Caye M. Drapcho Nghiem Phu Nhuan Terry H. Walker

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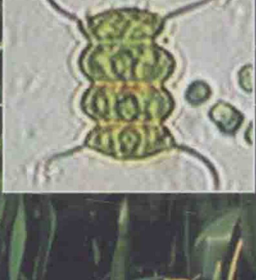

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Preface

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.

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Nghiem Phu Nhuan, Ph.D.
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Contents

Preface xi

Part 1 The Basics

1 Introduction **3**
1.1 Biorefinery 3
1.2 Description of Biofuels 5
1.3 Energy Use 6
1.4 Efficiency of Energy Use 8
1.5 Biofuels Production and Use 10
1.6 Alternative Energies 12
1.7 Environmental Impact 13
1.8 Book Overview 14
References 15

2 Harvesting Energy from Biochemical Reactions **17**
2.1 Introduction and Basic Definitions 17
2.2 Biochemical Pathways Review for Organoheterotrophic Metabolism 19
2.2.1 Aerobic Respiration 19
2.2.2 Anaerobic Respiration 23
2.2.3 Fermentation 25
2.3 Biochemical Pathways Overview for Lithotrophic Growth 30
2.4 Biochemical Pathways Overview for Phototrophic Metabolism 31
2.4.1 Light Reactions 32
2.4.2 Anabolic (Dark) Reactions 33
2.5 Definition and Importance of Chemical Oxygen Demand 33
Acknowledgments 35
References 36

3 Microbial Modeling of Biofuel Production **37**
3.1 Introduction 37
3.2 Summary of Microbial Growth Models 37
3.2.1 Unstructured, Single Limiting Nutrient Models 38
3.2.2 Inhibition Models 39

3.2.3 Models for Multiple Limiting Substrates 42
3.2.4 Yield Parameters 44
3.3 Kinetic Rate Expressions 45
3.3.1 Temperature Effects 47
3.4 Bioreactor Operation and Design for Biofuel Production 48
3.4.1 Batch Reactors 50
3.4.2 Continuous Stirred Tank Reactors 50
3.4.3 CSTR with Cell Recycle 52
3.4.4 Fed-Batch Systems 54
3.4.5 Plug Flow Systems 55
3.5 Bioreactor Design Strategies 57
3.6 Modeling of Glucose Utilization and Hydrogen Production 58
3.6.1 Batch Fermentations and Simulations 59
3.6.2 CSTR Fermentations and Simulations 61
Summary 64
References 65

Part 2 Biofuels

4 Biofuel Feedstocks 69
4.1 Starch Feedstocks 69
4.1.1 Cereal Grains 69
4.1.2 Other Grains 78
4.1.3 Tubers and Roots 78
4.2 Sugar Feedstocks 79
4.2.1 Sugarcane 79
4.2.2 Sugar Beet 80
4.3 Lignocellulosic Feedstocks 80
4.3.1 Forest Products and Residues 81
4.3.2 Agricultural Residues 82
4.3.3 Agricultural Processing By-Products 84
4.3.4 Dedicated Energy Crops 84
4.4 Plant Oils and Animal Fats 88
4.5 Miscellaneous Feedstocks 91
4.5.1 Animal Wastes 91
4.5.2 Municipal Solid Waste 94
References 94

5 Ethanol Production **105**
5.1 Ethanol Production from Sugar and Starch Feedstocks 105
5.1.1 Microorganisms 105
5.1.2 Process Technology 111
5.2 Ethanol Production from Lignocellulosic Feedstocks 133
5.2.1 Basic Concept 133
5.2.2 The Sugar Platform 134
5.2.3 The Syngas Platform 158
Acknowledgments 174
References 174

6 Biodiesel **197**
6.1 Introduction 197
6.1.1 Environmental Considerations 199
6.2 Biodiesel Production Chemistry and Thermodynamic Aspects 201
6.2.1 Transesterification 202
6.2.2 Esterification 202
6.2.3 Lipase-Catalyzed Interesterification and Transesterification 203
6.2.4 Side Reactions: Saponification and Hydrolysis 203
6.2.5 Alcohol Effect 204
6.2.6 Base or Alkali Catalysis 204
6.2.7 Acid Catalysis 206
6.2.8 Enzyme Catalysis 208
6.2.9 Supercritical Esterification and Transesterification 208
6.2.10 Thermodynamics and Reaction Kinetics 210
6.3 Oil Sources and Production 219
6.3.1 Plant Oils 219
6.3.2 Microbial and Algal Oils 223
6.3.3 Used Cooking Oils 233
6.3.4 Straight Vegetable Oil 233
6.3.5 Biosynthesis of Oils and Modification 234
6.4 Coproducts 236
6.5 Methods of Biodiesel Production 238
6.5.1 General Biodiesel Production Procedures 239
6.5.2 Pilot and Commercial Scale 245
6.5.3 Quality Control Analytical Technique 247

6.6 Economics ... 250
6.6.1 Feedstock Cost ... 252
6.6.2 Manufacturing Cost ... 255
6.6.3 Capital Cost ... 255
6.6.4 Operating Cost ... 257
6.7 Summary and Conclusions ... 258
Acknowledgments ... 259
Problems ... 260
References ... 262

7 Biological Production of Hydrogen ... 269
7.1 Introduction ... 269
7.1.1 Important Enzymes ... 269
7.1.2 Abiotic H_2 Production ... 271
7.2 Photobiological H_2 Production ... 271
7.2.1 Direct Biophotolysis ... 272
7.2.2 Indirect Biophotolysis ... 273
7.2.3 Photofermentation ... 273
7.2.4 Photobiological H_2 Production Potential ... 274
7.3 Hydrogen Production by Fermentation ... 274
7.3.1 Overview ... 274
7.3.2 Energetics ... 275
7.3.3 Thermotogales ... 276
7.3.4 Biochemical Pathway for Fermentative H_2 Production by *Thermotoga* ... 276
7.3.5 Hydrogen Production by Other Bacteria ... 277
7.3.6 Coproduct Formation ... 279
7.3.7 Batch Fermentation ... 280
7.3.8 Hydrogen Inhibition ... 281
7.3.9 Role of Sulfur—Sulfidogenesis ... 281
7.3.10 Use of Other Carbon Sources Obtained from Agricultural Residues ... 284
7.3.11 Process and Culture Parameters ... 287
7.4 Hydrogen Detection, Quantification, and Reporting ... 290
7.4.1 Hydrogen Detection ... 291
7.4.2 Total Gas Pressure ... 292
7.4.3 Water Vapor Pressure ... 292
7.4.4 Hydrogen Partial Pressure ... 292
7.4.5 Hydrogen Gas Concentration ... 293
7.4.6 Hydrogen Concentration Expressed as mol H_2/L Media ... 294

7.4.7 Hydrogen Production Rate 294
7.4.8 Dissolved H_2 Concentration in Liquid 294
7.5 Fermentation Bioreactor Sizing for PEM Fuel Cell Use 297
Acknowledgment 299
References 299

8 Microbial Fuel Cells 303
8.1 Overview 303
8.2 Biochemical Basis 303
8.3 Past Work Summary 305
8.4 Fuel Cell Design 308
8.4.1 Anode Compartment 308
8.4.2 Microbial Cultures 309
8.4.3 Redox Mediators 310
8.4.4 Cathode Compartment 311
8.4.5 Exchange Membrane 312
8.4.6 Power Density as Function of Circuit Resistance 313
8.5 MFC Performance Methods 314
8.5.1 Substrate and Biomass Measurements 314
8.5.2 Basic Power Calculations 315
8.5.3 Calculation Example 317
8.6 MFC Performance 318
8.6.1 Power Density as Function of Substrate 318
8.6.2 Single-Chamber Versus Two-Chamber Designs 320
8.6.3 Single-Chamber Designs 320
8.6.4 Wastewater Treatment Effectiveness 321
8.7 Fabrication Example 322
8.8 Future Directions 323
References 325

9 Methane 329
9.1 Introduction 329
9.2 Microbiology of Methane Production 329
9.2.1 Methanogenic Environments 329
9.2.2 Methane Process Description 330
9.2.3 Microbial Communities 332
9.3 Biomass Sources for Methane Generation 334

9.4 Systems 338
9.4.1 Reactor Conditions 339
9.4.2 Process Design 340
9.5 Biogas Composition and Use 343
References 344

Appendix: Conversion Factors and Constants 347

Index 351

PART 1

The Basics

CHAPTER 1
Introduction

CHAPTER 2
Harvesting Energy from Biochemical Reactions

CHAPTER 3
Microbial Modeling of Biofuel Production

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

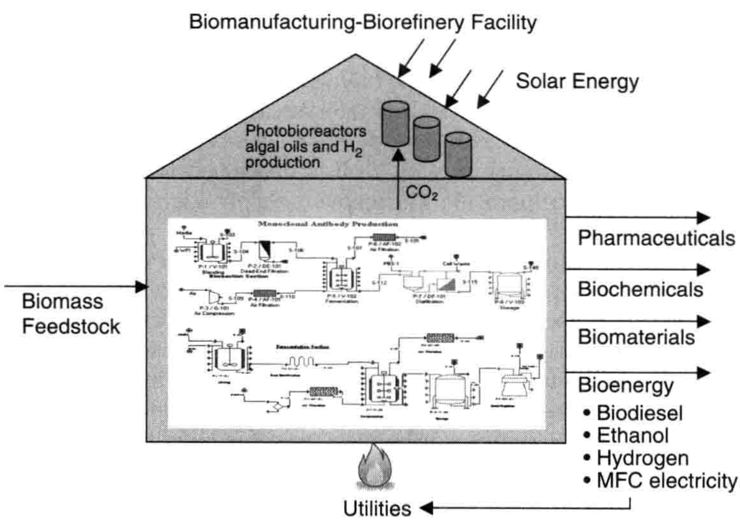

FIGURE 1.1 Integrated biorefinery showing example bioprocesses of monoclonal antibody and ethanol production. (*Adapted from Walker, 2005.*)

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/m^3)	Energy content (GJ/m^3)
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,

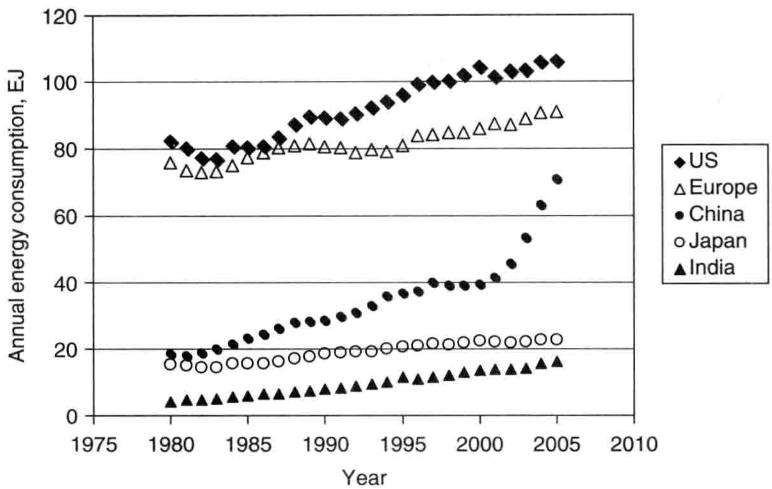

FIGURE 1.2 Annual energy consumption values for selected countries. (*Adapted from Energy Information Agency, 2007.*)

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.