Biofuels

Chapter 5

5.1 INTRODUCTION

The surface of the Earth is bathed by solar energy totaling 3.8×10^{24} J during the course of a year, which is equivalent to a power of about 120,000 TW. Of that amount, less than 0.1% is converted via photosynthesis to plant matter, and yet that tiny percentage is over six times greater than all the energy used by humans in a year. The term biomass is used to describe plant and animal matter, living or dead, the wastes from such organisms, and the wastes of society that has been generated from these organisms. The stored chemical energy biomass contains is referred to as bioenergy. Fossil fuels could be said to contain bioenergy from ancient plant material, but unlike recently created biomass fossil fuels are of course nonrenewable. Thus, the three terms bioenergy, biomass, and biofuels (fuels made from biomass) generally exclude fossil fuels. Biofuels include liquids, such as ethanol alcohol, biodiesel, and various vegetable oils, gases such as methane, and solids such as wood chips and charcoal.

An important advantage of biofuels over fossil fuels, apart from their being renewable, is that biofuels in principle can be used without adding any net CO_2 to the atmosphere provided that during the growth of the biomass CO_2 was removed from the atmosphere by no more than the amount it is later added when the fuel is consumed. In this case, we would describe the biofuel as being carbon-neutral (or perhaps even carbon-negative) over their life cycle. Of course, this assertion assumes that the CO_2 emitted during the planting, cultivating, and harvesting the biomass, along with that released when it is converted to a biofuel and finally transported and used are not great enough to alter the balance, which need not be the case. Nevertheless, biofuels generally are considered to come under the heading of renewable energy sources, and in fact comprise about 63% of them.

On the other hand, that amount mainly includes traditional fuels such as wood and dung used by about half the world's population for heating and cooking. In fact, in some developing countries firewood accounts for 96% of their total energy consumption. When used in this manner biofuels are hardly renewable, and can be extremely destructive to the environment, since trees are usually harvested as needed for firewood, with no replanting. Regrettably, there are excellent low-tech alternatives to firewood readily available for cooking in developing nations that need to be better known—see the solar cookers described in Chapter 10.

Apart from wood and dung for heating, most biofuels in use today throughout the world are still of the "first generation" variety, meaning that they are made from the sugars, starches, and vegetable oils found in food crops, from which they can readily be extracted using

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well-established technology. The two biofuels in greatest usage worldwide are bioethanol and biodiesel, which are almost always produced using edible crops such as corn, sugarcane, or sugar beets. Starting from near-zero in 1975, bioethanol production has risen dramatically in recent years, reaching over 30 billion gallons annually. These biofuels are also surprisingly concentrated in particular nations or regions, thus 90% of all bioethanol is produced in just two nations: Brazil and the United States, while a majority of the world's biodiesel is produced by the European Union (EU). Most biofuels are of course used in the transportation sector, where they can offset a certain percentage of a nation's petroleum consumption, either as an additive to gasoline or diesel fuel, or in some cases as a one-for-one replacement, provided the engines have been modified to allow this substitution. Worldwide biodiesel and bioethanol now account for just under 3% of the fuel used for road transportation, although the International Energy Agency has estimated that they could supply more than 25% of the world demand by 2050 (EIA, 2011). Thus, the use of biofuels, especially biodiesel and bioethanol has been growing rapidly, and is expected to continue its increase in the future (Figure 5.1).

In general, biofuels come in either a liquid, gaseous, or solid form. However, since the large majority of biofuels are used in the transportation sector, liquids or gases are far preferable to solids, which tend to be used largely for either heating or electric power generation. When gaseous biofuels are produced, it is useful if they can easily be liquefied at room temperature, owing to the greater energy density of liquids, and the difficulties of storing gases under very high pressures. Liquids also have

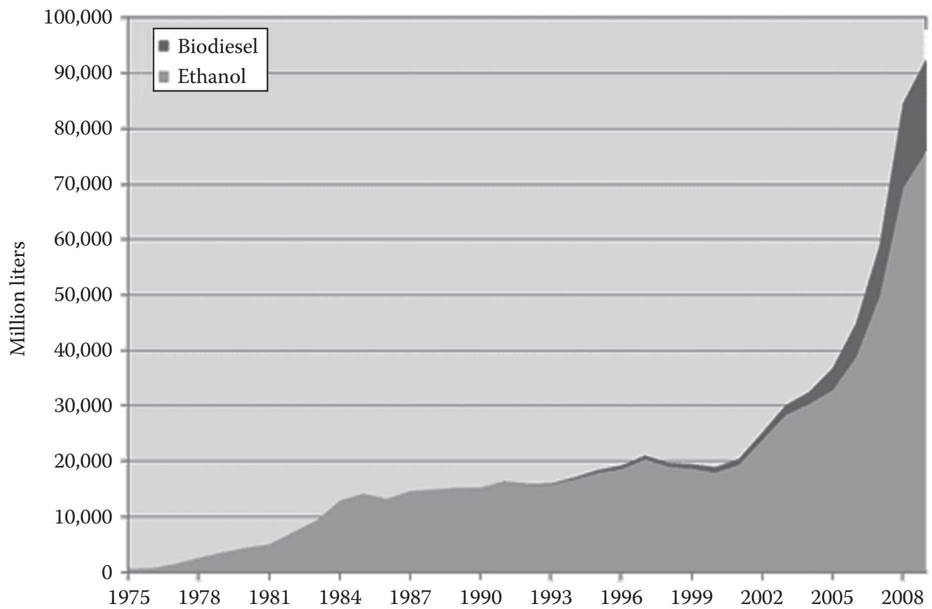

Figure 5.1 Worldwide bioethanol and biodiesel production, 1975–2009. (Image courtesy of Worldwatch Institute; http://arizonaenergy.org/News_10/News_Nov10/GrowthofBiofuelProductionSlows.html)

many other advantages as transportation fuels, including being cleaner burning, easier to transport and store (because they can be pumped and sent through pipelines), and of course being usable in an internal combustion engine.

5.2 PHOTOSYNTHESIS

Photosynthesis is the process whereby energy-rich organic compounds such as sugars and starches are created from carbon dioxide and water by sunlight. When sugar and oxygen are the end products of the reaction, the overall chemical equation may be written as

$$6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2 \tag{5.1}$$

Thus, photosynthesis plays an important part of the "carbon cycle," whereby the element carbon is exchanged among the biosphere, atmosphere, oceans, and land. The process of photosynthesis occurs in plants, algae, and some species of bacteria, such as cyanobacteria (also known as blue-green algae), and it is the ultimate source of energy for most life on Earth, including us.

BOX 5.1 CYANOBACTERIA

Cyanobacteria often caused by runoff of sewage or fertilizers sometimes causes algae "blooms" in lakes and rivers. In fact, according to the U.S. Department of Agriculture such nonpoint sources as sewage and fertilizers constitute the primary pollution hazard in the nation. The bacteria causing these algae blooms can be harmful to humans and other living creatures, and cause significant environmental and economic damage, e.g., through its impact on seafood harvests. In humans, studies show these bacteria are harmful to the liver and nerves, and can be responsible for several serious diseases.

The only organisms not ultimately dependent on photosynthesis are some bacteria and other single-celled organisms known as archaea living deep underground or undersea. Many deep undersea organisms live near thermal vents and use heat as their energy source, although recently researchers have discovered that some of them, in fact, also live off the dim light from thermal vents as well (Blankenship, 2005). Of course, most photosynthesis in the oceans occurs at the surface or at moderate depths (the "euphotic zone") that typically extend between 10 and 200 m depending on the murkiness of the water. The extent of oceanic photosynthesis also depends on the amount of incident sunlight reaching the ocean surface, which in turn depends on latitude and time of year. On land, the amount of photosynthesis also depends on the richness of the soil, which is a function of specific geographic features, such as forests, deserts, and mountain ranges—for the color-coded amounts of photosynthesis occurring on both land and sea.

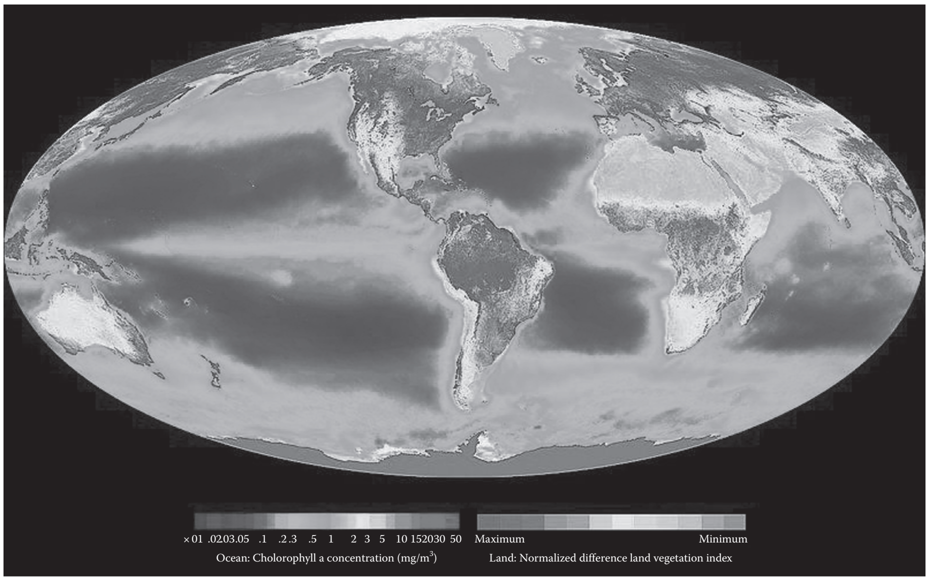

Figure 5.2 (See color insert.) Composite image showing the global distribution of photosynthesis, including both oceanic phytoplankton and vegetation. The composite color-coded image gives an indication of the magnitude and distribution of global primary production of chlorophyll in units of mg/m^3 chlorophyll. It was compiled from satellite imagery taken over the period September 1997–August 1998. (Image courtesy of NASA/Goddard Space Flight Center and ORBIMAGE, and is in the public domain; http://en.wikipedia.org/wiki/Photosynthesis)

Sea-based photosynthesis mainly occurs as a result of single-celled plants known as plankton. It has been estimated that these marine plankton produce perhaps half of the Earth's oxygen, even though their total biomass is orders of magnitude below that of terrestrial plants (Figure 5.2).

Photosynthesis absorbs about 10^{14} kg of CO_2 per year from the atmosphere converting it to biomass, which of course is returned to the atmosphere when that biomass decays. Thus, there is no net removal or addition to the atmospheric CO_2, unless the total biomass should shrink or grow, e.g., through deforestation or reforestation.

The process of photosynthesis is known to occur in two stages. In the first stage, light is captured primarily using the green pigment chlorophyll, and the energy is stored in energy-rich molecules such as adenosine triphosphate (ATP) and nicotinamide adenine dinucleotide phosphate (NADPH) (Figure 5.3). In the second stage, light-independent reactions occur and CO_2 is captured from the atmosphere. It is in this stage that the carbon is "fixed" or converted to plant matter such as sugar or starch in a series of reactions known as the Calvin cycle. Certain wavelengths of light are especially important in the first stage process, and while most photosynthetic organisms rely on visible light, there are some that use infrared or heat radiation—hence the existence of those organisms capable of living deep underground or near undersea thermal vents. The details of the reactions in both stages of photosynthesis need not concern us here, as they involve some complex biochemistry.

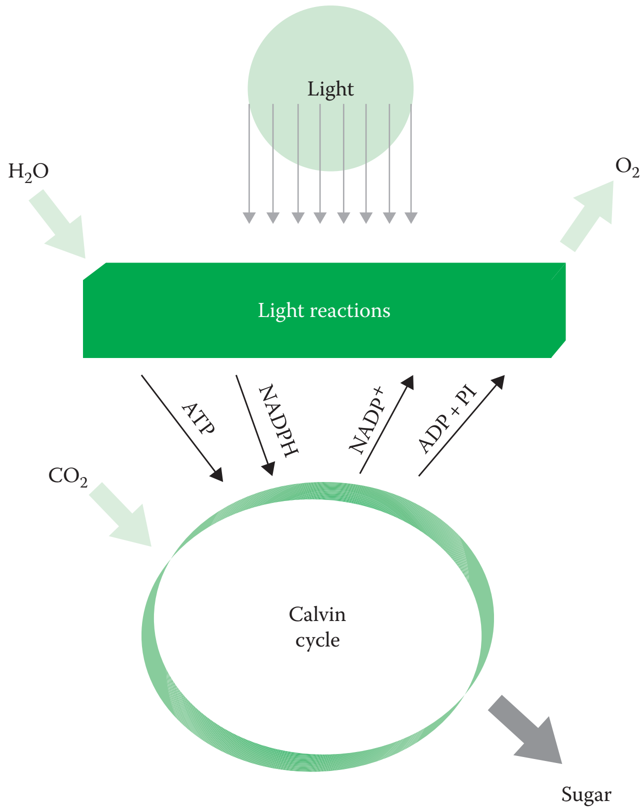

Figure 5.3 Simplified version of the two phases of the chemical reactions taking place during photosynthesis.

5.2.1 Example 1: Efficiency of Photosynthesis

The total energy stored worldwide in the sugar produced by photosynthesis is about 8.4×10^{21} J per year. Assuming that the process is 3%–6% efficient in collecting sunlight, find the fraction of sunlight that is stored in sugars, and approximately what area of the Earth's surface is covered by photosynthetic organisms.

Solution

As noted previously, the annual incoming solar energy totals 3.8×10^{24} J in a year, so the fraction of incoming solar energy creating sugars via photosynthesis is therefore about $8.4 \times 10^{21}/(3.8 \times 10^{24}) = 0.002$ (0.2%). If the actual efficiency of the overall reaction is 3%–6%, this implies that the fraction of the surface covered by photosynthetic organisms is between 1/3 (0.2) = 0.067 and 1/6 (.02) = 0.033, or between 3.3% and 6.7%.

What does the actual efficiency of photosynthesis depend on in a given location? The most important variables are

- Light intensity
- Light spectrum, i.e., wavelengths of light present
- Atmospheric carbon dioxide concentration
- Ambient temperature

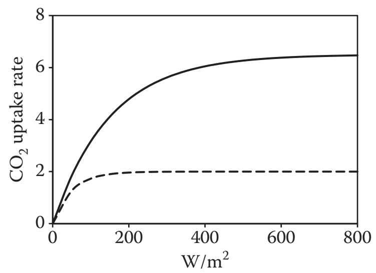

Figure 5.4 CO_2 uptake rate (a measure of photosynthetic activity level) versus the light intensity in watts/m^2 for a typical sun plant (solid curve) and shade plant. Full sun might correspond to around 750 W/m^2. Note how typical shade plants have a photosynthetic activity level that saturates at levels much less than full sun.

Some of these variables affect only one part of the overall process; thus, for example, although photochemical reactions of stage one are unaffected by temperature, the rate of carbon fixation during stage two does. There is also the matter of a limiting factor in regard to plant growth, whereby a variable such as moisture or light intensity assumes much greater importance when it is below some critical value.

How well does nature do in gathering solar energy compared to human's best efforts? Although photosynthetic efficiency lies in the 3%–6% range, commercial solar panels convert between 6% and 20% of sunlight into electricity, and their efficiency can reach over 40% in the laboratory. Of course, while less efficient in terms of energy conversion, plants also are capable of assembling themselves out of the absorbed energy and soil nutrients—something that humans have not yet designed solar panels to achieve! One of the other reasons that photosynthesis has a rather low efficiency is that the reaction saturates at a low light intensity—much less than full sunlight (Figure 5.4). It is not known why evolution would favor this fact, but of course evolution favors reproductive success, which need not be the same as efficiency of energy conversion by a plant.

5.2.2 Example 2: Best Wavelengths of Light for Photosynthesis

What parts of the visible spectrum would you imagine are most effective in promoting photosynthesis in green plants?

Solution

The color of any opaque surface viewed under white light is directly linked to the apparent color of that surface. Thus, a surface that appears green, such as nearly all plant leaves, is reflecting green wavelengths more so than those at either larger and smaller wavelengths, i.e., toward the red and blue ends of the spectrum—see Figure 5.5. If plants have evolved to maximize the rate of photosynthesis under white light illumination, this must mean that the wavelengths away from the green middle of the spectrum are more effective in promoting photosynthesis. In fact, studies have shown that chlorophyll A and B (the two primary compounds responsible for photosynthesis) absorb wavelengths of light with highest efficiency in wavelength regions: $\lambda_1 = 439–469\,\text{nm}$ (in the blue), and $\lambda_2 = 642–667\,\text{nm}$ (in the red). For this reason, plants grown under artificial lighting (using LEDs with the appropriately chosen wavelengths can be made to grow with greater efficiency than if one attempts to recreate natural lighting indoors. Note that for plants grown under natural light the fraction of the incident solar energy that they utilize is the ratio of the areas under the black absorption curve to that of the full spectrum in Figure 5.5.

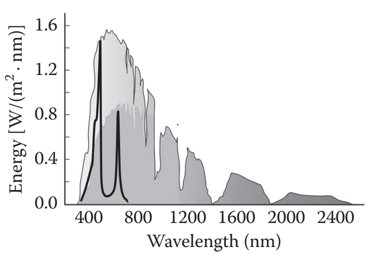

Figure 5.5 Spectrum of sunlight at sea level and the absorption curve for chlorophyll b, one of two important pigments found in almost all plants, algae, and cyanobacteria.

BOX 5.2 IS CO_2 "GREEN"?

As already noted, atmospheric CO_2 levels are a factor in the rate at which photosynthesis occurs, with higher CO_2 levels having a fertilizing effect, especially for some types of plants. Climate change skeptics therefore sometimes argue that atmospheric CO_2 is "green" in promoting plant growth, so the more atmospheric CO_2 the better. In fact, one nonprofit organization known as "CO_2 is green" with ties to the oil and gas industry lobbies against limiting CO_2 on precisely these grounds. The claim that CO_2 is "green" like any effective propaganda effort does have some element of truth. Thus, experiments with crops grown in plots of land subject to normal and elevated CO_2 levels do show that at least for some types of crops growth is enhanced by about 13% when CO_2 levels are elevated (Chandler, 2007). However, the effects appear to level off after a few years, and for most crops the other variables—especially moisture and temperature assume greater importance. For example, a 20 year study of rainforest plots in the tropics has shown that local temperature rises of more than 1°C reduce tree growth in half (Fox, 2007). Thus, in a world with higher CO_2 levels, which by the greenhouse effect will also be a warmer world, the higher temperatures will very likely have more of an inhibitory effect on plant growth than any benefit that higher CO_2 levels might have. This negative effect is likely to be compounded by drier conditions in continental interiors, which would also have a negative impact on the 95% of plants that fix carbon according to the "C3" metabolic pathway, since such plants, including rice and barley, do very poorly in hot dry climates.

5.3 BIOFUEL CLASSIFICATIONS

Three ways to characterize biofuels are in terms of (a) their feedstocks, i.e., the inputs; (b) the process used to produce the fuels from their feedstocks; and (c) the outputs of these processes. The importance of considering the feedstocks and processes as well as the end product is nicely illustrated by a comparison of two nations' approaches to the production of the same product, bioethanol.

5.3.1 Choice of Feedstock for Biofuels

The United States and Brazil between them produce 88% of all the bioethanol in the world, but the experiences of the two nations have been quite different. Brazil has been in the ethanol production business longer than the United States—ever since the 1973 Arab Oil embargo—and its program is far larger in scope considering the relative sizes of the two nations. Thus, while the United States produces about a third more ethanol than Brazil, that amount offsets only a meager 4% of the U.S. demand for gasoline, while in Brazil it offsets fully half the demand. In the United States, ethanol is primarily used as a gasoline additive—up to

Table 5.1 Brazil and the U.S. Ethanol Production

Criterion Feedstock	Brazil Sugarcane	U.S. Corn
Fuel production	6472 Mgal	9000 Mgal
Share of gas market	50%	4%
Arable land used	1.5%	3.7%
Fuel per hectare	1798 gal	900 gal
Net energy ratio (NER)	8.3–10.2	1.3
GHG reduction	61%	19%
Blend for existing vehicles	E25	E10
Blend for new vehicles	E 25–E 100	E10
Subsidy	None	Substantial
Use of waste	Energy generation	Livestock feed

GHG reductions include land use changes.

15%, while in Brazil, many cars now can run on any blend up to 100% ethanol (E100). In fact, such cars now constitute over 90% of all new cars and light trucks sold in Brazil.

Ethanol can be produced from a variety of crops, including sugarcane, cassava, sorghum, sweet potato, corn, and wood. The primary difference between ethanol production in the United States and Brazil involves their choice of feedstock—corn for the United States and sugarcane for Brazil (Table 5.1).

The Brazil–United States ethanol experiences also differ in many other respects, with the Brazilians generating nearly twice as much ethanol per acre of crop—in part, the result of the different sugar content of the two crops, but also the result of a 40 year Brazilian R&D program for agriculture. Brazil has now achieved the most efficient technology for sugarcane cultivation in the world, and it has tripled its production per acre over a recent 30 year period. This high production efficiency also translates directly into energy efficiency, which is often defined in terms of the "net energy ratio" (NER), or the ratio of the energy a biofuel supplies to that required to produce it. For Brazilian ethanol the NER is as high as 10, while for the United States it is a meager 1.3. Effectively, this means that U.S. corn ethanol yields 30% more energy than was used to create it, while for Brazilian ethanol it is 900% more. Part of the high energy efficiency for Brazilian ethanol results from the practice of harvesting the sugarcane residue ("bagasse"), and burning it to produce electricity that powers the operation.

An equally impressive comparison (favoring the Brazil model over the United States) lies in the relative greenhouse gas reductions, which is far greater for Brazil—even when the loss of Amazon rainforest to create agricultural land is taken into account. In fact, studies have shown that the extra greenhouse gas emissions resulting from the loss of rainforest when the land is used for sugarcane to produce ethanol can be recouped in about 4 years if the ethanol replaces gasoline, while in the case of U.S.

forest land replaced by corn ethanol, the corresponding figure is 167 years (Searchinger et al., 2008).

Finally, all the Brazilian sugarcane used for ethanol production has been accomplished without government subsidies, while the United States has taken the opposite course, largely for political (not economic or environmental) reasons. Interestingly, these subsidies totaling about $5 billion annually are paid not to farmers (who would plant the corn anyway) but to the oil industry to induce them to include the ethanol into their product. At the time of this writing (mid-2011), it seems likely that these federal subsidies that have been in place for 30 years may not survive a new round of budget austerity, but it is always a mistake to underestimate the oil industry's political clout and resources for influencing public opinion, and more importantly Congressional voting patterns.

Let us now broaden the possible feedstock choices beyond just sugarcane and corn, and consider the six feedstocks shown in Table 5.2, three of which could be used in the production of ethanol, and three in biodiesel. These feedstocks have been rated here on their "greenness" based on three important criteria: (a) their contribution to CO_2 emissions per unit energy the fuels contain, (b) their usage of various resources (water, fertilizer, pesticide, and energy), and (c) their availability. Availability has been expressed in terms of the percentage of existing U.S. cropland they would consume to produce enough fuel to displace half the gasoline needed for road transportation. The entries in the greenhouse gas emissions column of Table 5.2 are those for the complete life cycle of the fuel, and should be compared to those of gasoline, i.e., 94 kg CO_2/MJ, but note that some are actually negative, which requires that more carbon is removed from the atmosphere during their growth than

Table 5.2 Comparison of Six Biofuel Feedstocks Used to Make Ethanol and Biodiesel

Crop	NER	GHG kg CO_2/MJ	Resources Used W, F, P, E[a]	Yield (L/ha)	% U.S. Cropland
For ethanol					
Corn	1.1–1.25	81–85	H, H, H, H	1,135–1,900	157–262
Sugarcane Switch grass	8–10.2	4–12	H, H, M, M	5,300–6,500	46–57
	1.8–4.4	−24	L, L, L, L	2,750–5,000	60–108
For biodiesel					
Soybeans	1.9–6	49	H, L, M, M	225–350	180–240
Rapeseed	1.8–4.4	37	H, M, M, M	2,700	30
Algae	—	−183	M, L, L, H	49,700–109,000	1.1–1.7

Source: Groom, M. et al., *Conserv. Biol.*, 22(3), 602, 2007.
H, high; M, medium; L, Low.
The % U.S. cropland is that needed to supply half the nation's fuel for its road transportation.
[a] Resources include: water (W), fertilizer (F), pesticides (P), and energy (E).

is later returned to it. This carbon sequestration occurs because some grasses have been found to store carbon in the soil through their roots during their growth.

The vast differences between the numbers in Table 5.2 for the various feedstocks are quite striking, especially in regard to the percentage of cropland needed to satisfy half the U.S. transportation needs. The values here range from 1% to 2% for biodiesel made from algae to an impossible 262% of U.S. arable land for ethanol made from corn. It is clear from this table that if one wanted to select the worst possible choice of crop from these seven to use to generate a transport biofuel, corn ethanol probably would be at the top of the list. The best current candidate for an advanced biofuel (miscanthus) does not appear in Table 5.2 (Figure 5.6). It, like the best ones listed there (switch grass and algae), involves converting the nonsugar-based components of plants (cellulose and lignin) into biofuels, and this step involves technology not yet ready for economically viable widespread use.

Figure 5.6 Field of *Miscanthus giganteus*. (Image created by Pat Schmitz and licensed under the Creative Commons Attribution-Share Alike 3.0 Unported license; http://en.wikipedia.org/wiki/Miscanthus_giganteus#cite_note-5)

BOX 5.3 MISCANTHUS

Miscanthus is a tall grass that can grow to heights of more than 3.5 m in one growing season. It has been long hailed as a superb candidate for biofuel production, because of its rapid growth, high yield per acre (about 25 tons), and low mineral content. Most importantly, it is not used for food, and can grow in some places not well suited to many food crops. *Miscanthus* has very low nutritional requirements, which enable it to grow well on barren land without the aid of heavy fertilization.

5.3.2 Biofuel Production Processes

Having seen the importance of the choice of feedstock for a given biofuel, here we examine the differences in the various biofuel production processes. These processes can be classified into three broad categories, thermochemical, biochemical, and agrochemical, each of which has several subcategories (Figure 5.7).

Thermochemical processes based on their name obviously use heat to induce chemical reactions. The most well known of these would be the direct combustion of biomass—either for heating, cooking, generating electric power, or supplying energy to drive some industrial process. Direct combustion in its simplest form is thus not a process for creating a biofuel, but rather a usage of the original biomass as the fuel to produce energy. In this case, it is important that the biomass be completely dried, and preferably homogeneous in composition. Pyrolysis ("pyr" for fire and "lysis" for separating) is the process of anaerobic decomposition of organic material using heat. Pyrolysis differs from direct combustion in three important ways:

- Being anaerobic, the process occurs in the absence or near absence of oxygen.
- Moisture may be present and is sometimes essential.
- The decomposed material retains its stored energy afterward.

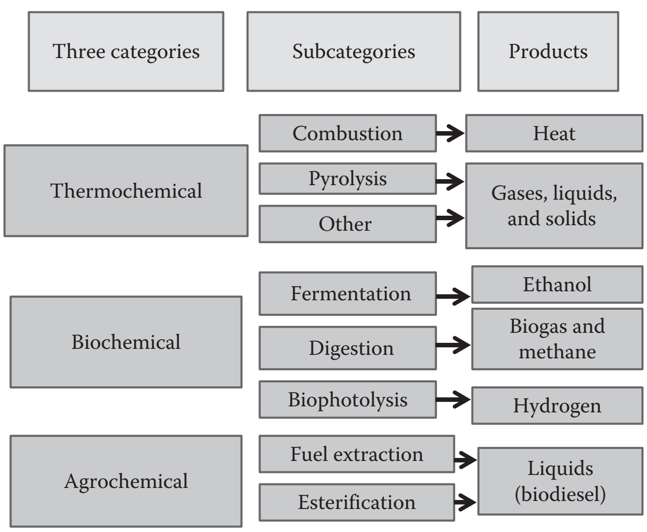

Figure 5.7 Summary of the categories of biofuel production processes.

The end product of pyrolysis may be a combustible solid, liquid, or gas, in which case the process is referred to as "gasification." A variety of other industrial thermochemical processes exist besides combustion and pyrolysis that involve sophisticated chemical control.

Biochemical processes obviously use biological organisms including bacteria, yeasts, or other microorganisms to induce chemical reactions in the original biomass. One biochemical subcategory involves the process of digestion. Our bodies use this process to convert food into substances that can be absorbed and assimilated. In its general meaning, digestion refers to the decomposition of organic matter by bacteria, either in the presence of oxygen (aerobically) or its absence (anaerobically). Anaerobic digestion, which also occurs in the stomachs of cattle and other ruminant animals, where one end product is biogas, a mixture of methane and CO_2 that is also known as sewage or landfill gas. Another biochemical process, fermentation usually refers to the conversion of carbohydrates such as sugars into ethyl alcohol. The third subcategory of a biochemical process for producing biofuels is biophotolysis. Photolysis as its name suggests involves making use of the energy in light to cause a chemical decomposition. Thus, biophotolysis involves having microorganisms help drive the process. In the present context, this involves splitting the water molecule into its constituent hydrogen and oxygen gas—the former being an energy-rich store of energy.

Agrochemical processes are the third way that biofuels can be created. One subcategory involves the direct extraction of useful products from living plants by tapping into their trunks or stems or by crushing them—molasses and latex rubber production being two examples of such extracts or "exudates." In many cases these plant exudates are fuels, which may serve as petroleum substitutes. Oils, for example, directly extracted from plant (or animal) matter may be used to power a diesel engine. In fact, some owners of diesel-powered cars fill up their tanks for free using the used vegetable oil from restaurants after it has been filtered. On the other hand, the high viscosity of these oils can cause engine problems, especially at low temperatures, so engines are usually modified to preheat the oils.

A better solution is to convert the oil into a chemical compound known as esters in order to produce the fuel known as biodiesel. In this process known as "esterification," the vegetable oils or animal fats are chemically reacted with an alcohol to produce the ester. In addition to having a lower viscosity than the pure oils, biodiesel fuel made this way has many highly desirable properties as a diesel fuel, including being

- Able to dissolve engine deposits
- Safer to handle than mineral-based diesel
- The cleanest burning form of diesel

Although normal (mineral) diesel fuel is known for having high emissions, according to the U.S. Environmental Protection Agency, biodiesel has between 57% and 86% less greenhouse gases compared to mineral diesel, depending on the feedstock (EPA, 2010). Particulate emissions, a significant health hazard, are also about half those of mineral diesel. In the United States, although bioethanol is the main biofuel for transport, the use of biodiesel is rapidly growing, and there remains considerable room for further growth in the United States, given that 80% of trucks and buses run on diesel.

5.3.3 Example 3: Loss of Energy When Combustible Material Is Moist

The energy density of dry wood is about 15 MJ/kg, while that of undried "green" wood is about 8 MJ/kg—the difference being due to some of the mass being simply water, and also the energy needed to drive off the water as vapor during combustion. Given the two energy densities, estimate the fraction f of moisture in green wood, assuming that it is essentially water.

Solution

A mass *m* kilograms of green wood will contain fm kg of moisture that needs to be driven off as vapor. Assume that the wood is initially at an ambient temperature of $T = 20°C$, and that it needs to be raised 80°C to its boiling point 100°C, and then vaporized. This will require 80 + 539 = 619 cal/g of water or 619,000fm cal = 2.60fm MJ total. Thus, the energy content in MJ of a mass *m* of green wood is 8*m* and can be expressed as

$$8m = E_{dry} - 2.60\,\text{fm} = 15m_{dry} - 2.60\,\text{fm} \tag{5.2}$$

The mass of the dry wood is $(1 - f)m$, so that Equation 5.2 yields

$$8m = 15(1 - f)m - 2.60\,\text{fm} \tag{5.3}$$

which when solved for f yields: $f = 0.40$ (40%).

5.3.4 Generation of Biofuels

The choice of feedstock for biofuels is closely related to the "generation" to which they belong (Table 5.3). At least four generations have been defined, although their definitions vary according to the source. For example, by some definitions biofuels in the second generation are said to come from a sustainable feedstock, which is defined more broadly than merely being a nonfood crop. Part of the reason for the confusion is that the vast majority of biofuels in commercial use still belong to the first

Table 5.3 A Possible Definitions of the Four Generations of Biofuels

Generation	Characteristics
First	Made from edible feedstocks (sugar, starch, and vegetable oil); unfavorable NER and CO_2 balance
Second	Use nonfood components of biomass, such as trees and grasses
Third	Specially engineered "energy crops" relying on genomics, e.g., algae based
Fourth	Crops that are very efficient in capturing CO_2—"carbon-negative"

generation, so the definitions of generations two, three, and four (often referred to as "advanced" biofuels) are a bit of a hypothetical exercise. The reason that generations two and higher are not yet widely used commercially has to do with the much greater difficulty of converting cellulose and lignin into a biofuel as compared to sugar, since there is the extra step of first converting these compounds into a sugar. This process is technically more difficult and remains to be perfected, although much research on the subject is underway. Scientists doing the work may have a lot to learn about this process if they could find a way to emulate nature, because livestock such as cattle, through a slow digestive process, turn the grass they eat into sugar.

BOX 5.4 HAD ENOUGH FIBER TODAY?

Lignin and cellulose, notoriously difficult to decompose, are complex chemical compounds that comprise an integral part of the cell walls of plants and many algae. They form the structural component of plants and trees and are often derived from wood. Cellulose is the most common organic compound on Earth, and together lignin and cellulose comprise a majority of all plant matter by weight, so that finding an economic way to harvest the stored energy they contain is essential to the future of second- and higher-generation biofuels. Although the digestive systems of some animals can decompose lignin and cellulose with the aid of helpful bacteria, the human ability to do so is much more limited. Nevertheless, these compounds do play a useful role in the human digestive process, because they are the "fiber" that plays such an important part of our diets—especially as we age!

Research is also underway in seeking to accomplish the goals of the third- and fourth-generation biofuels, which are likely to be still further in the future, with the science of genetic engineering playing a vital role in both cases. Algae are believed to be an especially promising feedstock for third-generation biofuels, and claims have been made that they might yield up to 100 times more energy per unit area than second-generation crops (Greenwell et al., 2010). In fact, the U.S. Department of Energy estimates that if algae-based fuel replaced all the petroleum-based fuel in the United States, the land area required would total 39,000 km^2 which is a mere 0.42% of total area—a far cry from the figure for corn-based ethanol (Hartman, 2008). Not surprisingly, the technology is not yet mature enough to economically produce algae-based biofuels, and more advanced genetics is probably needed to successfully engineer synthetic microorganisms. Optimists, however, predict that algae-based biofuels may reach cost parity with conventional fuels within this decade. On the other hand, even if the economic optimists are right, there are also the environmental effects to consider, since algae-based fuels so far require substantial amounts of water and their production emits more greenhouse gases than fuels generated than many second-generation feedstocks. These negative impacts are mainly the result of the heavy use of fertilizers needed to boost the algae production rate and the fossil fuels consumed in making those fertilizers (Clarens and Colosi, 2011).

Biofuels of the so-called fourth generation would be "carbon-negative," meaning that they would remove more carbon from the atmosphere during their growth than they would later return to it when they are consumed. In effect, they would need to somehow sequester captured carbon, and not release it all when the fuel is consumed. Various methods for doing this have been proposed. In one scheme, small pieces of wood would be pyrolyzed to produce charcoal and a gas. The gas would then be condensed into oil, which after processing is blended into biodiesel. The charcoal residue could be used as a fertilizer and put back into the ground where it would remain. Scientists have demonstrated by experiment using selected grassland plants that carbon sequestration in the soil works quite well for sandy soil that is agriculturally degraded and nitrogen poor (Tilman et al., 2006).

5.4 OTHER USES OF BIOFUELS AND SOCIAL–ENVIRONMENTAL IMPACTS

Although the primary use of biofuels is in the transportation sector, they also can play a role in electric power generation. For example, *Miscanthus*, which promises to be one of the best plants for producing biofuels is now grown in Europe mainly for mixing 50/50 with coal in electric power generation. Estimates are that it could supply 12% of the EU's electrical energy need by 2050 (Dondini et al., 2009). Direct combustion of solid biomass fuel does of course result in airborne pollutants, but their environmental impact is considerably less than fossil fuels. Apart from direct combustion of biofuels there is also research underway to explore how the plant and other biomass sources can be used to make plastics and other products usually made from petroleum.

There are many social, economic, and environmental issues with biofuels including their impacts on such matters as oil prices, the availability (and price) of food, CO_2 emissions, deforestation and biodiversity, water resources, and energy usage. As we have seen, some biofuels are far preferable than others in terms of minimizing the negative environmental impacts.

5.4.1 Biofuels from Wastes and Residues

One category of biofuels that still needs to be discussed is that produced from agricultural, residential, and industrial wastes. Various processes are used here depending on the input, with digestion (producing methane or landfill gas) followed by direct combustion to produce electric power being especially common. In order for the process to prove economically viable, widely distributed wastes need to be aggregated as part of some other goal, such as collection of garbage in a landfill. In the United States, for example, there are hundreds of landfills where methane is captured from decomposing trash and used to generate electricity totaling 12 billion kW-h/year. Burning landfill gas does create airborne emissions, which can vary widely, depending on the nature of the waste and the state of the technology. However, the CO_2 released from burning landfill gas is considered to be a part of the natural carbon cycle, and it is less harmful as a greenhouse gas than if the methane were released to the atmosphere. The generation of power from the wastes of society also is quite suitable in a rural setting in developing nations even in a community whose livestock produce 50 kg manure per day, which is an equivalent of about six pigs or three cows. In such a setting, a typical biogas plant that supplied gas for cooking could be built by a rural household with an investment of as little as \$300, depending on region. Several countries, especially China and India, have embarked on large-scale programs for producing biogas for domestic use in rural areas (Figure 5.8).

5.4.2 Agricultural Wastes

The same process of digestion of wastes followed by combustion of methane to produce electricity can also be done in an agricultural setting, which as noted earlier is routinely done in Brazil as a by-product of their ethanol production from sugarcane. Such usage of agricultural wastes is less common in the United States, however. One notable exception is the

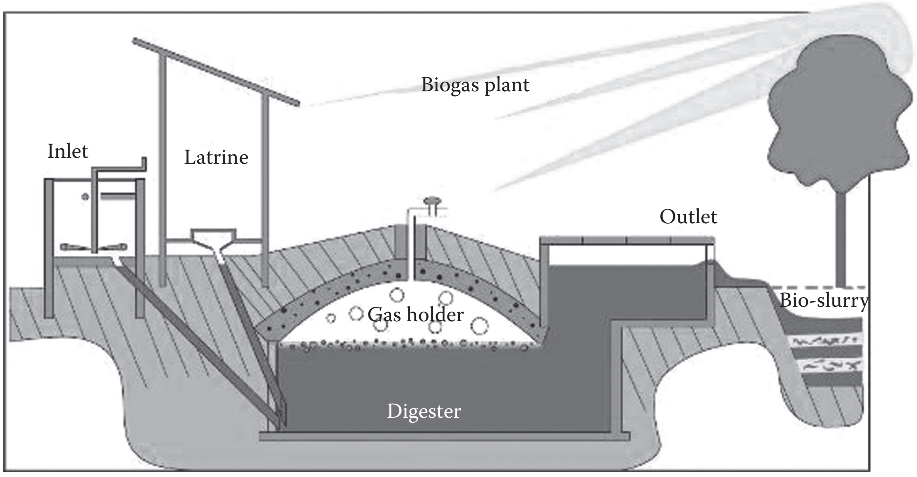

Figure 5.8 Design of a simple small-scale plant for generating biogas. (Image created by SNV and released to the public domain; http://en.wikipedia.org/wiki/Biogas)

Figure 5.9 Sculpture made from the residue of cow manure by the Mason-Dixon farm.

Mason-Dixon farm in Gettysburg, Pennsylvania. The Mason-Dixon farm where the motto is “Change is inevitable; success is optional,” stands as a model to the world for innovation in agricultural efficiency. Their 2000 cow herd of dairy cattle are housed in an extremely large barn where they are milked by robots that the cows seek out every few hours when their udders become uncomfortably full. Housing the cows in a barn also makes it easy to automatically gather their manure—not by robots but by slowly moving scraper bars that run the full length of the barn. The cow manure is then piped to a digester where methane is produced—enough to supply the whole farm with electricity, and sell some back to the power company. The residue of the cow manure is also sold as fertilizer, and what is left over from that is used to make sculptures sold to tourists who visit the farm from all over the world to learn about its practices! Visitors to the farm on noticing that the sculptures look strikingly like a recent U.S. Democratic president are likely to believe that they reveal the Republican leanings of the farm owner, particularly if they notice the inscription on the bottom (Figure 5.9). However, they might be of a different opinion if they knew that an equal number of sculptures of a recent Republican president had also been made, but they sold out very quickly.

5.4.3 Central Role of Agriculture in a Sustainable Future

The field of agriculture is of vital importance for the future sustainability of the human race. In fact, it plays a central role in many of the problems humanity faces, and will face in the future (Figure 5.10). Advances in agriculture are what have made possible the past growth in the number of humans on the planet this past century—for example, during 1950–1984, a period known as the “Green Revolution,” agriculture was transformed, and world grain production increased by 250%. Demographers now predict a continued growth in world population from the present 7 billion to as much as 10 billion by 2050. Whether

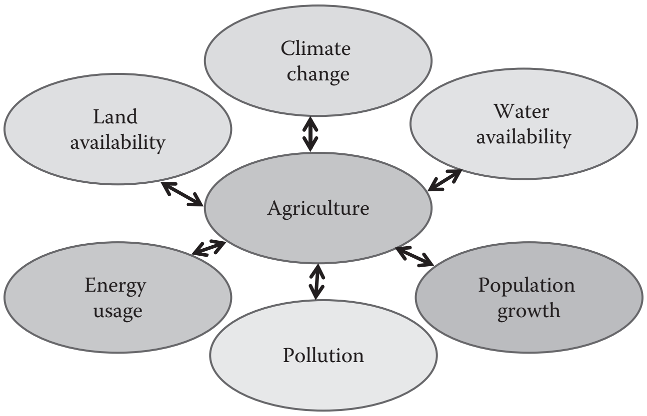

Figure 5.10 Central role of agriculture in relation to six major global problems.

these projections of population growth (or the less pleasant alternative massive famines) are realized will hinge in large measure over whether further comparable advances in agriculture are possible.

As it is, however, about 70% of the world's land area is either already used for agriculture or unsuitable to it, so simply planting crops on unused land does not offer a prospect for great expansion. Apart from the scarcity of land, that of freshwater also is becoming an increasingly serious problem in many heavily populated parts of the world plagued by drought. These problems may be exacerbated by climate change—which will likely decrease water availability and suitable cropland. Moreover, agriculture is a major factor in our usage of energy, another factor in promoting climate change. The Green Revolution was only made possible by a vast increase in the amount of energy used in agriculture, which increased by about 50 times what is used in traditional agriculture. This high energy usage (about 17% of all fossil fuel use in the United States) is primarily used for making fertilizer and operating farm machinery. Finally, the heavy usage of fertilizers relates to the sixth global problem—pollution, which as noted previously is caused to a major degree by agricultural runoff. All these global problems, in which agriculture plays a pivotal role, call out for a new way of doing agriculture if the human race is going to be able to sustain itself in the future.

5.4.4 Vertical Farming

The idea of "vertical farming" pioneered by Columbia University professor Dickson Despommier has the potential to revolutionize agriculture, and help solve all the six problems linked to it identified in Figure 5.10 (Despommier, 2010). The idea is to bring agriculture to the cities, and house it indoors in multistory buildings specially constructed for this purpose, using a combination of natural and artificial lighting. As Despommier explains, not a single drop of water, bit of light, or joule of energy is wasted in the operation, and in fact there is no "waste," with everything continually being recycled. The vertical farm essentially brings

Figure 5.11 Three proposed designs for a large-scale vertical farm designed by Chris Jacobs, Gordon Graff, SOA ARCHITECTES. (This image is made available under the Creative Commons CC0 1.0 Universal Public Domain Dedication; http://en.wikipedia.org/wiki/Vertical_farming)

the farm to the grocery store, and avoids both the large transportation costs (and energy expenditures), as well as the massive use of fertilizers and pesticides, which are no longer needed, because harmful pests are kept out. In this scheme which makes use of hydroponics and aeroponics, crops can be grown without soil, and it uses between 70% and 95% less water than conventional farming—one of the main consumers of freshwater in the world. The enclosed temperature-controlled system allows for year-round crops, and eliminates crop failures due to bad weather. Between such crop failures and those due to disease (also eliminated), as much as 70% of crops worldwide fail to be harvested. Despommier's scheme has yet to be implemented on a large scale, but a number of projects have already begun in Japan, the Netherlands, and the United States (Figure 5.11).

5.5 ARTIFICIAL PHOTOSYNTHESIS

The idea of artificial photosynthesis goes back to 1912 in the form of a challenge by Giacomo Ciamician to other scientists to search for a series of photochemical reactions that would mimic the process that plants use in storing energy. Recently, Daniel Nocera, an MIT chemist has met the challenge by developing an artificial leaf that uses photochemical reactions initiated by sunlight to produce hydrogen—an important energy-rich fuel (Nocera et al., 2011). Essentially, the process is a form of water-splitting, i.e., separating the hydrogen and oxygen in water using sunlight and catalysts that facilitate the reaction. Of course, real leaves do not generate hydrogen, but store the energy in other chemicals, such as carbohydrates, but the artificial leaf conforms to the basic functions taking place in nature, and it relies on earth-abundant materials and requires no wires. Quoting from an MIT press release:

> Simply placed in a container of water and exposed to sunlight, it quickly begins to generate streams of bubbles: oxygen bubbles from one side and hydrogen bubbles from the other. If placed in a container that has a barrier to separate the two sides, the two streams of bubbles can be collected and stored, and used later to deliver power: for example, by feeding them into a fuel cell that combines them once again into water while delivering an electric current (MIT, 2011).

5.6 SUMMARY

Following an overview of biofuels, and the process of photosynthesis from which nearly all biomass is created, the chapter considers various categories of biofuels, including their feedstocks, the processes used to make them, and their end products and uses. It is seen that all biofuels are far from equal, whether the measure be energy supplied, greenhouse gas emissions, or other impacts on society and the environment. Although much research on biofuels is ongoing, and some possibilities appear particularly promising (especially algae-based biofuels), most of the biofuels used worldwide continue to be either bioethanol or biodiesel produced from "first generation" feedstocks.

PROBLEMS

1. Suppose you wanted to supply half the U.S. demand for gasoline using ethanol from corn. It was stated in the chapter that this might require as much as 262% of U.S. cropland. Using data available on the web for the yield per acre of corn, its energy content, and the amount of energy needed to meet the needs of U.S. road transport, see if this estimate is about right.
2. How is it possible that marine plankton produce perhaps half of the Earth's oxygen from photosynthesis, even though their total biomass is orders of magnitude below that of terrestrial plants?
3. Consider this statement made in the chapter: "The amount of energy trapped by photosynthesis is approximately 100 TW, which is about 6× larger than the power consumption of human civilization." Assume the basic photosynthesis reaction can be written as $CO_2 + H_2O + \text{Energy} \rightarrow CH_2O + O_2$. (a) Given the original statement, how many tons of CO_2 does photosynthesis remove from the atmosphere each second, assuming that the absorbed energy consists of visible photons whose energy is about 2 eV each, and that absorption of one photon is sufficient to induce the aforementioned reaction, (b) What is the net effect on atmospheric CO_2 levels from photosynthesis over the course

of a year? (c) Explain why the net effect on CO_2 levels during the year due to plants is actually zero. (d) If 100 TW is in fact 6× larger than the power consumed by all humans, what does that imply about the average power consumed per person? How does that compare with the average power consumed by an American?

4. A farmer has a small herd of 100 pigs, and wishes to use their wastes to produce methane to generate part of the electricity used by the farm. Assume that each pig generates 1 kg of solid waste per day, which yields 0.8 m^3 of methane at STP. Methane contains about 38 MJ/m^3. Assume that you can convert 25% of this energy into electricity; find how many kilowatts would the farmer be able to generate in this manner?
5. During anaerobic digestion, glucose is converted to methane according to the overall formula $(CH_2O)_6 \rightarrow 3CH_4 + 3CO_2$. Calculate the percentage of methane produced by volume and by mass.
6. Over some range of sunlight power density and atmospheric CO_2 concentration, assume that the rate at which plant leaves take up CO_2 is a linear function of both variables. Suppose that the rate of CO_2 uptake by a leaf is 0.05 μmol/min/cm^2 when the solar power density is 50 W/m^2 and the atmospheric concentration is 330 ppm, and that the rate of CO_2 uptake by a leaf is 0.15 μmol/min/cm^2 when the solar power density is 100 W/m^2 and the atmospheric concentration is 400 ppm. Find the rate of CO_2 uptake when the solar power density is 200 W/m^2 and the atmospheric concentration is 450 ppm.
7. Using advanced fermentation technology for converting cellulose to ethanol can yield about 900 gal/acre. Assume that on average vehicles get 20 miles per gallon from gasoline. Estimate how many acres would need to be planted to replace 10% of the miles driven in the United States with ethanol generated in this way. The number of vehicles in the United States is about 250 million, and each vehicle is driven on average 12,000 miles. Note that ethanol provides 1/3 less miles per gallon than gasoline.
8. Estimate the number of tons of CO_2 added to the atmosphere for each square kilometer of Amazon rainforest that is cleared and burned to provide room for agriculture. You will need to make some assumptions on the average size and spacing of trees in the forest.
9. Normally, it would not make any sense to produce a biofuel that had an energy content that was lower than the energy required to produce it or an NER less than one. Are there exceptions and what are they?
10. The state of Massachusetts at one time had considered generating electric power by harvesting energy crops and burning them. Assume that the state requires 4000 MW of electricity, and that planted crops yield between 10,000 and 20,000 lb of dry biomass per acre per year that could be burned to produce electricity at 35% efficiency. How many acres would the state need to plant to supply all its electricity in this way?
11. Do some searching on the web to find estimates on the amount of carbon sequestered per acre of Amazon rainforest and also the amount of CO_2 emissions saved by using the ethanol produced each year by one acre's worth of sugarcane instead of gasoline. Based on the aforementioned two numbers see if the time (4 years) given in the chapter is correct for the time it takes for the extra greenhouse gas emissions

resulting from the loss of rainforest to be made up for by using sugar-cane-based ethanol instead of gasoline.

12. Ethanol has a 38% lower energy density by volume than gasoline. Partially offsetting this disadvantage is the higher octane rating of ethanol, which allows it to be used in engines having a higher compression ratio. In fact, a standard gasoline-powered engine typically runs at a compression ratio $r = 10$, while an ethanol-powered one can run at $r = 16$. Internal combustion engines can be approximated by the ideal Otto cycle, for which the efficiency is given by $e_O = 1 - r^{-0.4}$ Assume that a real engine has one-third the ideal Otto efficiency, and calculate how much improvement this would make to the efficiency of the ethanol-fueled engine over a standard gasoline engine. Is it enough to offset the lower fuel energy density of ethanol?
13. Assume that the rate of photosynthesis in some plants depends on the CO_2 concentration C (in ppm) according to $R = 50(1 - e^{-C/200})$. How does R change per unit change in C when $C << 200$ ppm, and when $C >> 200$ ppm? The units of R are mg CO_2 per m^2 per h.
14. Estimate the fraction of all sunlight harvested by the chlorophyll b pigment of plants—see Figure 5.5.
15. Find a pair of equations that describe the two curves in Figure 5.4. If "saturation" is defined as the point where each curve is at 80% of its asymptotic value, what is the ratio of the saturation light intensities for sun and shade plants based on this figure?

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