WOODHEAD PUBLISHING SERIES IN ENERGY

Membrane Reactors for Energy Applications and Basic Chemical Production

Edited by Angelo Basile, Luisa Di Paola, Faisal I. Hai and Vincenzo Piemonte

WP
WOODHEAD PUBLISHING

Woodhead Publishing Series in Energy:
Number 76

Membrane Reactors for Energy Applications and Basic Chemical Production

Edited by

Angelo Basile, Luisa Di Paola, Faisal I. Hai and Vincenzo Piemonte

ELSEVIER

AMSTERDAM • BOSTON • CAMBRIDGE • HEIDELBERG
LONDON • NEW YORK • OXFORD • PARIS • SAN DIEGO
SAN FRANCISCO • SINGAPORE • SYDNEY • TOKYO
Woodhead Publishing is an imprint of Elsevier

WP
WOODHEAD PUBLISHING

Woodhead Publishing is an imprint of Elsevier
80 High Street, Sawston, Cambridge, CB22 3HJ, UK
225 Wyman Street, Waltham, MA 02451, USA
Langford Lane, Kidlington, OX5 1GB, UK

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library

Library of Congress Control Number: 2014954543

ISBN 978-1-78242-223-5 (print)
ISBN 978-1-78242-227-3 (online)

For information on all Woodhead Publishing publications visit our website at http://store.elsevier.com/

Printed in the United States of America

List of contributors

A. Aghaeinejad-Meybodi Sahand University of Technology, Tabriz, Iran

P. Argurio University of Calabria, Rende, Italy

A. Arratibel Eindhoven University of Technology, Eindhoven, The Netherlands

A.A. Babaluo Sahand University of Technology, Tabriz, Iran

A. Basile University of Calabria, Rende, Italy

V. Calabrò University of Calabria, Rende, Italy

S. Chakraborty University of Calabria, Rende, Italy

P. Chiesa Politecnico di Milano, Milan, Italy

A. Comazzi Università degli Studi di Milano, Milan, Italy

S. Curcio University of Calabria, Rende, Italy

F. Dalena University of Calabria, Rende, Italy

R. Datta Worcester Polytechnic Institute, Worcester, MA, USA

L. Di Paola Campus Bio-Medico di Roma University, Rome, Italy

X. Dong Arizona State University, Tempe, AZ, USA

K.P. Fattah American University of Sharjah, Sharjah, UAE

F. Galli Università degli Studi di Milano, Milan, Italy

F. Gallucci Eindhoven University of Technology, Eindhoven, The Netherlands

G. Genduso KU Leuven, Leuven, Belgium

K. Ghasemzadeh Urmia University of Technology, Urmia, Iran; Sahand University of Technology, Tabriz, Iran

F.I. Hai University of Wollongong, Wollongong, NSW, Australia

J.T.S. Irvine University of St. Andrews, St. Andrews, UK

N. Itoh Utsunomiya University, Utsunomiya, Japan

A. Iulianelli University of Calabria, Rende, Italy

S. Klinsrisuk Khon Kaen University, Khon Kaen, Thailand

C. Lavorato University of Calabria, Rende, Italy

S. Liguori University of Calabria, Rende, Italy

Y.S. Lin Arizona State University, Tempe, AZ, USA

P. Luis Université Catholique de Louvain, Louvain-la-Neuve, Belgium

F. Manenti Politecnico di Milano, Milan, Italy

G. Manzolini Politecnico di Milano, Milan, Italy

D.J. Martino Worcester Polytechnic Institute, Worcester, MA, USA

E.R. Minardi University of Calabria, Rende, Italy

M. Miyamoto Gifu University, Gifu, Japan

R. Molinari University of Calabria, Rende, Italy

M.T. Moreira University of Santiago de Compostela, Santiago de Compostela, Spain

Y. Nakashimada Hiroshima University, Higashi-Hiroshima, Japan

D.A. Pacheco Tanaka Tecnalia, San Sebastian, Spain

V. Piemonte Campus Bio-Medico di Roma University, Rome, Italy

C. Pirola Università degli Studi di Milano, Milan, Italy

M.R. Rahimpour Shiraz University, Shiraz, Iran

M.C. Romano Politecnico di Milano, Milan, Italy

V. Russo Campus Bio-Medico di Roma University, Rome, Italy

D.P. Saroj University of Surrey, Guilford, UK

H. Takamura Tohoku University, Sendai, Japan

S. Tao University of Strathclyde, Glasgow, UK

J. Tong Colorado School of Mines, Golden, CO, USA

S. Uemiya Gifu University, Gifu, Japan

B. Van der Bruggen KU Leuven, Leuven, Belgium

M. van Sint Annaland Eindhoven University of Technology, Eindhoven, The Netherlands

H. Wang Arizona State University, Tempe, AZ, USA

J. Yang East China University of Science and Technology, Shanghai, P.R. China

C. Yang East China University of Science and Technology, Shanghai, P.R. China

P.-S. Yen Worcester Polytechnic Institute, Worcester, MA, USA

Woodhead Publishing Series in Energy

1 **Generating power at high efficiency: Combined cycle technology for sustainable energy production**
Eric Jeffs
2 **Advanced separation techniques for nuclear fuel reprocessing and radioactive waste treatment**
Edited by Kenneth L. Nash and Gregg J. Lumetta
3 **Bioalcohol production: Biochemical conversion of lignocellulosic biomass**
Edited by Keith W. Waldron
4 **Understanding and mitigating ageing in nuclear power plants: Materials and operational aspects of plant life management (PLiM)**
Edited by Philip G. Tipping
5 **Advanced power plant materials, design and technology**
Edited by Dermot Roddy
6 **Stand-alone and hybrid wind energy systems: Technology, energy storage and applications**
Edited by John K. Kaldellis
7 **Biodiesel science and technology: From soil to oil**
Jan C. J. Bart, Natale Palmeri and Stefano Cavallaro
8 **Developments and innovation in carbon dioxide (CO_2) capture and storage technology Volume 1: Carbon dioxide (CO_2) capture, transport and industrial applications**
Edited by M. Mercedes Maroto-Valer
9 **Geological repository systems for safe disposal of spent nuclear fuels and radioactive waste**
Edited by Joonhong Ahn and Michael J. Apted
10 **Wind energy systems: Optimising design and construction for safe and reliable operation**
Edited by John D. Sørensen and Jens N. Sørensen
11 **Solid oxide fuel cell technology: Principles, performance and operations**
Kevin Huang and John Bannister Goodenough
12 **Handbook of advanced radioactive waste conditioning technologies**
Edited by Michael I. Ojovan
13 **Membranes for clean and renewable power applications**
Edited by Annarosa Gugliuzza and Angelo Basile
14 **Materials for energy efficiency and thermal comfort in buildings**
Edited by Matthew R. Hall
15 **Handbook of biofuels production: Processes and technologies**
Edited by Rafael Luque, Juan Campelo and James Clark
16 **Developments and innovation in carbon dioxide (CO_2) capture and storage technology Volume 2: Carbon dioxide (CO_2) storage and utilisation**
Edited by M. Mercedes Maroto-Valer

17 **Oxy-fuel combustion for power generation and carbon dioxide (CO_2) capture**
Edited by Ligang Zheng
18 **Small and micro combined heat and power (CHP) systems: Advanced design, performance, materials and applications**
Edited by Robert Beith
19 **Advances in clean hydrocarbon fuel processing: Science and technology**
Edited by M. Rashid Khan
20 **Modern gas turbine systems: High efficiency, low emission, fuel flexible power generation**
Edited by Peter Jansohn
21 **Concentrating solar power technology: Principles, developments and applications**
Edited by Keith Lovegrove and Wes Stein
22 **Nuclear corrosion science and engineering**
Edited by Damien Féron
23 **Power plant life management and performance improvement**
Edited by John E. Oakey
24 **Electrical drives for direct drive renewable energy systems**
Edited by Markus Mueller and Henk Polinder
25 **Advanced membrane science and technology for sustainable energy and environmental applications**
Edited by Angelo Basile and Suzana Pereira Nunes
26 **Irradiation embrittlement of reactor pressure vessels (RPVs) in nuclear power plants**
Edited by Naoki Soneda
27 **High temperature superconductors (HTS) for energy applications**
Edited by Ziad Melhem
28 **Infrastructure and methodologies for the justification of nuclear power programmes**
Edited by Agustín Alonso
29 **Waste to energy conversion technology**
Edited by Naomi B. Klinghoffer and Marco J. Castaldi
30 **Polymer electrolyte membrane and direct methanol fuel cell technology Volume 1: Fundamentals and performance of low temperature fuel cells**
Edited by Christoph Hartnig and Christina Roth
31 **Polymer electrolyte membrane and direct methanol fuel cell technology Volume 2: *In situ* characterization techniques for low temperature fuel cells**
Edited by Christoph Hartnig and Christina Roth
32 **Combined cycle systems for near-zero emission power generation**
Edited by Ashok D. Rao
33 **Modern earth buildings: Materials, engineering, construction and applications**
Edited by Matthew R. Hall, Rick Lindsay and Meror Krayenhoff
34 **Metropolitan sustainability: Understanding and improving the urban environment**
Edited by Frank Zeman
35 **Functional materials for sustainable energy applications**
Edited by John A. Kilner, Stephen J. Skinner, Stuart J. C. Irvine and Peter P. Edwards
36 **Nuclear decommissioning: Planning, execution and international experience**
Edited by Michele Laraia
37 **Nuclear fuel cycle science and engineering**
Edited by Ian Crossland
38 **Electricity transmission, distribution and storage systems**
Edited by Ziad Melhem

39 **Advances in biodiesel production: Processes and technologies**
Edited by Rafael Luque and Juan A. Melero
40 **Biomass combustion science, technology and engineering**
Edited by Lasse Rosendahl
41 **Ultra-supercritical coal power plants: Materials, technologies and optimisation**
Edited by Dongke Zhang
42 **Radionuclide behaviour in the natural environment: Science, implications and lessons for the nuclear industry**
Edited by Christophe Poinssot and Horst Geckeis
43 **Calcium and chemical looping technology for power generation and carbon dioxide (CO_2) capture: Solid oxygen- and CO_2-carriers**
Paul Fennell and E. J. Anthony
44 **Materials' ageing and degradation in light water reactors: Mechanisms, and management**
Edited by K. L. Murty
45 **Structural alloys for power plants: Operational challenges and high-temperature materials**
Edited by Amir Shirzadi and Susan Jackson
46 **Biolubricants: Science and technology**
Jan C. J. Bart, Emanuele Gucciardi and Stefano Cavallaro
47 **Advances in wind turbine blade design and materials**
Edited by Povl Brøndsted and Rogier P. L. Nijssen
48 **Radioactive waste management and contaminated site clean-up: Processes, technologies and international experience**
Edited by William E. Lee, Michael I. Ojovan, Carol M. Jantzen
49 **Probabilistic safety assessment for optimum nuclear power plant life management (PLiM): Theory and application of reliability analysis methods for major power plant components**
Gennadij V. Arkadov, Alexander F. Getman and Andrei N. Rodionov
50 **The coal handbook: Towards cleaner production Volume 1: Coal production**
Edited by Dave Osborne
51 **The coal handbook: Towards cleaner production Volume 2: Coal utilisation**
Edited by Dave Osborne
52 **The biogas handbook: Science, production and applications**
Edited by Arthur Wellinger, Jerry Murphy and David Baxter
53 **Advances in biorefineries: Biomass and waste supply chain exploitation**
Edited by Keith Waldron
54 **Geological storage of carbon dioxide (CO_2): Geoscience, technologies, environmental aspects and legal frameworks**
Edited by Jon Gluyas and Simon Mathias
55 **Handbook of membrane reactors Volume 1: Fundamental materials science, design and optimisation**
Edited by Angelo Basile
56 **Handbook of membrane reactors Volume 2: Reactor types and industrial applications**
Edited by Angelo Basile
57 **Alternative fuels and advanced vehicle technologies for improved environmental performance: Towards zero carbon transportation**
Edited by Richard Folkson
58 **Handbook of microalgal bioprocess engineering**
Christopher Lan and Bei Wang

59 **Fluidized bed technologies for near-zero emission combustion and gasification**
Edited by Fabrizio Scala
60 **Managing nuclear projects: A comprehensive management resource**
Edited by Jas Devgun
61 **Handbook of Process Integration (PI): Minimisation of energy and water use, waste and emissions**
Edited by Jiří J. Klemeš
62 **Coal power plant materials and life assessment**
Edited by Ahmed Shibli
63 **Advances in hydrogen production, storage and distribution**
Edited by Ahmed Basile and Adolfo Iulianelli
64 **Handbook of small modular nuclear reactors**
Edited by Mario D. Carelli and Dan T. Ingersoll
65 **Superconductors in the power grid: Materials and applications**
Edited by Christopher Rey
66 **Advances in thermal energy storage systems: Methods and applications**
Edited by Luisa F. Cabeza
67 **Advances in batteries for medium and large-scale energy storage**
Edited by Chris Menictas, Maria Skyllas-Kazacos and Tuti Mariana Lim
68 **Palladium membrane technology for hydrogen production, carbon capture and other applications**
Edited by Aggelos Doukelis, Kyriakos Panopoulos, Antonios Koumanakos and Emmanouil Kakaras
69 **Gasification for synthetic fuel production: Fundamentals, processes and applications**
Edited by Rafael Luque and James G. Speight
70 **Renewable heating and cooling: Technologies and applications**
Edited by Gerhard Stryi-Hipp
71 **Environmental remediation and restoration of contaminated nuclear and NORM sites**
Edited by Leo van Velzen
72 **Eco-friendly innovation in electricity networks**
Edited by Jean-Luc Bessede
73 **The 2011 Fukushima nuclear power plant accident: How and why it happened**
Yotaro Hatamura, Seiji Abe, Masao Fuchigami and Naoto Kasahara. Translated by Kenji Iino
74 **Lignocellulose biorefinery engineering: Principles and applications**
Hongzhang Chen
75 **Advances in membrane technologies for water treatment: Materials, processes and applications**
Edited by Angelo Basile, Alfredo Cassano and Navin Rastogi
76 **Membrane reactors for energy applications and basic chemical production**
Edited by Angelo Basile, Luisa Di Paola, Faisal I. Hai and Vincenzo Piemonte

Preface

Integration of reaction and separation in a single unit is an elegant approach to increase efficiency and economic advantages of many chemical processes. In particular, the integration of membrane separation units to (bio)chemical reactors can yield the following multidimensional benefits:

1. The ability of such a reactor to circumvent thermodynamic limitations of an equilibrium-controlled process by separating reaction products, as they are produced, allows operation at lower temperatures than the conventional reactors to obtain the same reactant conversion or to convert more reactant at the same temperature.
2. Operating lower reaction temperatures allows reconsideration of heat integration strategy to supply heat duty to reactors.
3. Lower operating temperatures reduce materials cost along with increasing operation safety.
4. The expected significant process simplification and intensification offered by the membrane reactors due to combination of reaction and separation in one step would pave the way to a new industrial paradigm.

The potential of membrane reactors is substantial: they could play a key role not only in case of reversible reactions which conventionally cannot reach high conversions, but also in case of endothermic reactions since the equilibrium shift would allow a higher reactant conversion at lower temperature. In this book, an extensive list of the main reactions (or, better, reaction systems) carried out in membrane reactors is presented. Generally, a comparison with the so-called traditional reactors is also presented in order to better understand the benefits of membrane reactors in terms of conversion, yield, by-product recovery and so on.

The book is composed of three parts: (One) membrane reactors for syngas and hydrogen production (Chapters 1–9); (Two) membrane reactors for other energy applications (Chapters 10–15); and (Three) membrane reactors for basic chemical production (Chapters 15–21).

In detail, Chapter 1 (Iulianelli, Pirola, Comazzi, Galli, Manenti and Basile) delineates the importance of the water gas shift reaction, which is an equilibrium-limited reaction, moderately exothermic, thus, favored at lower temperature. It can be considered the most important reaction involved in all the other system reactions. The chapter describes the recent advancements on this reaction in membrane reactors, paying particular attention to the hydrogen selective membrane utilization for high temperature applications. In Chapter 2 (Basile, Liguori, Iulianelli) the relevant progress achieved in carrying out the methane steam reforming reaction via membrane reactor technology and the effects of the most important parameters affecting this reaction are described and critically reviewed. An overview on the mathematical models used for simulating the reaction is also presented and discussed. Chapter 3 (Arratibel, Tanaka, van Sint Annaland and Gallucci) discusses the application and the recent advances of membrane reactors for hydrogen production through autothermal reforming reactions, with a focus to the autothermal reforming of methane, methanol and ethanol. Two different configurations of membrane reactors, namely the fluidized bed and the packed bed configuration, are presented and compared. The modeling aspects of both types of reactors are also discussed. The methane dry reforming reaction, discussed in Chapter 4 (Minardi, Chakraborty and Curcio), yields a mixture of hydrogen and carbon monoxide (syngas), and is an important process for many applications. The reaction, from the stoichiometry, produces a higher concentration of carbon monoxide if compared to the methane steam reforming. However, there are some limitations such as the high endothermicity, the catalyst deactivation due to the carbon deposition on the solid active surface and the strong equilibrium limitations. In this chapter it is shown that membrane reactors can help in partially solving the last problem. Chapter 5 (Wang, Dong and Lin) presents the state of the art of hydrogen- and CO_2-selective membranes and membrane reactors for hydrogen production from coal with CO_2 capture. After introducing the traditional technologies for converting coal to hydrogen, the chapter focuses on the advantages and opportunities of membrane reactors with respect to the traditional ones. Finally, the recent progress in membrane reactors for the conversion of gasifier syngas and separation of hydrogen or CO_2 is presented. Another important aspect of membrane reactors is related to the possibility to produce highly pure hydrogen to be fed in a polymer electrolyte membrane fuel cell. In this context, Chapter 6 (Basile, Iulianelli and Tong) deals with the recent findings on both ethanol and methanol reforming reactions, paying attention to the utilization and the potentiality of the membrane reactors technology as well as its advantages over the conventional reactor technology. A short overview of the most representative scientific results on these reforming processes performed in membrane reactors is also discussed. How membrane reactors can improve the conversion and selectivity in water decomposition process for hydrogen production, as well as in NO_x and CO_2 decomposition, is the main focus of Chapter 7 (Ghasemzadeh, Babaluo and Aghaeinejad-Meybodi). In Chapter 8 (Iulianelli, Dalena, Liguori, Calabrò and Basile), glycerol and acetic acid as a bio-derived source are shown as attractive candidates for producing hydrogen through reforming reactions in both conventional and membrane reactors. The recent findings on these reactions are highlighted, with a specific care about the role of the catalyst and the potential of membrane reactor technology with respect to the conventional systems. The main biological reactions involved in the waste-to-biohydrogen process, pointing out the involved enzymatic and cellular systems, are outlined in Chapter 9 (Di Paola, Russo and Piemonte), where the authors also show how membrane reactors, compared with traditional technologies, allow to producing high-purity hydrogen in compact systems and with low environmental impact. Another important fuel for hydrogen production is biodiesel, which is considered as an alternative renewable energy, and has recently received great attention. In Chapter 10 (Rahimpour) it is discussed how all conventional methods in biodiesel production and purification have limitations leading to an expensive and non-environmental friendly process. It is further demonstrated how membrane reactors can minimize the limitations of the conventional methods. Membrane reactors for bioethanol production and processing are introduced and discussed in Chapter 11 (Hai, Fattah, Saroj and Moreira). In particular, the authors illustrate how membrane technology integrates several process steps that are conventionally separate. The scope of this important chapter is to provide a critical review of the application of membrane technology in various steps of bioethanol production. Moreover, the challenges to widespread deployment of full-scale bioethanol facilities equipped with membrane systems are also discussed. Chapter 12 (Miyamoto, Nakashimada and Uemiya) deals with biomethane that is considered one of the most promising carbon neutral energy. Anaerobic membrane bioreactors are presented as an attractive application for biomethane production. In this context, both the basic principles of anaerobic digestion and the fundamentals of anaerobic membrane bioreactors, including their configurations and membrane materials, are introduced, and their recent progress from the full-scale to lab-scale is also reviewed. Chapter 13 (Chiesa, Manzolini and Romano) considers the application of membranes for oxygen and hydrogen separation in coal gasification plants for power generation and hydrogen production. In this chapter, the focus is on the integration of polymeric and palladium based membranes for hydrogen separation. Different membrane module configurations are illustrated along with the key principles that guide plant design. It is underscored that carbon capture is one of most promising applications of membranes in the energy sector.

In Chapter 14 (Ji and Yang), a brief description of the chemical principles, industrial applications and advantages of the membrane reactors for the desulfurization is firstly given. Secondly, the theory, design and future trends of the use of membrane reactors for the desulfurization of gases and fuels are presented. A discussion and potential of a fuel cell as electrocatalytic membrane reactor is given in Chapter 15 (Datta, Martino and Yen). After introducing the concept and the principles behind the multifarious functions of this membrane reactor, various examples of its application as conventional fuel cells for producing power, unitized regenerative fuel cells for storing power, and a few industrial processes in which electrocatalytic synthesis or separation are presented. Chapter 16 (Itoh) takes into consideration the use of inorganic membrane reactors for the dehydrogenation of hydrocarbons, especially cycloalkanes (cyclohexane and methylcyclohexane), and alkanes (*n*-hexane, and ethyl-side group of aromatics like ethylbenzene). Chapter 17 (Takamura) describes the concept of oxygen permeable membranes based on mixed oxide-ion and electronic conductors and the trend in the related material development. In this chapter, after discussing the various membrane materials, and the development of tape-cast membranes, the fabrication of a prototype of planar-type methane reformer utilizing the ceramics membranes is also described. An exergy analysis is used to show that methane can be reformed to syngas under dry and low S/C conditions by using the membrane reformer. Ammonia, among many other important characteristics, can be considered an alternative energy source with zero CO_2 emission. It also is an important chemical feedstock in chemical industry, and liquid ammonia and ammonium salts have been widely used as fertilizer in farms and these industries have experience in handling ammonia safely. These aspects, and others, are taken into consideration in Chapter 18

(Klinsrisuk, Tao and Irvine) where, after an introduction of the traditional reactors for ammonia production, the advantages of membrane reactors are highlighted. Solid state proton conductors such as perovskites, pyrochlores, fluorites and polymers are reviewed and discussed with particular emphasis on their application in ammonia synthesis. In Chapter 19 (Genduso, Luis and Van der Bruggen) ester compounds are presented together with esterification methodologies and their main industrial applications. This is followed by a comparison between traditional reactors and membrane reactors for esterification reactions. Finally, the state of the art of pervaporation membrane reactors for esterification is presented. Another important application of membrane reactors is related to photocatalysis. In particular, in Chapter 20 (Molinari, Argurio and Lavorato) the photocatalytic hydrogenation of organic compounds in membrane reactors is shown as an alternative to conventional catalytic hydrogenation because it appears a more sustainable method to synthesize organic compounds under mild conditions in the presence of suitable photocatalysts. The chapter, after reviewing the basic principles of both photocatalysis and membrane photoreactors, then discusses photocatalytic hydrogenation of organic compounds. An in-depth overview of the recent progresses in this field, the latest developments of semiconductors and several possible applications of photocatalytic membrane reactors are also demonstrated. In the last chapter, Chapter 21 (Rahimpour), various reactions, such as butene oligomerization, phenol synthesis from benzene, butane partial oxidation and other reactions (e.g. cyclohexane dehydrogenation, ethylbenzene dehydrogenation, and water splitting) carried out in membrane reactors are presented and discussed.

The editors wish to take this opportunity to thank all the authors for their hard work. Special thanks also to the editorial team of Woodhead for their continued helpful support.

Angelo Basile
Luisa Di Paola
Faisal I. Hai
Vincenzo Piemonte

Contents