided invaluable assistance in converting many of my hand-drawn sketches, used off and on for years, into diagrams for this book. Two staff assistants, Carol Brantner and Nicole Arias, typed some of the versions of hand-written notes and created some of the diagrams. Their work was of great help in pulling the manuscript together. Lee Ann Nolan and Linda Musser, of the Fletcher Byrom Earth and Mineral Sciences Library at Penn State, helped in tracking down information, particularly biographical sketches of fuel scientists. I am also indebted to the staff of the Shakopee branch of the Scott County (Minnesota) Library, who made me welcome and provided a quiet room to work on visits to Minnesota. Many friends and colleagues at Penn State, especially Gary Mitchell and Caroline Clifford, helped in many different ways to provide information or ideas. Professor Christien Strydom, Director of the School of Physical and Chemical Sciences, North-West University, Potchefstroom, South Africa, helped by providing office space and computer access, as well as many splendid discussions. Many other friends at North-West and at Sasol provided assistance in various ways as well. Mohammad Fatemi, President of Middle East PetroChem Engineering and Technology, generously provided the software used to create the chemical structures and reactions. The two people at Cambridge University Press with whom I have worked, Michelle Carey and Sarah Marsh, deserve thanks for their long-suffering perseverance that would make Job seem a pretty impatient fellow. Finally, special thanks are due to the generations of students in Chemistry of Fuels, whose comments and suggestions were actually listened to, and often useful. Despite all this help, which I am very pleased to acknowledge and thank, any mistakes are my own.

## Acknowledgments for permissions to use illustrations

Figure 1.1	U.S. National Aeronautics and Space Administration, Greenbelt, Maryland
Figure 1.6	U.S. National Oceanic and Atmospheric Administration, Boulder, Colorado
Figure 2.1	Dr. David Pearce, <a href="http://general-anesthesia.com">general-anesthesia.com</a>
Figure 2.2	Dr. Ian Musgrave, Adelaide, Australia
Figure 3.1	Lawrence Berkeley National Laboratory, Berkeley, California
Figure 6.1	Dr. Wayne Armstrong, Palomar College, San Marcos, California
Figure 8.8	Dr. Robert Sullivan, Argonne National Laboratory, Chicago, Illinois
Figure 12.4	Carmel Barrett, Marketing Director, Amistco, Alvin, Texas
Figure 13.6	Chris Hunter, Curator of Collections and Exhibitions, Schenectady Museum and Suits-Bueche Planetarium, Schenectady, New York
Figure 13.18	Bart Eggert, Aerodyne, Chagrin Falls, Ohio
Figure 14.1	Dean Rodina, German Postal History, Brush, Colorado
Figure 14.5	Jon Williams, Hagley Museum and Library, Wilmington, Delaware, and Joseph McGinn, Sunoco Corporation, Philadelphia, Pennsylvania
Figure 14.8	Professor Carmine Collela, Facoltà d'Ingegneria, Università Federico, Napoli, Italy
Figure 14.9	Dr. Geoffrey Price, Department of Chemical Engineering, University of Tulsa, Tulsa, Oklahoma
Figure 14.16	Dr. Lars Grabow, Department of Chemical and Biomolecular Engineering, University of Houston, Houston, Texas
Figure 15.1	United Kingdom government (public domain)
Figure 15.3	David Aeschliman, <a href="http://Stamp.Collecting.World.com">Stamp.Collecting.World.com</a>
Figure 16.7	Roger Efferson, Process Engineering Associates, Oak Ridge, Tennessee
Figure 16.8	Helmut Renner, Graphite COVA, Roethenbach/Pegnitz, Germany
Figure 16.9	Gareth Mitchell, The EMS Energy Institute, Penn State University, University Park, Pennsylvania
Figure 17.1	Reprinted with permission from ASTM D720–91 (2010) Standard Test Method for Free-Swelling Index of Coal, copyright ASTM International, West Conshohocken, Pennsylvania
Figure 17.6	Dr. Caroline Clifford, The EMS Energy Institute, Penn State University, University Park, Pennsylvania

- Figure 17.10 Dr. Atul Sharma, Energy Technology Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan
- Figure 17.11 Dr. Mhlwazi Solomon Nyathi, Indiana Geological Survey, Indiana University, Bloomington, Indiana
- Figure 17.12 Public domain
- Figures 17.13–17.15 Gareth Mitchell, The EMS Energy Institute, Penn State University, University Park, Pennsylvania
- Figure 18.5 Le Huynh, Jameson Cell Manager, Xstrata Technology, Brisbane, Australia
- Figure 19.16 Stephanie Rahn, PUBLICIS Munich, Munich Germany. Copyright Siemens AG.
- Figure 19.17 Dr. Fred Starr, Claverton Energy Group, [www.claverton-energy.com/energy-experts-online](http://www.claverton-energy.com/energy-experts-online).
- Figure 21.16 Manuela Gebhard, Max-Planck-Gesellschaft zur Förderung der Wissenschaften, München, Germany
- Figure 22.5 Permission granted by [www.dullophob.com](http://www.dullophob.com)
- Figure 23.8 Jeannie Van Lew, Arizona Trailblazers Hiking Club, Chandler, Arizona
- Figure 23.9 U.S. Library of Congress
- Figure 25.1 Catherine Gatenby, US Fish and Wildlife Service

# Contents

<i>Preface</i>	<i>page xv</i>
<i>Acknowledgments</i>	<i>xvii</i>
<i>Acknowledgments for permissions to use illustrations</i>	<i>xviii</i>
<b>1 Fuels and the global carbon cycle</b>	<b>1</b>
Notes	8
<b>2 Catalysis, enzymes, and proteins</b>	<b>10</b>
2.1 Catalysis	10
2.2 Proteins	11
2.3 Enzymes	13
Notes	17
<b>3 Photosynthesis and the formation of polysaccharides</b>	<b>19</b>
3.1 Water splitting in photosynthesis	20
3.2 Carbon dioxide fixation	24
3.3 Glucose, cellulose, and starch	27
Notes	32
<b>4 Ethanol</b>	<b>35</b>
4.1 Fermentation chemistry	35
4.2 Commercial production of ethanol via fermentation	38
4.3 Ethanol as a motor vehicle fuel	42
4.4 Issues affecting possible large-scale production of fuel ethanol	47
4.5 Cellulosic ethanol	48
Notes	49
<b>5 Plant oils and biodiesel</b>	<b>53</b>
5.1 Biosynthesis of plant oils	53
5.2 Direct use of vegetable oils as diesel fuel	57
5.3 Transesterification of plant oils	59
5.4 Biodiesel	62
Notes	66

<b>6</b>	<b>Composition and reactions of wood</b>	<b>69</b>
6.1	Wood combustion	78
6.2	Wood pyrolysis	79
6.2.1	Charcoal	79
6.2.2	Methanol	81
6.3	Wood gasification	82
6.4	Wood saccharification and fermentation	83
	Notes	84
<b>7</b>	<b>Reactive intermediates</b>	<b>87</b>
7.1	Bond formation and dissociation	87
7.2	Radicals	89
7.2.1	Initiation reactions	89
7.2.2	Propagation reactions	91
7.2.3	Termination reactions	94
7.3	Radical reactions with oxygen	95
7.4	Carbocations	97
7.5	Hydrogen redistribution	100
	Notes	101
<b>8</b>	<b>Formation of fossil fuels</b>	<b>103</b>
8.1	Diagenesis: from organic matter to kerogen	104
8.2	Catagenesis: from kerogen to fossil fuels	109
8.3	Catagenesis of algal and liptinitic kerogens	111
8.4	Catagenesis of humic kerogen	117
8.5	Summary	127
	Notes	128
<b>9</b>	<b>Structure–property relationships among hydrocarbons</b>	<b>132</b>
9.1	Intermolecular interactions	132
9.2	Volatility	134
9.3	Melting and freezing	142
9.4	Density and API gravity	145
9.5	Viscosity	148
9.6	Water solubility	151
9.7	Heat of combustion	152
9.8	The special effects of aromaticity	156
	Notes	158
<b>10</b>	<b>Composition, properties, and processing of natural gas</b>	<b>161</b>
10.1	Gas processing	164
10.1.1	Dehydration	164
10.1.2	Gas sweetening	166

10.1.3	Separation of $C_2^+$ hydrocarbons	168
10.2	Natural gas as a premium fuel	170
	Notes	171
<b>11</b>	<b>Composition, classification, and properties of petroleum</b>	<b>174</b>
11.1	Composition	174
11.1.1	Alkanes	174
11.1.2	Cycloalkanes	175
11.1.3	Aromatics	177
11.1.4	Heteroatomic compounds	179
11.1.5	Inorganic components	180
11.2	Classification and properties of petroleum	181
11.2.1	API gravity	181
11.2.2	Carbon preference index	181
11.2.3	Age–depth relationships	182
11.2.4	Composition relationships	183
11.3	Asphalts, oil sands, and other unconventional oils	187
	Notes	189
<b>12</b>	<b>Petroleum distillation</b>	<b>192</b>
12.1	Desalting	193
12.2	Principles of distillation	194
12.3	Refinery distillation operations	198
12.3.1	Atmospheric-pressure distillation	198
12.3.2	Vacuum distillation	199
12.4	Introduction to petroleum distillation products	200
12.4.1	Gasoline	200
12.4.2	Naphtha	201
12.4.3	Kerosene	201
12.4.4	Diesel fuel	202
12.4.5	Fuel oils	202
12.4.6	Lubricating oils	203
12.4.7	Waxes	203
12.4.8	Asphalt	204
	Notes	204
<b>13</b>	<b>Heterogeneous catalysis</b>	<b>206</b>
13.1	Catalytic materials	207
13.1.1	The active species	207
13.1.2	The support	207
13.1.3	The promoter	209
13.1.4	Preparation	209
13.2	Adsorption on catalyst surfaces	210
13.3	Mechanisms of catalytic reactions	216

13.4	Measures of catalyst performance	217
13.5	Surface effects on catalysts	219
	Notes	221
<b>14</b>	<b>Catalytic routes to gasoline</b>	<b>224</b>
14.1	Gasoline combustion	224
14.2	Specifications and properties of gasoline	229
14.3	Refinery routes to enhanced yield and quality	231
14.4	Alkylation and polymerization	232
14.5	Catalytic cracking	234
14.5.1	Cracking catalysts	235
14.5.2	Cracking reactions	241
14.5.3	Practical aspects	243
14.6	Catalytic reforming	245
14.6.1	Reforming catalysts	245
14.6.2	Reforming reactions	246
14.6.3	Practical aspects	249
14.7	Methanol to gasoline	251
	Notes	253
<b>15</b>	<b>Middle distillate fuels</b>	<b>256</b>
15.1	Middle distillate fuel products	256
15.1.1	Kerosene	256
15.1.2	Jet fuel	256
15.1.3	Diesel fuel	260
15.1.4	Fuel oils	265
15.2	Hydroprocessing	266
15.2.1	Hydrodesulfurization	267
15.2.2	Hydrodenitrogenation	272
15.2.3	Hydrodemetallation	273
15.2.4	Hydrofining	273
15.2.5	Hydrocracking	274
15.2.6	Hydrogenation	276
15.2.7	Sources of hydrogen	277
	Notes	278
<b>16</b>	<b>Thermal processing in refining</b>	<b>281</b>
16.1	Thermal cracking	281
16.2	Visbreaking	284
16.3	Coking processes	286
16.3.1	Delayed coking	287
16.3.2	Fluid coking and Flexicoking	292
	Notes	293

<b>17</b>	<b>Composition, properties, and classification of coals</b>	<b>295</b>
17.1	Classification of coal by rank	295
17.2	The caking behavior of bituminous coals	298
17.3	Elemental composition	299
17.4	The macromolecular structures of coals	306
17.5	Coals as heterogeneous solids	312
17.6	Physical properties	314
	Notes	320
<b>18</b>	<b>The inorganic chemistry of coals</b>	<b>323</b>
18.1	The origin of inorganic components in coals	324
18.2	Inorganic composition of coals	324
18.3	Minerals in coals and their reactions	326
18.4	Coal cleaning	329
18.5	Behavior of inorganic components during coal utilization	334
	Notes	340
<b>19</b>	<b>Production of synthesis gas</b>	<b>342</b>
19.1	Steam reforming of natural gas	342
19.2	Partial oxidation of heavy oils	344
19.3	Coal and biomass gasification	345
19.3.1	Fundamentals of the carbon–steam and related reactions	346
19.3.2	Coal gasification processes	352
19.3.3	Fixed-bed gasification	354
19.3.4	Fluidized-bed gasification	356
19.3.5	Entrained-flow gasification	357
19.3.6	Underground coal gasification	359
19.3.7	Biomass gasification	360
	Notes	361
<b>20</b>	<b>Gas treatment and shifting</b>	<b>363</b>
20.1	Gas clean-up	363
20.2	Acid gas removal	365
20.3	The water gas shift	371
	Note	373
<b>21</b>	<b>Uses of synthesis gas</b>	<b>375</b>
21.1	Fuel gas	375
21.2	Methanation	375
21.3	Methanol synthesis	378
21.4	Fischer–Tropsch synthesis	381
21.5	Kölbel reaction	389



21.6	Oxo synthesis	390
21.7	Gas to liquids	391
21.8	The potential of synthesis gas chemistry	392
	Notes	393
<b>22</b>	<b>Direct production of liquid fuels from coal</b>	<b>396</b>
22.1	Pyrolysis	396
22.2	Solvent extraction	398
22.3	Direct coal liquefaction	402
	22.3.1 Principles	402
	22.3.2 Direct liquefaction processing	406
	Notes	413
<b>23</b>	<b>Carbonization and coking of coal</b>	<b>415</b>
23.1	Thermal decomposition of coals	415
23.2	Low- and medium-temperature carbonization	417
23.3	The special case of bituminous coals	418
23.4	Chemistry of coke formation	420
23.5	Industrial production of metallurgical coke	426
	Notes	432
<b>24</b>	<b>Carbon products from fossil and biofuels</b>	<b>435</b>
24.1	Activated carbons	435
24.2	Aluminum-smelting anodes	440
24.3	Carbon blacks	443
24.4	Graphites	445
	24.4.1 Natural graphite	445
	24.4.2 Graphitization processes	446
	24.4.3 Electrodes	447
	24.4.4 High-density isotropic graphites	449
	Notes	450
<b>25</b>	<b>Carbon dioxide</b>	<b>453</b>
25.1	Carbon capture and storage	455
	25.1.1 Algae	455
	25.1.2 Biochar	457
	25.1.3 Chemical uses of CO <sub>2</sub>	459
	25.1.4 Coalbed methane recovery	460
	25.1.5 Enhanced oil recovery	461
	25.1.6 Mineral carbonation	462
	25.1.7 Photocatalysis	464