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Gasoline, Diesel, and Ethanol Biofuels from Grasses and Plants

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Preface

The world is currently faced with two significant problems: fossil fuel depletion and environmental degradation. The problems are continuously being exacerbated due to increasing global population and per capita energy consumption. To overcome the problems, renewable energy has been receiving increasing attention due to a variety of environmental, economic, and societal benefits. First-generation biofuels (ethanol from sugar or corn, and biodiesel from vegetable oils) are already in the market, and second-generation biofuels from nonfood biomass are under development. The goal of this book is to introduce readers to the biofuels obtained from nonfood biomass, and for reference to provide the technologies involved in first-generation biofuels derived from food sources.

Chapter 1 discusses various nonrenewable (petroleum, natural gas, coal) and renewable forms of energy, and describes air pollution and greenhouse gas emission caused by the use of fossil fuels. Recent concern about carbon dioxide emissions, carbon sequestration, and carbon credits are discussed in Chapter 2. Chapter 3 provides an in-depth description of various renewable energy sources, including biomass; hydropower; geothermal, wind, solar, and ocean energy; and biogas. For the production of biofuels, the global availability of biomass is discussed in Chapter 4 along with the characterization and variations of biomass.

Conventional ethanol production from corn or sugarcane by fermentation technology is discussed in Chapter 5. Current techniques and various unit operations involved are presented, including saccharification, fermentation, distillation, and dehydration. The second-generation ethanol from cellulose is described in Chapter 6. It provides an in-depth coverage of various pretreatment techniques that are critical to the cost-effective production of cellulosic ethanol. In addition, xylose fermentation to improve the ethanol yield is discussed.

Chapter 7 discusses the production of biodiesel from vegetable oil by transesterification. The fuel properties of biodiesel are compared with those of petroleum diesel. Chapter 8 concerns the production of diesel from biomass. Processing of biomass gasification followed by Fischer–Tropsch synthesis of diesel and other liquid fuels is discussed. Chapter 9 outlines the production of bio-oil from biomass by the pyrolysis process. Various reactor designs for fast pyrolysis are described along with the fuel properties of bio-oil, including its upgradation. Chapter 10 deals with the production of biocrude by hydrothermal liquefaction of biomass, in which various aspects of production and upgradation are presented to obtain fuel comparable to petroleum liquids.

Chapter 11 discusses the use of wind and solar energies to enhance biofuel production from biomass. The process heating and electricity needs can be satisfied so that a higher amount of biomass carbon is converted to liquid fuels. Chapters 12 and 13 discuss the environmental and economic impacts of biofuels, respectively. Chapter 14 summarizes current biofuel policies of major countries that are promoting biofuel production and use.

This book strives to serve as a comprehensive document to present various technological pathways and environmental and economic issues related to biofuels. As petroleum reserves are depleted, the world is faced with finding alternatives. Currently, the transport sector depends almost entirely on petroleum liquids (diesel, gasoline, jet fuel, kerosene), and to fill the gap, biofuel can provide a replacement. However, alternatives to petroleum must be technically feasible, economically competitive, environmentally acceptable, and easily available.

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GASOLINE, DIESEL, AND ETHANOL BIOFUELS FROM GRASSES AND PLANTS

The world is currently faced with two significant problems – fossil fuel depletion and environmental degradation – which are continuously being exacerbated due to increasing global energy consumption. As a substitute for petroleum, renewable fuels are receiving increasing attention due to a variety of environmental, economic, and societal benefits. First-generation biofuels – ethanol from sugar or corn and biodiesel from vegetable oils – are already on the market. The goal of this book is to introduce readers to the second-generation biofuels obtained from nonfood biomass, such as forest residue, agricultural residue, switchgrass, corn stover, waste wood, and municipal solid wastes. Various technologies are discussed, including cellulosic ethanol, biomass gasification, synthesis of diesel and gasoline, biocrude by hydrothermal liquefaction, bio-oil by fast pyrolysis, and the upgradation of biofuel. This book strives to serve as a comprehensive document presenting various technological pathways and environmental and economic issues related to biofuels.

Dr. Ram B. Gupta is the PWS Distinguished Chair Professor and Chair of the Chemical Engineering Graduate Program at Auburn University. He has published numerous research papers and holds several patents on biofuels, nanotechnology, hydrogen fuel, and supercritical fluid technology and is the recipient of several national awards. He is a Fellow of the Alabama Academy of Science. He served on the editorial advisory boards of *Industrial & Engineering Chemistry Research* and *Nanomedicine: Nanotechnology, Biology and Medicine* and is currently serving on the editorial boards of *Journal of Biomedical Nanotechnology, Research Letters in Nanotechnology, Open Nanomedicine Journal, International Journal of Chemical Engineering*, and *Research Letters in Chemical Engineering*. His recent books are *Nanoparticle Technology for Drug Delivery, Solubility in Supercritical Carbon Dioxide*, and *Hydrogen Fuel: Production, Transport, and Storage*.

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Contents

1 Introduction

1.1 Energy

Energy is defined as the ability to do work and provide heat. There are different ways in which the abundance of energy around us can be stored, converted, and amplified for our use. Energy sources can be classified into three groups: fossil, renewable, and nuclear (fissile). Fossil fuels were formed in an earlier geological period and are not renewable. The fossil energy sources include petroleum, coal, bitumen, natural gas, oil shale, and tar sands. The renewable energy sources include biomass, hydro, wind, solar (both thermal and photovoltaic), geothermal, and marine. The main fissile energy sources are uranium and thorium. Despite adequate reserves, some classifications include fissile materials along with the nonrenewable sources.

For over ten thousand years, humans have used biomass for their energy needs. Wood was used for cooking, water, and space heating. The first renewable energy technologies were primarily simple mechanical applications and did not reach high energetic efficiencies. Renewable energies have been the primary energy source in the history of the human race. But in the last two hundred years, we have shifted our energy consumption toward fossil fuels. Industrialization changed the primary energy use from renewable resources to sources with a much higher energy density, such as coal or petroleum. During the last century, the promise of unlimited fossil fuels was much more attractive, and rapid technical progress made the industrial use of petroleum and coal economical.

Petroleum is the largest single source of energy consumed by the world's population (about 4.8 barrel/year/person), exceeding coal, natural gas, nuclear, or hydroelelctric, as shown in Figure 1.1. The United States' energy consumption and supply is shown in Figure 1.2. In fact, today, over 88% of the global energy used comes from three fossil fuels: petroleum, coal, and natural gas. Although fossil fuels are still being created today by underground heat and pressure, they are being consumed much more rapidly than they are created. Hence, fossil fuels are considered nonrenewable, that is, they are not replaced as fast as consumed. Unfortunately, petroleum oil is in danger of becoming short in supply. Hence, the future trend is

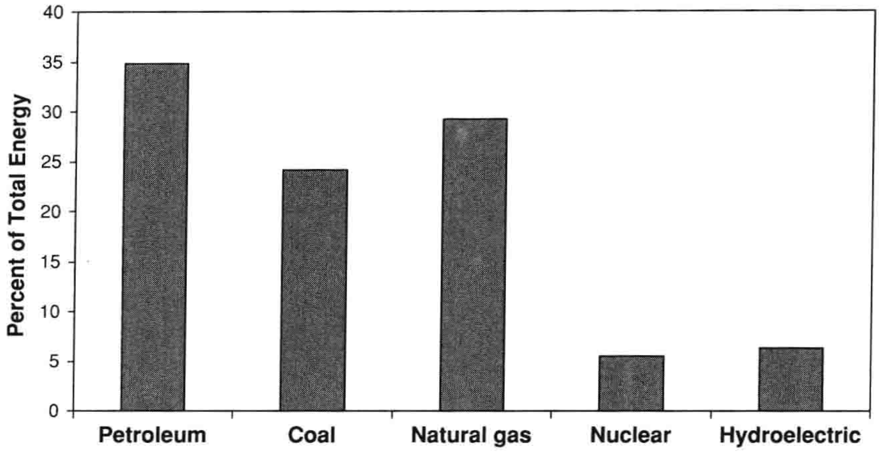

Figure 1.1. World consumption of various energies in 2008 out of the total consumption of 11.3 billion tons oil equivalent (BP, 2009).

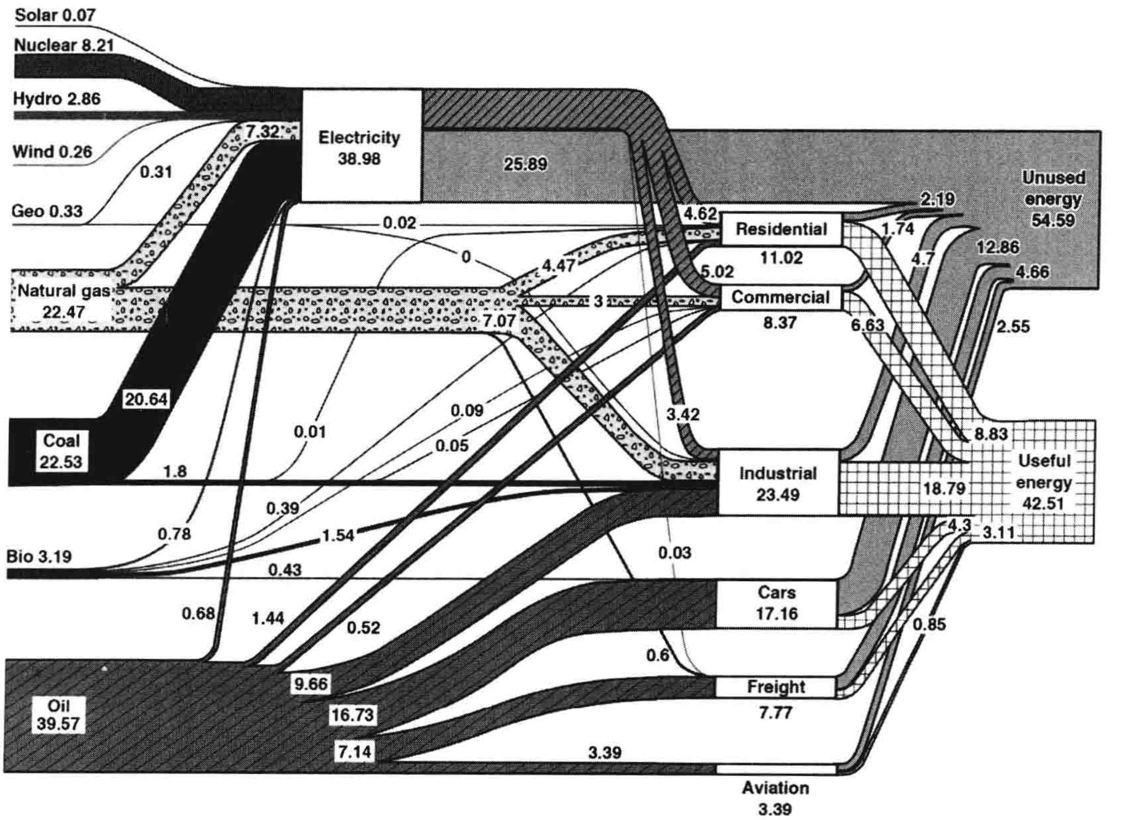

Figure 1.2. Energy consumption and supply in the United States for 2006 (U.S. DOE, 2008). Energies are shown in quad units (1 quad = 10^{15} BTU = 1.055×10^{15} J).

toward using alternate energy sources. Fortunately, technological development is making the transition possible.

A major problem with petroleum fuels is their uneven distribution in the world; for example, about 2% of the world population in the Middle East has 63% of the global reserves and is the dominant supplier of petroleum. This energy system is unsustainable because of equity issues as well as environmental, economic, and geopolitical concerns that have far-reaching implications. Interestingly, renewable energy resources are more evenly distributed than fossil or nuclear resources. Also, the energy flows from renewable resources are more than three orders of magnitude higher than current global energy need. Hence, renewable energy sources, such as biomass, hydro, wind, solar (both thermal and photovoltaic), geothermal, and marine, will play an important role in the world's future supply. For example, it is estimated that by year 2040 approximately half of the global energy supply will come from renewables (EREC, 2006), and the electricity generation from renewables will be more than 80% of the total global electricity production.

Another major problem with fossil fuel is the greenhouse gas emissions; about 98% of carbon emissions result from fossil fuel combustion. Reducing the use of fossil fuels would considerably reduce the amount of carbon dioxide and other pollutants produced. This can be achieved by either using less energy altogether or by replacing fossil fuels with renewable fuels. Hence, current efforts focus on advancing technologies that emit less carbon (e.g., high-efficiency combustion) or no carbon, such as nuclear, hydrogen, solar, wind, and geothermal, or on using energy more efficiently and sequestering carbon dioxide that is emitted during fossil fuel combustion.

Despite the above challenges, it is not easy to replace fossil fuels, as our modern way of life is intimately dependent on fossil fuels, specifically hydrocarbons, including petroleum, coal, and natural gas. For example, the majority of commodity products (e.g., plastics, fabrics, machine parts, chemicals, etc.) are made using crude oil or natural gas feedstock. And, more importantly, the major energy demand is fulfilled by fossil fuels, resulting in a major role for crude oil and natural gas in driving world economy.

1.2 Petroleum

Petroleum [word derived from Greek *petra* (rock) and *elaion* (oil) *or* Latin *oleum* (oil)] or crude oil, sometimes colloquially called black gold or "Texas Tea," is a thick, dark brown or greenish liquid. Petroleum consists of a complex mixture of various hydrocarbons, largely of the alkenes and aromatic compounds, but may vary much in appearance and composition. Petroleum is a fossil fuel because it was formed from the remains of tiny sea plants and animals that died millions of years ago and sank to the bottom of the oceans (Figure 1.3). This organic mixture was subjected to enormous hydraulic pressure and geothermal heat. Over time, the mixture changed, breaking down into compounds made of hydrocarbons by reduction

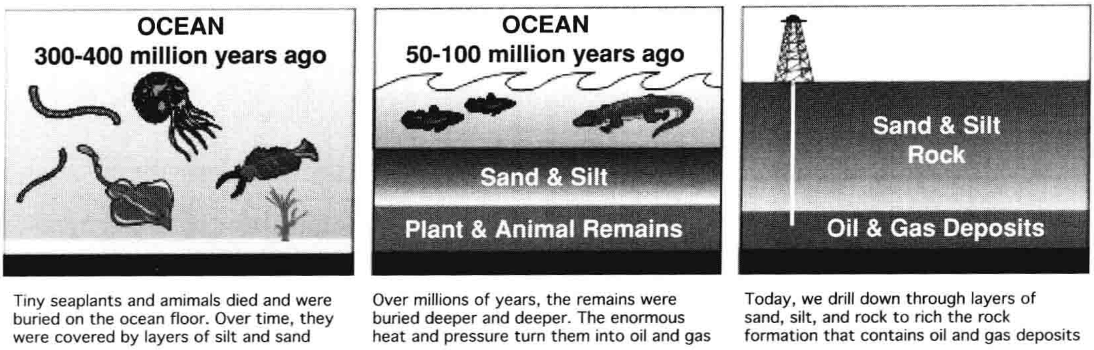

Figure 1.3. Cartoon showing formation of petroleum and natural gas (U.S. DOE, 2009).

reactions. This results in the formation of oil-saturated rocks. The crude oil rises and gets trapped under nonporous rocks that are sealed with salt or clay layers.

According to the well-accepted Biogenic theory (Walters, 2006), fossil fuels – crude oil, coal, and natural gas – are the product of compression and heating of ancient vegetation and animal remains over geological time scales. According to this theory, an organic matter is formed from the decayed remains of prehistoric marine animals and terrestrial plants. Over many centuries, this organic matter, mixed with mud, is buried under thick sedimentary layers. The resulting high pressure and heat transformed the organic matter first into a waxy material known as kerogen, and then into liquid and gaseous hydrocarbons. The fluids then migrate through adjacent rock layers until they become trapped underground in porous rocks called reservoirs, forming an oil field, from which the liquid can be removed by drilling and pumping. The reservoirs are at different depths in different parts of the world, but typical depth is 4–5 km. The thickness of the oil layer is about 150 meters, generally termed "oil window." Three important elements of an oil reservoir are a rich source rock, a migration conduit, and a trap (seal) that forms the reservoir.

According to not-well-accepted Abiogenic theory (Mehtiev, 1986), petroleum origin is natural hydrocarbons. This theory proposes that large amounts of carbon exist naturally in the planet, some in the form of hydrocarbons. Due to its lower density than aqueous pores fluids, hydrocarbons migrate upward through deep fracture networks. The two theories are reviewed by Mehtiev (1986).

1.2.1 History of Petroleum Exploration

According to historical accounts, the early oil wells were drilled in China before the fifth century (ACE, 2009). Wells, as deep as 243 meters, were drilled using bits attached to bamboo poles. The crude oil was burned to produce heat needed in the production of salt from brine evaporation. By the end of the tenth century, extensive bamboo pipelines connected oil wells with salt springs.

Separately, ancient Persian tablets indicate the medicinal and lighting uses of petroleum in the upper echelons of their society. Tar, the heavy component of the oil, was used in the paving of the street in Baghdad in the eighth century. In Baku