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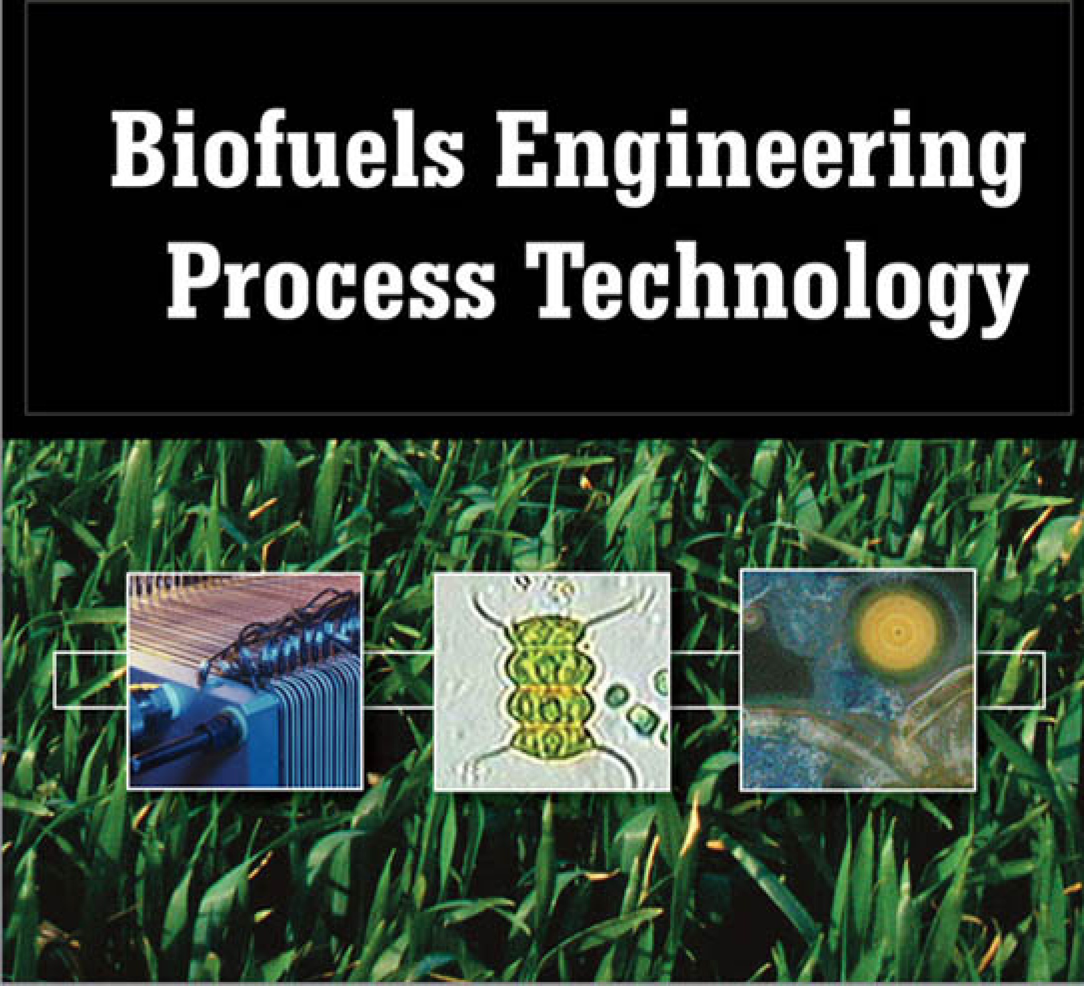

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To our parents Catherine and Cyril Drapcho and Pam and George Walker. They would have been proud of their children for trying to improve the world.

—Caye and Terry

To my wife, Minh Dzung, and to all the children of tomorrow with love and hope.

—Nhuan

About the Authors

Caye M. Drapcho, Ph.D., is an Associate Professor and the Graduate Coordinator in the Biosystems Engineering program at Clemson University. She has over 13 years of teaching and research experience in bioprocess and bioreactor design.

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Terry H. Walker, Ph.D., is a Professor in the Biosystems Engineering program at Clemson University. He has over 10 years of experience in bioprocess engineering, specializing in fungal fermentation, bioproduct separations, and bioavailability studies.

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Preface

The development of renewable energy has attracted a great deal of interest not only because of the steady rise in oil prices, but also because of the limit of fossil fuel reserves. One day not very far into the future, refineries and coal-fire power plants may be closed forever because their reserves have been depleted. It took nature a very long time to create gas, oil, and coal, but it takes us just a blink of an eye within the geological time scale to burn them all.

There are many sources of renewable energy. Biofuels are just one source, but a very important one. Biofuels can be defined as fuels that are derived from biological sources. Among them, methane produced by anaerobic digestion has been used by the human race for hundreds, if not thousands, of years. More recently, ethanol produced from sugar- and starch-based feedstocks has become another important biofuel. Other biofuels such as lignocellulosic ethanol, biodiesel, biohydrogen, and bioelectricity have been the focus of vigorous research, and the technologies for their production are being developed, although most of these are not quite ready for commercialization.

This book is written with two objectives. First, it may be a reference book for those who are interested in biofuels. Second, it may be used as a textbook to teach biofuel technologies to science and engineering students who want to contribute to the development and implementation of processes for production of these important renewable energy sources. In this book, readers will find the fundamental concepts of important biofuels and the current state-of-the-art technology for their production.

We hope our book will serve our readers well. We will be very grateful to receive comments and suggestions for improvement from our colleagues in this field and also from the students who will use this book in their educational endeavors.

Caye M. Drapcho, Ph.D.
Nghiem Phu Nhuan, Ph.D.
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PART 1

The Basics

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CHAPTER 1
Introduction

1.1 Biorefinery

Renewable energy deriving from solar, wind, and biomass sources has great potential for growth to meet our future energy needs. Fuels such as ethanol, methane, and hydrogen are characterized as biofuels because they can be produced by the activity of biological organisms. Which of these fuels will play a major role in our future? The answer is not clear, as factors such as land availability, future technical innovation, environmental policy regulating greenhouse gas emissions, governmental subsidies for fossil fuel extraction/processing, implementation of net metering, and public support for alternative fuels will all affect the outcome. A critical point is that as research and development continue to improve the efficiency of biofuel production processes, economic feasibility will continue to improve.

Biofuel production is best evaluated in the context of a biorefinery (Fig. 1.1). In a biorefinery, agricultural feedstocks and by-products are processed through a series of biological, chemical, and physical processes to recover biofuels, biomaterials, nutraceuticals, polymers, and specialty chemical compounds.[2,3] This concept can be compared to a petroleum refinery in which oil is processed to produce fuels, plastics, and petrochemicals. The recoverable products in a biorefinery range from basic food ingredients to complex pharmaceutical compounds and from simple building materials to complex industrial composites and polymers. Biofuels, such as ethanol, hydrogen, or biodiesel, and biochemicals, such as xylitol, glycerol, citric acid, lactic acid, isopropanol, or vitamins, can be produced for use in the energy, food, and nutraceutical/pharmaceutical industries. Fibers, adhesives, biodegradable plastics such as polylactic acid, degradable surfactants, detergents, and enzymes can be recovered for industrial use. Many biofuel compounds may only be economically feasible to produce when valuable coproducts are also recovered and when energy-efficient processing is employed. One advantage of microbial conversion processes over chemical processes is that microbes are able to select their substrate among a complex mixture of compounds, minimizing the need for isolation and purification of substrate prior to processing. This can translate to more complete use of substrate and lower chemical requirements for processing.

Early proponents of the biorefinery concept emphasized the *zero-emissions* goal inherent in the plan—waste streams, water, and heat from one process are utilized as feed streams or energy to another, to fully recover all possible products and reduce waste with maximized efficiency.[2,3] Ethanol and biodiesel production can be linked effectively in this way. In ethanol fermentation, 0.96 kg of CO_2 is produced per kilogram of ethanol formed. The CO_2 can be fed to algal bioreactors to produce oils used for biodiesel production. Approximately 1.3 kg CO_2 is consumed per kilogram of algae grown, or 0.5 kg algal oil produced by oleaginous strains. Another example is the potential application of microbial fuel cells to generate electricity by utilizing waste organic compounds in spent fermentation media from biofuel production processes.

Also encompassed in a sustainable biorefinery is the use of "green" processing technologies to replace traditional chemical processing. For example, supercritical CO_2 can be used to extract oils and nutraceutical compounds from biomass instead of using toxic organic solvents such as hexane.[4] Ethanol can be used in biodiesel production from biological oils in place of toxic petroleum-based methanol traditionally used. Widespread application of biorefineries

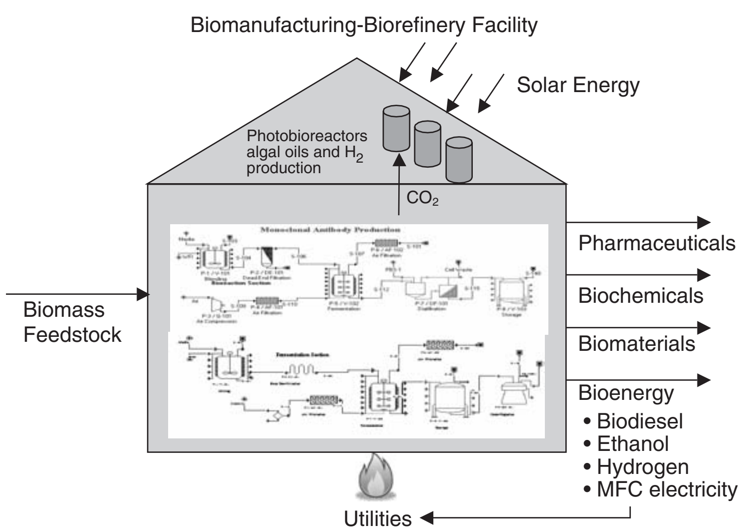

Figure 1.1 Integrated biorefinery showing example bioprocesses of monoclonal antibody and ethanol production. (*Adapted from Walker, 2005.*)

would allow for replacement of petroleum-derived products with sustainable, carbon-neutral, low-polluting alternatives.

In addition to environmental benefits of biorefining, there are economic benefits as new industries grow in response to need.[2,3] A thorough economic analysis, including ecosystem and environmental impact, harvest, transport, processing, and storage costs must be considered. The R&D Act of 2000 and the Energy Policy Act of 2005 recommend increasing biofuel production from 0.5 to 20 percent and biobased chemicals and materials from 5 to 25 percent,[5] a goal that may best be reached through a biorefinery model.

1.2 Description of Biofuels

The origin of all fuel and biofuel compounds is ultimately the sun, as solar energy is captured and stored as organic compounds through photosynthetic processes. Certain biofuels, such as oils produced by plants and algae, are direct products of photosynthesis. These oils can be used directly as fuel or chemically transesterified to biodiesel. Other biofuels such as ethanol and methane are produced as organic substrates are fermented by microbes under anaerobic conditions. Hydrogen gas can be produced by both routes, that is, by photosynthetic algae and cyanobacteria under certain nutrient- or oxygen-depleted conditions, and by bacteria and archae utilizing organic substrates under anaerobic conditions. Electrical energy produced by microbial fuel cells—specialized biological reactors that intercept electron flow from microbial metabolism—can fall into either category, depending on whether electron harvest occurs from organic substrates oxidized by organotrophic cultures or from photosynthetic cultures.

A comparison of biofuel energy contents reveals that hydrogen gas has the highest energy density of common fuels expressed on a mass basis (Table 1.1). For liquid fuels, biodiesel, gasoline, and diesel have energy densities in the 40 to 46 kJ/g range. Biodiesel fuel contains 13 percent lower energy density than petroleum diesel fuel, but combusts more completely and has greater lubricity.[7] The infrastructure for transportation, storage, and distribution of hydrogen is lacking, which is a significant advantage for adoption of biodiesel.

Another measure of energy content is energy yield (Y_E), the energy produced per unit of fossil fuel energy consumed. Y_E for biodiesel from soybean oil is 3.2 compared to 1.5 for ethanol from corn and 0.84 and 0.81 for petroleum diesel and gasoline, respectively.[8] Even greater Y_E values are achievable for biodiesel created from algal sources or for ethanol from cellulosic sources.[9] The high net energy gain for biofuels is attributed to the solar energy captured compared to an overall net energy loss for fossil fuels.

Fuel source	Energy density (kJ/g)	Density (kg/m³)	Energy content (GJ/m³)
Hydrogen	143.0	0.0898	0.0128
Methane (natural gas)	54.0	0.7167	0.0387
No. 2 diesel	46.0	850	39.1
Gasoline	44.0	740	32.6
Soybean oil	42.0	914	38.3
Soybean biodiesel	40.2	885	35.6
Coal	35.0	800	28.0
Ethanol	29.6	794	23.5
Methanol	22.3	790	17.6
Softwood	20.4	270	5.5
Hardwood	18.4	380	7.0
Rapeseed oil	18.0	912	16.4
Bagasse	17.5	160	2.8
Rice hulls	16.2	130	2.1
Pyrolysis oil	8.3	1280	10.6

*Values reported at standard temperature and pressure
Source: Adapted from Brown, 2003.

Table 1.1 Energy Density Values* for Common Fuels

1.3 Energy Use

The motivation for development and use of alternative fuels include (1) diminishing reserves of readily recoverable oil, (2) concern over global climate change,[10] (3) increasing fuel prices, and (4) the desire for energy independence and security. The U.S. Energy Information Administration determined that total world energy consumption in 2005 was 488 EJ (exajoule, 10^{18} J) or 463 Quad (quadrillion Btu, 10^{15} Btu), with U.S. consumption of 106 EJ (100.6 Quad) or 22 percent of the world total.[11] World consumption is expected to surpass 650 EJ by 2025.[11] The rates of increase in energy usage vary greatly by nation. Between 1985 and 2005, annual energy consumption increased 31 percent in the United States, while only 18 percent in Europe, and an overwhelming 250 percent in China and India,

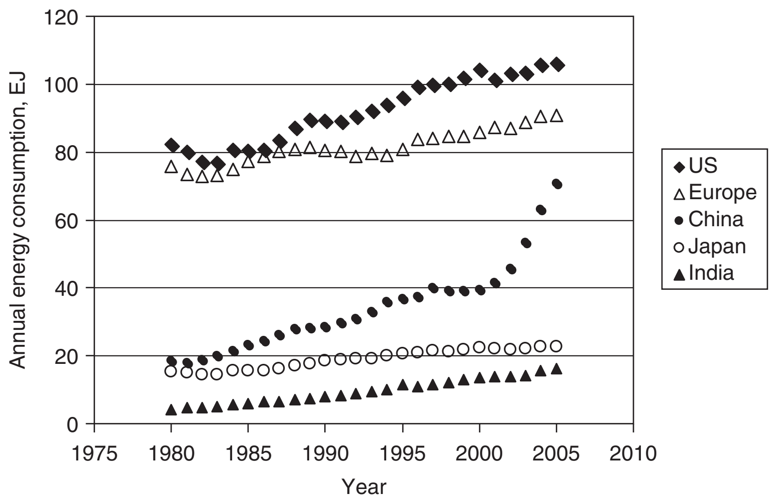

FIGURE 1.2 Annual energy consumption values for selected countries. (*Adapted from Energy Information Agency, 2007.*)

although India's total consumption is small at only 3 percent of the world total (Fig. 1.2). These values reflect a host of factors, including degree of industrialization, gross domestic product, relative efficiency of primary energy source used, and energy conservation. In the United States, fossil fuels accounted for 86 percent of our total energy consumption in 2004. Petroleum fuels, natural gas, and coal accounted for 40, 23, and 23 percent, respectively, with an additional 8 percent from nuclear power and only 6 percent from renewable sources, including hydroelectric (2.7 percent), biomass/biofuels (2.7 percent), and 0.6 percent from solar, wind, and geothermal energy sources combined.[11,12] Currently available fossil fuel sources are estimated to become nearly depleted within the next century, with petroleum fuel reserves depleted within 40 years.[11,13] The United States imports 10 million barrels of oil per day of the existing world reserves (1.3 trillion barrels) (Table 1.2). Peak oil, the maximum rate of oil production, is expected to occur between 2010 and 2020.[11] Even with increasing attention on hydrogen as an alternative fuel, 95 percent of worldwide production of hydrogen gas is from fossil fuel sources, primarily the thermocatalytic reformation of natural gas.[14]

Approximately 50 percent of the U.S. trade deficit is attributed to the import of crude oil. Crude oil prices have risen from less than \$20/barrel in the 1990s to nearly \$100/barrel in 2007. Accounting for military aid and subsidies to protect and maintain an uninterrupted flow of crude oil from unstable regions of the world, the true cost of oil[15] has been estimated as greater than \$100/barrel since 2004.

Country	Oil reserves (billion barrels)	U.S. oil imports (million barrels/day)
Saudi Arabia	267	1.50
Canada	179	1.62
Iran	132	—
Iraq	115	0.66
Kuwait	104	0.24
United Arab Emirates	98	—
Venezuela	80	1.30
Russia	60	—
Libya	39	—
Nigeria	36	1.08
United States	21	—
China	18	—
Qatar	15	—
Mexico	13	1.60
Algeria	11	0.22
Brazil	11	—
Other	91	1.84
Total	**1290**	**10.06 (60%)**

Source: Adapted from Energy Information Agency, 2007.

TABLE 1.2 World Oil Reserves and U.S. Imports Based on Leading Producers

1.4 Efficiency of Energy Use

The main fossil fuels (coal, natural gas, and oil) are about 33 percent efficient when used for energy generation, and emit high levels of CO_2 (Fig. 1.3) and nitrogen oxides. Geothermal and solar energy are less than 20 percent efficient with current technology, but are nearly zero-emission energy sources. Wind power has both high efficiency and zero-emissions, but is restricted to certain regions. Home heating by natural gas has a high efficiency, with lower emissions than other fossil fuels.

Spark-ignition (SI) gasoline engines, the most commonly used for transportation in the United States, are the most inefficient of current technologies, with an average efficiency of 16 percent (Fig. 1.4) compared to biodiesel in diesel engines (29 percent efficiency).[15] The most efficient engines—hybrid diesel and hybrid hydrogen fuel cell—achieve nearly 50 percent efficiency. Further, emissions for hybrid hydrogen fuel cell (390 g CO_2/mile) are substantially less than diesel (475 g CO_2/mile) and SI gasoline engines (525 g CO_2/mile).[16]