

Green Chemistry and Sustainable Technology

Series editors

Prof. Liang-Nian He, State Key Lab of Elemento-Organic Chemistry, Nankai University, Tianjin, China

Prof. Robin D. Rogers, Department of Chemistry, McGill University, Montreal, Canada

Prof. Dangsheng Su, Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang, China; Department of Inorganic Chemistry, Fritz Haber Institute of the Max Planck Society, Berlin, Germany

Prof. Pietro Tundo, Department of Environmental Sciences, Informatics and Statistics, Ca' Foscari University of Venice, Venice, Italy

Prof. Z. Conrad Zhang, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China

Aims and Scope

The series *Green Chemistry and Sustainable Technology* aims to present cutting-edge research and important advances in green chemistry, green chemical engineering and sustainable industrial technology. The scope of coverage includes (but is not limited to):

- Environmentally benign chemical synthesis and processes (green catalysis, green solvents and reagents, atom-economy synthetic methods etc.)
- Green chemicals and energy produced from renewable resources (biomass, carbon dioxide etc.)
- Novel materials and technologies for energy production and storage (biofuels and bioenergies, hydrogen, fuel cells, solar cells, lithium-ion batteries etc.)
- Green chemical engineering processes (process integration, materials diversity, energy saving, waste minimization, efficient separation processes etc.)
- Green technologies for environmental sustainability (carbon dioxide capture, waste and harmful chemicals treatment, pollution prevention, environmental redemption etc.)

The series *Green Chemistry and Sustainable Technology* is intended to provide an accessible reference resource for postgraduate students, academic researchers and industrial professionals who are interested in green chemistry and technologies for sustainable development.

More information about this series at <http://www.springer.com/series/11661>

Peter C.K. Lau
Editor

Quality Living Through Chemurgy and Green Chemistry

 Springer

Editor

Peter C.K. Lau
Tianjin Institute of Industrial Biotechnology,
Chinese Academy of Sciences
Tianjin
China

and

McGill University
Montreal
Québec
Canada

ISSN 2196-6982 ISSN 2196-6990 (electronic)
Green Chemistry and Sustainable Technology
ISBN 978-3-662-53702-2 ISBN 978-3-662-53704-6 (eBook)
DOI 10.1007/978-3-662-53704-6

Library of Congress Control Number: 2016954596

© Springer-Verlag GmbH Germany 2016

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.

Printed on acid-free paper

This Springer imprint is published by Springer Nature
The registered company is Springer-Verlag GmbH Germany
The registered company address is: Heidelberger Platz 3, 14197 Berlin, Germany

*To those who care though not necessarily
understand*

“There does not exist a category of science to which one can give the name applied science. There are science and the applications of science, bound together as the fruit and the tree that bears it.”

—Louis Pasteur, 1871

Foreword

As we all know from our school years, George Washington Carver sought to transform the U.S. agricultural sector of his day by paving the way for crop diversity and bioproduct manufacturing, which allowed the American South to move away from cotton monoculture.

Carver and his students developed more than 300 industrial uses for peanuts, sweet potatoes, and other crops that could be grown in rotation with cotton and corn. Carver's inventions included plastics, glues, soaps, paints, dyes for cloth and leather, medicines, and cosmetic ingredients. He was a prime mover in the early twentieth century chemurgy movement, which created ways to replace petrochemicals with farm-derived bioproducts. Industrial biotechnology pioneers restarted the movement in the late twentieth century and continue it today. The discovery of the structure of DNA, the development of modern genetic engineering methods and their application in industrial biotechnology accelerated the innovations and transformed the chemurgy space.

In June 2008, *The Economist* magazine published an article, "Better living through chemurgy," directly evoking the "Better Things for Better Living" branding campaign of a prominent traditional chemical manufacturer. The article outlined the economic potential for agricultural feedstocks to replace petroleum in everyday consumer products and the breakneck pace of industrial biotechnology developments enabling this substitution. It also highlighted the efforts of a growing breed of entrepreneurs to replace petrochemicals with renewable ones, boldly stating, "[C]hemurgy is back with a vengeance in the shape of modern industrial biotechnology." This book's title, "Quality Living through Chemurgy and Green Chemistry," further evokes that economic and technological potential.

In the 2008 *Economist* article, one pioneer of industrial biotech marveled that genetic engineering "processes that once took five years now take just one." Since 2008, the pace of technological development has accelerated still further. Synthetic biology and other new genetic engineering techniques have increased the speed and improved the precision of engineering biology. The processes that once took one year can now be accomplished more quickly. In Chap. 6 of this volume, Chun You

of the Chinese Academy of Sciences and Y.H. Percival Zhang of Virginia Tech describe a proposed consolidated biomass to ethanol process, in which cellulose is both hydrolyzed and fermented in the same vessel. Advanced enzyme engineering and new methods for pretreating cellulosic biomass would enable this proposed methodology, according to the authors.

Industrial biotech companies continue to accelerate the process of bringing products to market as they expand the universe of renewable products available to replace petroleum. In Chap. 3 of this volume, Liang Wu of the DSM Biotechnology Center describes the successful commercialization of biobased succinic acid, a precursor to polyesters and a replacement for fossil-based polyesters. Commercialization of succinic acid paved the way for proof-of-principle fermentation of adipic acid and caprolactam, nylon intermediates that can replace additional fossil-based polyesters, according to Wu. In Chap. 8, Jerald Lalman and colleagues from the University of Windsor and Aberystwyth University review the feedstocks and biofuels currently being produced and developed and find that additional resources are needed to fully displace petroleum. They describe options for fourth generation feedstocks, which could include genetically engineered aquatic plants that are also designed for CO₂ uptake and sequestration. Biohydrogen may also be a biofuel of the future, they find.

The need for additional biobased resources continues to push companies toward novel feedstocks, even as commercial development of cellulose, algae, solid waste streams, and methane continues. In Chap. 5, Huimin Zhao and colleagues from the University of Illinois at Urbana-Champaign provide an overview of the potential use of macroalgae biomass as a feedstock for biofuels and renewable chemicals. They also detail the advances in metabolic engineering that enable microorganisms to metabolize algal biomass sugars to ethanol and possible chemicals. And in Chap. 9, Jairo Lora of Lora Consulting LLC, describes the various uses of lignin—a component of biomass—as a feedstock for polymers and carbon materials. Companies have made progress in commercializing ingredients for consumer products from lignin. In Chap. 10, Fanny Monteil-Rivera of the National Research Council of Canada evaluates those green technologies including biocatalysis that could possibly be commercialized to convert lignin to valuable aromatic chemicals. She further identifies research gaps in the most promising approaches.

Renewable chemicals have made their way into consumer products, with some brand name manufacturers actively seeking commercial-scale quantities of renewable chemicals. Back in 2008, the global management firm McKinsey & Co. projected that the industrial biotech sector would capture \$100 billion in value by 2010, primarily through biofuels and plant extracts. The focus of the sector has now shifted as new technologies, applications and opportunities have come into view. More recently, the business consultancy Lux Research examined the subsector of renewable chemical production and found that it was experiencing the most rapid growth within industrial biotechnology, potentially reaching 13.2 million metric tons of annual capacity by 2017.

In addition to the economic potential of the sector, there is the promise of better living. A 2007 report from EPA, “Bioengineering for Pollution Prevention,” noted

that industrial biotechnology processes are naturally consistent with the principles of green chemistry and cleaner than petrochemical processes, since they reduce pollution at the source, save energy, and make use of renewable carbon. In the first chapter of this volume, David Constable, director of the American Chemical Society's Green Chemistry Institute, examines in detail how biobased and renewable chemicals can fit into the principles of green chemistry. He notes that chemurgy both influenced and continues to be influenced by the concept of green chemistry. In Chap. 4, Dunming Zhu of the Chinese Academy of Sciences and Ling Hua of DuPont Industrial Sciences expand on the unique benefits of using enzyme catalysis to replace chemical reactions in industry. They provide several examples of the positive environmental impacts—such as reduced chemical waste and production costs as well as improved energy efficiency—achieved through enzyme applications in chemical manufacturing.

There is also the promise of sustainably providing better living to people around the world. The availability and affordability of petroleum-based products and transportation has improved the standard of living of consumers in the United States and many other countries. The imbalance in living standards is also reflected in competition for natural resources. World population is expected to reach 9 billion by 2050, according to UN estimates, with rapid growth in Asia and Africa. Growing populations combined with economic growth will increase demands for food and consumer goods; at the same time, changing climate conditions could exacerbate resource constraints.

In Chap. 2 of this volume, Dongming Xie, Quinn Zhu and colleagues at DuPont Industrial Biosciences describe progress in commercializing an omega-3 fatty acid nutrition and feed supplement. The fatty acid is conventionally derived from fish, which are a scarce natural resource. With industrial biotechnology, the nutritional supplement can be produced in large quantities by yeast in a fermentation vessel, reducing demand for fish. Further, the omega-3 fatty acid can supplement fish food for farm raised salmon, further reducing demand for wild caught fish. And in Chap. 11, Baixue Lin and Yong Tao of the Chinese Academy of Sciences discuss progress in using metabolic engineering for production of sialic acids, which have applications in medicine, including antiviral drugs, and as a nutraceutical. These ingredients are traditionally derived from milk whey and egg yolks with typically low yields, which make them insufficient to meet growing demand.

Jim Lane at Biofuels Digest put the challenge of providing economic opportunity to growing worldwide populations in stark terms, saying, "Either we find a second planet to provide the resources. Or we in the United States find a way to tell the rest of the world that they can't have the material lifestyle we enjoy." The better option is to transition to a biobased economy that can generate the food, material goods and fuels needed to meet the demands of the world's growing population while providing new economic opportunities and creating a cleaner environment. Chemurgy—the technology needed to build the biobased economy—can also become the basis for manufacturing and economic growth, providing a means for people around the world to achieve a quality living standard.

In Chap. 7 of this book, Mingyu Wang and Jin Hou of Shandong University review the economic and technical hurdles that the industrial biotechnology and biorefinery industry must continue to address. Progress has been made in reducing the cost of converting cellulosic biomass to fermentable sugars as feedstock for biofuels and renewable chemicals; metabolic engineering provides tools for further cost reductions as well as the ability to produce new and more cost-effective fine chemicals. And in Chap. 12, Krista Morley of the National Research Council Canada and Peter C.K. Lau of Tianjin Institute of Industrial Biotechnology (Chinese Academy of Sciences) and McGill University map out the value chain for new functional polymers, detailing the steps from biomass to phenolic acids to monomers and finally proof-of-concept polymers. The biotech advances that enabled the development of these new polymers include the discovery of new enzymes.

In Chap. 13 of this volume, Manfred Kircher of CLIB2021 details how traditional chemical manufacturers can work with biomass producers to develop infrastructure and value chains to build state and international bioeconomies. The example of Europe's leading chemical cluster straddling Belgium, the Netherlands and Germany is presented as a bottom up approach to chemurgy. If George Washington Carver were alive today he might be very pleased and gratified to see how far chemurgy has come. Chemurgy has evolved to be modern-day industrial biotechnology. The chemurgy story is far from finished and more innovation and problem solving is in our future.

Brent Erickson

Preface

Control of consciousness determines the quality of life.

Mihaly Csikszentmihalyi

The impetus to editing this book stemmed from the overarching needs to fuel the fledgling bioeconomy or circular economy by realizing industrial and environmental sustainability through knowledge-based solutions, innovation, and cleaner production. The heart of this matter is promoting a greater awareness and deployment of environmentally benign biological processes to achieve various bioconversions by using naturally occurring or genetically improved enzymes, whole cells and associated bioprocesses. Whenever possible, renewable bio-based materials should be the feedstock of choice for the supply of chemicals and alternative energy sources to meet human societal needs.

This book, *Quality Living through Chemurgy and Green Chemistry*, is designed to give a deep appreciation of what the future holds, empowered by the synergy of two biomasses—a renewable feedstock and an infinite microbial biomass and its diversity as “game changers” in value addition and creation. Biocatalysis is integral to the 12 principles of green chemistry, an environmental priority and gateway to sustainability. Putting green chemistry to work on renewable feedstocks besides the conventional biomass is an extension of the original definition of chemurgy—applying “chemistry” (chemi) to “work” (ergon—Greek) on agricultural residues or simply on the farm.

I am deeply honored to have Brent Erickson writing a Foreword. He is Executive Vice President of the Industrial and Environmental Section of the Biotechnology Innovation Organization (BIO, formerly Biotechnology Industry Organization), and recently his name made the upper 10 % list of the Biofuels Digest “Top 100 people in the Advanced Bioeconomy,” a premier trade publication for the industrial biotechnology sector. I am equally honored to have Dr. David Constable, Director of the American Chemical Society’s Green Chemistry Institute to contribute a key chapter on Green Chemistry and Sustainability.

This book comprises 13 chapters and they have been written by scientists and engineers who are experts in their own fields. I am most grateful to these authors and colleagues who kindly accepted to undertake the charitable task of writing an informative chapter beyond their call of duty. The contents of the book are organized as follows:

- Chapter 1 serves as an introduction to the concept and practice of green chemistry and outlines the opportunities for applying sustainable (green) chemistry to maximize biobased resource efficiency.
- Chapters 2 and 3 highlight the industrial needs and perspectives in the bio-production of key commodity chemicals, e.g., dicarboxylic acids and omega-3 fatty acids.
- Chapters 4 and 5 are directed toward the development of a potpourri of biocatalysts to meet chemical and pharmaceutical needs, chiral building blocks, in particular; and also specialized enzymes from underexplored feedstock such as macroalgae for the production of biofuels and biochemicals.
- Chapters 6–8 focus on value creation from cellulosic and lignocellulosic materials to produce starch and derivatives thereof, as well as to gain access to a variety of biochemicals and biofuels including hydrogen, methane and butanol. Novel approaches to fermentation, e.g., simultaneous enzymatic biotransformation and microbial fermentation are highlighted. In the latter two chapters, various socioeconomic factors and technical bottlenecks that researchers and industries face in the biorefinery of lignocellulosics are discussed.
- Chapters 9 and 10 are devoted to the depolymerization and valorization of lignins from cleaner production (green approaches) point of view, and an updated review on the wide range of polymeric products that can be derived from this abundant aromatic feedstock. Notably, a great number of patents are cited in Chap. 9.
- Chapter 11 discusses the production of a family of amino sugars, sialic acid and its derivatives, and Chap. 12 presents a value chain in phenolic acids and polymeric production from agricultural feedstocks as well as the development of new enzymes and associated bioprocesses.
- Last but not least, Chap. 13 is considered a lagniappe—baker’s dozen. Without an infrastructure and receptors any technology development will be futile. Extrapolations of present day pillars of competitiveness in fossil-based economy to those of chemurgy and green chemistry in the bio- or circular economy are discussed by Dr. Manfred Kircher using a European model.

All in all, this book provides invaluable insights and perspectives in biobased economy and bioproduction from academia, national laboratories, health and environment industries as well as consulting enterprises. Although there is no shortage of books in the general context of biomass and nonbiological green chemistry approaches, *Quality Living through Chemurgy and Green Chemistry* is considered unique while adding knowledge to current advances in the literature. Graduate and undergraduate students in various disciplines, aspiring “sustainability scientists,” practitioners of industrial biotechnology and biobased industry,

researchers and engineers, granting officers and policy makers, etc., are expected to benefit from this book.

Started in the 1930s, a “chemurgic movement” was said to have taken place, formalized by the 1935 “Declaration of Dependence upon the Soil and of the Right of Self-Maintenance” and initiated by Dr. William J. Hale of Dow Chemical Company, among prominent proponents like Henry Ford and George Washington Carver: “When in the course of the life of a Nation, its people become neglectful of the laws of nature..., necessity impels them to turn to the soil in order to recover the right of self-maintenance.” Sustainability in either environmental or industrial setting is the new framework in which we all have a role to play.

I will be remiss if I do not express my gratitude to June Tang of Springer Beijing who first approached me for a project on Sustainable Development but agreed on this alternative title. Support and assistance in contacting the authors, preparing and realizing the final launching of the book came from the unyielding effort and patience on the part of June Tang and her team, Heather Feng, in particular. The interactions and exchanges of information with the Publisher, not forgetting the timely cooperations of the authors, have been a most gratifying experience. Thank you all. I hope readers will enjoy the book. Any suggestions or comments are welcome.

Tianjin, China and Montreal, Canada
September 2016

Peter C.K. Lau

Contents

1	Green Chemistry and Sustainability	1
	David J.C. Constable	
2	Sustainable Production of Omega-3 Eicosapentaenoic Acid by Fermentation of Metabolically Engineered <i>Yarrowia lipolytica</i>	17
	Dongming Xie, Edward Miller, Bjorn Tyreus, Ethel N. Jackson and Quinn Zhu	
3	Toward Fermentative Production of Succinic Acid, Adipic Acid, and Caprolactam: An Industrial Perspective	35
	Liang Wu	
4	Specialty Enzymes for Chemical Needs	61
	Dunming Zhu and Ling Hua	
5	Characterization and Engineering of Seaweed Degrading Enzymes for Biofuels and Biochemicals Production	99
	Eva Garcia-Ruiz, Ahmet Badur, Christopher V. Rao and Huimin Zhao	
6	Ex Vivo Enzymatic Conversion of Non-food Cellulose Biomass to Starch	129
	Chun You and Y.H. Percival Zhang	
7	Biorefinery of Lignocellulosics for Biofuels and Biochemicals	143
	Mingyu Wang and Jin Hou	
8	Biofuels Production from Renewable Feedstocks	193
	Jerald A. Lalman, Wudneh A. Shewa, Joe Gallagher and Sreenivas Ravella	
9	Lignin: A Platform for Renewable Aromatic Polymeric Materials	221
	Jairo H. Lora	

10	Green Processes for Lignin Conversion	263
	Fanny Monteil-Rivera	
11	Production of Sialic Acid and Its Derivatives by Metabolic Engineering of <i>Escherichia coli</i>	301
	Baixue Lin and Yong Tao	
12	Phenolics Value Chain and L-Lactic Acid Bioproduction from Agricultural Biomass	319
	Krista L. Morley and Peter C.K. Lau	
13	Regional Pillars of Competitiveness in Chemurgy and Green Chemistry	349
	Manfred Kircher	

Contributors

Ahmet Badur Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL, USA; Illumina, San Diego, CA, USA

David J.C. Constable American Chemical Society, Green Chemistry Institute, Washington, DC, USA

Joe Gallagher Institute of Biological, Environmental and Rural Sciences, Aberystwyth University, Aberystwyth, Ceredigion, UK

Eva Garcia-Ruiz Department of Chemical and Biomolecular Engineering, Carl R. Woese Institute for Genomic Biology, University of Illinois at Urbana-Champaign, Urbana, IL, USA

Jin Hou State Key Laboratory of Microbial Technology, School of Life Sciences, Shandong University, Jinan, China

Ling Hua DuPont Industrial Biosciences, Experimental Station, Wilmington, DE, USA

Ethel N. Jackson Industrial Biosciences, E.I. Du Pont de Nemours and Company, Wilmington, DE, USA

Manfred Kircher KADIB Kircher Advice in Bioeconomy, Frankfurt, Germany; CLIB2021, Düsseldorf, Germany

Jerald A. Lalman Department of Civil and Environmental Engineering, University of Windsor, Windsor, ON, Canada

Peter C.K. Lau Tianjin Institute of Industrial Biotechnology, Chinese Academy of Sciences, Tianjin, China; McGill University, Montreal, QC, Canada

Baixue Lin CAS Key Laboratory of Microbial Physiological and Metabolic Engineering, Institute of Microbiology, Chinese Academy of Sciences, Beijing, China

Jairo H. Lora Lora Consulting LLC, Media, PA, USA

Edward Miller Industrial Biosciences, E.I. Du Pont de Nemours and Company, Wilmington, DE, USA

Fanny Monteil-Rivera National Research Council of Canada, Aquatic and Crop Resource Development, Montreal, QC, Canada

Krista L. Morley National Research Council Canada, Montreal, QC, Canada

Christopher V. Rao Department of Chemical and Biomolecular Engineering, University of Illinois at Urbana-Champaign, Urbana, IL, USA

Sreenivas Ravella Institute of Biological, Environmental and Rural Sciences, Aberystwyth University, Aberystwyth, Ceredigion, UK

Wudneh A. Shewa Department of Civil and Environmental Engineering, University of Windsor, Windsor, ON, Canada

Yong Tao CAS Key Laboratory of Microbial Physiological and Metabolic Engineering, Institute of Microbiology, Chinese Academy of Sciences, Beijing, China

Bjorn Tyreus Industrial Biosciences, E.I. Du Pont de Nemours and Company, Wilmington, DE, USA

Mingyu Wang State Key Laboratory of Microbial Technology, School of Life Sciences, Shandong University, Jinan, China

Liang Wu DSM Biotechnology Center, Delft, The Netherlands

Dongming Xie Industrial Biosciences, E.I. Du Pont de Nemours and Company, Wilmington, DE, USA; Department of Chemical Engineering, University of Massachusetts-Lowell, Lowell, MA, USA

Chun You Tianjin Institute of Industrial Biotechnology, Chinese Academy of Sciences, Tianjin, China; Biological Systems Engineering Department, Virginia Tech, Blacksburg, VA, USA

Y.H. Percival Zhang Tianjin Institute of Industrial Biotechnology, Chinese Academy of Sciences, Tianjin, China; Biological Systems Engineering Department, Virginia Tech, Blacksburg, VA, USA

Huimin Zhao Department of Chemical and Biomolecular Engineering, Carl R. Woese Institute for Genomic Biology, University of Illinois at Urbana-Champaign, Urbana, IL, USA; Departments of Chemistry, Biochemistry, and Bioengineering, University of Illinois at Urbana-Champaign, Urbana, IL, USA

Dunming Zhu National Engineering Laboratory for Industrial Enzymes and Tianjin Engineering Research Center of Biocatalytic Technology, Tianjin Institute of Industrial Biotechnology, Chinese Academy of Sciences, Tianjin, China

Quinn Zhu Industrial Biosciences, E.I. Du Pont de Nemours and Company, Wilmington, DE, USA