CHAPTER

Introduction

1.1 Transitions

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Mankind has gone outside the biotic (i.e., derived from living organisms) environment for the majority of its material needs only recently. Plant-based resources were the predominant source of energy, organic chemicals, and fibers in the West as recently as 150 years ago, and they continue to play important roles in many emerging economies. The transition to non-biological sources of energy and materials was relatively swift and recent in the history of the world. Many assumed that the transition was irreversible. Indeed, in the 1960s it appeared that fossil fuels were only a short bridge to the nuclear age, with fission reactors supplying energy for power and transportation fuels in the waning decades of the twentieth century, while fusion reactors would ultimately provide limitless supplies of energy. In this scenario, petroleum and natural gas would continue as the source of building blocks for organic chemical synthesis.

Reality has proved more complicated, uncertain, and unsettling. In many parts of the world, nuclear fission has not lived up to its promise and has become a political pariah in the face of reactor safety concerns and unresolved questions about radioactive waste disposal. Nuclear fusion has a lively history of tokamaks, inertial confinement, and cold fusion, but no breakeven in energy output. Petroleum continues to supply most of the world's demand for transportation fuels and commodity chemicals but the remaining reserves are increasingly concentrated in the hands of a few capricious nations. Coal is plentiful but introduces tremendous burdens on the environment, ranging from acid rain to mercury poisoning. Concerns about global climate change due to carbon dioxide emissions raise questions about the future use of all fossil fuels. In this political and social climate, there are calls for the development of reliable and long-term resources that have fewer areas of environmental impact than fossil resources. This book explores a return to the biotic environment for energy, chemicals, fuels, and fibers.

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1.2 Definitions

Biorenewable resources, also known as biomass, are organic materials of recent biological origin. Biomass is obtained from the thin region near the surface of the Earth known as the *biosphere* that supports living organisms. Biomass may be grown as crops, but the vast majority of the world's biorenewable resources are forests, prairies, marshes, and ocean biomes. The energy to build the chemical bonds of these organic materials comes mostly from sunlight. Solar energy collected by photosynthetic organisms is converted into energetic chemical bonds to produce proteins, oils, and carbohydrates. This stored chemical energy is raw material that can be used as a resource of renewable carbon and energy for the production of bioenergy and biobased products. In contrast, coal, oil, and natural gas are thought to be derived from microorganisms and plants buried and transformed into fossil fuels eons ago. In this view, the only difference between biomass and fossil fuels is the degree that nature processes biogenic materials.¹

Biorenewable resources, by definition, are sustainable natural resources. Sustainable implies that the resource renews itself at such a rate that it will be available for use by future generations. Thus, a stand of grass cut every year for a hay crop represents a biorenewable resource, while a field cleared in a tropical rainforest for "slash and burn" agriculture is not.

Human societies, like living organisms, require sources of energy and carbon to survive and grow. Most living organisms obtain energy and carbon from the biosphere. In contrast, most modern human societies rely on fossil resources for energy and carbon, although this is a relatively recent historical development. Before wide-scale exploitation of fossil resources starting in the eighteenth century, human societies were almost completely dependent on biorenewable resources. The challenge of the twenty-first century is to create a bioeconomy, in which human societies obtain sustainable sources of energy and carbon from the biosphere.

Energy from biorenewable resources is used to produce bioenergy. Carbon from biorenewable resources is used to produce biobased products. Of course, bioenergy is based on fuels that contain carbon and biobased products contain chemical energy in their carbon bonds, but it is useful to distinguish between these two kinds of products from biorenewable resources as either sustainable sources of energy or carbon.

Bioenergy includes process heat, biopower, and biofuels. *Process heat* is often thought of thermal energy for industrial processing, but it also includes energy used for residential and commercial thermal energy demand such as space and water heating.

¹For a fascinating presentation of an abiogenic hypothesis on the origin of fossil fuels, see Thomas Gold's The Deep Hot Biosphere.

Biopower is the conversion of biorenewable resources into electrical power. When power generation is based on heat engines, the chemical energy of biorenewable resources is first converted into thermal energy before conversion into power. When power generation is based on electrochemical fuel cells, the chemical energy of biorenewable resources is first converted into hydrogen before conversion to power.

Biofuels are chemicals derived from biorenewable resources that have sufficient volumetric energy densities (enthalpies of reaction per unit volume) and combustion characteristics to make them suitable as transportation fuels. Most biofuels are liquids such as ethanol or green diesel, but compressed gases have also been proposed and evaluated for use in vehicular propulsion. It should be kept in mind that another way to use biorenewable resources for transportation is to convert it to biopower and store the electricity in vehicular batteries—electric cars.

Biobased products include chemicals and materials. Biobased chemicals include fine chemicals like pharmaceuticals and nutraceuticals, but the emphasis is on high-volume commodity chemicals. Biobased materials can be thought of as finished products manufactured from biorenewable resources. Most prominent in this category are biobased fibers, including both natural fibers and synthetic fibers. Natural plant fibers are bundles of long, thin plant cells with durable walls of lignocellulose (animal fibers are also natural fibers but are not treated in this book). Synthetic fibers are spun from synthetic polymers, manufactured from chemical building blocks known as monomers. Petroleum is the source of the vast majority of monomers and hence synthetic fibers, but synthetic fibers can also be manufactured from monomers derived from biorenewable resources.

1.3 Brief History of Biorenewable Resource Utilization

Many of the advances in early human society were based on the exploitation of biorenewable resources. The first campfire, dating to as early as 500 000 years before the present (BP), was most surely kindled from wood rather than coal. Evidence that vegetable oils and animal fats were sources of illumination by 40 000 years BP is found at Upper Paleolithic cave sites in Europe. Draft animals represented mankind's first use of prime movers other than their own muscle power. Grasses and cultivated grains, fed to draft animals, provided power and transportation needs in early societies.

Except for stone tools, virtually all possessions until the advent of the Bronze Age were biobased products. Wood was a versatile composite material for the construction of hunting and farming implements. Cotton fibers were spun and twined in Peru as long ago as 12 000 years BP. Fermentation of sugars to ethanol was mastered as long ago as 6000 BP, but the product remained too precious for any but convivial purposes for thousands of years afterward.

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Wood remained the primary fuel for most pre-twentieth-century societies, although there are traditions of using grass for steel making in Africa and "lightly processed" grass in the form of dried buffalo dung for cooking fires in the American West. The preeminence of bioenergy began to wane when the great forests of the Northern Hemisphere were depleted by the voracious fuel demand in the manufacture of copper, iron, and glass and the powering of steam engines. By the mid-eighteenth century, coal had supplanted wood as the primary energy source for European and North American countries.

Biorenewable resources continued to be important as sources of chemicals and materials for another 75 years aided by advances in industrial chemistry. Gum turpentine, rosins, and pitches, collectively known as naval stores, were extracted from coniferous trees for maintaining wooden ships and ropes. Natural latex from the hevea rubber tree was vulcanized to an elastic, waterproof material used in numerous consumer products. The "destructive distillation" of wood yielded methanol (wood alcohol) and other industrially important compounds. Wood pulping was developed to separate cellulose fibers used in paper and cardboard products. From cellulose came the first semi-synthetic plastic, celluloid. Advances in the brewery industry eventually led to commercial fermentation of a variety of organic alcohols and acids with applications far beyond the beverage industry.

With the exceptions of lumber production for building materials, fiber production (wood pulping and cloth manufacture), and ethanol fermentation, the manufacture of biobased products rapidly declined in the twentieth century. This decline was not the result of resource scarcity, as was the case for bioenergy. Instead, rapid advances in the chemistry of coal-derived compounds during the late nineteenth century followed by the development of the petrochemical industry in the early twentieth century provided less expensive and more easily manipulated feedstock for the production of chemicals and materials.

1.4 Motivation for Returning to a Bioeconomy

Despite gradually rising prices for fossil fuels since that time, economics currently do not favor bioenergy and biobased products. However, other factors are coming into play that increases the attractiveness of biorenewable resource utilization. These factors include desires to improve *environmental quality*, concerns that national security is compromised by overreliance on foreign sources of fossil fuels, the presence of excess agricultural production capacity in many developed nations, and the importance of rural development in improving economies of many agricultural regions.

1.4.1 Environmental Quality

The production and utilization of fossil fuels introduce several environmental burdens of increasing concern. These burdens have *local*, regional, and global impacts.

Production includes mining for coal and drilling for petroleum and natural gas. Most of the impacts are local in nature. Mining leaves behind spoil piles and acid drainage. Drilling can result in oil spills or sites contaminated by drilling mud or brackish water.

Utilization of fossil fuels can yield a plethora of local, regional, and environmental impacts. Local impacts can arise from solid waste disposal sites for ash from coal combustion or coke or sulfur from petroleum refineries. Combustion of coal or petroleum-based motor fuel also produces carbon monoxide, fine particulate matter, and smog as local pollution problems. Regional impacts of fossil energy utilization are mostly the result of acid rain, which is generated from sulfur dioxide and nitrogen oxides released during combustion. Acid rain can affect environments half a continent away from the point of pollutant emission. Global impacts are of two kinds: ozone depletion in the stratosphere and global climate change. Ozone depletion is usually associated with the release of chlorofluorocarbons from refrigeration equipment and aerosol cans. Nitrogen oxides have also been implicated in upper atmosphere reactions that destroy ozone molecules. However, the greatest concern with regard to global impact is the possible role of carbon dioxide released during combustion in contributing to the greenhouse effect in the atmosphere. Although the magnitude of this problem is still being assessed, there have been calls to greatly reduce the net rate of emission of carbon dioxide from the use of fossil fuels.

Bioenergy and biobased products are not a panacea for these problems. However, the environmental burden from the use of biorenewable resources is generally much less than from the use of fossil resources. An exact accounting of the benefits of using biorenewable resources is a difficult and sometimes politically charged process. For example, some argue that the benefits of using a 10% blend of ethanol in gasoline to reduce carbon monoxide emissions from spark-ignition engines are outweighed by the increased volatility of this fuel blend, which increases the release of unburned hydrocarbons to the atmosphere, a factor in smog formation.

1.4.2 National Security

In 1974, a severe economic crisis developed in many parts of the world as a result of disruptions in the distribution of petroleum to markets. The so-called energy crisis was commonly ascribed to dwindling reserves of petroleum resources, and many experts predicted that looming energy scarcity would drive petroleum prices from a few dollars per barrel to over \$100, plunging the world into an economic depression that would be difficult to reverse. These concerns provided the impetus for a short-lived effort in the United States to commercially implement alternative energy sources, including solar, wind, biomass, and coal, to provide future energy. However, by 1980 petroleum prices had considerably moderated, and it was understood that an actual shortage of energy had never existed. Instead, a decision by Arab nations to boycott the sale of petroleum to the United States was responsible for temporary escalations in the world price of oil. The boycott

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was an effort to influence US foreign policy in the Middle East, which favored the state of Israel in its conflicts with surrounding Arab states. Although disruptive in the short term, ultimately the boycott and various production quotas were lifted and the world price for petroleum dropped. This threat to national security failed because the United States and other nations responded by reducing their dependence on foreign sources of oil through energy conservation and energy efficiency improvements and by switching to domestic energy sources, mostly coal, natural gas, and petroleum. As demand for Middle Eastern petroleum dropped, these countries saw the major source of their revenues evaporating; economic survival forced them to suspend their efforts to use "the oil weapon," as it was called.

The lesson is that effective national security incorporates an energy policy that reduces heavy reliance on foreign cartels for energy resources. However, there is some evidence that this lesson is not being heeded in the United States, where dependence on petroleum imports now exceeds that of 1974. As a percentage of petroleum demand, the role of imported petroleum into the United States exceeded 50% in 2001 and is expected to fall only slightly to 48% by 2020. With two-thirds of world petroleum reserves located in the Middle East (including the Caspian basin), increased dependence is inevitable unless domestic energy sources such as biorenewable resources are developed.

1.4.3 Excess Agricultural Production

A frequently expressed concern about shifting agriculture toward production of biobased products is the potential impact on food production. Securing a safe and inexpensive food supply is the keystone of agricultural policy in the United States. Many people oppose the use of agricultural lands for the production of bioenergy and biobased products on the grounds that, at best, domestic food prices will rise and, at worse, starvation will increase in developing countries that are dependent on agricultural imports.

In fact, agricultural production in excess of domestic use and export demands exists in the United States as well as in a growing number of other countries. The United States in 1990, with a population of 250 million people, had 12% less land in agricultural production than it did in 1929, when the population was only 120 million. The reason for this decline in agricultural lands is primarily due to increasing crop productivity. For example, US corn yields between 1929 and 1990 increased from 22–30 bushels per acre to 101–139 bushels per acre. These improvements are the result of advances in plant genetics, fertilizers, pesticides, and production practices. In an effort to keep production in balance with demand, the US government encouraged development of export markets for agricultural products in the last half of the twentieth century. However, this strategy did not adequately anticipate the developing world's ability to feed itself. Even China, often viewed as an unlikely candidate for self-sufficiency because of its burgeoning

population of over one billion people, has in recent years become a net exporter of agricultural products.

Recognizing that overproduction threatens the stability of agriculture, the US government instituted a program called the Conservation Reserve Program to deliberately remove marginal lands from production. Producers are allowed to grow grasses or trees on enrolled acreage but cannot harvest this biomass. Almost 34 million acres were enrolled in this program in 2001 compared to about 900 million acres in production. Millions of additional acres are currently devoted to low productivity uses such as pasturage or woodlots that could provide additional land for the production of feedstocks for biobased products. Thus, devoting some land to biorenewable resources poses no immediate threat to food prices in the United States or to feeding the developing countries of the world.

1.4.4 Rural Development

The impact of modern agriculture has not been completely positive. Increases in labor productivity in agriculture have reduced labor costs but contributed to the depopulation of rural communities. Improvements in transportation have expanded opportunities for trade but put US farmers in direct competition with producers in developing nations, where land values are a fraction of what they are in the United States. The highly integrated agricultural processing industry is successful in capturing value from agriculture, of which producers share little. Whereas return in investment in the food processing industry is typically 15%, production agriculture rarely yields returns greater than 1-3%.

As a result, agriculture in developed nations is increasingly dependent on government subsidies to be viable. In the United States, government payments represent in excess of 50% of gross income for typical producers. Farm subsidies in 1997 reached \$23 billion. Despite this assistance, producers are increasingly turning to off-farm jobs for supplemental income to support their families. US farming has also consolidated during the twenty-first century, with a larger share of production being attributed to a small number of very large (and often corporate) farmers in an effort to reduce costs via economies of scale.

Both producers and rural communities are looking for new opportunities to boost income and economic development. Development of crops for new markets, especially those that are processed locally into value-added products, would provide significant opportunities for rural development. US biofuels policy has already proven very successful in this regard, with 40% of the US corn crop now being diverted to a high-value fuel ethanol industry that consumed only a small fraction of the amount at the turn of the century. Advanced biorenewable pathways could further increase these opportunities by providing markets for agricultural residues and other waste products, providing a new revenue stream for producers, and by developing higher-value products from existing feedstocks.

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1.5 Challenges in Using Biorenewable Resources

Biorenewable resources have a number of disadvantages compared to the fossil resources with which they compete. These include the fact that most biorenewable resources are solid materials of low bulk density, high moisture content, low heating value, and high oxygen content compared to fossil fuels.

The solid nature of biomass is both blessing and curse. Solids are easily collected by hand and can be stored in bins. These advantages were especially important to early human societies, which did not have technology to handle large quantities of liquids and gases. However, solids are notoriously difficult to handle and process in the automated industries of the modern world.

Gases and liquids can be moved hundreds and even thousands of miles through pipelines and stored in tanks with a minimum of human intervention. These fluids do not clog pumps and pipes unless they are carrying solids along with them. The flow of gases and liquids are easily metered with relatively simple instruments and their flow rates can be regulated by the turn of a valve. Gases and liquids can be rapidly and easily dispersed or mixed, which allows them to be readily processed into heat, power, fuels, and chemicals.

Monolithic solids, of course, do not have the property of flow that expedites the handling of gases and solids. However, if solids are broken up into small particles and aerated, they acquire flow properties resembling those of liquids, a fact that has been widely exploited in the twentieth century. Grain is sucked from the holds of ships by giant vacuum cleaner-like devices rather than carried up in 50 kg sacks on the backs of stevedores. Coal is blown as fine powders into giant steam boilers rather than shoveled onto grates by firemen. Even the backbreaking work of shoveling snow from driveways has been replaced by snow blowers that chop up the snow and convey it pneumatically.

Nevertheless, the handling of solids remains a problem. The process of converting solids into granular or powdered materials is an energy intensive process—as little as 10% of the energy consumed by crushing, grinding, or cutting machines actually goes into dividing the materials, the rest dissipated as thermal energy. Particulate materials do not flow as smoothly or predictably as gases and liquids. Particles as coarse as woodchips or as fine as flour can easily clog hoppers and transport lines. Solids metering and control devices are not as reliable or available as for gas and liquid flows. Finely divided solids can present special erosion problems and explosion hazards. Solids handling systems are uniformly acknowledged as high maintenance items in industrial processes.

Typically, the density of biomass is so low that the volume rather than the weight of biomass that can be transported will limit the capacity of the transportation systems. Accordingly, the number of trucks or railcars required to supply a conversion facility will increase as the volumetric density of the fuel decreases. For example, a conventional steam power plant with a relatively modest electric power output of 50 MW would require up to 75 tractor-trailer loads of biomass per day

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to stoke the boilers compared to as few as 28 weight-limited loads of coal. Similar arguments apply to the size of the boiler. A boiler designed to burn biomass must be much larger than a coal-fired boiler of comparable thermal output because of the lower energy density of biomass compared to coal. The moisture content of green biomass also detracts from its performance as fuel. Freshly harvested biomass can have moisture content of 50% or more. This additional weight needlessly adds to the cost of transporting the fuel to a conversion facility. In some conversion processes, such as anaerobic digestion, high moisture content may be beneficial to the conversion process. In other cases, such as direct combustion, high moisture exacts a high penalty on the conversion process. Field drying is feasible for many biomass crops but may only reduce moisture content from 20% to 25%. For some processes, additional drying at the conversion plant is required. Freshly mined coal also contains moisture: in some western coals it can be as high as 30%. However, moisture is generally much less of a problem in coal.

Biomass must compete with a variety of fossil resources, including petroleum, natural gas, and coal. Since they are both solid fuels, substituting biomass for coal might seem a more competitive entry into energy markets dominated by fossil fuels. However, on a purely thermodynamic basis, biomass is generally inferior to coal. Coals have heating values typically in the range of 23-28 MJ/kg. On a mass basis, the heating values of biomass are 16-20 MJ/kg, which is 20-30% lower than coal. Exacerbating this situation is the significantly lower densities of biomass compared to coal: mined coal has a bulk density of around 880 kg/m³ compared to 545 kg/m³ for hybrid poplar logs and 230 kg/m³ for baled switchgrass. On a volumetric basis, the heating value of biomass is only 20-50% that of coal. Volumetric heating value is an important consideration both in the transport of biomass to a conversion facility and in the conversion process itself.

Most biorenewable resources contain a significant portion of oxygen, up to 45 wt% for lignocellulosic biomass. In contrast, fossil resources contain substantially less oxygen, which may be as high as 25 wt% in lignite coal and virtually absent in natural gas and petroleum. Although "oxygenated" fuels are touted for their environmental performance as motor fuels, in general, chemically bonded oxygen is responsible for the lower heating values of biobased fuels as well as many of the difficulties of substituting biobased chemicals for petroleum-based chemicals. This difficulty can be resolved by removing oxygen from compounds derived from biorenewable resources to yield hydrocarbons, although this increases the energy consumption for the overall process.

1.6 Foundations for a Bioeconomy

An economy built upon biorenewable resources must be able to supply transportation fuels, commodity chemicals, natural fibers for fabrics and papermaking, and energy for process heat and electric power generation. There is precedence for 1 🗆

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producing all of these products from biorenewable resources. However, many of the conversion technologies currently do not yield products that are cost-competitive with the fossil-based products that dominate today's markets. This situation is likely to change as technologies improve for producing biobased products, and environmental and political factors make green products from indigenous resources more attractive. The remaining chapters of this book explore various opportunities for making biobased products.

Further Reading

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