



# Bioenergy Systems for the Future

Prospects for Biofuels  
and Biohydrogen

Edited by Francesco Dalena, Angelo Basile  
and Claudio Rossi

**Woodhead Publishing Series in Energy**

# **Bioenergy Systems for the Future**

**Prospects for Biofuels and Biohydrogen**

*Edited by*

***Francesco Dalena, Angelo Basile and  
Claudio Rossi***



**WP**

WOODHEAD  
PUBLISHING

An imprint of Elsevier

Woodhead Publishing is an imprint of Elsevier

The Officers' Mess Business Centre, Royston Road, Duxford, CB22 4QH, United Kingdom  
50 Hampshire Street, 5th Floor, Cambridge, MA 02139, United States  
The Boulevard, Langford Lane, Kidlington, OX5 1GB, United Kingdom

© 2017 Elsevier Ltd. All rights reserved.

No part of this publication may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording, or any information storage and retrieval system, without permission in writing from the publisher. Details on how to seek permission, further information about the Publisher's permissions policies and our arrangements with organizations such as the Copyright Clearance Center and the Copyright Licensing Agency, can be found at our website: [www.elsevier.com/permissions](http://www.elsevier.com/permissions).

This book and the individual contributions contained in it are protected under copyright by the Publisher (other than as may be noted herein).

### Notices

Knowledge and best practice in this field are constantly changing. As new research and experience broaden our understanding, changes in research methods, professional practices, or medical treatment may become necessary.

Practitioners and researchers must always rely on their own experience and knowledge in evaluating and using any information, methods, compounds, or experiments described herein. In using such information or methods they should be mindful of their own safety and the safety of others, including parties for whom they have a professional responsibility.

To the fullest extent of the law, neither the Publisher nor the authors, contributors, or editors, assume any liability for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions, or ideas contained in the material herein.

### Library of Congress Cataloging-in-Publication Data

A catalog record for this book is available from the Library of Congress

### British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library

ISBN: 978-0-08-101031-0 (print)

ISBN: 978-0-08-101026-6 (online)

For information on all Woodhead publications visit our website at <https://www.elsevier.com/books-and-journals>



Working together  
to grow libraries in  
developing countries

[www.elsevier.com](http://www.elsevier.com) • [www.bookaid.org](http://www.bookaid.org)

*Publisher:* Joe Hayton

*Acquisition Editor:* Raquel Zanol Pinheiro da Silva

*Editorial Project Manager:* Mariana Kuhl

*Production Project Manager:* Priya Kumaraguruparan

*Cover Designer:* Matthew Limbert

Typeset by SPi Global, India

# Bioenergy Systems for the Future

## **Related titles**

*Bioenergy – Biomass to Biofuels*  
(ISBN 978-0-12-407909-0)

*Biomass gasification, pyrolysis and torrefaction: practical design and theory*  
(ISBN 978-0-12-396488-5)

*Membrane Reactors for Energy Applications and Basic Chemical Production*  
(ISBN 978-1-78242-223-5)

# List of contributors

- N. Abatzoglou** Université de Sherbrooke, Sherbrooke, QC, Canada
- N. Abdoulmoumine** University of Tennessee, Knoxville, TN, United States
- S. Adhikari** Auburn University, Auburn, AL, United States
- Muhammad Afzal** KTH Royal Institute of Technology, Stockholm, Sweden
- Amjad Ali** COMSATS Institute of Information Technology, Lahore, Pakistan
- Sarfraz Arshad** COMSATS Institute of Information Technology, Lahore, Pakistan
- A. Bakhtyari** Shiraz University, Shiraz, Iran
- A. Basile** Institute on Membrane Technology (ITM-CNR), Rende, Italy
- P. Biniiaz** Shiraz University, Shiraz, Iran
- C. Bonechi** University of Siena, Siena, Italy
- A. Cassano** Institute on Membrane Technology (ITM-CNR), Rende (Cosenza), Italy
- C. Conidi** Institute on Membrane Technology (ITM-CNR), Rende (Cosenza), Italy
- M. Consumi** University of Siena, Siena, Italy
- A.K. Dalai** University of Saskatchewan, Saskatoon, SK, Canada
- F. Dalena** University of Calabria, Rende, Italy
- A. Donati** University of Siena, Siena, Italy
- Liangdong Fan** Shenzhen University, Shenzhen, PR China
- L.T. Fuess** University of São Paulo, São Carlos, Brazil
- M.L. Garcia** São Paulo State University, Rio Claro, Brazil

**K. Ghasemzadeh** Urmia University of Technology, Urmia, Iran

**J. Grams** Lodz University of Technology, Lodz, Poland

**Chuanxin He** Shenzhen University, Shenzhen, PR China

**H. Honkanen** JAMK University of Applied Sciences, Tarvaala, Finland

**C. Italiano** Institute for Advanced Energy Technologies (ITAE), “Nicola Giordano,” National Research Consilium (CNR), Messina, Italy

**A. Iulianelli** University of Calabria, Rende, Italy

**E. Jalilnejad** Urmia University of Technology, Urmia, Iran

**Muhammad Kaleem Ullah** COMSATS Institute of Information Technology, Lahore, Pakistan

**J. Kataja** JAMK University of Applied Sciences, Tarvaala, Finland

**J.A. Kozinski** York University, Toronto, ON, Canada

**G. Leone** University of Siena, Siena, Italy

**K. Li** Western Michigan University, Kalamazoo, MI, United States

**A. Magnani** University of Siena, Siena, Italy

**M.A. Makarem** Shiraz University, Shiraz, Iran

**M. Martino** University of Salerno, Salerno, Italy

**E. Meloni** University of Salerno, Salerno, Italy

**H. Nam** Auburn University, Auburn, AL, United States

**S. Nanda** York University, Toronto, ON, Canada

**O. Oyedeji** University of Tennessee, Knoxville, TN, United States

**V. Palma** University of Salerno, Salerno, Italy

**S. Pepi** University of Siena, Siena, Italy

**L. Pino** Institute for Advanced Energy Technologies (ITAE), “Nicola Giordano,” National Research Consilium (CNR), Messina, Italy

**Asia Rafique** COMSATS Institute of Information Technology, Lahore, Pakistan

**M.R. Rahimpour** Shiraz University, Shiraz, Iran; University of California, Davis, CA, United States

**Rizwan Raza** COMSATS Institute of Information Technology, Lahore, Pakistan; KTH Royal Institute of Technology, Stockholm, Sweden

**A. Ricca** University of Salerno, Salerno, Italy

**C. Rossi** University of Siena, Siena, Italy

**C. Ruocco** University of Salerno, Salerno, Italy

**A.M. Ruppert** Lodz University of Technology, Lodz, Poland

**A. Senatore** University of Calabria, Rende, Italy

**G. Tamasi** University of Siena, Siena, Italy

**A. Tursi** University of Calabria, Rende, Italy

**A. Vita** Institute for Advanced Energy Technologies (ITAE), “Nicola Giordano,” National Research Consilium (CNR), Messina, Italy

**Bin Zhu** KTH Royal Institute of Technology, Stockholm, Sweden; Hubei University, Wuhan, PR China





# Preface

Fossil fuels are and have been the major source of energy in the last century. However, mainly in the last decade, there are developing researches to find alternative energy sources. This is mainly due to the fact that fossil fuel reserves are depleting across the world; this creates instability in the global market, which leads to a corresponding instability in fuel prices. Furthermore, fossil fuels are primarily responsible for the production of greenhouse gas (GHG) emissions (e.g., CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O), and concerning the global warming, there are other factors contributing to the transition toward bioenergy.

As documented in a 2015 report of the European Environment Agency (EEA), the recent atmospheric concentration of CO<sub>2</sub> indicating a 31% increase from its 1750 levels. A secure and alternative supply of energy is therefore indispensable for a sustainable future global economy.

In addition, in another report of the same year of the US Environmental Protection Agency (EPA), it was provided alarming information on the excessive amount of waste products in the world. In fact, rapid economic and tremendous population growths have caused municipal solid waste (MSW). This report informed that the world generates an estimated 1.7–1.9 billion metric tons of MSW each year. In the United States alone, about 254 million tons of MSW were generated in 2013, among which about 34% was recycled. Also nowadays, one of the methods for disposal of MSW is landfills that dispose wastes by burning. The burning of organic waste and producing a large amount of CO<sub>2</sub> and CO in the air enter a huge amount of methane gas produced through anaerobic decomposition of solid waste; that is a more harmful GHG than carbon dioxide.

To simultaneously solve the dilemma of energy demand, waste management, and greenhouse gas emission for communities globally, the waste-to-energy (WTE) supply chain as district energy system should be a viable method toward industrial economy. WTE technologies convert solid waste into various forms that can be used to supply energy. Energy can be derived from waste that has been treated and pressed into solid fuel and from waste that has been incinerated. In fact, WTE can be used to produce biogas (CH<sub>4</sub> and CO<sub>2</sub>), syngas (H<sub>2</sub>, CO<sub>2</sub>, and CO), liquid biofuels (ethanol and biodiesel), or pure hydrogen.

The specialized literature documents that the WTE is able to produce 1,430 MWh/d of heat and 480 MWh/d of electricity from 1000 t/d of MSW.

In particular, in recent years, scientific industrial research has been particularly focused in the transformation of lignocellulosic feedstocks originating mainly from agricultural residues and from MSW into energy or, in other words, from biomass to bioenergy.

The transformation of these wastes to bioenergy was introduced as one of the most promising options. Examples are (a) the production of hydrogen from bioalcohols and biomethane by steam reforming reaction, (b) the last technologies such as nanocomposites for “Nano Green Energy,” and (c) the application of fuel cells at low temperatures to optimize the production of bioenergy from bioalcohol.

Demonstrating the great interest of this conversion, there is a the renewable fuel standard (RFS) program in the United States, which predicts that about 44.5% of 36 billions of gallons of renewable fuel will be made with cellulosic biofuels, of which approximately 56.9% will originate from agricultural residue by 2022. The International Energy Agency (IEA), in the 2010, has also suggested that the use of bioenergy is expected to triple by 2050 to about 135 exajoules (EJ) per year; screenings of potential bioenergy range from 100 to 300 EJ by 2050.

The aim of this book is to provide, with contributions from some of the best scientists in the field, an overview on the status of the most recent research efforts. In fact, the book wants to provide a gradual knowledge starting from the characteristics of biomasses to arrive at the most innovative transformation processes in bioenergy.

In detail, the volume opens with a chapter edited by one of the editors (Rossi) and his coworkers (Bonechi, Consumi, Donati, Leone, Magnani, and Tamasi). The chapter provides a systematic overview on available biomass. Chapter 2 (Honkanen and Kataja) focuses on the technological aspects of nonfood agricultural lignocellulose transformations. It highlights the use of local biomass as energy source supports the development of the region toward self-sufficiency and helps to tackle the growth of GHG emissions at the local and regional level. Chapter 3 (Ghasemzadeh, Jalilnejad, and Basile) introduces the details of production of bioalcohol/biomethane and various feedstocks, followed by the use of membrane technologies for biofuel production. Chapter 4 (Bakhtyari, Makarem, and Rahimpour) provides an overview on the production of olefins and gasoline (aromatics) from biomass feedstocks; focusing on pyrolysis or liquefaction for the production of bio-oil followed by hydrodeoxygenation or catalytic cracking for bio-oil upgrading to olefins and gasoline type fuel. Chapter 5 (Fuess and Garcia) deals on the application of anaerobic digestion (AD) as a core treatment technology in industrial plants. This chapter concentrates on important advantages on an environmental and energetic basis, associating wastewater pollution control with bioenergy generation from biogas. Chapter 6 (Tamasi, Bonechi, Magnani, Leone, Donati, Pepi, and Rossi) reports the thermodynamic theoretical analysis of ethanol steam reforming (SR) process for hydrogen production. Chapter 7 (Palma, Ruocco, Martino, Meloni, and Ricca) focuses on catalysts for conversion of synthesis gas. This reforming process represents the most important reactant mixture for other processes devoted to the production of methanol, higher hydrocarbons (Fischer-Tropsch synthesis), and ammonia. Chapter 8 (Vita, Italiano, and Pino) analyzes the distribution of the hydrogen production from different biomass-derived fuels (bioethanol, biobutanol, glycerol, and biomethane) by conventional SR process. Chapter 9 (Iulianelli, Dalena, and Basile) considers the  $H_2$  production from bioalcohols and biomethane in more environmentally friendly processes, based on the exploitation of bio-sources. In particular, the chapter is focused on a particular production process: SR in membrane reactors. Chapter 10 (Grams and Ruppert) is devoted to the presentation of the methods of the production of hydrogen rich gas via conversion of

this renewable feedstock and its decomposition products. This chapter is divided into two parts: (a) the high-temperature processes are discussed focusing on the influence of the composition and physicochemical properties of the used catalyst on the  $H_2$  yield and (b) the production of hydrogen by formic acid decomposition and application of the obtained  $H_2$  for hydrogenation reactions. Chapter 11 (Nanda, Li, Abatzoglou, Dalai, and Kozinski) gives an overview of different hydrogen production technologies involving thermochemical, electrochemical, and biological routes. The primary focus of this chapter is to evaluate both advantages and limitations of several hydrogen production methods based on the available technology options, feedstock selection, end uses, and economical aspects. Chapter 12 (Fan, Afzal, He, and Zhu) summarizes the research activities in a range of nanocomposite materials in solid oxide fuel cells (SOFCs) in finding the positive roles to improve the cell components (anode, electrolyte, and cathode), electrochemical performances, and cell efficiency for green energy applications. Chapter 13 (Cassano and Conidi) deals with the most relevant applications of integrated membrane operations in specific areas of the agrofood production including fruit juice, wine, and whey processing, where the combination of different membrane technologies has been largely explored on both laboratory and industrial scales. Chapter 14 (Rahimpour, Biniiaz, and Makarem) shows various stages of fuel production from microalgae. In particular, downstream procedures including microalgae cultivation, biomass harvesting, dehydration, cell disruptions, and oil extraction are discussed in details, followed by upgrading processes such as transesterification, fermentation, pyrolysis, liquefaction, and anaerobic digestion. Chapter 15 (Raza, Ullah, Afzal, Rafique, Ali, Arshad, and Zhu) is focused on the development of low-temperature solid oxide fuel cell (LT-SOFC) operated by direct bioalcohol (bioethanol and biomethanol) for sustainable developments. The content of this chapter is divided into three parts: (a) development of materials, (b) characterization and analysis, and (c) demonstration of the nanocomposite materials in a bioalcohol fuel cell (FC). Chapter 16 (Adhikari, Abdoulmoumine, Nam, and Oyedeji) discusses primary contaminants, the impact of operating conditions on them, their mitigation, and regulations governing their emissions. Additionally, best available technology (BAT) is discussed for select contaminants. The last chapter, Chapter 17 (Dalena, Senatore, Tursi, and Basile), aims to provide an update of the state of art of existing feedstocks for biofuel production from lignocellulosic biomasses. The chapter also presents a critical analysis of published data on both applications and potentiality of the bioenergy production from second- and third-generation of feedstocks.

To conclude, the editors would like to express special thanks to each one of the authors for their valuable contributions to this volume. Other very special thanks are surely addressed to all the staff of Elsevier that helped us in all the various steps for realizing this work in the best way.

**Angelo Basile**  
**Francesco Dalena**  
**Claudio Rossi**



# Contents

<b>List of contributors</b>	<b>xi</b>
<b>Preface</b>	<b>xv</b>
<b>Section A Biomass to bioenergy</b>	<b>1</b>
<b>1 Biomass: An overview</b>	<b>3</b>
<i>C. Bonechi, M. Consumi, A. Donati, G. Leone, A. Magnani, G. Tamasi, C. Rossi</i>	
1.1 Introduction	3
1.2 Chemical characterisation of biomass	5
1.3 Agriculture and forestry biomass for energy production	18
1.4 Energy from biomass, a resource to exploit	24
1.5 Conclusions	40
Acknowledgments	40
References	40
Further Reading	41
<b>2 Technological aspects of nonfood agricultural lignocellulose transformations</b>	<b>43</b>
<i>H. Honkanen, J. Kataja</i>	
Abbreviations	43
2.1 Introduction	43
2.2 Material flows of biomasses from agriculture	43
2.3 Energy use pathways of biomasses from agriculture	48
2.4 Conclusions	58
References	58
Further Reading	59
<b>3 Production of bioalcohol and biomethane</b>	<b>61</b>
<i>K. Ghasemzadeh, E. Jalilnejad, A. Basile</i>	
Abbreviations	61
3.1 Introduction	61
3.2 Biofuels	62
3.3 Membrane processes for biofuels production	80
3.4 Conclusion and future trends	83
References	83
Further Reading	86

<b>4</b>	<b>Light olefins/bio-gasoline production from biomass</b>	<b>87</b>
	<i>A. Bakhtyari, M.A. Makarem, M.R. Rahimpour</i>	
4.1	Introduction	87
4.2	Gasoline and olefins	88
4.3	Why bio-gasoline and bio-olefin?	89
4.4	Feedstocks obtained from biomass	90
4.5	Routes to bio-olefin and bio-gasoline	91
4.6	Gasification	96
4.7	Bio-oil upgrading	97
4.8	Hydrodeoxygenation	97
4.9	Catalytic upgrading	102
4.10	Biomass/bio-oil to olefins	104
4.11	Glycerol to olefins	114
4.12	Biomass/bio-oil to gasoline	117
4.13	Catalyst deactivation and coke formation	134
4.14	Food vs fuel	136
4.15	Conclusion, further studies, and outlook	136
	References	136
	Further Reading	148
<b>5</b>	<b>Anaerobic biodigestion for enhanced bioenergy generation in ethanol biorefineries: Understanding the potentials of vinasse as a biofuel</b>	<b>149</b>
	<i>L.T. Fuess, M.L. Garcia</i>	
5.1	Introduction	150
5.2	Vinasse characterization: Suitability for bioenergy generation	153
5.3	Bioenergy generation from vinasse: Input data and estimates	154
5.4	Potentials of vinasse as a bioenergy source	162
5.5	Outlook: Prospects for AD as the core treatment technology in ethanol plants	174
5.6	Concluding remarks	176
	Acknowledgments	176
	References	177
<b>Section B</b>	<b>Hydrogen production</b>	<b>185</b>
<b>6</b>	<b>Thermodynamic analysis of ethanol reforming for hydrogen production</b>	<b>187</b>
	<i>G. Tamasi, C. Bonechi, A. Magnani, G. Leone, A. Donati, S. Pepi, C. Rossi</i>	
6.1	Introduction	187
6.2	Calculation method	195

---

6.3	Analysis of thermodynamic properties for the single reactions	196
6.4	Conclusion	212
	Acknowledgments	212
	References	212
<b>7</b>	<b>Catalysts for conversion of synthesis gas</b>	<b>217</b>
	<i>V. Palma, C. Ruocco, M. Martino, E. Meloni, A. Ricca</i>	
7.1	Introduction	218
7.2	Fischer-Tropsch synthesis	220
7.3	Methanol synthesis	245
7.4	NH <sub>3</sub> synthesis	254
7.5	Other Processes	260
	References	265
<b>8</b>	<b>Distributed H<sub>2</sub> production from bioalcohols and biomethane in conventional steam reforming units</b>	<b>279</b>
	<i>A. Vita, C. Italiano, L. Pino</i>	
8.1	Introduction	280
8.2	Biomass feedstocks: routes and technologies for biofuels generation	283
8.3	Biofuels reforming for distributed hydrogen production	290
8.4	Novel catalytic formulations for steam reforming process	297
8.5	Conclusion	314
	References	314
	Web List	320
<b>9</b>	<b>H<sub>2</sub> production from bioalcohols and biomethane steam reforming in membrane reactors</b>	<b>321</b>
	<i>A. Iulianelli, F. Dalena, A. Basile</i>	
	Abbreviations	321
	Symbols	321
9.1	Introduction	322
9.2	Inorganic MRs	323
9.3	Hydrogen production in MRs from bio-alcohols reforming	329
9.4	Conclusions	337
	References	339
	Further Reading	344
<b>10</b>	<b>Formation of hydrogen-rich gas via conversion of lignocellulosic biomass and its decomposition products</b>	<b>345</b>
	<i>J. Grams, A.M. Ruppert</i>	
10.1	Introduction	345



10.2	High-temperature conversion of lignocellulosic biomass towards hydrogen rich gas	345
10.3	Hydrogen not only as a source of energy	358
10.4	Catalysts used for FA decomposition	360
10.5	Decomposition of formic acid to hydrogen and subsequent hydrogenation reaction	364
10.6	Summary	365
	References	366
<b>11</b>	<b>Advancements and confinements in hydrogen production technologies</b>	<b>373</b>
	<i>S. Nanda, K. Li, N. Abatzoglou, A.K. Dalai, J.A. Kozinski</i>	
11.1	Introduction	373
11.2	Hydrogen generation technologies	375
11.3	Advancements in hydrogen production technologies	392
11.4	Confinements in hydrogen production technologies	403
11.5	Conclusion and future prospects	409
	Acknowledgements	410
	References	410
<b>Section C</b>	<b>Bioenergy technology aspects/status</b>	<b>419</b>
<b>12</b>	<b>Nanocomposites for “nano green energy” applications</b>	<b>421</b>
	<i>Liangdong Fan, Muhammad Afzal, Chuanxin He, Bin Zhu</i>	
12.1	Introduction	422
12.2	Nanocomposite electrolytes	425
12.3	Nanocomposite anodes	435
12.4	Nanocomposite cathodes	439
12.5	Conclusions and outlook	443
	Acknowledgments	444
	References	444
<b>13</b>	<b>Integration of membrane technologies into conventional existing systems in the food industry</b>	<b>451</b>
	<i>A. Cassano, C. Conidi</i>	
13.1	Introduction	452
13.2	Fruit juice processing	453
13.3	Wine processing	459
13.4	Agrofood wastewaters	463
13.5	Conclusions and future trends	474
	References	475