GREEN CHEMISTRY AND CHEMICAL ENGINEERING

Biofuels and Bioenergy

Processes and Technologies

Sunggyu Lee and Y.T. Shah

CRC Press
Taylor & Francis Group

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CRC Press
Taylor & Francis Group
Boca Raton London New York

CRC Press is an imprint of the
Taylor & Francis Group, an **informa** business

CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

Printed in the United States of America on acid-free paper
Version Date: 20120611

International Standard Book Number: 978-1-4200-8955-4 (Hardback)

Library of Congress Cataloging-in-Publication Data

Lee, Sunggyu.
Biofuels and bioenergy : processes and technologies / Sunggyu Lee, Y.T. Shah.
p. cm. -- (Green chemistry and chemical engineering)
Includes bibliographical references and index.
ISBN 978-1-4200-8955-4 (hardback)
1. Biomass energy. I. Shah, Yatish T. II. Title.

TP339.L44 2012
662'.88--dc23 2012021353

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Biofuels and Bioenergy: Processes and Technologies
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Series Preface

Green Chemistry and Chemical Engineering

A Book Series by CRC Press/Taylor & Francis

The subjects and disciplines of chemistry and chemical engineering have encountered a new landmark in the way of thinking about, developing, and designing chemical products and processes. This revolutionary philosophy, termed *green chemistry and chemical engineering*, focuses on the designs of products and processes that are conducive to reducing or eliminating the use or generation of hazardous or potentially hazardous substances. In dealing with such substances, there may be some overlaps and interrelationships between environmental chemistry and green chemistry. Although environmental chemistry is the chemistry of the natural environment and the pollutant chemicals in nature, green chemistry proactively aims to reduce and prevent pollution at its very source. In essence, the philosophies of green chemistry and chemical engineering tend to focus more on industrial application and practice rather than academic principles and phenomenological science. However, as both a chemistry and chemical engineering philosophy, green chemistry and chemical engineering derive from and build upon organic chemistry, inorganic chemistry, polymer chemistry, fuel chemistry, biochemistry, analytical chemistry, physical chemistry, environmental chemistry, thermodynamics, chemical reaction engineering, transport phenomena, chemical process design, separation technology, automatic process control, and more. In short, green chemistry and chemical engineering is the rigorous use of chemistry and chemical engineering for pollution prevention and environmental protection.

The Pollution Prevention Act of 1990 in the United States established a national policy to prevent or reduce pollution at its source whenever feasible. And adhering to the spirit of this policy, the Environmental Protection Agency (EPA) launched its Green Chemistry Program in order to promote innovative chemical technologies that reduce or eliminate the use or generation of hazardous substances in the design, manufacture, and use of chemical products. Global efforts in green chemistry and chemical engineering have recently gained a substantial amount of support from the international community of science, engineering, academia, industry, and governments in all phases and aspects.

Some of the successful examples and key technological developments include the use of supercritical carbon dioxide as a green solvent in separation technologies, application of supercritical water oxidation for destruction of harmful substances, process integration with carbon dioxide sequestration steps, solvent-free synthesis of chemicals and polymeric materials, exploitation of biologically degradable materials, use of aqueous hydrogen peroxide for efficient oxidation, development of hydrogen proton exchange membrane (PEM) fuel cells for a variety of power generation needs, advanced biofuel production, devulcanization of spent tire rubber, avoidance of the use of chemicals and processes causing generation of volatile organic compounds (VOCs), replacement of traditional petrochemical processes by micro-organism-based bioengineering processes, replacement of chlorofluorocarbons (CFCs) with nonhazardous alternatives, advances in the design of energy-efficient processes, use of clean, alternative, and renewable energy sources in manufacturing, and much more. This list, even though it is only a partial compilation, is undoubtedly growing exponentially.

This book series on Green Chemistry and Chemical Engineering by CRC Press/Taylor & Francis is designed to meet the new challenges of the twenty-first century in the chemistry and chemical engineering disciplines by publishing books and monographs based upon cutting-edge research and development to effect reducing adverse impacts upon the environment by chemical enterprise. And in achieving this, the series will detail the development of alternative sustainable technologies that will minimize the hazard and maximize the efficiency of any chemical choice. The series aims at delivering to readers in academia and industry an authoritative information source in the field of green chemistry and chemical engineering. The publisher and its series editor are fully aware of the rapidly evolving nature of the subject and its long-lasting impact upon the quality of human life in both the present and future. As such, the team is committed to making this series the most comprehensive and accurate literary source in the field of green chemistry and chemical engineering.

Sunggyu Lee

Preface

Humans have a long history of using a wide variety of biomass resources as sources of energy and fuel. The discovery and use of fossil energy, represented largely by coal, natural gas, and petroleum, have drastically reduced the utilization of biomass fuels. Technologies for generating electricity using biomass, producing bioliquid fuels, and powering motor vehicles using bioalcohols and blended gasolines have been developed and practiced since the early twentieth century. Up until recently, however, development interest in biofuels had lessened due to the availability of relatively inexpensive fossil energy resources as well as the handling and transportation convenience of these conventional fuel sources.

Due to the strong growth of global transportation fuel demand, sharply escalating worldwide fossil energy prices, fear over the dwindling supply of petroleum and natural gas for the near future, and credible evidence linking global warming and climate change issues with the emission of greenhouse gases, global interest and R&D efforts in renewable alternative fuels have become intense and fiercely competitive, targeting both short- and long-term solutions to alternative energy needs. Although there are a number of options and routes for energy sustainability and independence via renewable alternative energy, bioenergy and biofuels certainly possess outstanding potential to provide solutions and relief to many of the immediate, intermediate, and long-term societal needs of clean energy and their associated challenges. Bioenergy and biofuels are quite broadly defined, including fuels derived from biological resources such as agricultural and forestry products, biomass and biomass-derived energy, fuels and fuel precursors secondarily derived from the primary biofuels and their by-products, fuels and energy derived from biological activities and processes, biodiesel from microalgae, and much more.

Accordingly, the resources for biofuels are ultimately renewable and totally independent of fossil energy availability and its distribution pattern. Biofuels are still, in some sense, similar to fossil fuels in that: (a) both are carbon energy sources, (b) direct combustion generates carbon dioxide emission, (c) both can be used as gas, liquid, and solid fuels, (d) both can be used for heat and power generation, and (e) both can be used as transportation fuels for conventional and futuristic motors. However, biofuels are drastically different from fossil energy in that biofuel resources are renewable, biomass is distributed worldwide, biomass typically contains much less sulfur, biofuels can also originate from nonmanufacturing and nonmining industrial sectors such as agriculture and forestry, and carbon dioxide generated by combustion of biofuels essentially originated from carbon dioxide removed from the atmosphere by plants through photosynthesis.

Because plant material in nature utilizes sunlight and carbon dioxide to produce energy and hydrocarbons, the combustion of biofuel derived from biomass by itself does not contribute to a net increase of carbon dioxide in the atmosphere. When biofuel is processed in conjunction with other carbon-neutral energies such as solar, wind, and hydrothermal energy, biofuels could be made available as a nearly carbon-neutral fuel. Furthermore, if biomass feedstock is chosen from abundantly available but nonfood crops whose growth does not require arable land, both sustainability and renewability would be warranted. Biofuel process R&D has directly benefited from the technological and scientific advances in C_1-chemistry, coal science and technology, petroleum science and technology, natural gas science and engineering, hydrocarbon processing, environmental science and engineering, separation science and technology, heat and mass transfer, catalysis and reactor engineering, materials science and engineering, biochemistry and biotechnology, agriculture, food science, and more. For example, the processes for fast pyrolysis, gasification, and liquefaction of biomass are quite similar to those developed and adopted for coal and oil shale processing. Gas cleaning and upgrading of bioliquid fuels also share common routes in conventional fuel processing with, in particular, those of natural gas and petroleum, with modifications and adaptations. Ingenious energy integration schemes are also receiving technological enhancements and know-how support from the well-practiced petroleum, petrochemical, and power generation industries. Biodiesel and bioethanol technologies have also benefited from the lessons-learned approaches of internal combustion engine developers and fuel engineers. Needless to say, the bioethanol industry is a direct and successful example of advances made in biotechnology, separation science and technology, agriculture, and animal food science. As such, the subject of biofuels cannot be treated as a new and independent stand-alone discipline, but rather as a multidisciplinary subject that has its foundation in C_1-chemistry, petroleum and coal science, natural gas engineering, environmental science and technology, process engineering and design, separation science and technology, biotechnology and biological engineering, heat and mass transfer, reactor engineering, catalysis and enzymology, energy management, public policies, and more. Therefore, this book is written as a comprehensive source book on the subject area covering all of the aforementioned subjects of relevance from the standpoints of fuel process engineers and fuel scientists as well as from the viewpoints of energy technologists.

This book is intended to provide the most comprehensive background in the science and technology of biofuels and bioenergy, including the most up-to-date and in-depth coverage of definitions and classifications of biofuels and related matters, characterization and analysis of biofuels, primary processing technologies of biofuel resources, secondary processing technologies of biofuels and biofuel precursors, upgrading of crude biofuels, issues involving the ethanol economy and the hydrogen economy, chemistry of process conversion, process engineering and design of biofuel production and associated environmental technologies, combined cycle processes, coprocessing of biomass with other fuels, energy balances and energy efficiencies, reactor designs and process configurations, energy materials and process equipment, commercial biofuel processes and significant practices, energy integration strategies and schemes, flowsheet analysis, relation to and integration with other conventional fossil fuel processes, by-product utilization, process economics of biofuel technology, environmental and ecological impacts and benefits, sustainability issues, governmental regulations and policies, global bioenergy trend and outlook, and much more.

Chapter 1 focuses on the introductory subjects of the book including the definition of biofuels, global energy outlook in reference to bioenergy and biofuels, issues of sustainability and carbon neutrality, generalized view of biomass feedstock and its availability, brief overview of technological trends of biofuel and bioenergy processes, and a general discussion of environment and ecology in relation to the utilization of bioenergy and biofuels.

Chapter 2 provides scientific and technological details of crop oils, algae fuels, and biodiesel. Vegetable oils, or plant oils, and their utilization as straight biofuels and biofuel feedstock are discussed in depth, including characterization, extraction, purification, and chemical conversion to biodiesel via transesterification. Also presented are algae biofuel and its technological details involving harvesting, extraction, and chemical conversion with detailed descriptions of the proposed or practiced technologies and their flowsheets.

Chapter 3 deals with the science and technology of producing bioethanol from starch crops, specifically corn. The fuel properties of ethanol as an oxygenated fuel for the internal combustion engine and as a blend fuel for conventional gasoline are presented. Particulars of corn ethanol process technologies, both dry milling and wet milling, are explained in necessary detail. Socioeconomic issues of "food versus oil" for corn ethanol production as well as technoeconomic issues of net energy balance of corn ethanol production are also discussed based on the literature data and recently published information. Also mentioned is the beneficial and profitable utilization of process by-products and coproducts in a variety of industrial sectors.

Chapter 4 is devoted to the production of ethanol from lignocellulose. An historical perspective of alcohol fermentation is presented along with its technological evolution and trend. Essential scientific and technological details of cellulose, hemicellulose, and lignin are provided and a variety of enzymes that are found and developed for processing these components are also discussed. Processing steps and options for lignocellulosic alcohol production involving prehydrolysis and pretreatment, hydrolysis and enzymatic treatment, and fermentation are elucidated. Particular attention is also paid to the fermentation of xylose, C_5-sugar, and to the co-fermentation of xylose with glucose, C_6-sugar, using genetically engineered micro-organisms. Also included in the chapter is the beneficial utilization of lignin in areas other than cellulosic ethanol production.

Chapter 5 is mainly focused on the thermochemical conversion of biomass into an assortment of gaseous products (biomass syngas), bioliquid (bio-oil), and solid fuel (biochar). Details of process technologies developed or proposed for fast pyrolysis of biomass as well as for gasification of biomass are presented with explanations of the merits and potential limitations associated with the specific technological steps. Process parameters, operating conditions, product spectra and properties, and pertinent reactor design issues are also discussed. Process options for further upgrading of crude products of thermochemical intermediates are also examined.

Chapter 6 provides an in-depth overview of the conversion of wastes to biofuels, bioproducts, and bioenergy. More specifically, the chapter deals with strategies for waste management, methods for waste preparation and pretreatment, an extensive list of waste-to-energy conversion technologies, socioeconomic and environmental issues of waste conversion, and the future of the waste management and conversion industry. Conversion technologies covered in the chapter include incineration, gasification, pyrolysis, plasma technology, supercritical processing, transesterification, anaerobic digestion, fermentation, and product upgrading.

Chapter 7 discusses various thermochemical technologies for processing a mixed feedstock such as a mixture of coal and biomass. The discussions are divided into two principal parts: (a) the technologies that are mainly generating gases such as combustion, gasification, and high-severity pyrolysis or plasma technology, and (b) those that are for generating liquids such as low-severity pyrolysis, liquefaction, and supercritical process. The chapter also reviews essential topics of reactor configurations and associated technologies, handling of product streams, process configurations, and examples of commercial processes, while discussing various technoeconomic benefits of the technology including early expansion of bioenergy utilization, mitigated environmental concerns, and enhanced thermal and economical efficiencies.

Even though this book covers in-depth knowledge on the subject of interdisciplinary biofuels and bioenergy, it is written for readers with college-level backgrounds in chemistry, biology, physics, and engineering. This book can be used ideally as a textbook for a three-credit-hour semester course in bioenergy or biofuels. If used as a textbook, two weeks each may be allocated for each chapter of this book, with one final week opted for open-ended discussions on regionally important topics or contemporary or arising issues related to the subject area. This book can also be adopted as a textbook or reference book for upper-level undergraduate or graduate-level courses in the fields of energy and fuels, renewable energy, alternative fuels, and fuel science and engineering.

This book will also serve as an excellent desk reference book for professionals who are engaged in renewable bioenergy- and biofuel-related industries as well as environmental engineering fields. Furthermore, this book will serve as a single source encompassing the most comprehensive and up-to-date scientific and technological information for researchers in the fields of biofuels as well as alternative and renewable energies.

Finally, the authors wish to acknowledge and thank their families, former and current graduate students, friends, and colleagues for their support and assistance in completing this book project.

Contents