

# Global Chemical Kinetics of Fossil Fuels

Alan K. Burnham

# Global Chemical Kinetics of Fossil Fuels

How to Model Maturation and Pyrolysis

 Springer

Alan K. Burnham  
Livermore, CA  
USA

Every effort has been made to contact the copyright holders of the figures and tables which have been reproduced from other sources. Anyone who has not been properly credited is requested to contact the publishers, so that due acknowledgment may be made in subsequent editions.

Additional material to this book can be downloaded from <http://extras.springer.com>.

ISBN 978-3-319-49633-7                      ISBN 978-3-319-49634-4 (eBook)  
DOI 10.1007/978-3-319-49634-4

Library of Congress Control Number: 2016958711

© Springer International Publishing AG 2017

This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.

The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

The publisher, the authors and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, express or implied, with respect to the material contained herein or for any errors or omissions that may have been made.

Cover figure: Schematic geologic cross-section showing the relationships among oil shale (a rich, immature source rock), active source rocks, and conventional (stratigraphic or structural trap) and unconventional (mature source rock) reservoirs. Coal follows a parallel maturity pathway, with lignite being immature, bituminous being mature, and anthracite being over-mature. Immature rocks can be analyzed in the laboratory to derive chemical kinetic parameters to model oil shale retorting, coal pyrolysis, and natural petroleum formation. Reproduced courtesy of Lawrence Livermore National Laboratory.

Printed on acid-free paper

This Springer imprint is published by Springer Nature  
The registered company is Springer International Publishing AG  
The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

# Preface

I started to write this book in 2014 because I was seeing so many erroneous papers on applied chemical kinetics. Methods for practical problems that were developed 20–40 years ago were too often ignored. This might be expected, because the literature on applied chemical kinetics is so vast that no one would be expected to be aware of all of it. Also, much of this literature has one or more serious flaws, and people entering the field may or may not be able to distinguish between the good and bad. Furthermore, certain mistakes are so common that seeing a particular approach in multiple papers can lead one to the erroneous conclusion that the approach is valid.

To be sure, I have made mistakes. If I knew 35 years ago what I know now, I would have done some things differently in my early papers. Learning from our mistakes is a central part of both science and a person's life. So in one sense, I hope that others can learn from my mistakes rather than repeating them. A first example is that I did not understand initially that kinetics derived from a single constant heating rate are very unreliable, so my early kinetics for oil-shale char gasification have serious flaws. I learned that lesson in the mid-1980s while working on the kinetics of natural petroleum formation, and I subsequently contributed to ICTAC papers in 2000 and 2011 addressing the need for multiple thermal histories to derive valid kinetics. Numerous papers in the thermal analysis literature had claimed to be able to identify the reaction mechanism by the quality of fit to data from a single heating rate, and they were wrong. The ICTAC papers have contributed to improving the quality of kinetic determinations in the thermal analysis field. A second example is that I derived kinetic parameters for oil cracking by varying temperature at roughly constant reaction time. Because different reactivities are sampled at different conversions and reactivity tends to decrease with conversion, this procedure results in artificially low activation energies. It is a common mistake in kinetic determinations for complex materials.

Another career lesson is that each of us should seek out and recognize the understandings of other research communities. Coming from the fossil fuel community, I was steeped in 1st-order,  $n$ th-order, and distributed activation energy models. Then I ran into linear polymers and a few well-preserved algal kerogens

that had sigmoidal reaction profiles. We found a mathematical form that worked quite well, but it was a few years later that we realized the mathematical form had been in the solid-state reaction literature for decades—an extension of the Prout–Tompkins model common in the Russian literature, also known as the truncated Šesták–Berggren model. We also discovered that other people were using that form for linear synthetic polymers. Even 20 years later, some petroleum geochemists fail to realize the importance of using a sigmoidal reaction model for some source rocks. At the same time, some recent kinetic work related to oil shale processing disregards the greatly superior quantity and quality of oil generation kinetics from the petroleum geochemistry community. It seems that the energy barrier between different application areas is too high for such lessons to transfer to the other communities. That is unfortunate, because amongst all the mediocre papers in the literature, there are numerous gems that have a lot to offer.

I am often dismayed that many people try to write their own chemical kinetics fitting software for analyzing complex systems, given that several powerful and versatile commercial programs are readily available. Perhaps it is a matter of cost, but the cost to develop one's own software is also high, and the cost of publishing mediocre kinetic work is even higher. I have reviewed papers in which inappropriate models were used, and where better models were available in commercial software. On multiple occasions, the editor accepted the paper after the authors said that their home-grown software was not capable of doing the more appropriate analysis. While writing such software serves an excellent educational objective, software-limited research that does not measure up to standard commercial practice is substandard and should not be tolerated in peer reviewed literature. As such, this book emphasizes the virtues of the Kinetics2015 program and precursors. While not the best at all types of kinetic optimizations, it is very good at the subset it does address and far better than most programs written by students.

Often in this book I draw upon my own work for specific issues. Although I try to cite the best papers on any given topic, this book is not intended to be a complete collection of all relevant work, and there may be papers by others that are either as good as or better than mine. Sometimes those papers are referenced in the works cited in this book, and sometimes they may have missed my attention. I apologize in advance for any such omissions.

This book took a few turns during its writing. One possibility was more of user's manual for specific software developed by Robert Braun and myself, but its final form was strongly influenced by a course I taught during the spring of 2016 in the Department of Energy Resources Engineering at Stanford University. It was designed for graduate students, although advanced undergrads could also take it. Exercises are included at the end of each chapter to help probe student understanding of both concepts and implementation of concepts. These specific exercises do not require specific software, although the classes I teach do in order to achieve more complete training. Solutions to the exercises and additional problem sets are available at <http://extras.springer.com>. While useful as a textbook, this book is intended to help the experienced practitioner, also.

There are numerous people who helped me along my career that made this book possible, with most of them being coauthors on one or more publications. Jack Campbell helped bring me to LLNL and introduced me to nonisothermal kinetics. Art Lewis supported my work there in oil shale and petroleum geochemistry that led to most of the applications covered here. Robert Braun, both before and after his retirement from LLNL, supplied the computer expertise that converted many of my ideas into efficient computer codes. Paul Lerwick of EGL Resources, Howard Jonas of IDT, and Pierre Allix of Total brought me back into the fossil energy area after a substantial absence, which rejuvenated my interest in writing a book such as this. Total continued my involvement in this field via the Stanford-Total Enhanced Modeling of Source Rocks (STEMS) project, managed by Alex Lapene, Francois Gelin, Tony Kavscek, and Hamdi Tchelepi. Several reviewers gave helpful suggestions on the manuscript that improved it significantly: Ken Peters, Drew Pomerantz, Dan Jarvie, Justin Birdwell, Sergey Vyazovkin, and Andy Pepper, with Ken being the most thorough. However, their review does not imply that we agree on all things, and I take full responsibility for what I have written. And thanks, of course, to my wife, Mary, who endured my many long hours in front of the computer screen.

Livermore, USA

Alan K. Burnham

# Contents

|          |  |     |
|----------|--|-----|
| <b>1</b> | <b>Classification and Characterization</b> . . . . .             | 1   |
| 1.1      | Introduction to Fossil Organic Matter Types . . . . .            | 2   |
| 1.2      | Historical Usage of Fossil Organic Matter . . . . .              | 4   |
| 1.3      | Characterization Methods . . . . .                               | 9   |
| 1.4      | The Evolution of Modern Classification Systems . . . . .         | 14  |
|          | References. . . . .  | 22  |
| <b>2</b> | <b>Introduction to Chemical Kinetics</b> . . . . .               | 25  |
| 2.1      | The Activation Energy and Frequency Factor. . . . .              | 26  |
| 2.2      | Introduction to Conversion and Pressure Dependence . . . . .     | 28  |
| 2.3      | Integrating the Reaction Rate . . . . .                          | 31  |
| 2.4      | Methods of Kinetic Analysis . . . . .                            | 34  |
|          | 2.4.1 Isoconversional Methods. . . . .                           | 35  |
|          | 2.4.2 Model Fitting Methods . . . . .                            | 39  |
| 2.5      | Sigmoidal Reaction Models . . . . .                              | 42  |
| 2.6      | Distributed Reactivity Models . . . . .                          | 51  |
| 2.7      | Identifying and Fitting the Right Kinetic Model. . . . .         | 60  |
|          | References. . . . .  | 69  |
| <b>3</b> | <b>Structures of Coal, Kerogen, and Asphaltenes</b> . . . . .    | 75  |
| 3.1      | Molecular Structure of Coal and Type III Kerogen . . . . .       | 76  |
| 3.2      | Molecular Structure of Type I and II Kerogen . . . . .           | 80  |
| 3.3      | Molecular Structure of Asphaltenes . . . . .                     | 87  |
| 3.4      | Relationship Between Kerogen Structure and Pyrolysates . . . . . | 95  |
| 3.5      | Mechanistic Models of Kerogen Decomposition. . . . .             | 98  |
|          | References. . . . .  | 100 |
| <b>4</b> | <b>Pyrolysis in Open Systems</b> . . . . .                       | 107 |
| 4.1      | Types of Pyrolysis Apparatus. . . . .                            | 108 |
| 4.2      | Temperature Measurement Issues . . . . .                         | 110 |
| 4.3      | Kerogen Pyrolysis Kinetics. . . . .                              | 115 |

|          |   |            |
|----------|---|------------|
| 4.3.1    | Oil-Prone Kerogen Decomposition . . . . .   | 116        |
| 4.3.2    | Oil Generation and the Sequential Mechanism . . . . .                               | 118        |
| 4.3.3    | Effects of Pyrolysis Temperature on Oil Yields<br>and Properties . . . . .          | 123        |
| 4.4      | Fossil Fuel Kinetics by Programmed Micropyrolysis . . . . .                         | 127        |
| 4.4.1    | Measurement Issues for Global Hydrocarbon Kinetics . . . . .                        | 130        |
| 4.4.2    | Global Kinetics for Type I and II Organic Matter. . . . .                           | 134        |
| 4.4.3    | Global Kinetics for Bitumen and Asphaltenes. . . . .                                | 145        |
| 4.4.4    | Global Kinetics for Humic Coals<br>and Type III Kerogens . . . . .                  | 146        |
| 4.5      | Gas Generation Kinetics by Programmed Pyrolysis . . . . .                           | 156        |
|          | References. . . . .   | 163        |
| <b>5</b> | <b>Pyrolysis in Semi-Open Systems. . . . .</b>                                      | <b>171</b> |
| 5.1      | Coal Pyrolysis at Elevated Pressure . . . . .                                       | 172        |
| 5.2      | Secondary Cracking of Oil and Tar . . . . .   | 182        |
| 5.3      | Oil Shale Pyrolysis at Elevated Pressure. . . . .                                   | 187        |
|          | References. . . . .   | 200        |
| <b>6</b> | <b>Pyrolysis in Closed Systems . . . . .</b>  | <b>205</b> |
| 6.1      | Maturation of Coal and Evolution of Vitrinite Reflectance. . . . .                  | 206        |
| 6.2      | Compositional Models of Type III Organic Matter Pyrolysis . . . . .                 | 216        |
| 6.3      | Closed-System Pyrolysis of Type I and II Organic Matter . . . . .                   | 221        |
| 6.3.1    | Type I Organic Matter . . . . .   | 222        |
| 6.3.2    | Type II Organic Matter . . . . .  | 233        |
| 6.3.3    | Type II-S Organic Matter . . . . .  | 237        |
| 6.4      | Compositional Kinetic Models of Type I and II Organic<br>Matter Pyrolysis . . . . . | 244        |
| 6.5      | High-Pressure Pyrolysis with Supercritical and Reactive<br>Solvents . . . . .       | 257        |
| 6.5.1    | Coal Liquefaction . . . . .   | 258        |
| 6.5.2    | Thermal Solution of Green River Oil Shale . . . . .                                 | 261        |
| 6.5.3    | Thermal Solution of Other Oil Shales. . . . .                                       | 263        |
|          | References. . . . .   | 266        |
| <b>7</b> | <b>Applications to Fossil Fuel Processes . . . . .</b>                              | <b>273</b> |
| 7.1      | Petroleum Systems . . . . .   | 275        |
| 7.2      | Oil Shale Retorting . . . . .   | 288        |
| 7.2.1    | In Situ Retorting . . . . .   | 289        |
| 7.2.2    | Ex Situ Retorting . . . . .   | 296        |
| 7.3      | Coal Utilization . . . . .  | 301        |
| 7.3.1    | Coal Liquefaction . . . . .   | 301        |
| 7.3.2    | Coal Combustion . . . . .   | 304        |
|          | References. . . . .   | 308        |
|          | <b>Index . . . . .</b>  | <b>313</b> |



## About the Author



**Alan K. Burnham** is currently a consultant for Total E&P Research on a source rock modeling project at Stanford University, where he serves as an Adjunct Professor. He also continues in a partnership with GeoIsoChem improving Kinetics2015, a chemical kinetics analysis program, and PMod2, a source-rock chemical kinetic modeling program. Previously, he was Chief Technology Officer for American Shale Oil, LLC (AMSO), which had its technical headquarters in Rifle, Colorado, to test in-situ oil shale extraction technology in the Piceance Basin. Prior to becoming CTO for AMSO in 2008, Dr. Burnham worked for more nearly 31 years at Lawrence Livermore National Laboratory (LLNL) in the areas of oil shale processing, petroleum geochemistry, laser fusion targets, large optics for the National Ignition Facility, and energetic materials. He has a BS degree in Chemistry from Iowa State University and a Ph.D. degree in Physical Chemistry from the University of Illinois at Champaign-Urbana. Dr. Burnham has approximately 10 patents and 250 journal articles, conference proceedings, book chapters, and publicly available LLNL technical reports. He has been active in numerous professional societies, including being an officer in the Geochemistry Division of the American Chemical Society and the Energy Minerals Division of the American Association of Petroleum Geology. He serves on the editorial boards of Energy & Fuels and Thermochemica Acta. He received an Outstanding Chemistry Alumni Award from Iowa State University in 2014 and won a Federal Laboratory Consortium award for excellence in technology transfer in 1990.



*Left to right* Jerry Sweeney, Alan Burnham, and Robert Braun next to a Pyromat II in 1990 at the time of their selection for a Federal Laboratory Consortium award for Excellence in Technology Transfer. Alan is holding a core from the Green River Formation, Uinta Basin. The computer screen shows the output from an early version of Kinetics2015, originally written for DOS. Reproduced courtesy of Lawrence Livermore National Laboratory