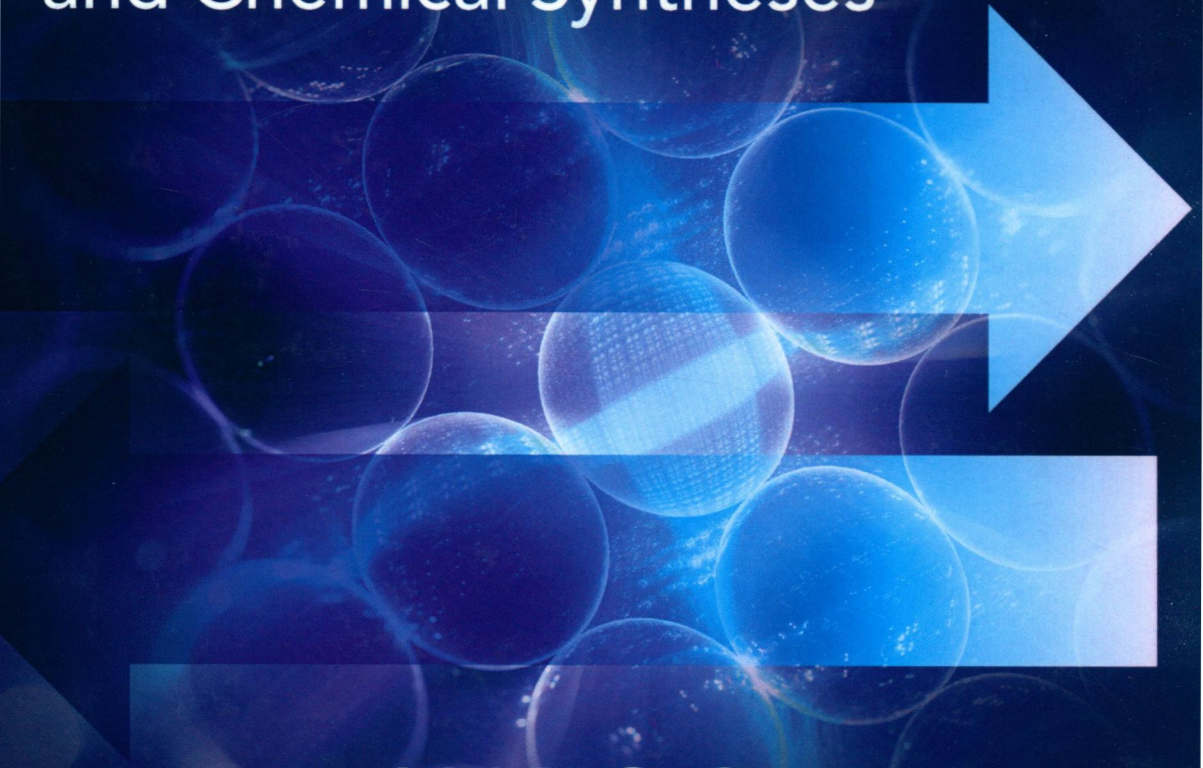
CHEMICAL LOOPING PARTIAL OXIDATION

Gasification, Reforming, and Chemical Syntheses



LIANG-SHIH FAN

CHEMICAL LOOPING PARTIAL OXIDATION

This is the first comprehensive guide to the principles and techniques of chemical looping partial oxidation. With authoritative explanations from a pioneer of the chemical looping process, you will:

- Gain a holistic overview of metal oxide reaction engineering, with coverage of ionic diffusion, nanostructure formation, morphological evolution, phase equilibrium, and recyclability properties of metal oxides during redox reactions.
- Learn about the gasification of solid fuels, the reforming of natural gas, and the catalytic conversion of methane to olefins.
- Understand the importance of reactor design and process integration in enabling metal oxide oxygen carriers to produce desired products.
- Discover other applications of catalytic metal oxides, including the production of maleic anhydride and solar energy conversions.

Aspen Plus® simulation software and results accompany the book online. This is an invaluable reference for researchers and industry professionals in the fields of chemical, energy, and environmental engineering, and students studying process design and optimization.

LIANG-SHIH FAN is Distinguished University Professor and the C. John Easton Professor in Engineering at The Ohio State University. He is a member of the U.S. National Academy of Engineering, Chinese Academy of Engineering, and Australian Academy of Technological Sciences and Engineering, and an Academician of Academia Sinica.

Online Resources
www.cambridge.org/fan

ASPEN simulation files and supporting documents

CAMBRIDGE
UNIVERSITY PRESS
www.cambridge.org

ISBN 978-1-107-19439-7

Cover illustration: original image © sakkmesterke

COVER DESIGNED BY HART McLEOD LTD

FAN

CHEMICAL LOOPING PARTIAL OXIDATION

CAMBRIDGE

Chemical Looping Partial Oxidation

Gasification, Reforming, and Chemical Syntheses

LIANG-SHIH FAN
Ohio State University

CAMBRIDGE
UNIVERSITY PRESS

CAMBRIDGE
UNIVERSITY PRESS

University Printing House, Cambridge CB2 8BS, United Kingdom

One Liberty Plaza, 20th Floor, New York, NY 10006, USA

477 Williamstown Road, Port Melbourne, VIC 3207, Australia

4843/24, 2nd Floor, Ansari Road, Daryaganj, Delhi – 110002, India

79 Anson Road, #06-04/06, Singapore 079906

Cambridge University Press is part of the University of Cambridge.

It furthers the University's mission by disseminating knowledge in the pursuit of education, learning, and research at the highest international levels of excellence.

www.cambridge.org
Information on this title: www.cambridge.org/9781107194397
DOI: 10.1017/9781108157841

First published 2017

Printed in the United Kingdom by TJ International Ltd. Padstow Cornwall

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

Library of Congress Cataloging-in-Publication Data
Names: Fan, Liang-Shih.
Title: Chemical looping partial oxidation : gasification, reforming, and chemical syntheses / Liang-Shih Fan, Ohio State University.
Description: Cambridge : Cambridge University Press, 2017. | Includes bibliographical references and index.
Identifiers: LCCN 2017014544 | ISBN 9781107194397 (Hardback : alk. paper)
Subjects: LCSH: Synthesis gas. | Biomass energy.
Classification: LCC TP243 .F36 2017 | DDC 662/.88–dc23 LC record available at https://lccn.loc.gov/2017014544

ISBN 978-1-107-19439-7 Hardback

Additional resources for this title are available at www.cambridge.org/fan

Chemical Looping Partial Oxidation

Gasification, Reforming, and Chemical Syntheses

This is the first comprehensive guide to the principles and techniques of chemical looping partial oxidation. With authoritative explanations from a pioneer of the chemical looping process, you will:

- Gain a holistic overview of metal oxide reaction engineering, with coverage of ionic diffusion, nanostructure formation, morphological evolution, phase equilibrium, and recyclability properties of metal oxides during redox reactions.
- Learn about the gasification of solid fuels, the reforming of natural gas, and the catalytic conversion of methane to olefins.
- Understand the importance of reactor design and process integration in enabling metal oxide oxygen carriers to produce desired products.
- Discover other applications of catalytic metal oxides, including the production of maleic anhydride and solar energy conversions.

Aspen Plus® simulation software and results accompany the book online. This is an invaluable reference for researchers and industry professionals in the fields of chemical, energy, and environmental engineering, and students studying process design and optimization.

Liang-Shih Fan is Distinguished University Professor and the C. John Easton Professor in Engineering at The Ohio State University. He is a Member of the U.S. National Academy of Engineering, Chinese Academy of Engineering, and Australian Academy of Technological Sciences and Engineering, and an Academician of Academia Sinica.

Cambridge Series in Chemical Engineering

Books in Series

Deen, *Introduction to Chemical Engineering Fluid Mechanics*
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*
De Pablo and Schieber, *Molecular Engineering Thermodynamics*
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*
Franses, *Thermodynamics with Chemical Engineering Applications*
Leal, *Advanced Transport Phenomena: Fluid Mechanics and Convective Transport Processes*
Lim and Shin, *Fed-Batch Cultures: Principles and Applications of Semi-Batch Bioreactors*
Marchisio and Fox, *Computational Models for Polydisperse Particulate and Multiphase Systems*
Mewis and Wagner, *Colloidal Suspension Rheology*
Morbidelli, Gavriilidis, and Varma, *Catalyst Design: Optimal Distribution of Catalyst in Pellets, Reactors, and Membranes*
Nicoud, *Chromatographic Processes*
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*
Shell, *Thermodynamics and Statistical Mechanics*
Sirkar, *Separation of Molecules, Macromolecules and Particles: Principles, Phenomena and Processes*
Slattery, *Advanced Transport Phenomena*
Varma, Morbidelli, and Wu, *Parametric Sensitivity in Chemical Systems*

In Memory of

My Sister, Liang-Chi Fan Subisak
Whose Passion, Devotion, and Selflessness as a Teacher
Inspired Generations of Students
in the Pursuit of Their Successful Future Endeavors

Dedicated to

Fan club members
For their past and continuing devotion
to the demonstration of the Syngas Chemical Looping Pilot Operation
at the National Carbon Capture Center in Alabama

In Cooperation with Professor Fan's Research Group Members

William Wang

Mandar Kathe

Niranjani Deshpande

Ankita Majumder

Elena Chung

Dikai Xu

Siwei Luo

Lang Qin

Zhuo Cheng

Dawei Wang

Sourabh Nadgouda

Qiang Zhou

Alan Wang

Cheng Chung

Tien-Lin Hsieh

Charles Fryer

Preface

This book is written as a sequel to an earlier book, entitled "Chemical Looping Systems for Fossil Energy Conversions," published in 2010 by Wiley/AICHE. For the earlier book, the motivation was to elucidate the rationale for the resurgence of chemical looping technology research and development related to the ease in CO_2 emission control and the enhancement in exergy conversion efficiency for combustion of carbonaceous fuels. The earlier book clearly indicated that the success of chemical looping technology depends strongly on the viability of the metal oxide materials for its redox applications. Knowledge of fundamental properties of these materials such as redox phase behavior, reactivity, recyclability, and metal oxide support is essential for characterizing chemical looping system performance for the conversion of coal, natural gas, petrochemicals, and biomass. Furthermore, it elaborated gasification or reforming processes involving syngas generation from traditional coal gasifiers, and the use of syngas as feedstock for hydrogen production through a steam–iron chemical looping reaction scheme. It also covered traditional methane–steam reforming applications that are coupled with chemical looping heating schemes, followed by water–gas shift reactions for hydrogen generation. Chemical looping process simulations based on Aspen Plus® utilizing reactors such as gasifier, reducer, oxidizer, combustor, and processes such as conventional gasification and chemical looping for electricity and liquid fuel production were presented.

My motivation for writing this book was precipitated by the exciting recent revelation of direct, one-step, chemical looping partial oxidation techniques in gasifiers and reformers using carbonaceous feedstock. These techniques can produce syngas of a high quality, leading to process efficiencies far greater than any traditional gasification or reforming techniques and other chemical looping techniques. The implications of this discovery are significant in that syngas compositions can reach to near the thermodynamic conversion limit with a H_2:CO molar ratio that can readily be used for direct downstream chemicals or liquid fuels synthesis. The uniqueness of these gasification and reforming techniques is that the syngas stream from the chemical looping reducer reactor will contain little CO_2, yielding a process of high carbon utilization efficiency. Even higher carbon utilization efficiencies can be achieved in a chemical looping process scheme for chemicals or liquid fuels production when the CO_2 generated from the process system can be fully recycled to the reducer reactor, yielding a CO_2 neutral chemical looping process system. Furthermore, in a CO_2 negative chemical looping process system, both the recycled CO_2 from the process stream and the fresh CO_2 can

be used as feedstock in the operation of the reducer. The CO_2 recycling along with the fresh CO_2 intake operation scheme also allows a reducer modularization strategy to be implemented, in order to optimize the downstream product synthesis functions in the gasification or reforming operation. Opportunities for direct synthesis of chemicals using natural gas, bypassing syngas formation, also exist and are of high academic and industrial interest. The consequence of process intensification with either the indirect or direct route for synthesis of chemicals can appreciably impact the process system economics. Also, recent advances in the science of mixed metal oxide materials have provided valuable insights into their chemical and physical behavior during redox reactions, and have assisted in their effective formulation and synthesis for chemical looping applications. Accounting for the characteristics of the mixed metal oxides as oxygen carrier at the molecular level, such as ion, defect, and electron transport during redox reactions and their effects on morphological transformation and solid phase equilibrium is further motivation for writing this book. The lattice oxygen diffusion discussed in the context of metal oxides serving purely as an oxygen carrier or as an oxygen carrier as well as a catalyst, referred to as "catalytic metal oxide," is also illustrated.

The book contains six chapters with accompanying supplemental material. Chapter 1 presents the underlying theme of the book and provides an update on the world and U.S. energy outlook based on the latest reports. It introduces the essence of redox reactions that are accompanied by the transport of ions and electrons, as well as defects and morphological variations in mixed metal oxides. It also highlights the importance of reactor design and process integration in successfully enabling mixed metal oxide oxygen carriers to produce the desired products. The use of Aspen Plus® simulation software as a valuable tool in process synthesis and techno-economic analysis of various chemical looping process schemes is also described. Chapter 2 provides details on the ionic diffusion, nanostructure, morphology, and phase equilibrium of complex mixed metal oxide based materials, their recyclability and physical properties, the effect of pressure on reaction kinetics, and oxygen carrier enhancement techniques. Chapter 3 discusses reforming processes represented by the oxidative coupling of methane (OCM) that produces chemicals such as olefins. The OCM reaction mechanism, catalytic metal oxide properties, and process concept and simulations using Aspen Plus® are given. Chapter 4 describes the chemical looping gasification and reforming techniques that are characterized by a one-step generation scheme of high purity syngas and desired H_2:CO ratios for immediate downstream chemicals or fuel synthesis, and the simplicity in their process schemes. They can be carried out in a co-feed mode with solid or gaseous feedstock in the presence or absence of H_2O. This chapter also discusses the unique oxygen carrier and feedstock contact mode that allows syngas quality to be easily maintained and novel CO_2 neutral or negative processes that can take recycled CO_2 and fresh CO_2 as feedstock in the reducer operation. Chapter 5 discusses examples of catalytic metal oxides used for other partial oxidation applications that were significant in the past or will be so in the future. These processes include DuPont's butane oxidation to produce maleic anhydride, solar energy conversions, partial oxidation of methane to formaldehyde, and partial oxidation of propylene and alcohols. Although

some of these examples are not based directly on the chemical looping concept per se, the oxidation mechanisms of catalytic metal oxides in the presence of molecular oxygen that are discussed elucidate the origin of the oxygen that participates in the selective or partial oxidation reactions, either from a metal oxide lattice or molecular oxygen. Chapter 6 provides general process simulation methodology and techno-economic analysis. The simulations through chemical looping gasification or reforming processes including coal to methanol, natural gas to liquid fuels, and biomass to olefins, in comparison with conventional gasification or reforming processes are also given. Supplemental material that contains various Aspen Plus® process simulation results is available on the book's website.

Like the first book, this book can be used as a research reference and/or used for teaching in courses at undergraduate and graduate levels related to energy and environmental engineering, reaction engineering, and process system engineering. It can also be used as a good technology and process example in teaching a senior design, optimization and strategy course. The book offers students a degree of appreciation of the depth and breadth of knowledge required to understand chemical looping technology for a wide spectrum of process applications. The subject matter for the knowledge required includes thermodynamics, reaction and reactor engineering, metal-oxide reaction engineering, catalysis, process system engineering and simulation, particle science and technology, and density functional theory.

The book was written in collaboration with some of the members of my research team who have worked or are working on chemical looping research and process development in my lab at The Ohio State University. They include one undergraduate student, 11 MS and PhD graduate students, and four post-doctoral research associates. This is an entirely different group of team members from those who participated in writing the earlier book. The current team members are William Wang, Dr. Mandar Kathe, Dr. Niranjani Deshpande (currently at Shell, India), Dr. Ankita Majumder (currently at Dow Chemical), Dr. Elena Chung (currently at EcoCatalytic Technologies), Dikai Xu, Dr. Siwei Luo (currently at Bay Environmental Technology, China), Dr. Dawei Wang, Sourabh Nadgouda, Dr. Qiang Zhou (currently Assistant Professor at Xi'an Jiaotong University, China), Dr. Lang Qin, Dr. Zhuo Cheng, Dr. Yao Wang (currently at ExxonMobil), Cheng Chung, Tien-Lin Hsieh, and Charles Fryer. Completion of this book would not have been possible without their extensive involvement and knowledge in the field. The technical contribution to this book from each one of them is apparent from the citations given in the text. Their devotion to the writing of this book is deeply appreciated. I am, however, solely responsible for the content and the presentation of the book, including the scope, topic selection, logic sequence, format, and style.

My team and I are grateful to Professor Andrew Tong, Fanhe Kong, Deven Baser, Mingyuan Xu, Yu-Yen Chen, Yaswanth Pottimurthy, Yitao Zhang, Mengqing Guo, Abbey Empfield, Elena Blair, and Peter Sandvik, who each reviewed one or more chapters of the book and provided valuable suggestions and comments. We are also grateful to our research collaborators, Dr. John Sofranko of EcoCatalytic Technologies, Professor Steven Chuang of University of Akron, and Professor Jonathan Fan of Stanford University, for their helpful insights into some aspects of chemical looping

technology that have been incorporated in the text of this book. We are thankful to the sponsors of our chemical looping gasification and reforming research and development work on which much of the contents of this book are based. They include U.S. Department of Energy, both ARPA-E and NETL, National Science Foundation, Ohio Department of Services Agency, and The Ohio State University. We have also benefitted from useful technical discussion and considerable engineering support for our demonstration activities from our industrial collaborators. They include Babcock and Wilcox Power Generation Group, WorleyParsons Group, American Electric Power, Southern Company, CONSOL Energy Inc, Particulate Solid Research Inc, First Energy Corporation, Clariant Corporation, IWI Incorporated, and Duke Energy Corporation. Our deep thanks are extended to Aining Wang, Yitao Zhang, and Mengqing Guo for their excellent figure drawings.

Liang-Shih Fan
Columbus, Ohio

Nomenclature

$1-\theta$	fraction of anion vacancies
a	total amount of active centers
A	surface area
A_i	attrition index
A_{tot}	attrition rate over 1 hr test period
C_{gT}	overall gas concentration
C_i	concentration of component i
C_{io}	concentration of component i at the grain surface
C_i^*	dimensionless concentration of component i
C_{io}^*	dimensionless concentration of component i at the grain surface
C_o	ion concentration in grain
C_o^*	normalized ion concentration
$C_{o,\,B}$	unreacted concentration of the diffusing ion in grain of solid B
C_{pi}	specific heat of component i
d	particle diameter
d_m	ion migration distance
$d_{o,\,B}$	number of the diffusing ion in the chemical formula of solid B
D	diffusivity
D_e	effective diffusivity constant
D_e^*	dimensionless effective diffusivity constant
D_i	diffusivity of component i
D_{int}	interstitial diffusivity
D_0	ionic diffusivity constant
D_o^*	dimensionless ionic diffusivity constant
D_{vac}	vacancy diffusivity
D^*	diffusion pre-exponential factor
D_{int}^*	interstitial diffusion pre-exponential factor
D_{vac}^*	vacancy diffusion pre-exponential factor
E_a	activation energy
$E_{a,int}$	activation energy of interstitial diffusion path
$E_{a,vac}$	activation energy of vacancy diffusion path
E_{ads}	adsorption energy
E_{DFT}	total energy calculated using DFT
$E(i)$	energy of system i