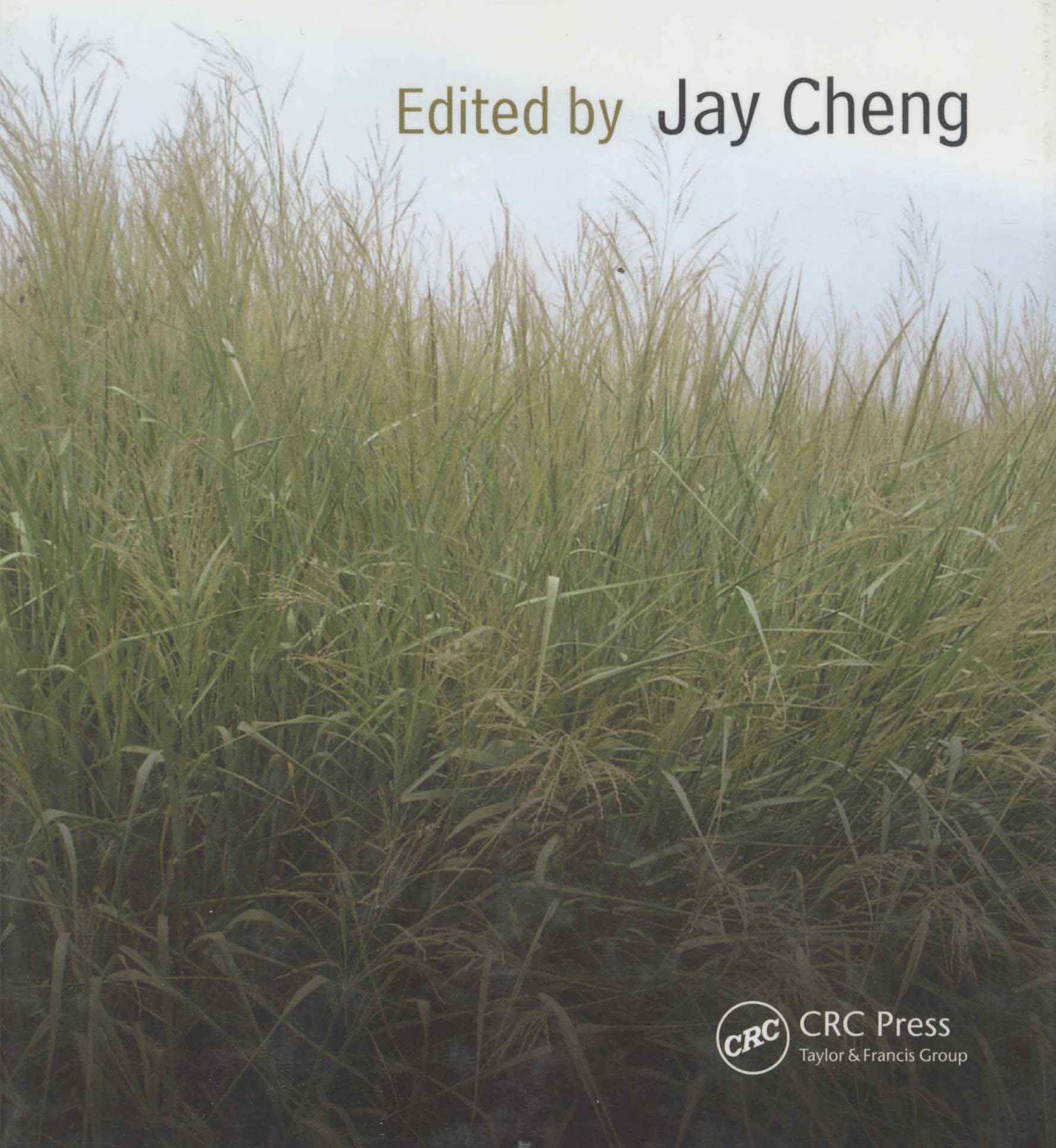
Biomass to Renewable Energy Processes

Edited by Jay Cheng



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Preface

A reliable and sustainable energy supply has been a major cause of concern for the global community, especially in the last decade, for the following reasons: the continuously increasing consumption of fossil fuels, our current major energy source, to support economic growth has had a significant impact on the global climate change; the price of fossil fuels has experienced huge fluctuation; and there is concern about the availability of fossil fuels in the near future. To respond to this energy supply crisis, a lot of effort has been made to explore renewable energy production technologies around the world, including hydroelectric, geothermal, wind, solar, and biomass.

Biomass energy products are generated from agricultural crops and residues, herbaceous and woody materials, and organic wastes. These materials can either be directly combusted for energy production or processed into energy products such as bioethanol, biodiesel, and biogas, which are then used as transportation fuels or for the production of electricity and heat. Although biomass energy production is a fast-growing area because of its renewable nature and the abundance of materials, its market share in total energy production is still very small (less than 5%). Currently, commercial biomass energy products mainly include bioethanol extracted from sugarcane and corn, biodiesel extracted from plants and waste oils, biogas produced from organic waste materials, and electricity and heat generated from the direct combustion of wood chips. The industry is very vulnerable to the fluctuation of feedstock prices. New technologies need to be developed to convert abundant biomass, such as lignocellulosic materials, into energy products in a cost-effective and environmentally friendly manner in order to tremendously increase the market share of biomass energy. The exploration of novel feedstocks is also important for the healthy development of the biomass energy industry.

This book describes fundamental principles and practical applications of biomass energy production processes for engineering and science students, and for professionals who are interested in this area and are well acquainted with the basic biological, chemical, and engineering principles. It explains the principal theories of biological processes, biomass materials and logistics, and technologies for bioenergy products, such as biogas, ethanol, butanol, biodiesel, and synthetic gases. Authors from several engineering disciplines have contributed to this book. I would like to thank them all for their hard work. I would also like to thank other colleagues who helped us in one way or another to make this book a reality.

Jay J. Cheng
Raleigh, North Carolina

Editor

Jay J. Cheng is a professor of bioprocessing and environmental engineering in the biological and agricultural engineering department at North Carolina State University, Raleigh. He joined the North Carolina State University faculty as an assistant professor in 1997. Prior to this, he served as a lecturer and the fermentation division director in the food engineering department at Jiangxi Polytechnic University (now renamed Nanchang University, China) and as a research associate at the University of Cincinnati, Ohio. He received his BS in chemical engineering from the Jiangxi Institute of Technology in China, his MS in biological engineering from St. Cyril & Methodius University in Macedonia, and his PhD in environmental engineering from the University of Cincinnati.

Professor Cheng has received several major awards including the Top Honors Award for Visual Aids in Teaching from Jiangxi Polytechnic University in 1988, first place (in the PhD category) in the Water Environment Federation Student Paper Competition in 1995, and a poster presentation award (first place) at the Water Environment Federation's 73rd Annual Meeting in 2000. He became a Fulbright scholar in 2005.

Dr. Cheng has taught courses in the areas of fermentation, environmental engineering, and bioenergy during his professional career. His research interests include brewing, anaerobic digestion of waste materials, nutrient recovery from wastewater with aquatic plants, and biomass conversion to biofuel. He has published over 30 articles in refereed scientific journals and presented more than 60 papers at national and international technical conferences on these topics. He has been invited to present over 25 keynote speeches and seminars in China, Europe, and the North and South Americas. He has served as an associate editor for the *Journal of Environmental Engineering* and on more than 15 international and national professional committees.

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Introduction

Jay J. Cheng

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1.1 Objectives of This Book

This book is written as a textbook for a graduate course in renewable energy production for both graduate and senior undergraduate students in the areas of agricultural, biological, chemical, and environmental engineering as well as crop, food, plant, and wood sciences. It is also intended to be a reference book for professional engineers and scientists who are interested in the processes of converting biomass into renewable energy sources.

This book introduces fundamental principles and practical applications of biomass-to-renewable energy processes, including biological, chemical, and thermochemical processes. Chemical properties of a variety of biomass are presented in this book. Resources of biomass that can be utilized for renewable energy production are also presented in this book, including their production and basic characteristics. Logistics of biomass handling such as harvesting, transportation, and storage are also included in this book. Biological processes include anaerobic digestion of waste materials for biogas and hydrogen production, and bioethanol and biobutanol production from sugars, starch, and cellulose. Pretreatment technologies, enzymatic reactions, fermentation, and microbiological metabolisms and pathways are presented and discussed in this book. The chemical process of biodiesel production from plant oils, animal fats, and waste oils and fats is described and discussed in this book. Thermal processes include combustion, gasification, and pyrolysis of woody biomass and of agricultural residues. Engineering principles of biomass combustion, gasification, and pyrolysis, and potential end-products are discussed in this book.

1.2 Renewable Energy versus Fossil Fuel Energy

Energy consumption has increased steadily over the last century as world population has grown and more countries have become industrialized since 1900. Fossil fuel, especially crude oil, is currently the predominant energy source around the world. Table 1.1 shows the top five crude oil–consuming countries in 2005 (Energy Information Administration, 2006). However, the reserves of fossil fuel are limited and will be depleted in the near future at its current consumption rate. Although there are debates about the exact year of peak oil production, it is generally believed that it would occur before 2025 after which significant reduction of oil production should be expected. Moreover, burning fossil fuels causes environmental concerns such as greenhouse gas (GHG) emission, which is generally believed as the major reason for global climate change. Because the world economy depends on oil, the consequences of inadequate oil availability could be severe. Therefore, there is a great interest in exploring alternative energy sources. The negative environmental impact of burning fossil fuels reminds us that the alternative energy source should be sustainable and environment-friendly. Energy production from biomass such as crop, herbaceous, woody, and waste materials has a great advantage over fossil fuels. The former is renewable annually or in several years, while the latter needs thousands or millions of years for reproduction. The energy production from biomass releases CO_2, which is believed as a major GHG to cause global climate change, but the CO_2 is utilized for biosynthesis during the growth of biomass. Thus, using biomass for

TABLE 1.1

Top Crude Oil–Consuming Countries in the World in 2005

Country	Crude Oil Consumption (Million Barrels/Day)
United States	20.3
China	6.2
Japan	6.1
India	2.2
South Korea	2.2

energy production can have a balanced CO_2 production and consumption or little net CO_2 release, compared to a huge discharge of CO_2 from burning fossil fuels. Currently, energy production from biomass is only a small portion of the total energy production. The sources of the 2005 energy consumption in the United States include 85% fossil fuel, 8.2% nuclear energy, 3.3% biomass, 2.7% hydroelectric power, 0.34% geothermal energy, 0.18% wind power, and 0.07% solar energy (Energy Information Administration, 2006). The resources of biomass materials such as crops, grasses, wood, agricultural residues, and organic wastes are quite abundant, so there is a great potential to substantially increase energy production from biomass materials.

Ethanol production from dedicated crops or agricultural residues is one form of renewable energy that addresses the critical need for sustainable fuels. There is already a well-developed market for ethanol in the United States; over 6.5 billion gal of ethanol were produced in 2007 according to the Renewable Fuels Association. Ethanol is primarily used as an additive to gasoline to improve emissions and boost octane. Biogas is generally produced from organic waste materials such as sewage sludge, agricultural wastes, industrial wastes, and municipal solid wastes. Proper treatment of these waste materials is necessary to protect our environment from pollution. At the same time, biogas production from the treatment facilities provides a renewable energy source. A number of commercial biogas production plants have been in operation utilizing sewage sludge, animal manure, and municipal solid wastes, and biogas is used for either electricity generation or direct combustion for heat production. Biodiesel is produced from vegetable oils and animal fats, and used as an alternative fuel of petroleum diesel for buses and trucks. The major benefits of producing and using bioenergy generated from biomass are as follows:

1. **Energy Independence.** Crude oil or natural gas reserves are located in limited regions in the world. Many countries have to rely on importing oils from limited oil-producing countries. For example, the U.S. Energy Information Administration reported that the United States imported 56% of its overall demand of petroleum in 2003, two-thirds of which were from the politically unstable Persian Gulf. The reliance makes the United States vulnerable to supply disruptions and nonmarket-related price instability, thereby jeopardizing the nation's energy and economic security according to the U.S. Congress's record that a dependence on foreign oil of greater than 50% is a peril to the country (NREL, 2000). On the other hand, biomass is almost everywhere. Renewable energy production from biomass could protect the oil-deficit countries from depending on foreign oil, and generate local jobs.
2. **Air Quality.** Oxygenated fuels such as ethanol typically promote more complete combustion as compared to fossil fuels. More

complete combustion translates into fewer emissions, particularly carbon monoxide (CO) emissions (National Science and Technology Council, 1997).

3. **Water Quality.** Ethanol is replacing methyl tertiary butyl ether (MTBE) as the preferred octane enhancer in the United States because of concerns over MTBE's persistence in the environment and possible negative effects to the water quality and human health. Ethanol breaks down quickly and spills of ethanol do not pose a critical threat to the environment.
4. **GHG Emissions.** The combustion of fossil fuels results in a net increase in the emission of GHGs (primarily carbon dioxide) into the atmosphere. According to the U.S. Energy Information Administration, the U.S. transportation sector is responsible for approximately one-third (1/3) of all carbon dioxide emissions. The impact of GHGs on global climate change is of increasing concern around the world. The use of biogas, bioethanol, and biodiesel as energy sources can significantly reduce the net GHG emissions. For example, use of E85 (85% ethanol and 15% gasoline) can reduce the net emissions of GHGs by as much as 25% on a fuel-cycle basis as compared to gasoline (Wang, 1999).

1.3 Life Cycle Assessment

The purpose of the life cycle assessment (LCA) of renewable energy production is to evaluate the environmental impacts of a product or process. LCA normally involves energy balance and GHG emissions. Energy balance determines the net energy production of a renewable energy product or process, while GHG emissions indicate its impact on climate changes. The first step to conduct an LCA is to define a boundary for the assessment, for example, from corn cultivation to ethanol combustion for corn-based fuel ethanol production process. All the unit operations inside the boundary need to be analyzed for energy input and output as well as GHG emissions. Again using corn-based fuel ethanol production process as an example, the unit operations generally include corn cultivation, corn harvest, transportation of corn to ethanol plant, conversion of corn to fuel ethanol, ethanol fuel distribution, and combustion of fuel ethanol to provide energy. Corn cultivation involves mainly land preparation, seeding, fertilization, irrigation, and weed control. Corn harvest includes corn kernel collection and residue handling. The conversion of corn to fuel ethanol consists of corn grinding, saccharification, fermentation, distillation, dehydration, and by-product processing. Similar procedures can be applied to the LCA of lignocellulose-based ethanol and

TABLE 1.2

Impact of Common GHGs on Global Climate Change

Greenhouse Gas	Global Warming Potential or CO_2 Equivalent
CO_2	1.0
CH_4	21.0
N_2O	310.0

Source: U.S. Environmental Protection Agency/U.S. Greenhouse Gas Inventory Program/Office of Atmospheric Programs, *Greenhouse Gases and Global Warming Potential Values*, 2002.

biodiesel production processes. For biogas production from organic waste materials, LCA usually needs to include the cost of the waste disposal to prevent environmental pollution as an offset to the biogas production process.

The major GHG emission in the energy production processes is CO_2. Other GHGs related to the unit operations of renewable energy production include methane (CH_4) and nitrous oxide (N_2O). The impact of the GHGs on global climate change can be expressed with global warming potential (GWP) or CO_2 equivalent. Their typical values are listed in Table 1.2.

In general, biogas production from waste materials needs little energy input or has a high net energy production. It also has a high impact on GHG emission reduction. A big challenge for biogas as a renewable energy source is its low energy density, which makes it economically unfavorable to transport from one location to another. Both corn- and lignocellulose-based ethanol productions are generally believed as net energy-producing processes. However, corn-based ethanol production has limited reduction in GHG emission, mainly because the corn residues are not utilized in the process, but lignocellulose-based ethanol production has significant reduction in GHG emission. Biodiesel usually has a much better net energy production than bioethanol, but it has limited impact on GHG emission because only a portion of the oil plant, that is, seeds, is utilized in biodiesel production.

1.4 Problems

1. How were the fossil fuels (petroleum, natural gas, and coal) formed? How long did it take for the formation? Discuss the alternative energy sources that are currently used in the world and their advantages and disadvantages.

2. Anaerobic lagoons are widely used for municipal and agricultural wastewater treatment. However, there are increasing concerns about GHG emissions from the lagoons. Thus, there have been efforts in covering the anaerobic lagoons to collect biogas that is used for energy generation or simply flared. Explain why the actions would help reduce the GHG emission and the effect of the GHG.
3. Switchgrass is considered as a promising biomass crop for renewable energy production, especially bioethanol as transportation fuel. Conduct a LCA of switchgrass-to-bioethanol process.

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Biomass Chemistry

Deepak R. Keshwani

CONTENTS

2.1 Introduction

Biomass-to-renewable energy processes involve the synthesis or breakdown of organic compounds that constitute different types of biomass. These organic compounds range in their complexity and contain numerous functional groups that influence the ultimate structure and chemistry of biomass. Familiarity with these organic compounds and their functional groups is important in understanding and developing biological and chemical processes that convert biomass into renewable energy and value-added products. This chapter summarizes relevant concepts from organic and carbohydrate chemistry followed by a discussion of the structure and chemistry of different types of biomass.

2.2 Review of Organic Chemistry

2.2.1 Alkanes

Alkanes are hydrocarbons that are exclusively made up of single bonds between carbon and hydrogen. They are called saturated hydrocarbons because of the absence of double or triple bonds. Saturated acyclic hydrocarbons have the general empirical formula C_nH_{2n+2}. The simplest alkanes are methane ($n=1$), ethane ($n=2$), and propane ($n=3$), whose structures are shown in Figure 2.1. When $n \geq 4$, more than one compound is possible for the same empirical formula. These compounds are called structural isomers and differ in the arrangement of the carbon atoms (straight chain or branched).

When $n=4$, there are two distinct compounds with the empirical formula of C_4H_{10}: normal butane (*n*-butane) and isobutane (Figure 2.2). Similarly,

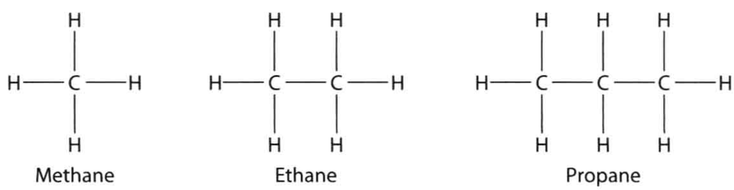

FIGURE 2.1
Structures of simple alkanes.

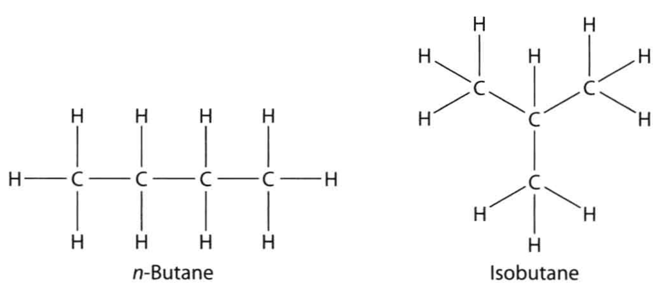

FIGURE 2.2
Structural isomers of butane (C_4H_{10}).

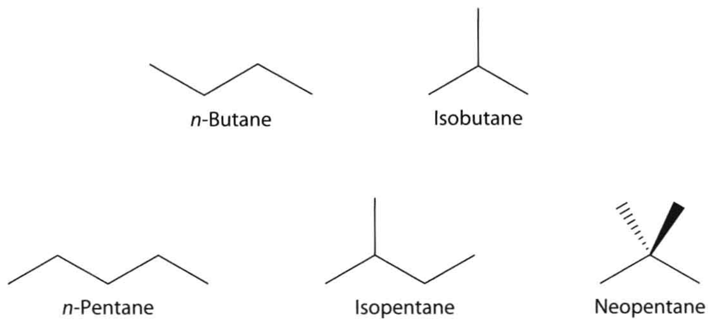

FIGURE 2.3
Simplified representations of the structural isomers of butane (C_4H_{10}) and pentane (C_5H_{12}).

when $n=5$ (pentane), there are three structural isomers with the empirical formula of C_5H_{12}. The number of structural isomers rapidly increases as the number of carbon atoms increases. For example, C_7H_{16} has nine structural isomers and $C_{10}H_{22}$ has 75 structural isomers.

Since including every carbon and hydrogen atom in structures can be cumbersome, representations of organic compounds are simplified by using chains of carbon atoms with hydrogen atoms assumed implicit. Figure 2.3 shows the simplified representations of the structures of *n*-butane and isobutane, along with the three structural isomers of pentane (*n*-pentane, isopentane, and neopentane). Note the use of wedged bonds in the case of isopentane. These bonds are often used in place of plain lines to provide a three-dimensional perspective of substituent groups attached to a central atom.

2.2.2 Alkenes

Alkenes are hydrocarbons that contain at least one double bond between adjacent carbon atoms. The simplest acyclic alkenes contain only one such double bond and have the general formula empirical C_nH_{2n}. The simplest examples of such alkenes are ethene ($n=2$) and propene ($n=3$), shown in Figure 2.4.

Structural isomers of alkenes are obtained by changing the position of the double bonds or by changing the way the carbon atoms are joined to each other. The presence of double bonds can lead to another type of isomerism: geometric isomerism (*cis–trans* isomerism). However, the presence of a double bond is not a guarantee for such geometric isomerism. In order for such isomerism to be exhibited, each carbon atom involved in the double bond must be attached to different functional groups. For example, Figure 2.5 shows the structural isomers with the

$H_2C{=}CH_2$	$H_2C{=}CH{-}CH_3$
Ethene	Propene

FIGURE 2.4
Structures of simple alkenes.