

Fossil Fuels and Fossil Energy

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A business with an income at its heels,
Furnishes always oil for its own wheels.

—William Cowper (1731–1800)

8.1 Introduction

8.1.1 Definition and types of fossil fuels

Coal, natural gas, and petroleum are called fossil fuels because they are the remains of prehistoric plants and animals that have been subjected to millennia of geologic processes. These remains have formed large deposits that are retrievable by humans and can release energy when burned. Most fuels release their energy by reacting with a separate substance (the *oxidant*), but there are cases (e.g., the explosive TNT) where the oxidant is actually part of the fuel itself. Thus, all fossil fuels are storehouses of chemical potential energy. Under the right circumstances (i.e., by chemical reaction with an appropriate oxidant), this chemical potential energy can be tapped for useful (e.g., home heating, propulsion) or destructive (e.g., fires) purposes. We typically think of oxidation as a chemical reaction that causes oxygen atoms to combine with some other substance, as in the oxidation of methane gas (the principal component of natural gas) by pure oxygen, to form carbon dioxide and water:



However, many different substances, including the halogens and CO_2 , can be oxidants; and some substances, such as boron, sulfur, and phosphorous (which are fuels when reacted with oxygen or fluorine), can themselves or as their oxides or halides be oxidants (Fristrom, 1995). When fuel oxidation is rapid and primarily produces heat, the process is called *combustion*. We use this definition to distinguish combustion from electrochemical oxidation of a fuel to produce electricity and small amounts of heat. The equipment used for these two processes are a *combustor* (or *burner*) in the former case and a *fuel cell* in the latter. To fathom the role of fuels in sustainable energy, we will study the two classes of fuels that are primarily responsible for supplying energy for human needs—fossil and biomass (chapter 10)—and we will illuminate some of the basic features of combustion, including effects that give rise to pollutants.

Naturally occurring fossil fuels are thus solid, liquid, or gaseous substances that contain *organic* or covalently bonded carbon and are produced by chemical and physical transformations of plant and animal remains over geological time periods. The time scale of the creation of fossil fuels is crucial to differentiate them from biomass fuels, which are produced and regenerated over time scales as short as 1 to 100 years (i.e., 1/1,000,000 or less of geological time scales).

8.1 Introduction

Basic Definitions

The *atomic weight* of any atom is the ratio of its mass to the mass of a prescribed standard, taken as a particular type (isotope) of the carbon atom, C, which is assigned a value of exactly 12 units. One atom of atomic hydrogen, H, weighs almost exactly one-twelfth of this form of the carbon atom, so the atomic weight of H is very close to 1 (1.00797 ± 0.00001 , to be more precise).

The *molecular weight* (MW) of any substance is the sum of the weights of all the atoms in the substance. Thus, the MW of CO_2 is the sum of the weights of one atom of carbon and two atoms of oxygen, i.e., $(1 \text{ atom C} \times 12 \text{ units}/(\text{atom of C})) + 2 \text{ atoms O} \times 16 \text{ units}/(\text{atom of O}) = 12 + 32 = 44$. As defined here, these atomic and molecular weights have no units. They are merely ratios (i.e., one molecule of CO_2 has approximately 44 times more mass than one atom of hydrogen).

We define a *mole*, better referred to as a *gram mole* for reasons given below, as the amount of that substance that has a mass in grams equal to its molecular weight. A mole of CO_2 has a mass of 44 grams. Because one atom has such a small absolute mass, we conclude that a gram mole of a molecule must contain a large number of molecules. This is correct, and that number is an important physical constant known as Avogadro's number, or N_a , which defines a mole as 6.023×10^{23} molecules of any substance. Thus, 6.023×10^{23} molecules of CO_2 have a mass of 44 grams.

The *pound mole* (or lb mole) is useful in many practical engineering calculations. It is defined as the amount of a substance of mass equal to the molecular weight of the substance in pounds rather than in grams.

Ideal gases have a volume directly proportional to the absolute temperature of the gas and inversely proportional to the pressure of the gas. For many fuel-related calculations, it is accurate to treat all gases as ideal. The relationship of the temperature, T , pressure, P , and volume, V , of any gas is described by a relationship known as an equation of state, which for an ideal gas takes the simple form:

$$PV = nRT$$

where n is the number of gram moles or lb moles of the gas (calculated by dividing the corresponding weight of the amount of gas present in grams or pounds, w , by the molecular weight of the gas), and R is the universal gas constant in consistent units.

The *standard volume* of a gram mole of any ideal gas occupies a volume of 22.414 standard liters. A standard liter is defined as a liter of an ideal gas at a pressure of 1 atm and a temperature of 0°C (273.15 K). A pound mole of any ideal gas occupies a volume of 380 standard cubic feet (SCF). One SCF is defined as a cubic foot of an ideal gas at a pressure of 30 in of mercury and a temperature of 60°F (519.7°R). Note the use of 60°F as the reference temperature, rather than 32°F , the Fahrenheit equivalent of 0°C .

The major naturally occurring fossil fuels are (Glasstone, 1982):

- *Coal*: A compact, stratified mass of metamorphosed plant that has, in part, undergone arrested decay to different extents of completeness. Coal originates from the arrested decay of the remains of trees, bushes, ferns, mosses, vines, and other forms of plant life that flourished in huge swamps and bogs many millions of years ago during prolonged periods of humid, tropical climate, and abundant rainfall. Peat is a coal precursor formed by bacterial and chemical action on the plant debris. Subsequent actions of heat, pressure, and other physical phenomena metamorphosed the peat to the various types (ranks, an index of geological age) of coal found today. Because of the various extents of transformation during coal's geological history, coal is not a uniform substance, and no two coals are ever exactly identical. Coal is a rocklike combustible material, generally rich in organic matter, but exhibiting substantial variability in chemical composition, molecular structure, inorganic content (e.g., minerals), and physical constitution, depending upon geologic age and other factors. Although coal is sometimes referred to as an "organic rock," all coal types contain some amount of inorganic material. Elemental sulfur and nitrogen are important components in coal, as they influence emissions (MIT, 2007; Hendricks, 1945; Corey et al., 1984).
- *Natural gas*: Found, among other locations, in underground reservoirs of porous rocks, alone or physically mixed with petroleum (see below), natural gas consists primarily of a mixture of simple paraffinic hydrocarbon gases of which methane (CH_4) is the major constituent (70–90% by volume). Ethane, propane, butanes, and higher paraffins occur in the gas in proportions that, in general, decline with the increasing carbon number of the hydrocarbon. Natural gas may also contain H_2S and inerts, such as N_2 and CO_2 (MIT, 2010).
- *Shale gas*: Natural gas also exists in some large shale deposits, but the low permeability of the shale impedes the rate at which the gas can be removed. Recent advances in horizontal drilling and hydraulic fracturing of shale formations have led to significant increases in production from such deposits, with wellhead prices at about \$6/MMBtu. The large amounts of fluids needed for fracturing raise environmental concerns, as the fluids could contaminate freshwater aquifers and their disposal could cause pollution (MIT, 2010).
- *Petroleum*: Literally "rock oil," petroleum (Elliott and Melchior, 1985) refers to deposits of oily material found in the upper strata of the earth's crust. Petroleum consists mainly (generally 90%) of a complex mixture of hydrocarbons spanning a wide range of molecular weight. It was formed by a complex series of chemical transformations of organic precursors deposited in previous geological periods. Although carbon and hydrogen make up the bulk of petro-

leum, it can also contain sulfur (trace to 8%), nitrogen (trace to 6%), and oxygen (trace to 2%), as well as nickel and vanadium.

- *Oil shale*: A fine-grained sedimentary rock made up of compact mineral matter (e.g., carbonates, sand, and clay) associated with kerogen, an organic material of complex and widely variable composition but consisting mainly of carbon and hydrogen and capable of producing petroleum-like liquids upon heating. (Typical yields are 10–30 gallons of liquid per ton of oil shale heated, depending primarily on the quality of the oil shale.)
- *Tar sands*: A sand or sandstone impregnated with a highly viscous, crude, asphalt-like hydrocarbon substance known as bitumen (Towson, 1985). *Bitumen* is defined as a hydrocarbon substance soluble in carbon disulfide. Typically, tar sands are a mixture of sand, water, and bitumen, with the latter ranging from trace to 18%. Roughly 50% of the bitumen can be recovered from the sand by heating without serious degradation. A typical bitumen H/C ratio is 1.4–1.5, and bitumen can contain 4.5–5.0% S and 0.4–0.5% N.

Most of the fuels we use in everyday life are refined or manufactured from the naturally occurring fossil fuels discussed above. Thus, gasoline, automotive diesel fuel, jet fuel, and home heating oil, as well as numerous chemicals, are refined (section 8.3.3) from petroleum. Coal is often washed or otherwise treated to effect physical separations of less-desired components before it is combusted to generate electricity. Even natural gas, a rather clean fuel in its own right, typically undergoes some processing (e.g., desulfurization and stripping of higher hydrocarbons and inerts to adjust its heating values) before use in the marketplace. Further information on the upgrading of naturally occurring fossil fuels for consumer applications is presented in section 8.3, and table 8.1 lists some of the attributes of a number of fuel types. The ratio of hydrogen to carbon atoms in the fuel (H/C ratio) and the fuel's higher heating value (HHV) are important properties that affect practical utilization. Fuels with higher H/C ratios produce lower CO_2 emissions per unit of combustion energy.

8.1.2 Historical and current contributions of fossil fuels to human progress

As of 2010, roughly 85% of the developed world's energy was supplied by fossil fuels—largely petroleum, natural gas, and coal—almost totally by means of combustion. Owing to a number of factors, the percentage contribution of fossil fuels will probably decline as time passes, but it is not known how rapidly this will occur. Undoubtedly, the drawdown in fossil-fuel use will vary from country to country. Moreover, in the US, fossil fuels dominate all major utilization sectors, with nuclear energy being the closest competitor in the electric sector, accounting for well over 20% of the kWh generated in recent years. In other countries, fossil fuel is less significant in electricity generation but still dominates total energy consumption in the developed world.

Table 8.1
Hydrogen-to-Carbon Ratio and Heating (Calorific) Value of Selected Fossil and Process-Derived Fuels

Fuel Type	H/C, Atomic ^a	Gross Heating Value (kcal/g) ^{b,c}
<i>Gaseous</i>		
<i>High-Btu</i>		
Methane	4.0	13.3
Natural gas	3.5–4.0	11.7–11.9
<i>Intermediate-Btu</i>		
Hydrogen	∞	33.9
Coke oven gas	4.9	9.6
Water gas (H_2 -CO)	2.0	4.3
<i>Low-Btu</i>		
Producer gas (N_2 -diluted; from bituminous coal)	1.2	1.2
<i>Liquid</i>		
Methanol	4.0	5.3
Gasoline	2.0–2.2	11.2–11.4
No. 2 fuel oil	1.7–1.9	10.7–11.0
No. 6 fuel oil	1.3–1.6	10.0–10.5
Crude shale oil	1.6	10.3–10.4
Bitumen (Athabasca tar sands)	1.4–1.5	9.8–10
<i>Solid</i>		
Kerogen (Green River oil shale)	1.5	10
Lignite	0.8	3.9–5.4
Subbituminous coal	0.8	5.5
Bituminous coal	0.5–0.9	6.7–8.8
Anthracite	0.3	8.4
Low-temperature coke	0.4	8.2
High-temperature coke	0.06	8.0

Source: Howard (1981) and references cited therein.

^a Mineral-matter-free C and total organic H (i.e., including H bound with O, S, and N).

^b Coals: moist, free of mineral matter; cokes: dry, ash-free; 1 kcal/g = 1,800 Btu/lb.

^c Gross heating value is equivalent to the higher heating value of the fuel (HHV).

Fossil fuel has gained its dominant position because of its convenience for consumers and the attractive costs of fossil-fuel-derived energy products and services, such as electricity, transportation fuels, industrial process energy, and home heating. The maturity and size of the fossil industry, its existing infrastructure, and its attractive economics are major challenges to the penetration of alternative energy technologies. To appreciate the magnitudes involved, consider the following facts (NRC, 2009; OECD, 2009).

- In the US, the price of premium gasoline, even with taxes, is about half or less of the cost of bottled water.
- During fueling of a motor vehicle with gasoline or diesel fuel, energy flows into the fuel tank at a rate of 5–10 MW. If this were electricity, it would be equivalent to running an electric generating station to supply the needs of 5,000–10,000 people.

8.1 Introduction

- World crude oil production is roughly 70 million bbl/day or 3.8 billion tons/yr. World steel production is about one-fifth this value.
- World coal production is 5.2 billion tons/yr, about seven times that of steel.
- World primary energy production was about 470 quads (quadrillion Btu) in 2008, before dropping by about 1% in 2009 due to a global recession. If this were entirely petroleum, it would be the equivalent of 220 million bbl/day.
- The world population in 2010 was approaching 7 billion people and growing. Sadly, 2 billion of these people had no electricity and lived in poverty.
- In the Organisation for Economic Co-operation and Development (OECD) countries, roughly 50 million new passenger cars are sold each year.
- The daily market value of electricity production in the US is over \$0.5 billion.
- The daily cash flow associated with global trade in crude oil is over \$1 billion.
- The cost to replace the global infrastructure for liquid transportation fuels is estimated at \$3–5 trillion.
- For comparison, the 2009 US gross domestic product (GDP) was \$14.2 trillion.

Selected Fuel Properties Affecting Performance and Environmental Impacts

The *heating value* of a fuel is the maximum amount of energy obtainable by combusting unit weight or volume of fuel and then cooling all the products of combustion to room temperature. Chemical enthalpy is released by the cumulative effects of breaking and forming bonds during combustion. Moreover, the process of cooling contributes additional energy if combustion products condense. This energy equals the enthalpy of vaporization (also known as the latent heat of vaporization) of the condensed product. Water is the most common condensable combustion product, so cooling the products of combustion to room temperature releases an additional 971.2 Btu for each pound of water condensed (or, equivalently, 539.6 cal/g). Tabulated values of the heating value of a fuel may take credit for the additional heat released by condensation of water. For fossil fuels, the tables rarely account for the small amount of heat liberated by condensation of other combustion products such as metal vapors or for the conversion of gaseous sulfur and nitrogen oxides into acid aqueous solutions (i.e., to form sulfuric and nitric acid, respectively). If a tabulated heating value does include the energy released by condensation of the water of combustion, it is called the *gross or higher heating value* (HHV). Similarly, if the value does not include this latent heat, it is called the *net or lower heating value* (LHV).

Another common term is the *adiabatic flame temperature*. This is a useful idealization that signifies the maximum temperature that would be obtained if the fuel in question were completely combusted with exactly the right amount of oxidant and with no loss of heat to the surroundings. In such an idealized case, the fuel is completely oxidized to the lowest energy state products obtainable from its constituent atoms.

- Time scales in the fossil fuels and related large throughput industrial sectors:
 - Conceptualizing new ideas for technological innovation: hours to months.
 - Research and development to test the technical and economic promise of new ideas at scales up through pilot (1/1,000 to 1/100 of commercial scale) and demonstration (1/10 of commercial scale): 2 to 10 years.
 - Design, siting, permitting, construction, commissioning, and shakedown of commercial facility: 1 to 10 years.
- Time scales in the political sector:
 - Single term of chief executive (president, prime minister): 3 to 5 years or less.
 - Single term of legislative branches (Senate, House of Representatives, Parliament): 2 to 6 years.
 - Global-scale jeopardy to international shipments of energy: 6 years, i.e., 1939 through 1945 during World War II.
- Time between successful negotiations of major international economic treaties: 50 years from the General Agreement on Trade and Tariffs (GATT) to the World Trade Organization (WTO).

These numbers delineate the magnitude of materials flows and monetary transfers in the global fossil energy sector, the long times typically needed for technological transformation in this sector, and the gargantuan sums of money that would be needed to completely replace the supply infrastructure for just one of the four major fossil utilization sectors (e.g., transportation fuels) with a nonfossil alternative. The sums involved could total the entire GDP of the US. Such a transformation is arguably feasible, but would be challenging to accomplish more than once in a century. Likewise, the listed time scales for terms of elected officials in democracies and between treaties show that institutional transformation typically proceeds slowly.

8.1.3 Sustainability: Challenges and opportunities

Were it not for the climate-forcing potency of CO₂ emissions produced by fossil-fuel combustion and the CH₄ emissions leaking from pipelines and the like, fossil fuels might not face serious environmental challenges. This is because it seems probable that technological advances would conquer environmental impacts at costs acceptable to consumers. However, based on present understanding, we can't project whether technological measures would make possible an economically viable fossil option if serious restrictions on carbon emissions to the atmosphere are called for. The potential conflict between continuing to harvest the benefits of fossil fuels and preventing adverse global climate impacts from greenhouse gases (GHG) emitted by the use of fossil fuels epitomizes the difficulty of translating the laudable ideals of sustainability into practicality. As discussed in section 8.4.3, the quest to over-

come this difficulty has spurred proposals, research, pilot testing, and field studies to mitigate GHG emissions or their adverse climate effects through geoengineering, emissions reduction, and GHG removal from the atmosphere. However, each of these approaches has "sustainability" challenges.

8.2 The Fossil-Fuel Resource Base

8.2.1 How long will fossil fuels last?

Nobody knows when we will "run out" of oil or other fossil fuels. In seeking a glimpse into the future, one always looks at the cost of incremental production from a given source. When that exceeds the then-prevailing costs of other wells or mines that produce fossil fuels, production at that source is suspended—either forever or until that source again becomes economical (e.g., owing to some technological advance). Indeed, the production of petroleum and other fossil fuels is a grand example of how the advance of technology has created pleasant surprises. The amounts of fossil fuels recoverable from the earth are determined by competition between depletion of the best resources and advances in technology that open up previously unavailable stocks. So far, technology has won this battle.

Table 2.4 shows that additions to petroleum reserves over the period 1944–1993 outpaced cumulative production. Table 8.2 shows estimates of the earth's resources of coal, petroleum, natural gas, tar sands, and oil shale, as well as peat and uranium as ²³⁵U. Such data are useful in making approximate comparisons of how much various energy resources may contribute to future consumption, as well as rudimentary forecasts of the time scale to deplete a set fraction of these resources under a prescribed drawdown schedule. Sample problem 8.1 illustrates such a calculation. However, any specification of a fixed value of a fossil-fuel resource automatically brings with it assumptions about how well technology can liberate the resource from the earth. Again, the record has always been in the direction of better and better technology liberating previously unrecoverable stocks. This will ultimately

Table 8.2
Estimates of Various Energy Resources on Earth, ca. 1999 (see also sample problem 8.1)

Fuel	10^{15} kJ ^a
Coal	290,000
Petroleum	2,600
Natural gas	5,400
Tar sands	5,700
Oil shale	11,000
Peat	3,000
Uranium (²³⁵ U)	2,600

^a 1 kJ = 0.948 Btu

change because the time scale for replenishment of naturally occurring fossil fuels is so much longer than any imaginable societal utilization time.

8.2.2 “Unconventional” naturally occurring fossil fuels

Two other categories of naturally occurring fossil fuels are “ultraheavy” (i.e., high-specific-gravity) oil and natural gas hydrates. Both are considered “unconventional” in that the form of their occurrence in the earth is substantially different from forms in which oil and natural gas are found. Both resources are of appreciable interest because the deposits are believed to be so large that, if they could be exploited, they would increase total global deposits of petroleum and natural gas severalfold.

Ultraheavy oil (Glasstone, 1982) is a highly viscous and dense mixture of hydrocarbons. Its viscosity (resistance to flow) is typically so high that less than 10% of the oil can be recovered from the earth by conventional pumping. To lower the oil’s viscosity, the oil is heated (e.g., by injecting steam from the surface of the well). The oil can also be heated *in situ* by injecting air to burn gas within the well or to burn some of the oil itself (called *fire flooding*). Combustion of the oil is maintained by continuously injecting air so that a slow-burning wave moves through the oil, heating it sufficiently to allow it to be pumped. Water may be introduced ahead of the burning front to yield hot water and steam to facilitate flow of the oil. In some locations, heavy oil is mined by penetrating oil deposits with holes that allow the oil to flow into collection sumps from which it is pumped to the surface. Heavy oil has a low H/C ratio and must be extensively processed to derive fuel products comparable in quality to present-day liquid transportation fuels (section 8.3.3).

Gas hydrates (Malone, 1990) are crystalline, icelike solid cages in which frozen water molecules surround natural gas. For certain ranges of temperature and pressure, natural gas hydrates form naturally in sediments beneath the earth’s oceans and permafrost. By some estimates, global deposits of natural gas hydrates are so vast that they may exceed all the earth’s other deposits of fossil fuels combined. The challenge is learning how to safely and economically harvest the natural gas locked up in hydrates. Natural gas is an attractive fuel because of its high H/C elemental ratio. However, it is also a potent GHG, and so fugitive emissions of natural gas to the atmosphere during recovery and processing need to be avoided. Moreover, in hydrates, there are many water molecules for each molecule of gas. Thus, it would be wasteful to “lift” the complete hydrate with all that water. Instead, we need to devise economical and efficient *in situ* processes to separate the natural gas from its water cage; then the gas can either be harvested for use above the surface or used in place (e.g., to produce electricity or hydrogen for transmission to *ex situ* locations where they can be used). The methane hydrates exist primarily in the deep ocean, but some are found in more accessible regions. By 2015, the first research-scale tests on promising concentrated deposits will be conducted by the

Sample problem 8.1a: Fossil-fuel lifetimes at present consumption rates

Question: Take coal as an example. If the world suddenly switched all its energy consumption to coal, how long could the estimated resource last?

Solution: Resource for world = $290,000 \times 10^{15} \text{ kJ} \times 0.948 \text{ Btu/kJ}$

$$= 275,000 \times 10^{15} \text{ Btu.}$$

$$\text{At world total energy consumption rate in 2010} = \frac{275,000 \times 10^{15}}{470 \times 10^{15}} = 585 \text{ yrs.}$$

Sample problem 8.1b: Fossil-fuel lifetimes with exponential growth in consumption

Question: What effect would growth in energy consumption rate have? With Q = energy, t = time, m = growth rate:

$$\frac{dQ}{dt} = ce^{mt}.$$

Solution: Take $t = 0$ at 1995 for convenience in data use:

$$\left(\frac{d}{dT} \right)_{t=0} = ce^{m(0)} = c = \left(\frac{dQ}{dT} \right)_{1995},$$

$$\frac{dQ}{dT} = \left(\frac{dQ}{dT} \right)_{1995} e^{mt}.$$

With Q_∞ ≡ the coal resource originally available (before any use), and $Q_\infty - Q_{1995}$ = resource yet to be consumed:

$$\int_{Q_{1995}}^{Q_\infty} dQ = \left(\frac{dQ}{dt} \right)_{1995} \int_0^{\Delta t_{\text{lifetime, growth}}} e^{mt},$$

$$Q_\infty - Q_{1995} = \left(\frac{dQ}{dt} \right)_{1995} \frac{1}{m} [e^{m\Delta t_{\text{lifetime, growth}}} - 1],$$

$$m \left\{ \frac{[Q_\infty - Q_{1995}]}{(dQ/dt)_{1995}} \right\} + 1 = e^{m\Delta t_{\text{lifetime, growth}}},$$

$$\Delta t_{\text{lifetime, growth}} = \frac{1}{m} \ln \{m\Delta t_{\text{lifetime, no growth}} + 1\}.$$

Take $m = 2\%$ /yr:

$$\Delta t_{\text{lifetime, growth}} = \frac{1}{0.02 \text{ yr}^{-1}} \ln \{(0.02 \text{ yr}^{-1})(585 \text{ yrs}) + 1\}$$

$$= 127 \text{ years (would be 97 years for 3%/year).}$$

Therefore, even small exponential growth can significantly reduce depletion times even for large resources.

US DOE on the Alaskan North Slope and by the Japanese MH21 project for the Nankai Trough deepwater gas hydrates (MIT, 2010).

8.2.3 Fossil resources and sustainability

As we established earlier, the driving force for sustainability is *not* that the world is running out of fossil fuels and needs to seek alternative energy sources. To the contrary, the weight of evidence is that the combination of known deposits exploitable with current technologies plus the opening of additional deposits through advances in technology will continue to keep pace with demand growth for many decades. However, alternative energy sources do need to be developed, preferably in the context of a sustainability view of earth-human ecology, for any or all of the following reasons:

- as insurance in case the higher levels of global warming predicted from a doubling of current atmospheric concentrations of CO₂ prove to be correct;
- as a means to smooth the transition to lower fossil dependency at whatever rate of transformation circumstances call for;
- as a way to diversify global sources of energy to prevent overreliance on any one source and the resultant vulnerability to source unavailability, whether due to political, environmental, regulatory, or technological factors.

8.3 Harvesting Energy and Energy Products from Fossil Fuels

8.3.1 Exploration, discovery, and extraction of fuels

Since coal deposits are plentiful and globally distributed, most coal companies focus on issues of extraction and bulk transportation. In contrast, major petroleum companies devote substantial resources to the so-called upstream portion of their industry (i.e., to finding additional exploitable deposits of oil and natural gas). Modern seismic and other technologies for illuminating underground and undersea geology are identifying previously well-camouflaged deposits of petroleum and gas for profitable development. Likewise, new generations of drilling and production hardware and software are liberating oil and gas from reservoirs that in the past were unassailable by human intervention. One example is deep-sea production. In the 1970s, offshore drilling was technically feasible only in water a few feet deep. By 2003, oil and gas were routinely produced from water depths of a mile or more.

8.3.2 Fuel storage and transportation

The storage and transport of fossil fuels pose considerable safety and environmental risks. (These topics are discussed in more detail in chapter 17.) Spills of liquid fuels, such as gasoline or liquefied natural gas (LNG), or pressurized releases of gases/

aerosols from liquefied petroleum gas (LPG) or natural gas can ignite and pose a risk of explosion, as can the combustion of solid fuels. Careless handling of fuels during shipment, loading, or unloading may create flammable or even explosive mixtures of the fuel with air at particular locations, so that the presence of an ignition source can instigate a catastrophic fire or explosion. Unfortunately, effective ignition sources are ubiquitous, and the risks of human injury or death, as well as property damage, can be substantial. Common ignition sources are tiny electrical discharges (sparks) formed by flipping a light switch or by relaxation of static electricity accumulated on a rubber conveyor belt or other electrically low-conducting material.

Fuel spills can also cause serious environmental damage. The tragic contamination of the Prince William Sound ecosystem by a major oil spill from the *Exxon Valdez* in 1989 and of the west coast of Spain by an oil tanker breakup in 2002 illustrate the tragic consequences of human or technological failures in environmentally sensitive areas. In 2010, a blowout during exploratory drilling in the Gulf of Mexico of a well at water depths of a mile led to an oil spill that caused significant damage to large ecologically sensitive areas; it was technologically challenging to stop and to mitigate its damages. Because every region of the planet is laden with its own unique ecological sensitivities and vulnerabilities, great caution must be exercised in planning and implementing the shipment of anthropogenic goods regardless of their location. The risk of human injury and environmental damage from fuel storage and transport can be reduced through modern technology and energetic vigilance by owners and operators to avoid human errors and prevent mechanical failures. However, the risk can never be entirely eliminated unless the activity itself is stopped. Once again, we witness a compelling example of the trade-offs in the real world of sustainable energy—finding the proper balance in protecting humans and their environment through regulations, monetary expenditures, and monitoring of employees' on-the-job performance to assure minimal risk in the production, storage, and transport of oil, natural gas, and other fossil fuels.

Economics are another issue in fuel storage and transport. Many otherwise attractive deposits of natural gas go undeveloped because it would be too expensive to ship the gas to consumers. Because shipping costs scale with volume, research and development have been spurred to increase the volumetric density of this so-called remote or stranded gas by economically converting it to useful liquid or solid fuels. (Recall that solids and liquids are about 1,000 times denser than gases at atmospheric pressure.)

8.3.3 Fuel conversion

Fuel conversion, known as fuel processing, is the chemical or physical transformation of a naturally occurring or already modified fuel to improve its quality. A fuel conversion process (figure 8.1) may result in one or more upgraded fuel products that may be solid, liquid, or gaseous, and may also generate chemicals or raw

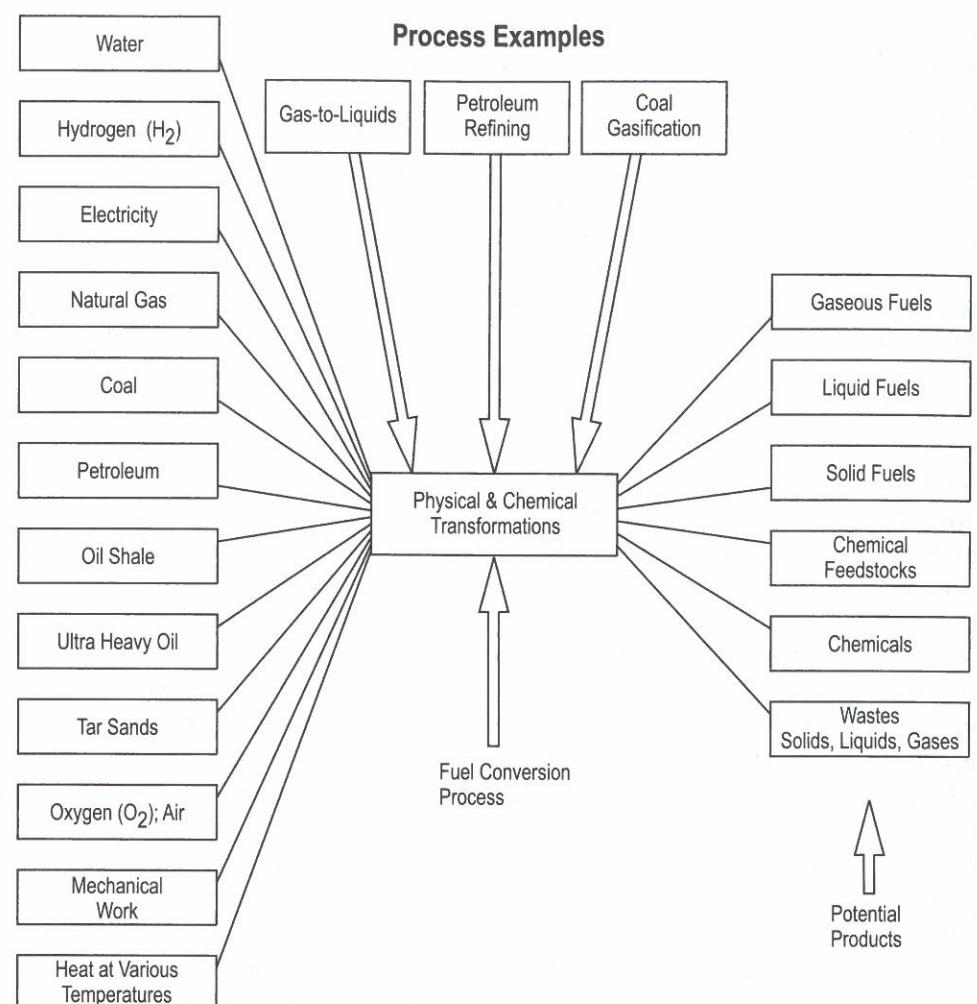


Figure 8.1

Typical inputs to and products of fuel conversion processes.

materials for chemical manufacture (chemical feedstocks). Each raw fuel feedstock has its own conversion requirements. Coal typically requires size reduction, washing, and removal of inert species. Natural gas may need removal of H_2S and CO_2 , along with separation of gas liquids such as LPGs and C_2 compounds. Petroleum refining and coal gasification are examples of more complex fuel conversion processes. Quality upgrades are typically driven by the need for a fuel that is more compatible with existing utilization equipment or by the need to remove environmentally offensive components in the fuel. Examples are the manufacture of automotive gasoline by “cracking” (thermal decomposition) of petroleum components in a refinery and removal of sulfur and nitrogen from liquid fuels by reacting the fuel with hydrogen. An example of a nonchemical conversion of a fuel is the fractional distillation of a crude oil to separate it into several fractions of different volatility (boiling point) ranges.

The essence of fuel conversion is the prescribed modification of fuel composition, chemically or physically, to augment fuel quality. In general, fuels of higher H/C ratio exhibit higher “quality” as measured by environmental impacts, ease of storage, handling, combustion (section 8.3.4), and overall consumer convenience. Two basic mechanisms of fuel conversion are the rejection of carbon and the addition of hydrogen. Often both are practiced in a comprehensive fuel conversion plant. The detailed design and operating requirements of a fuel conversion plant are dictated by the properties of the raw material (fuel) being processed, by the properties desired in the product (or refined) fuel, and by considerations of overall energy consumption, process economics, and process safety and environmental impacts.

Technology for fuel conversion has been studied for roughly a century. The art is highly sophisticated and successful for petroleum refining. Major progress has been made in coal conversion, in thermal extraction of oil from shale and tar sands, and in upgrading the liquids derived from coal, shale, and tar sands. There is still abundant opportunity to develop improved fuel processing technologies for all fossil substances (as well as nonfossil substances; see chapter 10).

There are also opportunities for applying biotechnology to fuel conversion (e.g., to removal of heteroatoms and improvement of volatility). However, thermal and catalytic (largely heterogeneous catalysis, i.e., fluid-solid processing) reactions dominate fuel conversion chemistry. Moreover, diverse physical separations are employed in fuel upgrading. Detailed information is found in Elliott (1981), Lowry (1963, 1945), Hottel and Howard (1971), Gary and Handwerk (2001), Satterfield (1991), and Shreve and Brink (1984). Recent progress can be found in publications from the US Department of Energy and the International Energy Agency. Katzer, Ramage, and Sapre (2000) summarize the historical trajectory of enabling technologies in producing liquid transportation fuels from petroleum, and provide

insight on expected technological changes such as diversification of the raw materials base to include natural gas.

Petroleum refining is currently the dominant technology for fuel conversion. Modern refineries convert crude oil to an array of fuels and other valuable products. Refining technology is remarkable in that it transforms a low-quality, highly complex mixture of naturally occurring and often polluted substances (i.e., hydrocarbons and affiliated compounds) to a host of clean fuels, chemicals, and other products essential to modern living. In a modern refinery, all of this is accomplished at modest expenditures of energy, in an environmentally sound manner, while generating products so inexpensive that they are readily accessible to most consumers. The details of petroleum refining are discussed in Gary and Handwerk (2001), Satterfield (1991), Shreve and Brink (1984), and Mark (1985). Katzer, Ramage, and Sapre (2000) look at where refining technology may take us in the first half of the twenty-first century.

All refineries perform a series of physical and chemical operations to achieve three basic functions that we will call the three Cs: *compartmentalization*, *conversion*, and *cleaning*. These operations may occur sequentially or together, and they may be repeated at different stages of refining (i.e., they may be applied to the crude oil and to various products generated from the oil). *Compartmentalization* denotes separation into simpler components. It is exemplified by fractional distillation of crude oil but also includes any of a number of separations that occur at various stages of product manufacture and cleaning throughout the refinery (e.g., separation of H₂ gas from CO₂). *Conversion* refers to modification of the chemical composition of fuels to instill desired properties (e.g., catalytic cracking of higher molecular weight fractions to obtain hydrocarbons suitable as gasoline components). *Cleaning* encompasses the removal of pollutants from the fuel (for example, catalytic hydrodesulfurization, hydrodenitrogenation, and hydrodemetalation, in which the dirty fuel is reacted with H₂ in the presence of a catalyst to reduce sulfur, nitrogen, and metals, such as Ni and V).

Although most refineries exhibit these essential features, each refinery is unique. Refineries must adapt their operations to accommodate appreciable variations in the quality of the crude oil they process. Moreover, refineries must adjust the yield and the specific properties of their various products to meet regional and temporal variations in customer and regulatory requirements. For example, in the US, refineries are “tuned” to produce more gasoline in the summer to meet the demands of increased driving and more middle-distillate-range fuel in the winter months to meet increased demands for home heating oil. More and more specialization of product quality over shorter and shorter time frames will be a trend for refineries of the future (Katzer, Ramage, and Sapre, 2000). In addition, US refineries must be operated to meet region-specific air quality regulations. Consequently, a refinery in

one part of the country with excess output cannot, without substantial adjustments, help allay shortages of fuel in a different region.

During the last 80 years, there has been substantial on-again, off-again interest in producing so-called substitute or synthetic fuels from coal and other nonpetroleum sources, such as oil shale and biomass (chapter 10). There is substantial governmental and industrial interest in developing technologies to use the vast coal resources of the US as raw materials for the production of clean fuels comparable in environmental quality and consumer convenience to petroleum-derived stocks. The Clean Coal Technology Program of the US Department of Energy exemplifies current efforts. Section 8.8 contains more discussion of emerging clean coal technologies. The term “synthetic fuels” is somewhat unfortunate because, for commercial use, fossil fuels are rarely used “as received” (i.e., they have undergone some measure of cleaning or other processing), and therefore most fossil fuels that we encounter are synthetic to some degree. A more precise nomenclature would be *non-petroleum-derived synthetic fuels*. As a compromise, we will refer to these as *substitute* or *alternative fuels*.

Historically, the development of technologies to manufacture alternative fuels has been motivated by concern that depletion of domestic supplies or political interference with access to foreign sources would create scarcity of petroleum or natural gas. More recently, environmental factors, such as carbon management and reduced sulfur emissions, have helped spur interest in the use of natural gas and of biomass (chapter 10) as raw materials for alternative fuels manufacture. At various times, the objectives of alternative fuels initiatives have been to manufacture cleaner, more versatile fuels from coal or oil shale.

Here, we illustrate basic processes for converting coal to various alternative fuels. Most processes entail thermal treatment, at some stage causing the coal to undergo *pyrolysis* (i.e., thermal decomposition in the absence of oxygen), producing a mixture of gaseous, liquid, and solid products in proportions that depend on the type of coal and on the treatment conditions (figure 8.2). Although each of these products could be used as fuels, they generally require further processing to be compatible with today’s utilization equipment and environmental requirements.

Pyrolysis itself can be a coal conversion process, and many technologies have been developed to actualize pyrolysis commercially. The most common and successful process is the manufacture of metallurgical coke for steelmaking. There have been a plethora of process variations, including heating the coal in the presence of hydrogen (*hydropyrolysis*) and combining pyrolysis of the coal with downstream processing or combustion of (some of) the pyrolysis products.

Coal liquefaction involves converting coal, a solid at room temperature, to a liquid suitable, either directly or with further upgrading, as a substitute for petroleum-derived, consumer-grade liquid fuel. Coal is deficient in hydrogen, a

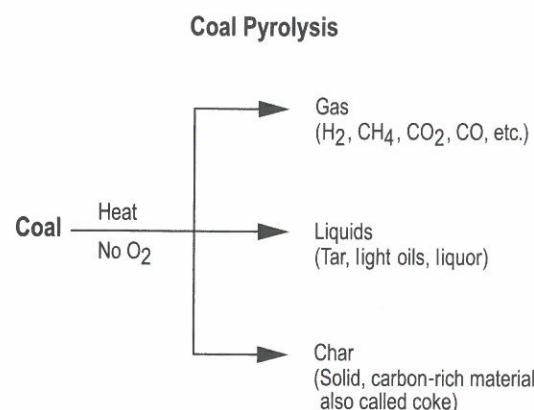


Figure 8.2
Schematic of coal pyrolysis showing three major product categories.

typical empirical formula being CH_{0.8} versus CH_{1.8} for diesel fuel or No. 2 fuel oil used to heat single-family homes. Thus, coal liquefaction entails the rejection of carbon or the addition of hydrogen, or both. Pyrolysis is a carbon rejection process (figure 8.2) and produces a liquid (tar), so pyrolysis is a means of coal liquefaction. In general, coal pyrolysis tars require further upgrading before they are suitable as petroleum-substitute fuels. Another means of coal liquefaction entails reaction of the coal, perhaps slurried in coal-derived oil, with hydrogen:



Although only a schematic equation, reaction (8.2) provides a lot of information about the requirements of coal liquefaction technology. Note that the key to a good liquefaction process is having an adequate source of low-cost hydrogen to upgrade the coal. This typically means having a good coal gasification process, because in most cases, unless there is access to low-cost natural gas, the H₂ needs to be manufactured by gasification of the coal (see below). Note also that there are coproducts, including solids and gas. The gas may include H₂S, NH₃, or HCN formed by reaction of hydrogen with S and N from the coal. These gases would need to be separated from the liquid products and processed further to extract valuable products, such as elemental sulfur and ammonia for conversion to fertilizer or other substances. Somewhat paradoxically, solid by-products are a major challenge in coal liquefaction technology. They consist of inorganic matter in the coal, which cannot be converted to hydrocarbon liquid, as well as solids derived from the organic portion of the coal. These solids need to be separated from the liquid product so that the latter can be conveniently pumped and used in modern combustion equipment. If possible, these solids are used in road paving or similar applications, or they are

Table 8.3
The Basic Chemical Reactions for Simulation of Coal Gasification Chemistry^a

C(s) + H ₂ O(g) → CO(g) + H ₂ (g)	(8.3)
CO(g) + 2H ₂ O(g) → CO ₂ (g) + H ₂ (g)	(8.4)
C(s) + 2H ₂ (g) → CH ₄ (g)	(8.5)
C(s) + ½O ₂ (g) → CO(g)	(8.6)
C(s) + H ₂ O(g) → ½CH ₄ (g) + ½CO ₂ (g)	(8.7)
CO(g) + 3H ₂ (g) → CH ₄ (g) + H ₂ O(g)	(8.8)
C(s) + O ₂ (g) → CO ₂ (g)	(8.9)

Source: Adapted from Hottel and Howard (1971).

^a A reasonable empirical formula for the organic, i.e., nonmineral portion of coal is CH_{0.8}S_xN_yO_z, where x, y, and z vary but typically are each < 0.1. Here, for simplicity, coal mineral matter is neglected and the organic fraction of coal is represented as solid elemental carbon C(s), often taken as graphite in thermodynamic calculations.

disposed of as wastes. The gas by-products can be separated and burned to provide some of the energy needed for the process.

Coal gasification is the production of gas from coal. Table 8.3 summarizes the major chemical reactions that occur in coal gasification, with the recognition that coal is approximated by solid carbon (see footnote to this table). Reaction (8.3) is endothermic (i.e., it requires an input of energy to proceed from left to right as written). The energy needed to drive reaction (8.3) can be generated by a suitable heat-liberating (exothermic) chemical reaction. Examples are burning some of the coal, partially to form CO (reaction (8.6)) or more fully to form CO₂ (reaction (8.9)). These reactions can occur in a separate section of the gasifier or in a separate reactor equipped with some means to transfer the heat back into the gasifier. Reaction (8.4), the water-gas shift reaction, is important in fuels technology as it provides a simple means of generating hydrogen from carbon monoxide merely by reacting it with steam at temperatures between 500° and 1,000°C. Reaction (8.5) depicts direct production of methane by so-called hydrogasification (i.e., reacting the coal directly with hydrogen gas).

In the US in the late 1960s and early 1970s, many observers believed that substitute or synthetic natural gas (SNG) from coal would be needed because conventional domestic natural gas reserves appeared to be nearing depletion. This precipitated substantial R&D by government and the private sector to develop technically and economically viable means to capitalize on basic gasification chemistry. Reaction (8.7) is the result of reactions (8.3), (8.4), and (8.5), and depicts every coal-gasification technologist's "dream" reaction, namely the direct production of methane by reacting coal with steam in a single step. Unfortunately, this reaction is slow at temperatures where thermodynamics favor a decent yield of methane, ca. 500°C, and so a suitable catalyst would be needed to accelerate the reaction rate without going to higher temperatures unfavorable to methane production.

A “suitable” catalyst would be one that is inexpensive or readily separable and recoverable from the reacted (gasified) coal and without interference or catalyst poisoning by the coal mineral matter. In the 1970s, the Exxon catalytic gasification process accomplished this to a high degree of technical success, but the process was never commercialized at large scale due to declining interest in producing SNG from coal.

Reaction (8.8) is another process chemistry for making methane from coal, this time indirectly, in that the reactants are gases, CO and H₂, that can be produced from coal, e.g., by reactions such as (8.3), (8.4), and (8.6). Reaction (8.8) is referred to as *methanation*. As with reaction (8.7), it is slow at temperatures sufficiently low to obtain high yields of methane, and it also requires a catalyst. Moreover, reaction (8.8) releases tremendous amounts of heat, and, because reaction (8.8) operates at low temperatures, this heat emerges at a low “availability” (i.e., it cannot be used to directly drive other reactions in coal gasification that require a high temperature, such as reaction (8.3)). Some of the heat can be recovered to preheat coal and steam fed to a gasification reactor. (Note that reaction (8.8) is the same as reaction (8.5) subtracted from reaction (8.3).)

Figure 8.3 shows the wide range of gas heating values obtainable by coal gasification. Low-heating-value gas¹ is of interest for electric power generation at locations proximate to the gasifier because its low quality precludes economical shipment over extended distances (e.g., >100 miles). Intermediate-heating-value gas can be stored and shipped more economically because of its higher energy density. Suitable applications are power generation and industrial process heat. Synthesis gas is a mixture of H₂ and CO in various proportions. Many valuable fuels, including high-heating-value gas (mainly methane, see reaction (8.8) and table 8.1) and chemicals, can be manufactured by reacting synthesis gas with the appropriate H₂/CO ratio over a suitable catalyst (figure 8.4).

Over the last twenty-five years, there has been substantial interest in the development of technologies to convert natural gas to liquid fuels capable of displacing petroleum-derived transportation fuels, in particular diesel and gasoline. Drivers include the known and probable deposits of natural gas throughout the world. Some of this gas is in remote locations and would require densification for economical shipment to major markets. Other deposits are of so-called unconventional gas such as hydrates, but these could potentially swamp all known petroleum deposits.

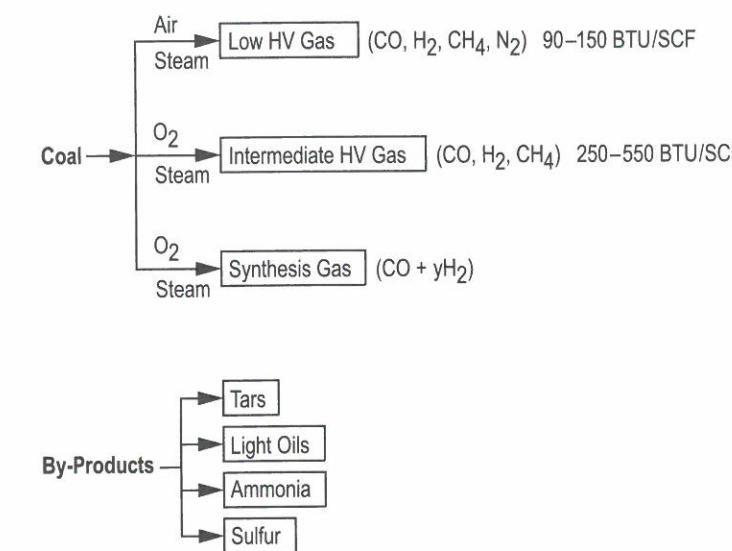


Figure 8.3
Major products and by-products of coal gasification with steam, using various process options.

Sample problem 8.2

Question: What is the mass of (a) 0.5 g mole of carbon dioxide, and (b) 0.25 g mole of water vapor?

Solution: First find the molecular weights.

For CO ₂ :	1 atom C × atomic wt of C	1 × 12 = 12
	2 atoms O × atomic wt of O	2 × 16 = 32
		Total = 44
For H ₂ O:	1 atom O × atomic wt of O	1 × 16 = 16
	2 atoms H × atomic wt of H	2 × 1 = 2
		Total = 18

$$\text{Part (a): } 0.5 \text{ g mole} = 0.5 \times \text{MW in g} = [0.5 \text{ g mole CO}_2] \times [44 \text{ g CO}_2/(\text{g mole CO}_2)] = 22 \text{ g}$$

$$\text{Part (b): } 0.25 \text{ g mole} = 0.25 \times \text{MW in g} = [0.25 \text{ g mole H}_2\text{O}] \times [18 \text{ g H}_2\text{O}/(\text{g mole H}_2\text{O})] = 4.5 \text{ g}$$

¹ Low-heating-value gas means gas with less energy per unit weight or volume than higher-specific-energy gaseous fuels. It is different from the physical properties denoted as HHV (higher heating value) and LHV (lower heating value), which measure the amount of energy that can be extracted from completely combusting a fuel and cooling the products of combustion to ambient temperature. The HHV assumes that water vapor is condensed to liquid, releasing additional energy. The LHV assumes that the water vapor remains gaseous at ambient temperature.

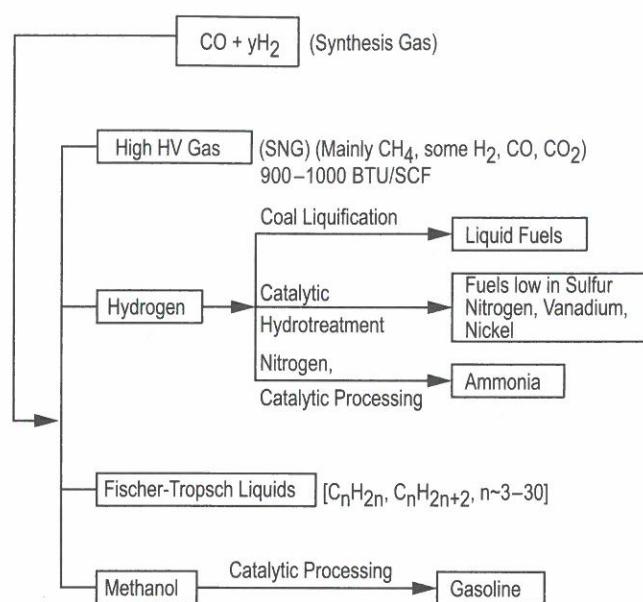
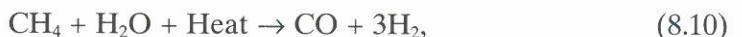


Figure 8.4
Examples of the wide variety of fuels and chemicals obtainable from synthesis gas.

Thus, technology to transform natural gas to storable and transportable liquid fuels capable of displacing petroleum-derived premium transportation fuels could have appreciable market appeal. Moreover, there are indications that substitute diesel of higher environmental quality than petroleum-derived diesel, in particular with near-zero sulfur and nitrogen content, can be manufactured from natural gas. (Schmidt et al. (2001) elaborate on the opportunities.) Here, using methane as a proxy for natural gas, we describe one of the basic approaches to *gas-to-liquids* fuel conversion, namely steam reforming of the gas to make synthesis gas, followed by Fischer-Tropsch (FT) catalytic synthesis of premium liquid fuels:



The quantity y denotes that different H_2/CO ratios are selected in FT processing according to the desired product.

Sample problem 8.3

Question: Estimate the amount of carbon dioxide, in lbs and in SCF, emitted by completely burning one gallon of gasoline with the following chemical analysis: 85.7% carbon and 14.3% hydrogen. Assume the only products of combustion are water and carbon dioxide and that the carbon dioxide behaves as an ideal gas.

Solution: We first need to find a chemical formula for the gasoline, so that we can then write a chemical equation for combustion of this fuel. Even though a gallon of gasoline has a mass of roughly 7 lbs, to make the calculations easier in finding the chemical formula, assume that we have 100 lbs of this gasoline. Then, from the analysis we know that there are 85.7 lbs of carbon and 14.3 lbs of hydrogen atoms in this gasoline. To find the corresponding number of each carbon and hydrogen atom, we simply divide by their atomic weights:

$$\text{Number of C atoms} = (85.7 \text{ lb C})/(12 \text{ lb C/lb-atom C}) = 7.14 \text{ lb atom C},$$

$$\text{Number of H atoms} = (14.3 \text{ lb H})/(1 \text{ lb H/lb-atom H}) = 14.3 \text{ lb atom H}.$$

The chemical formula for the gasoline is $\text{C}_{7.14}\text{H}_{14.3}$, or, normalizing to 1 atom of C, $\text{C}_{14.3/7.14} = \text{CH}_2$.

Assuming only H_2O and CO_2 as combustion products, the chemical reaction for combustion is:



Here y is an unknown *stoichiometric coefficient* equal to the number of moles of molecular oxygen needed so that the chemical reaction accurately accounts for all the atoms of each element involved in the combustion process. To compute y , we must “balance” this chemical reaction, which means that we must find the value of y so that the number of oxygen atoms is the same on both sides of the equation. This is already the case for the atoms of H and of C, but in more difficult problems it may be necessary to perform individual balances for several elements (i.e., to solve simultaneously for two or three or even more unknown stoichiometric coefficients). Equating the number of oxygen atoms on the left- and right-hand sides of the equation, we find:

$$2y = 2 \text{ (oxygen atoms from CO}_2\text{)} + 1 \text{ (oxygen atom from H}_2\text{O)} = 3, \text{ i.e., } y = 1.5,$$

and equation (8.3-1) becomes:



This chemical equation tells us that complete combustion of 1 lb mole of this particular gasoline in pure oxygen emits 1 lb mole each of water and of CO_2 . Note that if a ton mole of this gasoline were burned, the mass of water and CO_2 emitted would each be 1 ton mole. The present problem asks how much CO_2 is emitted by burning a gallon of gasoline, so we need to know how much mass is in 1 gal of gasoline; i.e., we need to know its mass density, ρ_m . A typical value is roughly 7 lb/gal. To use equation (8.3-2), we also need to compute how many lb moles of gasoline are in a gallon. As in sample problem 8.2, first find the MW:

For CH_2 :

1 atom C × atomic wt of C	$1 \times 12 = 12$
2 atoms H × atomic wt of H	$2 \times 1 = 2$
	Total = 14

Then from equation (8.3-2) we have:

$$(44 \text{ lbs CO}_2)/(14 \text{ lbs gasoline}) \times (7 \text{ lbs gasoline})/(1 \text{ gal gasoline}) = \\ 22 \text{ lbs CO}_2/\text{gal of gasoline}.$$

To express this as standard cubic feet of CO_2 , we then make the following conversion:

$$(22 \text{ lbs CO}_2)/(\text{gal of gasoline}) \times (1 \text{ lb mole CO}_2)/(44 \text{ lbs CO}_2) \times \\ (380 \text{ SCF CO}_2)/(1 \text{ lb mole CO}_2) = 90 \text{ SCF of CO}_2.$$

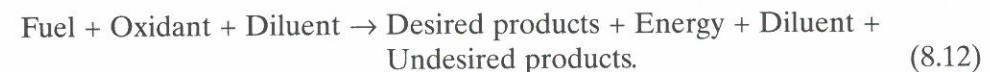
8.3.4 Fuel combustion

Combustion is the rapid release of heat by chemical reaction(s). The reactants are always a fuel (see section 8.3.3) and almost always a separate substance, an *oxidant*, which converts the chemical potential energy of the fuel to thermal energy. Combustion is enabled by feedback of some of its own output (e.g., energy, material, fluid motion, or various combinations). This is the case whether a small portion of fuel is burned over a short time (batch combustion), as occurs in the cylinder of an internal combustion engine (chapter 3), or fuel is continuously burned over many hours or longer, as occurs in a coal- or natural-gas-fired electricity utility boiler. Thus, combustion is inherently a feedback process. This feedback creates and maintains an environment in which fuel and oxidant are continuously “mixed” (i.e., brought into chemical intimacy) for temperatures and times needed to sustain the desired fuel-oxidant reactions. The energy feedback can occur by thermal radiation from the flame to the unignited combustible mixture, or by recirculated flow of hot combustion products entrained into the unignited turbulent fuel/air jet stream.

Other than rocket propulsion, most practical combustion reactions that produce energy for useful purposes involve combining the fuel with a source of molecular oxygen, typically air itself (a mixture of approximately 79 vol % N₂ and 21 vol % O₂) or oxygen-enriched air (air in which the percentage of oxygen exceeds 21%, up to essentially pure oxygen). For several reasons, a basic comprehension of combustion is essential to understand the challenges and opportunities of sustainable energy:

- Combustion is the dominant means of transforming fossil fuels (and biomass; see chapter 10) to other useful forms of energy and is virtually certain to remain so, even with major technological and marketing gains by fuel cells (see section 8.3.5).
- Combustion is the major source of anthropogenic emissions of carbon dioxide to the atmosphere.
- Uncontrolled combustion generates diverse pollutants with adverse ecological and human health impacts.
- Current scientific and engineering understanding of combustion is sufficient to allow design and operation of efficient, low-environmental-impact stationary (Beér, 2000) and mobile (Heywood, 1988) combustors.
- Combustion technology will continue to improve at an evolutionary rather than revolutionary rate, but with sufficient dispatch to keep pace with demands for increasingly better environmental performance.

Reaction (8.12) depicts a generalized combustion reaction in a form that illuminates issues relevant to sustainable energy:



Rapid release of the chemical potential energy of the fuel is essential to combustion (i.e., energy obtainable by breaking and/or forming *chemical bonds*). Continuous combustion requires that this release be self-perpetuating. In reaction (8.12), the *oxidant* is a chemical reactant that converts the chemical potential energy of the fuel into thermal energy. In general, the oxidant is initially separate from the fuel (although some “fuels,” such as the explosive TNT, come with their own “built-in” oxidant as part of the fuel molecule). The most common oxidant in energy practice is molecular oxygen (O₂), but a variety of solid, liquid, and gaseous substances can be oxidants. A *diluent* is a component of a combusting mixture that does not participate chemically in the main combustion reactions as either a fuel or an oxidant. The most common combustion diluent in practice is molecular nitrogen N₂, in air, but again, various solids, liquids, and gases may function as combustion diluents. In newer power plant designs that burn fuel in pure oxygen to facilitate the capture of CO₂ from the stack gases, CO₂ is recycled to the inlet oxygen stream as a diluent to control the temperature of the combustion process. Diluents can strongly influence the temperature, efficiency, and the environmental performance of combustion. They can serve as parasitic sinks for the energy liberated by combustion, causing energy to be lost as waste heat as diluent gases emerge from the combustor exhaust. Moreover, diluents can be a source of adverse emissions; perhaps the best example is nitric oxide, formed at high temperature by reactions of N₂ diluent with labile combustion intermediates, such as oxygen atoms, e.g.:



Reactions (8.13) and (8.14) are known as the Zeldovich “atom shuttle” reaction of “thermal NO” formation and allow the cycle to perpetuate as long as N₂ and O₂, i.e., air, is available.

Note that if combustion involved fuels containing only carbon and hydrogen in pure oxygen and worked perfectly, the only emissions product of concern would be CO₂. Concerns about this emission and its interactions with the climate are leading to major efforts to capture and sequester carbon emissions in order to help enable our continued future use of fossil fuels as energy sources (see section 8.4.3 as well as 4.3.5). The idealized case of burning perfectly pure methane, reaction (8.1), illustrates the point. However, reaction (8.12) better captures the reality that

combustion always creates some undesired products. These arise because of pollutants in the fuel and because combustion is an imperfect process. The amounts of unwanted coproducts and their propensity to cause environmental malfeasance will depend on the composition and inlet ratio of the fuel and oxidant, the amounts and types of diluents, and the specific forms of combustion behavior.

To gain an understanding of these ideas, we will examine steady combustion. For a given amount of fuel, there must be sufficient oxidant to fully combust all of the fuel, i.e., to chemically transform each of its reactive elements (generally carbon and hydrogen in practical fuels for energy production) to their highest oxidation state, i.e., CO_2 and H_2O , respectively. Next, combustion must release its energy fast enough to (a) heat up the fuel and oxidant (and any diluents) at least to a minimum temperature at which the enabling chemical reactions are sufficiently rapid to sustain the feedback(s) necessary to maintain combustion; and (b) compensate for heat and other forms of energy, such as the work of gas expansion, withdrawn or unavoidably lost from the combustion environment. Combustion energy is the product of chemical reaction(s) between the fuel and the oxidant. Thus, for any form of combustion, the requirements for a chemical reaction must be satisfied.

First, there must be physical contact between molecules of the fuel and the oxidant (i.e., there must be good molecular-level mixing—*micromixing*—between the two). In some combustors, the fuel and oxidant are mixed ahead of time or before these reactants have been heated to the combustion temperature. In others, the combustion equipment mixes the fuel and oxidant. Often, mixing is promoted by creating *turbulence* within and between flows of fuel and oxidant. Turbulence is fluid motion in which macroscopic, random (in both magnitude and direction) fluctuations in fluid properties, such as velocity and pressure, and potentially in temperature and density as well, are superimposed upon the main stream motion, resulting in eddying motions of the fluid and attendant mixing over length scales that are large compared to molecular dimensions.

Second, the reactants must be able to react fast enough to achieve the desired heat release rates. Because rates of chemical reactions increase with temperature, the fuel and oxidant must be heated up at least to a minimum temperature for fast reactions. Then the reactants must remain at this temperature for sufficient time for combustion to proceed essentially to 100% completion (i.e., the point in time at which most of the fuel has been productively consumed). We can summarize these requirements in terms of the three Ts of combustion: *temperature*, *time*, and *turbulence*, where the last is a proxy for mixing. The situation is depicted schematically in figure 8.5 for combustion of a single particle or droplet of fuel. Heat, fed back from combustion of the already burning fuel, raises the temperature of the particle or droplet. Moisture is evaporated and then combustible components in the fuel vaporize, owing to evaporation or to chemical decomposition creating volatile

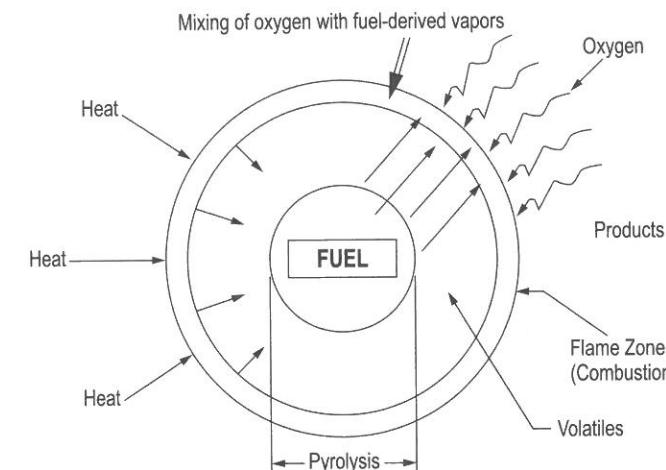


Figure 8.5

Schematic depicting heat transfer, the mixing of fuel vapors with oxidant (oxygen), and two regions of chemical reactions (pyrolysis and the flame zone), in the combustion of an individual particle or droplet of fuel.

products (or to both). These components migrate away from the fuel particle (droplet) and at some point come into contact with oxidant vapor (O_2 gas) and react, forming a combustion zone. This “region of burning” may surround the entire fuel particle (droplet), creating a so-called circumambient flame. Sufficient time must be allowed for combustion to proceed. Depending on the geometry and operating conditions of the combustor, mixing of fuel vapors and oxidant vapors may occur only by nonturbulent processes (e.g., molecular diffusion) or turbulent mixing may also play an important role. Note that while combustion always requires chemical changes, the operation of most practical combustors also requires contributions from the physical transport of heat, material, and momentum, with momentum transfer being the mechanism of macroscale mixing of the combustion fluids.

Figure 8.6 depicts a typical temperature-time history for the surface of a fuel particle or droplet heated from room temperature to a temperature high enough to allow stable combustion of a steady feed of such particles. The heating rates in practical combustors can be enormous. For example, a modern electric utility boiler heats up powdered coal (roughly $74 \mu\text{m}$ particle size) at a rate of $10,000\text{--}15,000^\circ\text{C/s}$. Pyrolysis of such small particles is complete in about 100 ms; burnout of the resulting char occurs in about 1 s.

In oil boilers and furnaces where the fuel is injected as an aerosol, the droplets do not burn as individual particles because they first vaporize in a fuel-rich flame zone. Then the generated vapor burns as a turbulent gaseous diffusion flame.

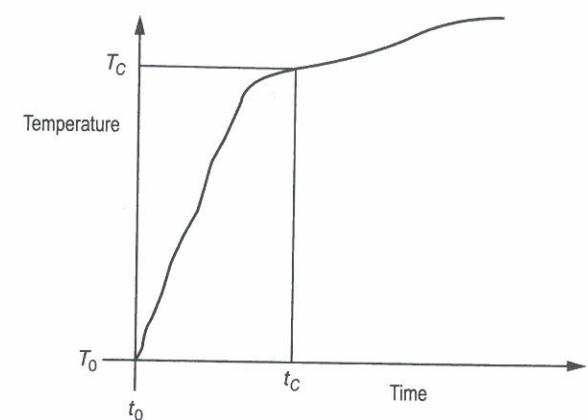


Figure 8.6

Schematic of a typical temperature-time history of the surface of a fuel particle or fuel droplet undergoing combustion (see figure 8.5). T_c is the minimum temperature that enables rapid and self-sustaining oxidation of the fuel vapors; t_c is the time it takes to reach this temperature, assuming the fuel was initially at a temperature T_0 .

Figure 8.7 illustrates a model of a spray combustion process. Some large droplets may survive the fuel-rich zone and burn with an envelope flame around them (as in figure 8.5), but over 95% of the fuel burns as a diffusion flame.

The basic reaction kinetics for NO formation are slower than those for the combustion reactions, but become more important at higher temperatures. In fact, in the 1960s, the quality of a combustion process (good mixing and high combustion temperature) was monitored using NO as an indicator. The formation of NO in combustion processes can involve several different pathways:

- In fuel-lean flames, nitrogen oxides (“thermal NO”) form by the attack of O atoms or OH⁻ radicals on molecular nitrogen in the air, as shown in reactions (8.13) and (8.14). These reactions are highly temperature-dependent; at 1,800 K the reaction rate doubles for every 35 K temperature rise.
- In fuel-rich regions of hydrocarbon-air flames, NO is formed by the attack of hydrocarbon radicals on molecular nitrogen, producing first HCN and then NO. This is a fast reaction that occurs at the flame front and produces what is termed “prompt NO.” Prompt NO formation is not strongly temperature-dependent.
- In combustion of fuels that contain organically bound nitrogen in their molecules (coals and oils), the pyrolysis and oxidation of these heterocyclic nitrogen compounds readily form NO in fuel-lean flame regions (“fuel NO”). The

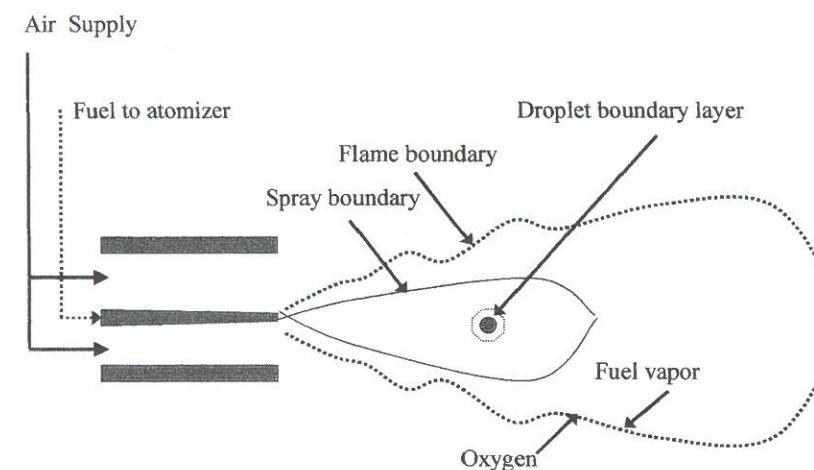


Figure 8.7

Typical behavior of atomized oil spray droplet flames in oil burners.

good news is that pyrolysis of these fuels for some extended residence time (100–300 ms) at high temperatures can convert these nitrogen species first from cyanides to amines, and then to N₂, which renders them innocuous for NO formation.

Examination of the chemical reaction paths and kinetics of nitrogen compound interconversions in flames has opened the opportunity for controlling NO emissions through process modifications. Some of these modifications include:

- reducing peak temperatures in fuel-lean combustion by heat extraction and/or by flue gas recirculation in boilers and furnaces. In gas turbines, NO formation can be greatly reduced by the use of a premixed ultralean feed stream.²
- staging the combustion air and/or the fuel injection to produce fuel-rich/fuel-lean flame zones that create conditions favorable for the conversion of fuel-bound nitrogen to molecular nitrogen.

Figure 8.8 schematically depicts a gas turbine–steam turbine (GT-ST) combined cycle for combustion of natural gas and other clean fuels. This cycle is used

² In gas turbines, the inlet temperature is limited by the structural integrity of the machine to about 1,570 K. At this temperature, an ultralean feed mixture will produce negligible NO over the short residence time (about 20 ms) in the gas turbine combustor. The problem is that this flame temperature is close to the lean limit of flammability. The combustion technologist and the turbine designer are challenged to reconcile the conflicting requirements of low NO_x emissions and good flame stability over a wide range of operation.

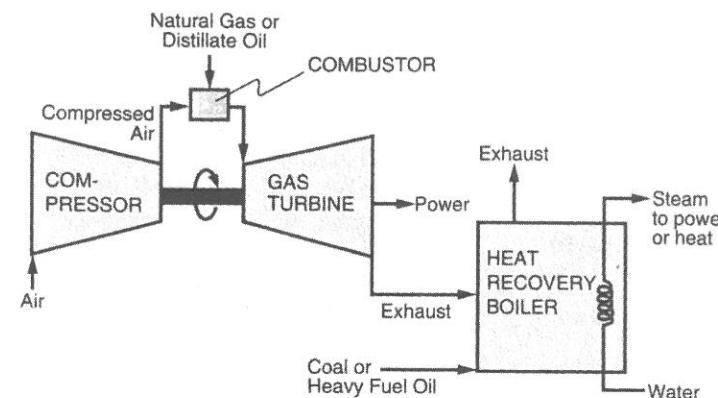


Figure 8.8

A schematic of a gas turbine–steam turbine combined cycle. Source: Beér (2000). Reprinted with author's permission.

extensively to generate electric power because it has relatively low capital cost and provides low-cost electricity even with high natural gas costs. (Quantitative details on these costs are presented in section 8.6.) A GT-ST generation scheme integrates the Brayton and Rankine cycles (chapter 3) and provides fuel-to-electricity generation efficiencies of about 60% with low NO_x emissions. Moreover, these cycles allow for incremental expansion of generation capacity in relatively small stages, avoiding the huge capital outlays of large nuclear and coal-fired plants. These cycles *do* require clean fuels, such as natural gas, petroleum middle distillates, or methanol.

The most typical example of a coal-fired power plant is sketched in figure 8.9. As discussed in chapter 3, this is a basic steam generator with a turbine that exhausts to a heat exchanger where spent (i.e., decompressed) steam is condensed and pumped up to pressure again. Typical operating efficiencies for such plants are about 35%, based on the lower heating value (LHV) of the fuel.

A more modern type of coal power plant utilizes a pressurized-fluid-bed combined cycle design as depicted in figure 8.10. Such plants are much more integrated for energy recovery than the basic plant and are capable of achieving 50% efficiencies, depending on the details of the design. As discussed in chapter 3, there are many possibilities for energy integration and other efficiency improvements in power plants, and individual designs vary considerably. Technology improvements have gradually increased the efficiency of coal-fired power generation by up to 1% per year over the past decade.

8.3.5 Direct generation of electricity: Fuel cells

A fuel cell can be thought of as an “electrochemical combustor.” Hydrogen or some other fuel is still oxidized, some heat is still released, and, as in any chemical

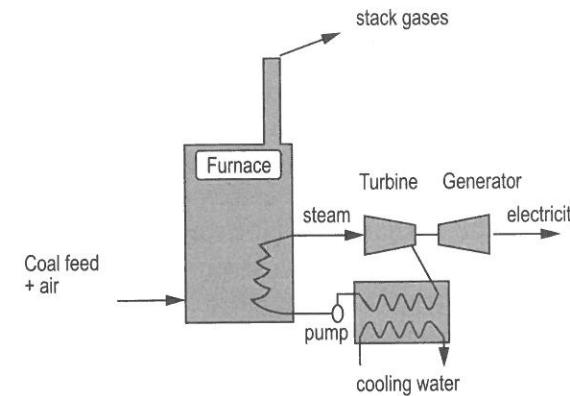


Figure 8.9

Typical coal plant.

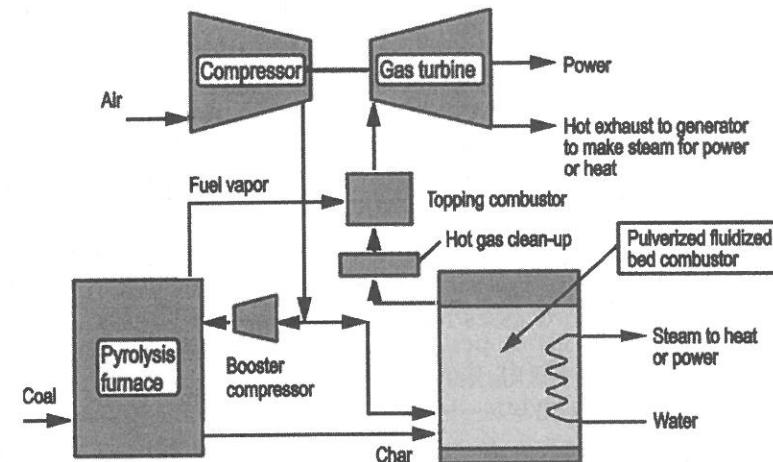


Figure 8.10

Typical pressurized-fluid-bed combined cycle.

reaction, electrons are exchanged (i.e., chemical bonds are broken). However, in a fuel cell, the fuel and the oxidant react separately in different regions that are connected to each other by two different conduits for charged particles. Each region contains a solid surface, an electrode, at which either the fuel is oxidized by giving up electrons or at which the oxidant is reduced by accepting electrons. The electrode for fuel oxidation is the anode, and the electrode for oxidant reduction is the cathode. In the fuel cell, the exchange of electrons among the reactants (the fuel and the oxidant) occurs through an electrical circuit outside the cell. The fuel cell converts chemical potential energy to usable electrical energy in the form of moving electrons. For electrons to journey through the external circuit, they must overcome any electrical barriers (impedance) to their transmission (i.e., they must do electrical work). Electrochemical reactions for use in fuel cells are purposely chosen so that the amount of electrical work attainable is sufficient to overcome the resistance to electron flow inherent in any circuit, but also to allow the electron flow to carry out useful electrical tasks (e.g., operating a motor or light bulb). The second conduit for charged particles is inside the cell and is called an “electrolyte.” This can be an aqueous or other solution, a solid polymer, or an ion-conducting ceramic. Its job is to allow charged particles much more massive than electrons to pass between the two electrodes; e.g., the particles could be positively charged hydrogen atoms, H^+ (if the electrolyte is an acidic solution); negatively charged hydroxyl ions, OH^- (if the electrolyte is a basic solution); or negatively charged oxygen, O_2^- (if a solid oxide ceramic is used).

Figure 8.11 shows a schematic of a fuel cell in which hydrogen (H_2) is converted to electricity using oxygen (O_2) as the oxidant and an acidic electrolyte. The essential chemical and physical processes for this cell to operate follow:

1. Oxidation of gaseous $H_2(g)$, the fuel, at a region of the anode in interfacial contact with the electrolyte:



2. Physical transport of the hydrogen ion from the anode through the electrolyte to the cathode:



3. Reduction of gaseous O_2 , the oxidant, at a region of the cathode in interfacial contact with the electrolyte:



4. Physical transport of electrons from the anode to the cathode through the external circuit:

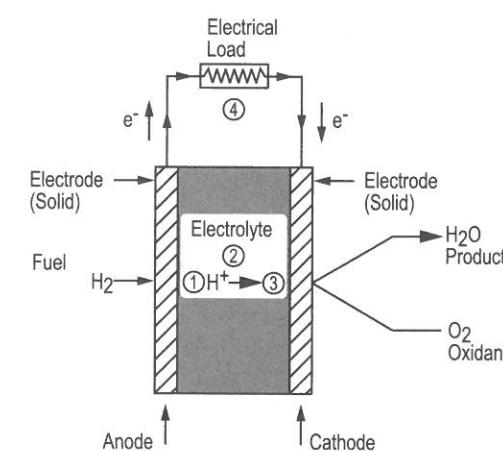
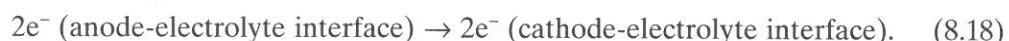


Figure 8.11
Schematic of a hydrogen-oxygen fuel cell with an acidic electrolyte and H^+ as the transfer ion.
D. Sadoway, personal communication, 1999.



Note that if we add up reactions (8.15) to (8.18), we get the same overall reaction as if we had directly combusted hydrogen in oxygen:



The difference is that, through use of the fuel cell, we are able to directly generate electricity. Fuel cells now command great interest as clean energy converters for use in producing electricity for consumers and as the energy source for electric vehicles. This interest is motivated by the potential for high fuel-to-electricity conversion efficiencies and by the fact that fuel cells fired with hydrogen emit only water. Table 8.4 summarizes several of the common types of fuel cells under development for stationary electric power and automobile propulsion applications, together with estimates of their fuel-to-electricity conversion efficiencies (assuming H_2 as the fuel). The ion flowing within the electrolyte may be H^+ or any of several negatively charged species (anions), e.g., OH^- , CO_3^{2-} , or O_2^- (the anions flow from the cathode to the anode). Advanced electrolyte systems (i.e., proton-conducting inorganic oxides) may enable fuel-to-electricity efficiencies as high as 70% based on H_2 and its LHV. Fuel cells are also attractive because of their high reliability, low noise levels, and potential for low maintenance. Because they operate at lower temperature than typical combustion processes, they do not produce NO_x emissions from reactions involving N_2 diluent in air (see reactions (8.13) and (8.14)).

Table 8.4
Summary of Common Fuel Cell Technologies

Fuel Cell	Anode Reaction	Electrolyte	Transfer Ion ^a	Operating Conditions		
				Cathode Reaction	Temperature (°C)	Pressure (atm)
Proton exchange membrane (PEM) ^b	H ₂ → 2H ⁺ + 2e ⁻	Solid polymer	H ⁺	2H ⁺ + ½O ₂ + 2e ⁻ → H ₂ O	80–100	1–8 ^c
Phosphoric acid (PAFC)	H ₂ +2OH ⁻ →2H ₂ O+2e ⁻	Phosphoric acid	H ⁺	2H ⁺ + ½O ₂ + 2e ⁻ → H ₂ O	150–250	1–8 ^c
Alkaline (AFC)	H ₂ → 2H ⁺ + 2e ⁻	Aqueous base	OH ⁻	H ₂ O + ½O ₂ + 2e ⁻ → 2OH ⁻	80–250	40
Molten carbonate (MCFC)	H ₂ +CO ₃ ²⁻ →H ₂ O + CO ₂ +2e ⁻	Molten salt (metal carbonate)	CO ₃ ²⁻	CO ₂ + ½O ₂ + 2e ⁻ → CO ₃ ²⁻	600–700	50–60+
Solid oxide (SOFC)	H ₂ + O ²⁻ → H ₂ O + 2e ⁻	Solid ceramic oxide	O ²⁻	2H ⁺ + ½O ₂ + 2e ⁻ → H ₂ O	800–1,000	1–10
						50–55

Source: Adapted from O'Sullivan (1999).

^a Positively charged ions (cations) travel through the electrolyte from the anode to the cathode; negatively charged ions (anions) traverse the electrolyte in the opposite direction.

^b Also called polymer electrolyte fuel cell.

^c Pressure must be sufficiently high to prevent boiling of water in PEM or aqueous electrolytes in PAFC and AFC.

8.3 Harvesting Energy and Energy Products from Fossil Fuels

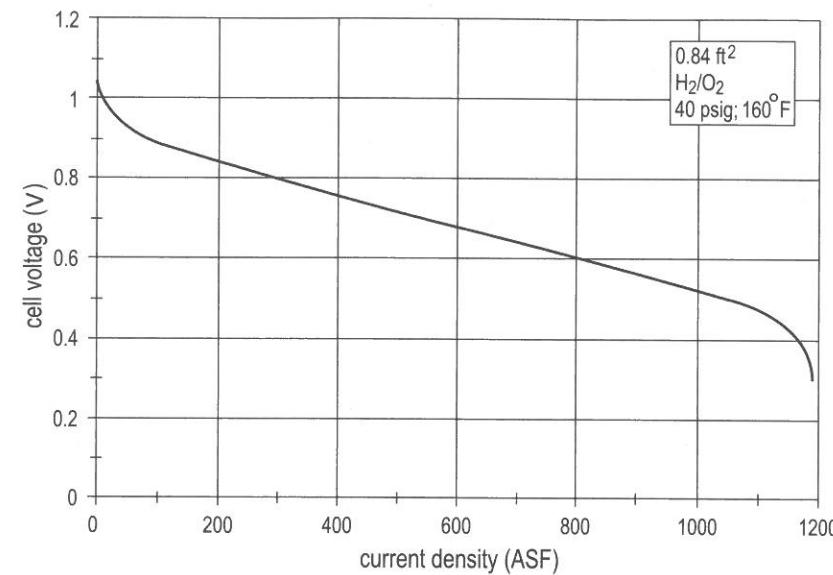


Figure 8.12

Typical plot of cell voltage (volts) as affected by current density (amps/ft²) (polarization curve) for a proton exchange membrane (PEM) fuel cell. Source: Babir (1999). Reprinted with author's permission.

Figure 8.12 shows that the output voltage of a fuel cell declines with the amount of current drawn from the cell. The decline at low current densities is caused by limitations on the rates of chemical reactions at the electrodes and at high current densities by the rates of ion transport through the electrolyte. The corresponding effect on power density (figure 8.13) creates a small plateau region where cell electrode area is used effectively at high current densities, but undergoes appreciable drawdown at lower and ultrahigh current densities. The latter means that fuel cells are best operated at steady power densities and lose much of their electrode capability during load following (continually adjusting output to meet a varying demand). Because each fuel cell unit generates only about 1 volt, fuel cell systems are composed of stacks of individual fuel cells that are interconnected to produce the desired voltage and power densities.

Other major challenges with fuel cells include reducing their capital cost, assuring long-term durability (particularly in challenging environments, such as automobiles), and providing a fuel compatible with the cell. So far, the most compatible fuel has been H₂, provided either directly from storage or by generating it in situ by reforming some other fuel such as gasoline, diesel, or natural gas. The latter option requires mating a fuel production technology to the fuel cell. Synchronization of the

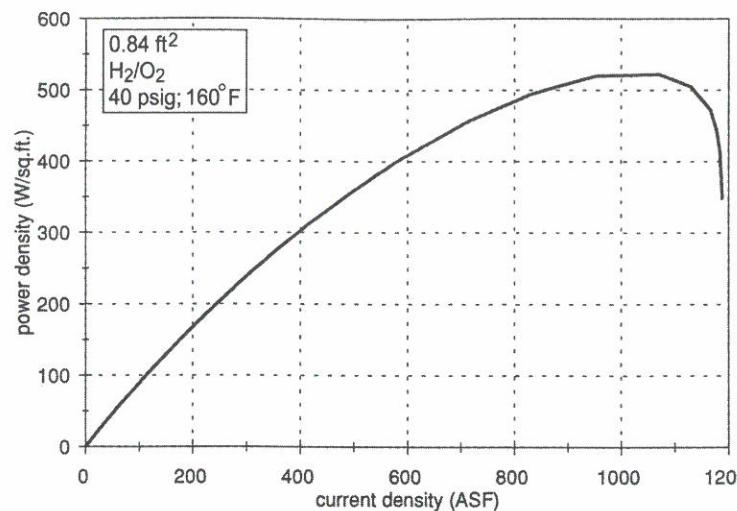


Figure 8.13
Power density (watts/ft²) as affected by current density (amps/ft²) curve for a typical PEM fuel cell. Source: Babir (1999). Reprinted with author's permission.

output of the fuel producer to the varying fuel input requirements necessary to load-follow will be difficult, so some form of postproduction storage will generally be required. There has been progress on direct firing of fuel cells with other fuels, such as methanol, and (for higher-temperature cells such as solid oxide) with hydrocarbons. At high temperatures, reforming of hydrocarbon fuels can be incorporated into the cell system. Of course, the carbon from the fuel ends up as waste CO₂. Fuel cell electrodes and electrolytes must be protected from poisoning (e.g., by sulfur in the case of platinum catalysis in the electrodes of low-temperature fuel cells, and by carbon monoxide or methanol in the case of polymer electrolytes). Figures 8.13 and 8.14 show that fuel cell power density varies appreciably with the current being drawn and the cell voltage. Consequently, fuel cell performance changes considerably with the load demand on the cell and degrades precipitously at high loads.

Opinion varies on the future role of fuel cells in stationary power generation and transportation propulsion. (See chapters 16 through 18.) Some observers see significant roles in the electrical sector, especially in distributed power generation, and huge contributions to the automotive sector owing to the potential for low to zero emissions of various pollutants and of CO₂ when fueled by H₂ (assuming the H₂ is generated without carbon emissions). Some major automobile makers (e.g., Toyota and General Motors) are carrying out programs to develop fuel cell vehicles. Other analysts see a less certain future, pointing to appreciable competition from alterna-

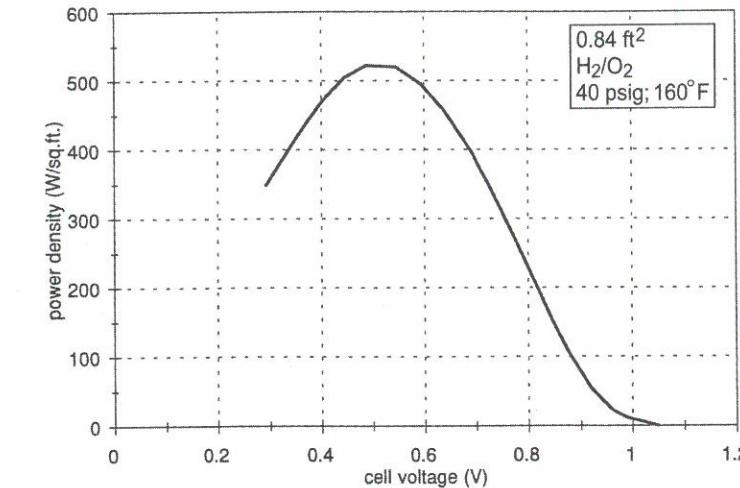


Figure 8.14
Power density (watts/ft²) as affected by cell voltage (volts) for a typical PEM fuel cell. Source: Babir (1999). Reprinted with author's permission.

tives, including natural-gas-fired turbines in the stationary power sector, and from hybrid and plug-in electric propulsion in the passenger vehicle sector.

8.3.6 Manufacture of chemicals and other products

As seen in figures 8.1 through 8.4, naturally occurring fossil fuels, as well as by-products of their upgrading, are the input raw materials, or feedstocks, for the manufacture of a host of valuable nonfuel products, from ammonia to plastics to valuable chemicals. (Chemicals and other products manufactured from petroleum, natural gas, and coal are discussed at length in Shreve and Brink, 1984; Elliott, 1981; and Mark, 1985.)

8.4 Environmental Impacts

8.4.1 Pollutant sources and remedies: The fuel itself

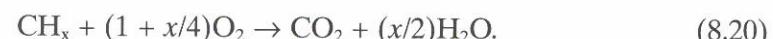
During handling, processing, and combustion, adverse emissions may arise from the fuel itself. Specific sources are:

- carbon dioxide (see section 8.4.3);
- products of incomplete combustion (PICs), resulting from escape of fuel or fuel components unchanged or partially modified by the process;

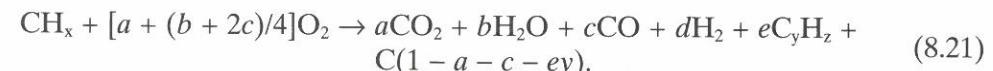
- fuel impurities chemically or physically liberated during combustion or other processing. Some impurities are present in only trace amounts (e.g., nickel and vanadium in heavy oil from certain regions of the world). Other impurities, such as the mineral matter, sulfur, and nitrogen in coal, occur in appreciable percentages (e.g., 1–10%).

When combustion systems have poor design or unanticipated transients, these fuel components reach elevated temperatures without sufficient oxygen to convert them completely to CO₂ and water; as a result, they have a strong tendency to form soot or smoke, as well as polycyclic aromatic hydrocarbons (PAHs), many of which are known genotoxins.

Fuel components that contribute substantially to the heating value of the fuel can also contribute to adverse pollutants. In an ideal combustor, all hydrocarbon components of the fuel, which we shall designate CH_x , will be completely converted to CO_2 and water, in the process making their maximum possible contribution to the energy obtainable from the fuel:



In practice, however, a combustor may temporarily or indefinitely fall short of this ideal chemical reaction. The reasons can be varied. For example, there may be an inadequate supply of air or oxygen (e.g., owing to poor design), excess feeding of fuel, plugging of oxidant feed lines, poor mixing of fuel with O₂, and vitiation of the O₂ by recirculation of combustion products. The temperature of the fuel and oxidant may not be high enough for reaction (8.20) to occur fast enough to consume all the fuel, or the fuel and oxidant may not spend enough time at the temperature needed for this reaction. The result is incomplete combustion, potentially including escape of the fuel totally unchanged, partially modified by physical processes (e.g., evaporation of more volatile components), or chemically transformed. The “combustion” chemistry may be represented by the following stoichiometry:



In addition to CO_2 and H_2O , reaction (8.21) identifies several other products of “incomplete” combustion. These products include carbon monoxide, CO , molecular H_2 , and, potentially, compounds of carbon and hydrogen with complex molecular structures, which we denote, collectively, as C_yH_z . Note that the products other than CO_2 and H_2O may represent a small percentage of the carbon and hydrogen in the original fuel (i.e., $[c + ey + f] \ll 1$, and $[2d + ez] \ll x$). Nevertheless, these parasitic products have important implications for the environmental performance of fuel combustion systems and are important to sustainable energy.

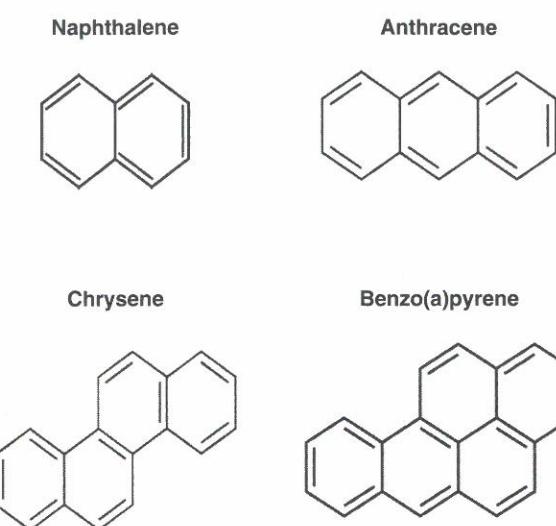


Figure 8.15
Examples of polycyclic aromatic hydrocarbons (PAHs). See Bjørseth (1983).

Carbon monoxide is a serious pollutant because it can bind to hemoglobin in human blood. For this reason, CO emissions from automobiles are severely restricted in North America and Europe. The substances C_yH_z may include PAHs, example structures of which are shown in figure 8.15. Fine particulate carbon matter, commonly called soot or smoke, may also form. For simplicity, we have denoted soot in reaction (8.21) by the symbol C, because, although it is typically rich in elemental carbon soot, it may also contain chemically bonded and physically absorbed components that contain other elements, including hydrogen. Soot and PAHs are of particular interest from a sustainability perspective because soot, soot extracts, and many PAHs exhibit toxicological activity in model systems, and some PAHs, such as benzo(a)pyrene, are classified as known carcinogens. Moreover, soot particles have high emissivities for thermal radiation (chapter 3). Thus, soot particles in flames increase radiative heat transmission, which is beneficial in boilers and furnaces but detrimental in gas turbine combustors, where they may lead to the overheating of combustion liners.

Given the “right” combustion conditions, any fuel containing carbon and hydrogen can form soot and PAHs. Moreover, the propensity to form these pollutants is exacerbated when the fuel contains aromatic structures or components. These substances, which have empirical compositions of approximately CH, abound in coal and in higher boiling fractions of petroleum-derived liquids. The underlying chemical and physical mechanisms responsible for soot and PAH formation and growth

in combustion are highly complex. Note that the pollutant products exhibited in reaction (8.21) may represent only a fraction of the total amount of carbon and hydrogen in the fuel but can degrade the energy efficiency and environmental performance of any given fuel-combustion combination.

Countermeasures to pollutants from the major components of fuels include combustion modification (see section 8.4.2) and fuel reformulation. Generally, hydrocarbon fuels of higher H/C ratio are cleaner burning. More of the energy they provide comes from forming water through bonding of their hydrogen atoms with oxygen atoms supplied by the oxidant. Because fuels of high H/C ratio supply less of their energy from their carbon atoms, there is less opportunity for that part of the combustion chemistry to go astray and form carbonaceous pollutants. For example, high-H/C fuels have less inherent tendency to form soot and PAHs compared to fuels of lower H/C ratio in the same combustion circumstances. The hydrocarbon fuel of highest H/C ratio is methane, CH_4 , the principal component (typically 85–90% by volume) of natural gas. Thus, there is great interest in the use of natural gas both as a stand-alone fuel and in cofiring with fuels of lower H/C ratio, an approach that increases the overall H/C ratio of the fuel. Some scholars (e.g., Socolow and Williams, 2002) point out that production of molecular hydrogen (H_2) may be the preferred fuel reformulation strategy for a greenhouse-gas-constrained energy economy, because carbon is then totally removed from the fuel, eliminating any possibility of adverse carbon-containing pollutants, as well as CO_2 emissions, if the carbon is stored outside of the atmosphere.

Fuel impurities contribute little to the heating value of the fuel, but they are another important source of pollutant emissions. Coal mineral matter can be volatilized from the coal during combustion and then condensed as fine particulate matter. If ingested into the lungs, these particles are toxic to human health. They can also degrade the efficiency of energy production by depositing on the surfaces of heat recovery tubes, where they impede heat transfer and exacerbate corrosion.

8.4.2 Pollutant sources and remedies: Combustion pathologies

As we have seen, combustion imperfections lead to pollutants and wasted energy. Sometimes the imperfections can be counteracted by redesign or the choice of a different fuel. Indeed, each of the essential ingredients of successful combustion (i.e., fuel and oxidant properties, stoichiometry, the three Ts) can be manipulated to improve the efficiency and environmental impacts of practical combustion equipment. On the other hand, uninformed adjustments of any of these can degrade combustion performance, resulting in incomplete utilization of the fuel and unacceptable releases of adverse emissions. Moreover, because of the complex interactions between chemical reactions and physical transport, simultaneous adjustments of two or more variables may produce negative results that are absent if each vari-

able is changed separately or when all are changed in sequence, rather than all at once. Given sufficient time, all chemical reactions, including combustion, will attain *thermodynamic equilibrium*—i.e., for the particular stoichiometry, temperature, and pressure of interest, the state in which all reactants and products are in their most chemically stable condition.

In actual combustors, realization of equilibrium for a given fuel/oxidant stoichiometry may be inhibited by slow chemical reactions or inadequate mixing of fuel and oxidant. Moreover, unwanted leakage (or inflows) of heat or material (air, fuel, etc.) may, at least for certain regions in the combustor, upset the prevailing temperature, pressure, and stoichiometry from that associated with the combustor as a whole. Any departure from design conditions can result in unburned fuel and creation of pollutants. A simple illustration of both is the example of inadequate mixing, in which there is not enough oxygen in contact with the fuel to completely convert it to CO_2 and H_2O . In consequence, the fuel is incompletely burned. Some escapes the combustor as unburned or partially converted fuel, so the combustor produces less energy than it could have if all the fuel had been completely combusted to CO_2 and H_2O . In addition, some of the products of partial (incomplete) combustion could well be pollutants such as soot or PAHs.

It is instructive to consider technological strategies to overcome these difficulties. Why can't we just return to the three Ts and employ higher temperatures, longer burning times, and more intense mixing to solve all our pollution and combustion inefficiency problems? The key to success is learning how to optimize these “control knobs,” economic costs, and performance objectives. For example, use of higher temperatures can only go so far owing to the following limitations:

- the maximum temperature any given fuel can provide (adiabatic flame temperature);
- operating costs (e.g., to separate O_2 in order to eliminate N_2 diluent and achieve a higher temperature);
- the availability of materials compatible with desired operating temperatures;
- the intended use of the combustion-generated energy, e.g., to raise steam of a given “quality,” i.e., temperature and pressure;
- the propensity to form certain pollutants, such as soot, PAHs, and NO_x , at high temperatures.

The time available for combustion can be increased by using a combustor with a larger volume, by reducing combustor throughputs, or by doing both. Volume increases are limited by capital costs, and volume increases and throughput reductions are both constrained by minimum requirements for power harvesting per unit volume of the combustor. Mixing improvements entail higher capital and operating

costs. Reduction of NO emissions through design and control of the combustor is discussed in section 8.3.4. Atmospheric emissions of CO₂ are a more specialized environmental impact of fossil-fuel combustion; approaches for carbon management are described in section 8.4.3.

8.4.3 Pollutant sources and remedies: Carbon management

Release of carbon dioxide and other carbon-bearing gases into the atmosphere by human activity is a human intervention in the environment. As discussed in chapter 4, there is growing evidence that climate is being seriously affected by human activities, but there is considerable uncertainty about the magnitude and timing of interventions and their effectiveness in mitigating future adverse consequences for global climate, as well as about the potential economic and environmental impacts of proposed curtailment strategies. Figure 8.16 summarizes a number of these measures. Before considering them in detail, we must remind ourselves of the amount of carbon involved. Each year, CO₂ emissions to the atmosphere due to human activity, almost all of it caused by the combustion of fossil fuels, is 22 gigatons (i.e., 2.2×10^{10} tons or about 3+ tons of CO₂ for every person on earth). A compact passenger sedan weighs about 1.5 tons, so, each year, the amount of CO₂ humans release to the atmosphere exceeds the weight of two Toyota Camrys or Ford Tauruses for every person on earth.

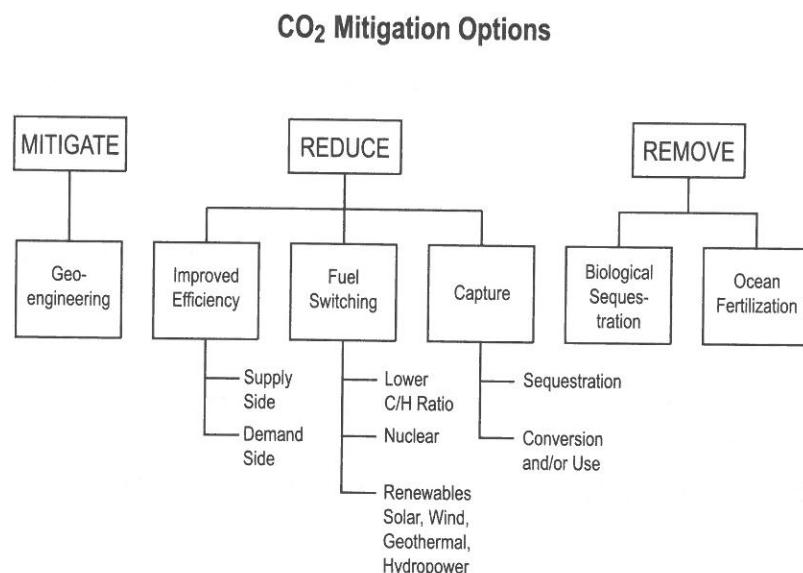


Figure 8.16
Options for mitigation of the release of fossil-fuel-derived carbon dioxide to the earth's atmosphere. Source: Herzog, Eliasson, and Kaarsted (2000).

ruses for every person in the world. Overall, there is wide variability around the average value of emissions, ranging from near zero for the poorest populations to many times the average for wealthy countries, especially the US.

One proposed approach to CO₂ management entails some sort of manipulation of the earth-atmosphere-sun relationship so as to counteract greenhouse warming. An example of this type of geoengineering mitigation is to cool the earth artificially by adjusting its albedo to increase the fraction of incident thermal radiation reflected back into the atmosphere. Several approaches to reducing the amount of CO₂ emitted to the atmosphere (figure 8.16) can be understood in terms of equations (8.22) and (8.23), as introduced in chapter 1:

$$SI = (P) \times (GDP/P) \times (E/GDP) \times (CO_2/E), \quad (8.22)$$

$$SI = (P) \times (GDP/P) \times (E/GDP) \times (CO_2/E) - (CO_2)_{sq}. \quad (8.23)$$

Improved energy efficiency (chapter 3 and chapters 16 through 20) brought about by less wasteful energy conversion equipment (supply-side management) or by reducing per capita reliance on energy (demand-side management) reduces CO₂ release by lowering the energy intensity term, i.e., (E/GDP), in these two reactions. Likewise, we can reduce the carbon intensity term, i.e., (CO₂/E), by so-called *fuel switching* (figure 8.16) or by placing greater reliance on fossil fuels of higher H/C ratio (e.g., natural gas instead of coal) and on energy sources that contain no fossil carbon, such as nuclear and renewables, including solar, wind, geothermal, and biomass. We can also capture CO₂ as it is emitted by human activity, such as from the stacks of electric power plants (where, around 2012, US power sector emissions amounted to 2.8 billion tons/year). This is equivalent to increasing the sink term $[-(CO_2)_{sq}]$ in reaction (8.23). There are various chemical and physical processes that will separate CO₂ from flue gas, but, at present, their broad-based application to flue gas capture would be expensive (Herzog, Golomb, and Zemba, 1991).

While it is certainly possible to remove carbon from the atmosphere (concentration of CO₂ around 400 ppm by volume, or 0.04%) through chemical and biological conversion, it is much easier to use industrial methods to separate CO₂ from power plant stack gases, which are about 10% CO₂. Therefore, despite many challenges, government and industry continue to pursue options for CO₂ capture. Roughly 10 capture plants (100–1,000 tons/day, corresponding to 5–50 MW_e) have been constructed since 1978 to provide CO₂ for industrial applications. In September 1996, Statoil, motivated by a Norwegian CO₂ emissions tax of about \$55/tonne, began operation of the world's first commercial plant for capture and sequestration of CO₂ explicitly built to respond to concerns about climate change. The natural gas produced contains about 9% CO₂, which is separated at the offshore platform and reinjected into a saline aquifer at about 1,000 m depth. About 1 million tonnes of

CO_2 have been successfully injected each year, and the formation is being monitored for integrity.

A recent study (MIT, 2007) concluded: “ CO_2 capture and sequestration (CCS) is the critical enabling technology that would reduce CO_2 emissions significantly while also allowing coal to meet the world’s pressing energy needs.” And a National Academies study (NRC, 2009) describes more recent CO_2 capture and storage projects, noting that a number of other large-scale projects are in advanced stages of planning:

- In Salah, Algeria: CO_2 separated from the produced natural gas is reinjected into salt water underlying the gas-producing formation.
- Snøvit (in the Barent Sea): CO_2 is separated onshore at a liquefied natural gas plant and reinjected into salt water underlying the gas-producing formation.
- Weyburn, Saskatchewan: CO_2 is captured from a North Dakota coal gasification plant and transported by pipeline 205 miles to an oil field where it is used for enhanced oil recovery and geologic storage.

Once captured, something must be done with the CO_2 (as implied in figure 8.16). It can be converted to other products, employed in some useful purpose, or locked up (i.e., *sequestered* in a suitable repository). Successful storage of CO_2 requires the “lockup” to be stable over time scales that are long compared to those for transitioning the global energy economy to nonfossil sources. The storage must cause negligible environmental damage over its lifetime and must be economical, acceptable to the public, and of sufficient capacity to accommodate potentially huge quantities of CO_2 (Szulczezski et al., 2012). Table 8.5 displays estimates of the capacity of various earthbound options for CO_2 sequestration. Recalling that current (2012) global releases are about 30 Gt CO_2 /year, the table shows that, in principle, the oceans, aquifers, and depleted oil and gas wells could each provide

Table 8.5
Estimates of the CO_2 Capacity of Various Sequestration Options

Sequestration Option	Worldwide Capacity (order of magnitude)
Ocean	100,000 Gt
Aquifers	10,000 Gt
Depleted oil and gas	1,000 Gt
Active oil	1 Gt/yr
Utilization	0.1 Gt/yr
Coal seams	?

Source: Herzog, Eliasson, and Kaarsted (2000).

Notes: Total CO_2 emissions worldwide = 22 Gt/yr; CO_2 emissions from US power plants = 1.7 Gt/yr.

8.4 Environmental Impacts

multidecade storage capacity. However, if only 10% of this capacity could be tapped and up to 50% of global CO_2 emissions required sequestration, depleted oil and gas wells would quickly become saturated, necessitating reliance on aquifers and the oceans. Environmentalists have expressed resistance to tapping aquifers and especially the oceans for carbon sequestration, so it remains to be seen whether these options could make a significant contribution as CO_2 storage reservoirs. Table 8.5 also shows that the yearly drawdown of oil wells worldwide would not provide enough storage capacity for even 5% of the yearly CO_2 releases even if 100% utilization were possible. In addition, at present the market for CO_2 is minute in comparison with the amounts emitted (i.e., less than 0.5% if all current uses doubled). However, there are many deep saline aquifers that are isolated from near-surface freshwater aquifers. Early CCS projects generally focus on disposal in deep geological formations.

Another option might be to use separated CO_2 as a chemical feedstock. Anthropogenic processes for chemical and biological conversion of CO_2 include manufacture of various industrial chemicals, growth of microalgae, production of carbonate minerals, and conversion to fuel. CO_2 is chemically far more stable than carbon and oxygen (chapters 1, 3). Thus, conversion of CO_2 to a useful fuel entails high inputs of energy that must be supplied from some other, non- CO_2 -emitting source, which would be more efficiently used to displace fossil-fuel use in the first place. CO_2 can also be removed directly from the atmosphere for carbon mitigation, as discussed earlier (figure 8.16). One approach is to use gas separation technologies to remove the CO_2 from the atmosphere. The challenge is that the concentrations (about 390 ppm in 2012) are low for efficient gas separation, although large-scale trace gas separation systems exist for other industrial applications. A recent paper (House et al., 2011) concludes that existing separation technologies would require more work input than 400 kJ/mol CO_2 —the authors estimate that direct air capture costs will be on the order of \$1,000/tonne CO_2 . The energy for such a system would have to be supplied by CO_2 -neutral sources in order for the process to be CO_2 -negative. These estimates suggest that capturing CO_2 from major emitting sources is likely to be significantly cheaper than direct atmospheric gas separation.

Another approach is *biological sequestration*, in which the growth of trees or other plants fixes atmospheric CO_2 . The mechanism is *photosynthesis* (chapters 7 and 10), in which catalysts that occur naturally in the plant harness a portion of the energy of sunlight to force CO_2 and water to react chemically to form carbohydrates that become the building blocks of the plant. Photosynthesis uses solar energy relatively inefficiently (e.g., converting only about 1% of the flux incident on the earth’s surface to plant matter). Biological sequestration requires huge amounts of land (or ocean) surface and copious amounts of water to significantly reduce atmospheric CO_2 concentrations (see problems, chapter 10).

Almost half of the earth's photosynthesis is carried out by phytoplankton, tiny cells occurring in the first 100 meters of the ocean's depth that use sunlight and dissolved inorganic nutrients (compounds of nitrogen, phosphorus, silicon, and iron) to convert CO₂ to organic carbon. Most of this carbon becomes food for creatures in surface waters and is emitted back to the atmosphere as CO₂. However, some of this carbon ends up in the deep ocean (>3,800 m), where it may reside up to 1,000 years before it is then returned to the atmosphere by upwelling of deep ocean water. It has been proposed that atmospheric CO₂ can be reduced by artificially fertilizing the ocean surface waters where phytoplankton growth is nutrient-limited, such as by iron in the equatorial Pacific and southern Pacific Ocean (Martin et al., 1994). This approach is controversial (see section 7.5.2). Small-scale experiments on artificial fertilization of ocean surface waters with iron have documented increased phytoplankton production. However, there was no evidence of increased transfer of carbon to the deep ocean, which would be essential for successful carbon sequestration.

Mann and Chisholm (2000) point out that artificial fertilization of the ocean in this way occurs over time scales much shorter than those used by the earth to adjust ocean inventories of iron, and that this form of human intervention entails risks of global ecosystem damage not worth the hoped for, and as yet unsubstantiated, benefits:

The earth system consists of elements distributed between the land, air, and oceans by biological and geological processes over millions of years. Many environmental problems stem from our moving elements between these compartments at unprecedented rates that the system cannot accommodate. (Chisholm, 2000)

Although vigorously challenged by some environmental groups, ocean sequestration offers by far the largest capacity for long-term CO₂ sequestration (table 8.5). The best near-term option for CO₂ injection appears to be dissolution at 1,000–1,500 m depths after release from pipelines or towed pipes. Research is needed to better understand the chemical and physical processes by which CO₂ interacts with seawater at depths relevant to sequestration, the efficiency of CO₂ incarceration as affected by ocean circulation, the effects on the ocean environment, and the infrastructure needed to operate effectively in the ocean.

8.5 Geopolitical and Sociological Factors

8.5.1 Globalization of fossil energy sources

Over the last 40 years, international trading in fossil fuels has given rise to complex, often fragile, political relationships between exporting and importing nations. On the “receiving end” are many of the world’s industrialized nations, some depending

8.5 Geopolitical and Sociological Factors

heavily or even predominantly on imported fossil fuels to power their economies. Imports make up about half of US petroleum consumption, and it has been argued that the economy of Japan would quickly collapse without the succor of Middle East oil. On the “sending end” are countries endowed with substantial deposits of oil, natural gas, or coal that can be profitably exploited in today’s markets. Exporters are often (although not always: witness Canada, Norway, and the UK) less well-developed nations that depend heavily on fossil sales abroad to finance domestic economic progress. This ensemble of symbiotic interdependencies is further complicated by stark differences in governmental philosophies, economic aspirations, environmental objectives, and regional as well as global political agendas. Indeed, given the number of players and these disparities, it is remarkable that the export-import compacts have persisted for so long with so few serious disruptions. Three notable exceptions, all of relatively short duration, were the oil embargo of 1973 and the oil price spikes of 1979 and 1991, the last two due in large measure to panic buying brought on by fears that the Iranian hostage seizure and the Gulf War (with Iraq) would precipitate sustained supply scarcities. In the first decade of the twenty-first century, continuing unrest in the Middle East, coupled with growing oil demand from China and a global recession, have led to consistently higher oil prices. Whatever the short-, near-, and longer-term prospects for fossil energy in the global economy, it is vital to understand the known and potential sustainability consequences of the globalization of fossil energy trading. (Chapter 2 analyzes petroleum availability and prices.)

International accords on fossil carbon management are only workable if accepted by all major producers and consumers. The proposition that a curtailment in fossil demand is sufficient overlooks the attendant economic upheaval that would ensue for numerous exporters. This dislocation would almost certainly give rise to political instabilities that could disrupt regional and even global economic equilibrium for months and perhaps years. During a speech in 1968, President Nixon, referring to the imperative for social and economic equity in the US, said, “This won’t be a good place for anyone to live unless it’s a good place for everyone to live.” In today’s global village, this idea applies to all citizens of the planet. Thus, a crucial message for sustainability is that plans to transition the earth to a reduced-fossil-fuel and eventually nonfossil economy must incorporate proactive measures to prevent contagious economic, social, and political instability in fossil-exporting nations.

In chapter 2, we learned that some exporters have been willing to band together and forgo sales to create artificial scarcities that bump up oil prices. However, economic forces invariably degrade these collegia in relatively short time scales (a year or less), as partners renege in favor of larger near-term profits and as lower-cost, more reliable alternatives become available. Sustainability depends upon orderly transitioning to alternatives as those options become technically and economically

available. Looking to the future, it must be asked whether other factors will spur exporters to use fossil exports as a political weapon for *economic terrorism*. Radical groups driven solely by political objectives could gain control of major oil-exporting nations and cut off exports or even demolish production infrastructure to propagate economic dislocation within and between importing nations. Serious advocates of sustainability must pay close attention to political developments around the planet and to the sociopolitical factors that breed popular support for institutionalized radicalism.

8.5.2 Equitable access, revenue scaffolds, American Graffiti

Sustainability requires people to reconcile the rates at which they consume goods and services with protecting the planet from the environmentally harmful human interventions that enable this consumption. But attitudes toward consumption, social entitlements, political freedom, economic progress, conservation, and environmental protection vary dramatically. Fossil energy plays a prominent role in shaping those attitudes because today's global economy is based primarily (ca. 85%) on affordable fossil fuels. Many scholars are convinced that this dependency must be reduced in the next 10 to 20 years in order to put the earth on a more sustainable path. However, technological or policy measures to wean the planet from fossil fuels must win popular support. This in turn requires a widespread appreciation of the current or potential role of affordable fossil energy in the day-to-day lives of people in industrialized nations and in poorer regions that aspire to some form of parity with their more industrialized kindred. Below, we discuss three examples.

Equity With substantial justification, petroleum fuels are broadly perceived as the least expensive source of transportation fuels and, in many cases, of electricity, residential/commercial energy, and industrial energy as well.³ Developing nations aspiring to the economic growth enabled in the developed countries by "cheap" fossil energy have little interest in adopting more expensive nonfossil alternatives without financing from the developed world. The issue is one of equity, as emerging economies desire to move rapidly to attain some of the socioeconomic benefits that their developed neighbors have.

³ Exceptions are nuclear and hydro-powered central station electricity generation in certain regions of the world, and occasional contributions from renewables, which are generally inconsequential (i.e., <5% regional penetration). Dissenters posit that opaque government subsidies for infrastructure, as well as lack of accountability for the adverse environmental effects of fossil fuels, distort energy economics in favor of fossil fuels. This reasoning ignores the gargantuan income taxes and other fees (e.g., for oil leases) paid by fossil industries and the fact that the costs of energy and health care in the US are about comparable, so that even if fossil fuels were responsible for every physiological and mental ailment suffered by Americans, they would be underpriced by, at most, a factor of two.

Likewise, already developed countries eager to hang on to their fossil-enabled economic amenities are reluctant to pay more for energy or to switch from fossil fuels. Advocates of higher energy taxes face an uphill road. In 1993, shortly after taking office, a new US federal administration, with a vice president, Al Gore, strongly identified with environmentalism, proposed a so-called Btu tax on various forms of energy utilized in the US. Although the administration enjoyed a huge majority in the House of Representatives and a majority in the Senate, this energy tax initiative failed miserably because elected representatives of both political parties correctly realized that a majority of the US public was strongly opposed to higher energy prices. For the same reason, the Senate also has not had enough votes to ratify international initiatives such as the Kyoto Protocol to address climate change by committing to reductions in GHG emissions.

Revenue scaffolds Owing to various taxes on gasoline, diesel, and other fuels, fossil energy sales are a tremendous "cash cow" for governments. Figure 8.17 shows the net earnings per barrel of oil in 1993 for Organization of Petroleum Exporting Countries (OPEC) and for various governments by fuel taxation. Even in the US, where there is no *ad valorem* or national sales tax and where fuel taxes are low compared to Europe and Japan, tax revenues somewhat exceeded those of the fuel supplier. In several other countries, as well as the G8 and the EU, government proceeds from fuel taxes dramatically outpace corresponding OPEC revenue (e.g., by almost twofold in Canada, and approaching sixfold in Denmark). In 2010, with

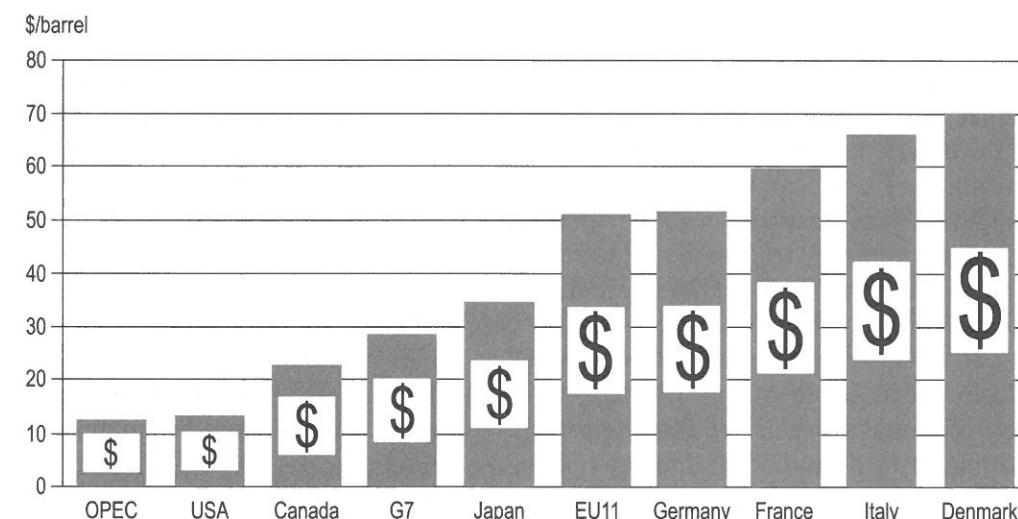


Figure 8.17
Net earning per barrel of crude oil in 1993 by OPEC and by various governments through fuel taxes. Source: Okogu (1995). Reprinted with permission of OPEC.

higher fuel prices, OPEC's profits per barrel have risen drastically and now are of the same order as the higher governmental taxes (non-OPEC producer profits are considerably less). Governmental taxes, however, have not decreased and remain a major revenue stream. Thus, transitioning away from fossil fuels must include a plan to offset the loss of government revenue from fuel taxes.

American Graffiti Sustainable progress is stultified by finger-pointing over “unsustainable” practices by global stakeholders. On occasion, developing countries have been identified with an overreliance on “dirty” technologies, while rich nations, especially the US, have been accused of unfair consumption rates, far exceeding those needed to maintain a decent standard of living. Much time can be spent weighing the merits of these claims. Alternatively, societies can focus on comprehending the forces that shape the current and expected behavior of energy stakeholders. That understanding can illuminate sustainable alternatives that would be responsive to stakeholder needs and aspirations.

Modern technologies for environmental protection require not only financial capital but also good physical infrastructure and well-trained people to operate and maintain technically sophisticated equipment. Many developing regions are short on all of these. Use of inefficient or strongly polluting fossil or other energy technologies in a developing region is most likely due not to a systemic indifference to environmental protection but to the imperative to concentrate limited resources on immediate problems, such as nutrition, sanitation, health care, and other foundations of social well-being and economic progress.

Most of the US consumption of energy-intensive goods and services is enabled by fossil fuels. But what underlies these consumption patterns, and must they be reformed to assure a sustainable future not only for the US but for the entire planet? Consider personal automobiles and light-duty trucks (see chapter 18 for more details on the transportation sector in general), which account for almost one-third of US fossil-fuel use. Some critics attribute much of this consumption to oversized “gas-guzzling” cars or sport utility vehicles (SUVs) that waste huge amounts of energy to provide unnecessary luxury to the driving public. But SUVs for everyday use didn't exist 20 years ago, and demand for them was promoted through advertising of features related to size and comfort. Increased fuel use was not an issue since fuel was inexpensive. Such perspectives did little to advance the cause of sustainable energy. More recent increases in fuel prices as a result of expansion of global markets are starting to reverse this trend, and more consumers are turning toward more fuel efficient vehicles.

The auto sector is a major economic engine, and Americans have an almost 60-year history of enjoying increasingly consumer-friendly private vehicles at affordable purchase and operating costs. Roughly 16 million passenger vehicles including light trucks are manufactured in the US yearly—roughly 64,000 vehicles per day, or one vehicle every 1.35 seconds (assuming 250 manufacturing days per

year). Large automobiles, especially SUVs, had become popular with US consumers, as well as with manufacturers that reap an average profit of several thousand dollars per larger vehicle sold. One view is that sustainable progress will be far better served by understanding that the automobile is ingrained in US popular culture, and thus auto industry effort is now being put into devising high-efficiency, low-pollution fuels and vehicle technologies that will produce a future fleet of fuel-efficient vehicles.⁴ Because of the higher gasoline prices and the recession which started around 2007, US consumers are now buying smaller or more efficient (e.g., hybrids) vehicles—yet feature-packed, comfortable automobiles continue to remain an integral part of American life and the economy.

8.6 Economics of Fossil Energy

Fossil fuels are available worldwide at attractive costs and affordable prices to end users. Fossil-fuel costs are low (see chapter 2 and below) in part because they benefit from over a century of steady technological improvements in our ability to discover and produce petroleum, natural gas, and coal and to transport, upgrade, distribute, and utilize these substances and their derivatives throughout the planet. These advances have created today's remarkable global fuel-supply infrastructure, and have enabled steadily improved efficiency and environmental performance at manageable costs in automobile engines, electric utility boilers, industrial furnaces, and other combustion technology. Moreover, these advances will continue, further improving our ability to obtain and cleanly use fossil fuels. Part of the development of the present infrastructure has been subsidized through government investment, tax breaks, and other mechanisms. Some externalities, such as pollution from local emissions, have been managed through regulations which incorporate environmental costs into operations. More vexing, however, will be the issue of CO₂ emissions from continued use of fossil fuels (see chapter 4 and section 8.4.3).

Petroleum It is sometimes stated that fossil fuels are “cheap.” If we ask in what sense this is true, we could answer, taking petroleum as a proxy for fossil fuels, that it is substantially lower in cost than several other liquid consumer products, such as Coca-Cola, milk, orange juice, and bottled water (figure 8.18). (As of 2010 in Boston, the price gap has lessened: gasoline costs about \$3.50/gal; Coca-Cola in cans costs \$4/gal; milk costs about \$5.20/gal; orange juice about \$6–8/gal; and bottled

⁴ The iconoclastic role of the automobile in US culture is aptly portrayed in a George Lucas motion picture that was a box office bonanza long before his *Star Wars* blockbusters. His *American Graffiti* depicts the exploits of several teenagers coming to grips with their post-high school futures on one Saturday evening (and Sunday morning) in a small town in California in 1962. The juxtaposition of diverse automobiles with the characters' lives transforms this movie from just another “teen flick” to an American masterpiece. Motor vehicles become central players, unifying some half-dozen subplots and instilling momentum, humor, and pathos. To appreciate why the private auto is likely to continue to play an important role in the US, study this movie carefully.

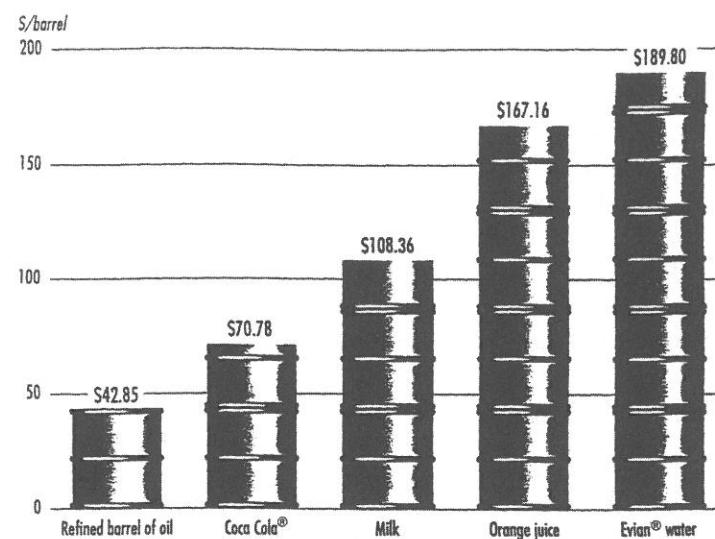


Figure 8.18

Prices paid by consumers for a barrel of refined oil (without taxes) and a barrel of various other consumable liquids in 1995. Source: Okogu (1995). Reprinted with permission of OPEC.

water about \$5–7/gallon.) Again, keep in mind typical consumption rates. The average US consumption of petroleum (about 3 gal/day) is substantially greater than that of the other consumer products shown in figure 8.18. But we can also argue that fossil fuels, on average, remain affordable. Recall figure 2.7, which shows gasoline prices (before taxes) in real dollars (i.e., corrected for inflation), on average, declining over time from 1900 to 1996. Over the same period, crude oil prices were more or less constant over stretches of 3 to 5 years, with shorter episodes of increasing but then decreasing prices. Since 1996, the basis for figure 2.7, inflation has raised prices by 35% as of 2010. The crude oil prices of about \$78/bbl in 2010 are worth \$58/bbl in 1996\$. However, prices have also risen because OPEC, with large reserves of crude that can be produced at prices well below \$20/bbl, has chosen to cap its production levels, so that additional demand is being met by non-OPEC producers developing more expensive resources to meet rapidly growing global demand. Higher market prices for crude oil encourage consumers to invest in more efficient energy technologies and to reduce wasteful energy behaviors. Consumers, who would likely oppose any politically imposed energy tax, are willing to grumble quietly and accept market price increases.

Natural gas There are two schools of thought on future US prices for natural gas: (1) they will follow classic commodity cycles and decline to \$2.00–2.50/MMBtu in two to three years as new supplies and transportation infrastructure become

available; or (2) they will be governed by a different paradigm in which long-range prices appreciably higher than historical norms will be commonplace. Jensen (2001) illuminates a number of the complexities and subtleties of North American natural gas markets, including the behavior of short-run prices and their relationships to oil prices. Moreover, he provides considerable evidence that gas drilling productivity has been declining with increasing drilling activity, which has important consequences for increasing US capacity for gas-fired electricity generation. To expand gas deliverability to meet the expected demand growth from the electricity sector (California alone is about 10 GW_e short on generating capacity), it will be necessary to accelerate the creation of new gas supplies. This will necessitate higher gas prices to attract the multibillion-dollar investments needed to capitalize long-term supply projects. Such investments are already producing new large quantities of natural gas from recently developed commercial technologies to exploit the large shale gas reserves in the US, and are stabilizing US natural gas prices around \$4/MMBtu.

Costs of electricity from fossil fuels Further appreciation for fossil energy economics is gained by comparing the costs of electricity (COE) generated in large central station plants fired by natural gas and by coal with the corresponding costs for nuclear-fired power. (See also chapter 16.) Tables 8.6 through 8.8 provide relevant data from circa 2000. Note first that typical coal costs were \$1.00–1.50 per million Btu (i.e., about \$24–36 per ton), and that representative natural gas costs fell in the range of roughly \$2.00–5.00 per million Btu (i.e., to \$12–30 per barrel oil on the basis of an equivalent energy content). By 2011, all fossil-fuel costs had escalated because of inflation and other factors. Typical coal costs had risen to \$2.24/MMBtu; natural gas to about \$11/MMBtu; and crude prices to \$20/MMBtu or about \$100/barrel. (See <http://www.eia.gov/forecasts/steo/> for current information; these data are from November 2011.)

Table 8.6 shows that subcritical and supercritical steam pulverized coal boilers have similar COEs for a given coal price, with the somewhat higher capital cost of supercritical units largely offset by their greater efficiency. Further, unless natural gas prices return to more traditional lows, i.e., below about \$2.70/MMBtu, the COE for coal is lower than that for gas. This assumes that US coal prices will remain low and stable in the coming years, continuing this industry's multiyear trend of thin margins and intense competition. However, Ellerman (2001) draws attention to price surges for coal earmarked for US regions experiencing high gas prices. This may be evidence of a coupling between short-run coal and gas prices. (In table 8.6, coal prices of \$1.00, \$1.25, and \$1.50 per MMBtu, respectively, correspond to \$24, \$30, and \$36 per ton coal, assuming a typical heating value for steam coal of 12,000 Btu/lb.)

Regardless of the coal prices, additional costs will be added to consumer prices as carbon sequestration and technologies are implemented. A recent study (MIT,

Table 8.6

Cost of Electricity Generated in the US from Coal and Natural Gas in 2000

Technology	Fuel Cost (\$/MMBtu)	Contributions to Cost of Electricity (COE, \$/MWh)			Total COE (\$/MWh)
		Fuel	O&M	Capital	
Pulverized coal with supercritical steam boiler ^a	1.00	8.50	3.50	19.62	31.62
	1.25	10.62	3.50	19.62	33.74
	1.50	12.75	3.50	19.62	35.87
Pulverized coal with subcritical steam boiler ^b	1.00	9.22	3.50	18.40	31.12
	1.25	11.52	3.50	18.40	33.42
	1.50	13.83	3.50	18.40	35.73
Natural gas combined cycle ^c	2.00	13.60	2.00	10.72	29.32
	3.40	23.12	2.00	10.72	38.38
	4.60	31.28	2.00	10.72	47.43

Source: J. M. Beér, personal communication, 2001. Data supplied by Byers Rogan of the Babcock & Wilcox (B&W) Co. for a 2000–2001 study by the National Coal Council Advisory Committee for the US Secretary of Energy.

Notes: Other assumptions: capacity factor: 85%; book life: 30 years for coal plants, 20 years for natural gas; leveled capital charge: data in table calculated assuming 85% capacity factor and 15% interest.

B&W information (supplied as bar charts, not shown) is from an “EPRI Technical Assessment Guide.” The table 8.6 data and the bar charts are in good agreement.

All heat rates are in HHV, but, consistent with the B&W bar charts, fuel contribution to COE for natural gas is based on LHV.

^a Basis: capital cost \$960/kW; O&M (nonfuel) \$3.50/MWh; average heat rge 8,500 Btu/kWh.

^b Basis: capital cost \$900/kW; O&M (nonfuel) \$3.50/MWh; average heat rate 9,220 Btu/kWh.

^c Basis: capital cost \$600/kW; O&M (nonfuel) \$2.00/MWh; average heat rate 800 Btu/kWh.

2007) estimated that a CO₂ emission price of about \$30/tonne would be sufficient to make new coal plants with CCS competitive with new plants without CCS, with \$25 of the cost for the capture and pressurization of the CO₂ and about \$5 for transportation and storage.

Table 8.7 illustrates that in the US, a *new* nuclear plant, based on today’s technology, has little hope of competing with coal or even rather highly priced gas (i.e., \$4.60/MMBtu). However, several existing US nuclear plants have generation costs as low as \$20/MWh because their capital costs have been paid off (Moore, 2000). This is consistent with the sum of the data for “Production Cost” and “Other Costs” (columns 3 and 4, table 8.7) for the top 50% of US nuclear plants averaged over 1997–1999. The prospect of attractive returns from these already-paid-down nuclear plants explains the resurgence of investor interest in acquiring existing US nuclear generation plants in the late 1990s (Moore, 2000). See chapter 9 for more discussion on nuclear power economics.

Table 8.7 also documents the dramatic impact of differences in nuclear plant performance on COE, owing to variations in capacity factor as well as safety performance, fuel costs, and operation and maintenance (O&M) charges. Table 8.8

Table 8.7
Costs of Electricity Generated in the US by Nuclear Fission Reactors in 2000

Relative Plant Performance	Average Capacity Factor (%) ^a	Contribution to Cost of Electricity (COE, \$/MWh)			\$/MWh @ \$1,500/kW ^e	\$/MWh @ \$2,000/kW ^f
		Production Cost ^b	Other Costs ^c	Capital @ \$1,500/kW		
Bottom 25% ^b	74.6	28	5-8	39.43	46.58	70.93
Second 25% ^b	82.3	18.4	5-8	31.67	42.22	58.07
Third 25% ^b	87.9	15.8	5-8	29.65	39.53	53.45
Best 25% ^b	91.4	13.3	5-8	28.51	38.02	49.81

Source: Fertel, Myers, and Kait (2000).

^a Three-year rolling average, 1997–1999.

^b Production Cost = Fuel + O&M + Waste Fee + Decommissioning.

^c Capital additions to existing plants, A&G, property tax, etc.

^d Assumes capacity factor given in column 2. Leveled cost calculated assuming 30-year plant life and 15% interest.

^e Assumes higher value of \$8/MWh for “other” costs.

^f Disaggregated data for fuel and nonfuel O&M are not provided by this source.

Table 8.8
Fuel (Uranium) and Nonfuel O&M Contributions to Cost of Electricity Generation in the US by Nuclear Fission Reactors^a

Year	Fuel	Nonfuel O&M	Total
1987	10	15.1	25.1
1991	7.4	17.4	24.8
1996	5.7	13.8	19.5

Source: Kazimi and Todreas (1999).

^a Three-year average median cost for all plants. Data in \$/MWh.

disaggregates fuel and nonfuel cost contributions (three-year average for all US nuclear plants) to the COE for 1987, 1991, and 1996. The overall improvement (additional data are provided by Kazimi and Todreas, 1999) is evident, but the relatively small contribution of these costs to total COE (i.e., <40% at most, tables 8.7 and 8.8) reaffirms that reduced capital costs, without compromising safety or overall performance, are essential to a competitive future for electricity generation from new nuclear plants in the US. On-site storage and eventual sequestration in a national depository are technically viable strategies for management of wastes from existing and future nuclear plants, but these options are virtually certain to face continuing political challenges.

Uncertainties in electricity costs The data in tables 8.6 through 8.8 are believed to be reliable. The capital costs for the fossil plants are probably accurate to within $\pm 5\%$. Nuclear capital costs are more variable. The Nuclear Regulatory Commission is working to reduce cost escalation due to the uncertainties caused by long delays in permitting (chapter 9). More stringent environmental regulations on pulverized coal plants would probably degrade plant efficiency by no more than 1% (i.e., fuel-to-electricity might drop from 40 to 39%). Plant location impacts the COE, because there is considerable regional variation in fuel costs and fuel use regulations (see table 8.6). These factors can be accounted for in cost projections. For example, increasing capacity factors clearly reduce capital charges per unit of output, but may jeopardize longevity and cumulative profitability by excessively delaying essential and preventative maintenance. Some natural gas plants facing “must run” contracts have learned how to achieve good returns on investment (ROIs) and operate at capacities as high as 90%. The profitability of these so-called merchant plants, which compete in a deregulated electricity market, depends on how much electricity they can sell and how much gas they can obtain reliably, and at what price. In contrast, a regulated electric utility agrees to provide electricity at high reliability in exchange for a guaranteed fixed, but generally lower, ROI. Somewhat less than 50% of the kilowatt-hours generated in the US are deregulated at this time.

8.7 Some Principles for Evaluating Fossil and Other Energy Technology Options

Chapter 5 provides analytical tools to estimate the economic feasibility of energy projects. Here, we present additional criteria to apply in forecasting the potential for success of an energy project. These performance metrics apply to both conventional and alternative energy projects. Many were rediscovered in the 1970s, when the public and private sector in the US and other countries, spurred on by fears of natural gas and petroleum scarcity, devoted financial and technological resources to produce substitute or synthetic fuels from coal, oil shale, and other nontraditional-fossil raw materials, as well as from biomass.

We can complement the three Ts of combustion and the three Cs of petroleum refining with the three Es of project evaluation: *environmental performance*, *efficiency*, and *economics*. In many countries today, no project has any hope of going forward without convincing governmental and private sector bodies (e.g., those developing or financing the project) that it can fully comply with strict environmental performance requirements—on its overall footprint, aesthetic impacts, air and water emissions, solid wastes, and occupational safety. Granted, environmental regulations are not universal and can vary substantially from jurisdiction to jurisdiction, especially between the developed and developing regions. Most proposed projects depend on the successful performance of various technologies to fulfill their environmental requirements. Thus, technical evaluations of various environmental subsystems are essential to a thorough project evaluation. Efficiency means not only the overall energy efficiency of the project (chapter 3) but how well the project minimizes waste of all substances (raw materials, cooling water, etc.); how easily its end products can be recycled; and how easily, at the end of the project life, the project hardware can be decontaminated or recycled and the project site made suitable for other uses. Assessments of various technological subsystems are critical to gauging overall “efficiency.”

Several principles are useful in determining the technical viability of systems and their components:

- **Energy balances.** Identify all energy inputs, including energy to operate equipment and the energy content of all raw materials. What fraction of the inputted energy is “recovered” in process outputs (First Law of Thermodynamics, chapters 1 and 3), and what is the availability of this energy output (Second Law of Thermodynamics, chapter 3)? In large fossil energy projects, capital costs scale roughly inversely with thermal efficiency. Projects to produce commodity fuels (e.g., substitute petroleum liquids) will face tremendous difficulty if their calculated thermal efficiencies are <50%. A lower overall efficiency is

tolerable if the energy is generated at a high availability (e.g., as electricity or high-temperature heat).

- *Material balances.* Have all needed inputs of raw materials, water, air, and the like been accounted for, and can the fate of these materials in the process be accounted for? Does the mass of material exiting the process equal that entering the process? Acceptance criteria for material balances depend on the scale of development of the project. In fossil fuels, during the research, development, and demonstration project phase, material balance closures to within ±25, 10, 5, and 1% would build confidence in work at laboratory, pilot, critical-subscale, and demonstration scale, respectively.
- *Technical feasibility essentials.* No project can succeed if it violates basic laws of science. Thus, projects that exhibit 100% efficiency are gibberish. This may seem obvious, but scientifically impossible notions can gain remarkable public visibility. Even when there is no violation of scientific principles, it is important to estimate the performance limits of a candidate process. Specifically, thermodynamic calculations (chapters 1 and 3) should always be performed to forecast upper bounds on thermal efficiency and yields and selectivities of desired products for the proposed operating conditions. If these results are encouraging, the kinetics of rate-limiting processes, chemical or physical, in the project next need to be estimated. A process can be totally feasible thermodynamically but so slow as to be of no practical use. In many cases, the necessary rate information can be assembled from the literature, but in other cases, considerable research involving experiments, as well as interpretive modeling, must be carried out to generate the necessary kinetic understanding.

Another important factor in determining technical viability is whether materials are available to build the hardware needed to operate the process over long periods of time without safety risks, vessel failure, or product contamination due to corrosion or erosion of process equipment. Successful performance by virtually all modern energy technologies depends on the synergistic operation of an array of process components. Of necessity, the formative stages of research and development are typically concerned with demonstrating and improving the technical and economic viability of one or a few key technical components. However, it is essential to determine whether there is a high probability that the proposed technology will operate as an integrated system of all crucial components. This evaluation must occur before committing to major investments in large-scale demonstration, and more preferably, to the extent feasible at the scale of development, it will be ongoing throughout the process of technology scale-up. Examining the process

from a life-cycle viewpoint (chapter 6) is also useful to assure that feedstock will continue to be available within economic limits and that wastes and emissions will conform to emerging regulatory standards.

Related questions include: Is the overall process composed of an elaborate assembly of numerous technical subsystems? Does it use temperatures, pressures, or chemical reaction environments that push or exceed the envelope of experience at commercial scale? Is there heavy reliance on high-performance materials of construction? If the answer to any of these three questions is "yes," extra caution is called for in approving further investments.

Scale at which performance has been satisfactorily proven In the energy sector, innovative technologies undergo substantial scale-up before becoming acceptable for commercial service. This is because most consumer and industrial applications require reliable delivery of heat, mechanical work, electricity, and fuels at rates many times greater than those used in embryonic research to create and validate technological innovations (table 8.6). For example, a fundamental experiment on the kinetics of coal thermal decomposition in a pulverized fuel boiler shows the ability to process 10 mg of coal in 0.1 min (i.e., 0.013 lb coal/hr). By comparison, a large pulverized-coal-fired electricity utility generating station might consist of three 340 MW_e boilers (for a total capacity of 1,020 MW_e, i.e., enough electricity to supply the needs of about 1 million people in a residential/light-industrial commercial setting). Each of these boilers would consume about 218,000 lb/hr (109 tons/hr) of a good-quality steam coal (14,000 Btu/lb HHV). Here, the difference in scale from research to full commercial service is about a factor of 16 million.

Many processes become less expensive per unit throughput as they are scaled up, but they also become more complex because components must be integrated and function harmoniously. For example, in the 1970s, unit capacity of pulverized coal boilers reached 1,300 MW_e in a Tennessee Valley Authority power plant. Since then, no significant scale-up has occurred. The problem of scale-up to such large boiler sizes is that, under conditions of geometrically similar scaling, the surface-to-volume ratio of the combustion chamber is reduced in inverse proportion to increasing size. This makes it difficult to maintain a furnace gas exit temperature below the softening point of the fly ash without installing extra heat transfer surface in the combustion chamber (steam-generating tube walls), changing the furnace geometry to a more slender form (taller and narrower), and/or reducing the volumetric heat rate in the combustion chamber. These design additions and changes, as well as the increased tendency for slagging and fouling that cut into boiler availability, have set practical limits on the technologically and economically feasible scale-up.

In evaluating any energy project, it is imperative to determine at what scale the process's performance has actually been demonstrated. Investors' confidence

typically increases as the scale of proven performance goes up. Scaling factors between testing depend upon the process's complexity and on the extent to which its performance relies on established versus new subsystems. In evaluating technologies for producing synthetic fuels from coal, scale-up occurred in three- to tenfold increments beginning with bench-scale tests at one to a few lbs of coal per hour. These scale-up factors are in part a consequence of the many technological challenges in processing coal and other solid raw materials: storage, size reduction, and feeding to pressure vessels of large quantities of erosive solids, some of which soften and become sticky upon heating; operation at elevated temperatures and often at high pressures under reactive gases such as oxygen, steam, and hydrogen; and difficulties in separating desired products in high yields without contamination. Some technologies reach a maximum unit size for optimal performance. For example, coal plant boiler units are much larger in generating capacity than a typical gas power turbine, so multiple turbines are installed to produce more capacity. Solar panel and fuel cell installations also use multiple smaller units to meet larger demands. Wind turbines are examples of multiple-unit systems.

As scales increase, throughputs and the number of interacting systems to be demonstrated also increase. The overall objective is to increase the understanding of the process so as to provide reliable technological, environmental, and economic bases for advancing to the next stage or for implementing changes that will make that next stage viable. It is also wise to test, at various scales, nontechnological proposals to achieve sustainability, such as regulations, company policies, and voluntary performance targets.

As a new technology moves from pilot scale to larger demonstration scales, the level of investment required increases substantially. Many promising technologies may die at this stage because of the large initial investments needed to commercialize a new technology. Returns on any investment of this type are subject to varying levels of risk. Before deregulation, vendors or large utilities, sometimes with financial support from the government, used to invest in new technology development. With deregulation, much of this ability has disappeared, and new ways are being found to promote the development of energy technology.

Other questions of diligence It is vital to assess the reliability of technical and economic assumptions that are crucial to the success of a project. Have alternatives to achieve the same objectives been thoroughly screened? How do these alternatives compare with the proposed technology? Does the proposed approach offer overwhelming advantages in one or more of the three Es—environmental impacts, efficiency, and economics—or does it face appreciable competition? Will developers, financiers, and regulators fairly credit the advantages offered by the proposed technology? Have adverse contingencies been adequately identified and appropriate countermeasures incorporated in the process implementation plan? What other

factors will challenge process performance or economics? To be successful, does the process depend on yet-to-be-demonstrated advances in some subsystem technology or yet-to-be-enacted environmental or fiscal regulations? What is the probability that these changes will occur in time scales relevant to developing this process?

Technology readiness levels (TRLs) For roughly 25 years, NASA has used a series of well-defined R&D performance metrics known as technology readiness levels (TRLs; table 8.9) to gauge the technical maturity of various products and processes important to space exploration and other NASA missions. In 1999, the US Army adopted TRLs (GAO, 1999; Kumagai, 2002) to assist decision makers in assessing the state of development of military systems. TRLs facilitate communication during technology assessment and assist planners in discriminating among candidate technologies and in formulating technology development plans, including the identification of where prescribed levels of R&D investment can have a greater impact in moving promising technologies closer to practical applications. TRLs are an important tool that can be applied in assessing the maturity and potential practical impacts of new energy technologies.

Time scales. Has the total time to transition from basic concept to commercial scale been reliably quantified and addressed? (For many fossil-fuel projects, this time can be of order 3 to 10 years.)

Supporting infrastructure. Abrupt or even gradual replacement of one fuel with another will require facilities for the manufacture, storage, transport, and distribution of the fuel. The capital and O&M costs for these facilities must be offset in the customer's price of the new fuel.

Project location. Remote or other unusual venues can substantially impact project costs and technical viability, due to the following factors (Weiss et al., 2000):

- the need to construct infrastructure to support the project,
- higher costs for construction and operation of project and infrastructure facilities,
- local costs of fuel, electricity, raw materials (note that resources located near the project site may be appreciably discounted if they are long distances from alternative lucrative markets),
- additional risks, e.g., from political instability, that must be countered by higher rates of return for investors.

The resulting differences in project costs can be substantial. For example, Weiss et al. (2000) cite US Department of Energy data that estimated the capital costs (in 1987US\$) of a 10,000 tonne/day methanol plant would vary from \$588 million in Trinidad to \$1,323 million on Alaska's North Slope.

Table 8.9
Technology Readiness Levels and Their Definitions

Technology Readiness Level	Description
1. Basic principles observed and reported.	Lowest level of technology readiness. Scientific research begins to be translated into applied research and development. Examples might include paper studies of a technology's basic properties.
2. Technology concept and/or application formulated.	Invention begins. Once basic principles are observed, practical applications can be invented. The application is speculative and there is no proof or detailed analysis to support the assumption. Examples are still limited to paper studies.
3. Analytical and experimental critical function and/or characteristic proof of concept.	Active research and development is initiated. This includes analytical studies and laboratory studies to physically validate analytical predictions of separate elements of the technology. Examples include components that are not yet integrated or representative.
4. Component and/or breadboard validation in laboratory environment.	Basic technological components are integrated to establish that the pieces will work together. This is relatively "low-fidelity" compared to the eventual system. Examples include integration of ad hoc hardware in a laboratory.
5. Component and/or breadboard validation in relevant environment.	Fidelity of breadboard technology increases significantly. The basic technological components are integrated with reasonably realistic supporting elements so that the technology can be tested in a simulated environment. Examples include "high-fidelity" laboratory integration of components.
6. System/subsystem model or prototype demonstration in a relevant environment.	Representative model or prototype system, which is well beyond the breadboard tested for TRL 5, is tested in a relevant environment. Represents a major step up in a technology's demonstrated readiness. Examples include testing a prototype in a high-fidelity laboratory environment or in a simulated operational environment.
7. System prototype demonstration in an operational environment.	Prototype near or at planned operational system. Represents a major step up from TRL 6, requiring the demonstration of an actual system prototype in an operational environment, such as in an aircraft, vehicle, or space. Examples include testing the prototype in a test bed aircraft.
8. Actual system completed and "flight qualified" through test and demonstration.	Technology has been proven to work in its final form and under expected conditions. In almost all cases, this TRL represents the end of true system development. Examples include developmental test and evaluation of the system in its intended system to determine if it meets design specifications.
9. Actual system "flight proven" through successful mission operations.	Actual application of the technology in its final form and under mission conditions, such as those encountered in operational test and evaluation. In almost all cases, this is the end of the last "bug fixing" aspects of true system development. Examples include using the system under operational mission conditions.

Source: GAO (1999).

8.8 Emerging Technologies

Cost elements for petroleum-derived fuels. The pretax cost of liquid fuels produced by refining petroleum (gasoline, diesel, jet fuel, home heating oil, heavy fuel oil, etc.) consists of the refiner's cost to purchase crude oil (i.e., the raw material for fuel manufacture), the cost to refine the oil into the desired product (e.g., gasoline), and the cost to distribute the refined product to customers (Weiss et al., 2000). Crude oil prices are the most volatile and most uncertain of these three (chapter 2), with spot prices varying from \$10/bbl in December 1998 to \$38/bbl in September 2000 to about \$22/bbl in March 2002 and now to over \$75/bbl in September 2010. Refining costs vary because each refinery is a unique collection of physical and chemical process operations that are harmonized in various ways to produce diverse marketable products whose specifications and throughputs vary by geographic region and season of the year. Weiss et al. (2000) point out that a convenient, although imperfect, proxy for refining costs is the *refiner's margin*, defined as the difference between the average price at which refiners sell a gallon of finished fuel at the refinery gate and the average price refiners pay for crude oil. From 1982 to 1999, refiners' margins for gasoline and diesel in the US went from 22¢ to 31¢ and 12¢ to 20¢/gal, respectively. Distribution costs in the US were about 15¢ to 16¢/gal for gasoline and diesel. They are expected to change little over the next 10 to 20 years (Weiss et al., 2000). These margins in 2010 are about \$10/bbl or 24¢/gal for gasoline.

8.8 Emerging Technologies

Research and development targets increased the utilization efficiency of fossil-fuel technology and decreased their environmental footprint. Numerous studies describe specific challenges and opportunities (see <http://www.doe.gov>). For example, table 8.10 (NRC, 2000) summarizes the goals of the US DOE Vision 21 Program for use of petroleum, natural gas, and coal in the US. Many programs concentrate on reducing atmospheric emissions of NO_x, SO_x, and particulates and, increasingly, on developing means to lower emissions of CO₂ and other greenhouse gases to the atmosphere (see chapters 4 and 7). Reduced adverse impacts on all media, including water, open space, and lower solid wastes, are related objectives. There are also breakthrough opportunities, such as technology to convert natural gas directly to premium liquid fuels that are economically competitive with petroleum-derived liquids. Such technologies must be demonstrated at full scale at the large throughputs typical of modern fuel-use patterns. Moreover, because the historical pattern of technological progress in the fossil-fuels industry has been evolutionary rather than revolutionary, true paradigm-shifting breakthroughs, while possible, will probably be rare. The encouraging news is that this sector of the energy industry has an impressive record of remarkable progress in improved efficiency and environmental performance through steady evolutionary improvements in technology.

Table 8.10

Goals of the US Department of Energy Vision 21 Program

Attributes	Goals
Efficiency: electricity generation	60% for coal-based systems (based on fuel HHV); ^a 75% for natural gas-based systems (LHV) ^b with no credit for cogenerated steam
Efficiency: combined electricity/heat	Overall thermal efficiency above 85%; also exceeds efficiency goals for electricity
Efficiency: fuels only, plant	When producing fuels, such as H ₂ or liquid transportation fuels alone from coal, 75% fuels utilization efficiency (LHV)
Environmental	Near-zero emissions of sulfur and nitrogen oxides, particulate matter, trace elements, and organic compounds; 40–50% reduction in CO ₂ emissions by efficiency improvement; 100% reduction with sequestration
Costs	Aggressive targets for capital and operating costs and RAM; ^c products of Vision 21 plants must be cost-competitive with market clearing prices when they are commercially deployed
Timing	Major benefits (e.g., improved gasifiers and combustors, gas separation membranes) begin by 2006 or earlier; designs for most Vision 21 subsystems and modules available by 2012; Vision 21 commercial plant designs available by 2015

Source: NRC (2000) and adapted from DOE (1999).

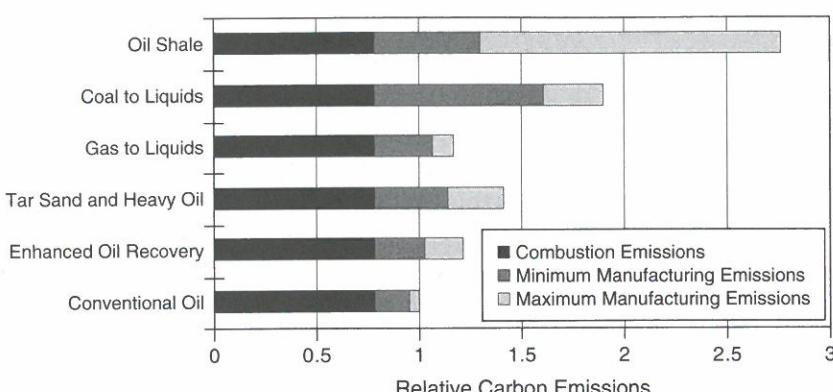
^a HHV = higher heating value.^b LHV = lower heating value.^c RAM = reliability, availability, maintenance.

Most engineers are familiar with the idea that successful new technologies experience rapid improvements in the early stages of development. Significant improvements are also made as the technology is commercialized—in streamlining production, in system integration, and in achieving economies of scale. As the technology matures, the rate of improvement decreases to small improvements in efficiency or in recovery of energy from waste streams.

However, because most major energy production systems consist of combinations of new and mature technologies, the introduction of a new control technology or new higher-temperature materials can contribute to additional improvements in a mature technology. This is an added challenge to alternative technologies, which compete not only with existing technology but with continuing improvements in that technology.

In 2008, the National Academies initiated a series of studies which resulted in the 2009 publication of *America's Energy Future: Technology and Transformation* (NRC, 2009). This report's stated aims are "to inform policy makers about technology options for transforming energy production, distribution, and use to increase sustainability, support long-term economic prosperity, promote energy security, and reduce adverse environmental impacts." The report explicitly looks at greenhouse gas emissions (CO₂-eq) as one sustainability parameter and uses a life-cycle basis for making comparisons among alternatives.

8.8 Emerging Technologies

**Figure 8.19**

Estimated relative CO₂ emissions of alternative sources of hydrocarbon fuels. Source: NRC (2009). © 2009 National Academy of Sciences. Reprinted with permission of National Academies Press.

As conventional oil resources are increasingly stressed, alternative methods of producing liquid fuels for the transportation sector (chapter 18) are being developed. Figure 8.19 shows the CO₂ emissions associated with the production and combustion of alternative sources of liquid fuel relative to conventional oil. Since the source quality and production technologies vary, minimum and maximum CO₂ emissions associated with manufacture of the fuel are shown. In some cases, the manufacturing emissions exceed those of the actual combustion of the fuel. Although there is potential for capturing and sequestering some emissions that occur in the production processes, this would entail additional investments without any incentive at present for them.

Coal and natural gas also play important roles in the production of electricity (plate 4 and chapter 17) and generate about 40% of total US GHG emissions, with coal-fired plants contributing about 80% of electric sector emissions. Because coal is a plentiful domestic resource, and because it is such an integral part of today's electricity systems, one major option for reducing GHG emissions is to capture CO₂ from power plant stacks and store it so that it does not reenter the atmosphere. Several challenges are now being explored to assess the viability of carbon capture and storage (CCS) and to find transitional strategies.

1. **Capturing CO₂:** Technologies are available for separation of CO₂ from stack gas streams (amine or similar absorption scrubbing, molecular sieves, etc.). Some have already been used on a large scale to remove CO₂ from raw natural gases to make pipeline-quality natural gas or to purify raw gas for liquefaction to LNG. Another family of options involves using oxygen instead of air in the

combustion process (with CO₂ recirculated to control combustion temperatures). This requires air separation facilities to produce the oxygen. Yet both flue gas separation technologies and air separation facilities for oxy-combustion are large additions to existing power plants. Since the separation plants of either type will require additional energy for operation, the power plants will divert some of their power for this purpose, thereby derating the power output of the facility. Consequently, it is useful to evaluate CO₂ capture technologies on the basis of costs per unit of CO₂ avoided—rather than CO₂ captured. Many power plants do not have the space on site to accommodate such retrofits. Even if land is available, the costs of retrofitted CCS are likely to be higher than for incorporating CCS into a new plant, so it is clear that building new power plants incorporating carbon capture is more efficient than retrofits. Studies indicate that the option of building “capture-ready” power plants is unlikely to be economically attractive (MIT, 2007). However, the over 400 existing coal plants in the US have many more years of operating life and US electricity demand is not expanding, so there is not a large demand for new power plants. The 500 natural gas power plants have much lower carbon emissions than the fleet of coal plants, but may also provide some less costly opportunities for CCS.

2. **Storage of CO₂:** Since power plants generating emissions are distributed across the continent, a variety of different types of deep geologic storage options are being investigated (figure 8.20), since the CO₂ will need to be transported by pipeline to the disposal location. Coastal power plants may also consider geologic formations located short distances offshore. Considerable monitoring of such repositories will be necessary to prove the integrity of the storage, especially for early projects.
3. **Economics:** With no economic incentive to employ CCS, little change can be expected. Subsidies and/or charges for carbon emissions will be needed to make progress on implementing demonstration and early projects. For example, the early CCS Sleipner project was motivated by a 1996 Norwegian carbon tax of \$55/ton CO₂.

Total estimated power plant costs (\$/kW) are presented in figure 8.21 for pulverized coal (PC), integrated gasification combined-cycle (IGCC), and natural gas combined-cycle (NGCC) technologies (NRC, 2009). For each technology, costs are given for two options: venting the stack gases to the atmosphere (V) and capturing and storing the CO₂ (CCS). The added cost for CCS for pulverized coal nearly doubles the cost of the plant. The IGCC plant is more expensive than the pulverized coal plant for the vented flue gas case, but because it can be adapted for CCS more readily, it is less expensive when CCS is added. The NGCC plants, even with CCS, are less expensive (\$/kW) than the pulverized coal plant with venting. However,

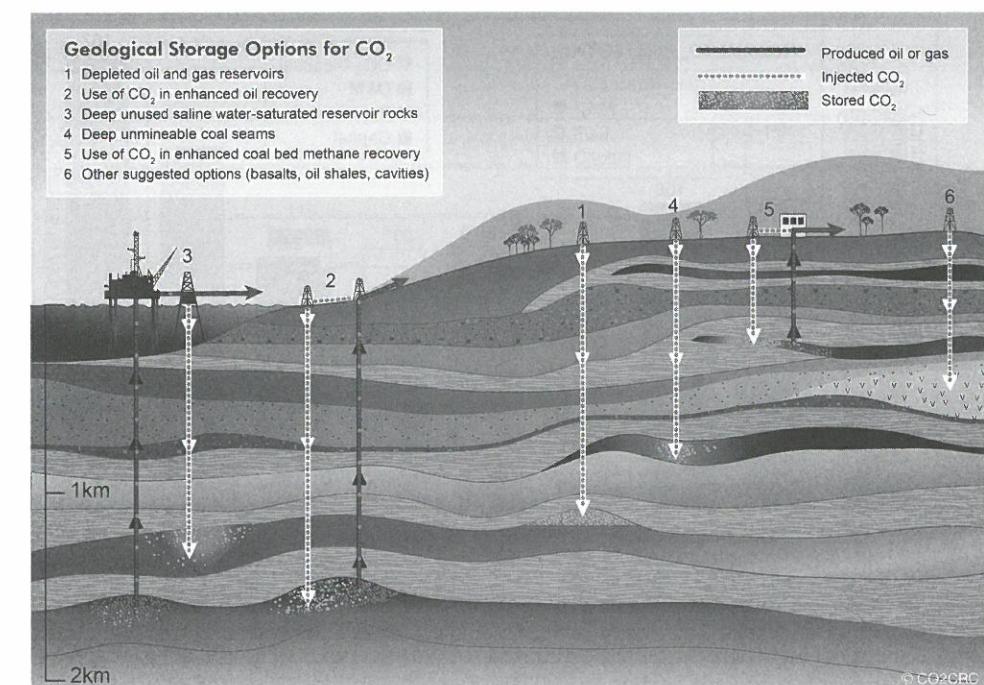


Figure 8.20
Overview of geological storage options. Source: Australian CO2CRC: <http://www.co2cc.com.au/aboutccs/storage.html>

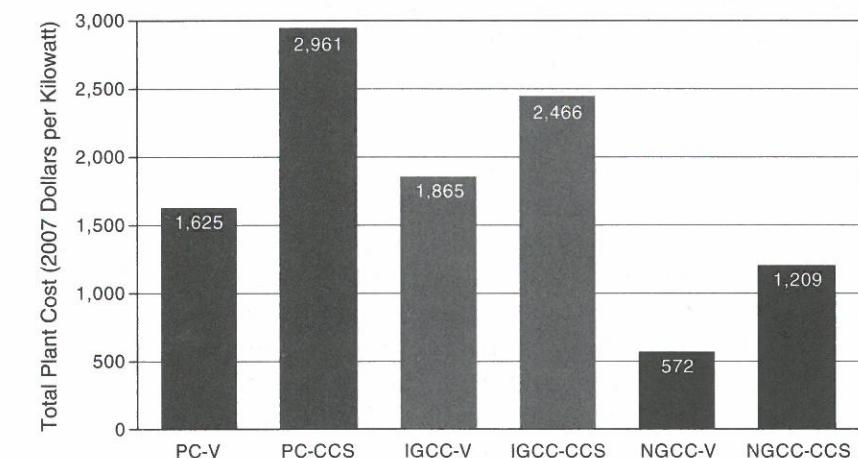


Figure 8.21
Total estimated plant cost in 2007 US\$ for three types of power plants, with and without carbon capture and sequestration (CCS). Note: V refers to CO₂ vented. Source: NRC (2009). © 2009 National Academy of Sciences. Reprinted with permission of National Academies Press.

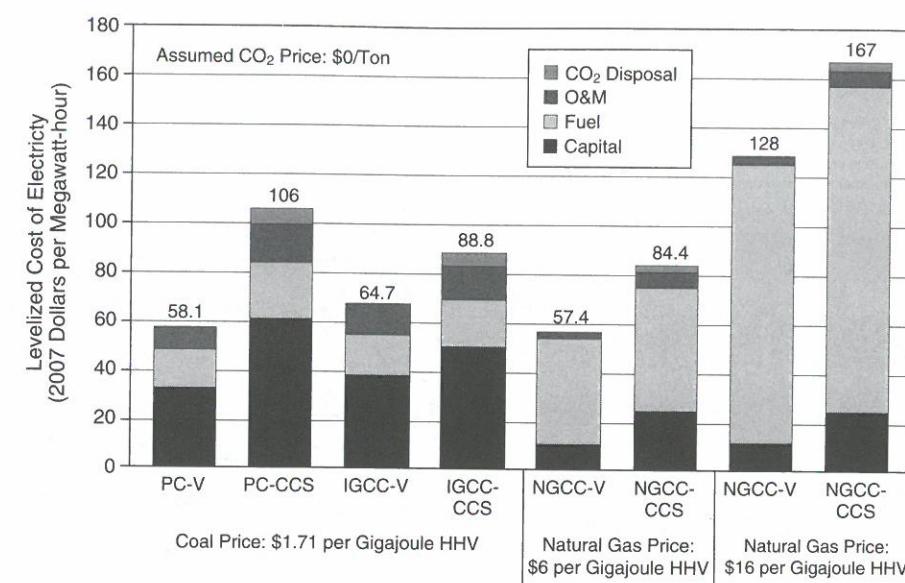


Figure 8.22

Levelized cost of electricity (LCOE) estimated for various types of coal-fired and natural-gas-fired power plants and zero-carbon price. These estimates, like those for other technologies, do not necessarily include all of the site-specific costs of building a plant, nor all of the real-world contingencies that may be needed depending on economic conditions. The price of coal is fixed at \$1.80/MMBtu (2007US\$), approximately equivalent to \$50/tonne, depending on the energy content of the coal. Results for two natural gas prices are shown (\$6/GJ or \$6.33/MMBtu HHV and \$16/GJ or \$16.88/MMBtu HHV) to illustrate how strongly the competitiveness of natural gas plants depends on fuel price. The cost shown for CO₂ disposal is estimated to be \$6.30/tonne CO₂ for PC-CCS, \$6.80/tonne CO₂ for IGCC-CCS, and about \$9/tonne CO₂ for NGCC-CCS. Note: V refers to CO₂ vented. Source: NRC (2009). © 2009 National Academy of Sciences. Reprinted with permission of National Academies Press.

the amount of CO₂ generated from natural gas combustion is much less per unit of output power than that from coal.

Figure 8.22 shows the levelized cost of electricity (see table 5.3) produced by this same set of technologies, with and without CCS. However, since fuel cost is the major factor in NGCC plants, two levels of gas prices are also shown. The lower price of \$6/GJ HHV (note that 1 MMBtu=1.055 GJ) is representative of prices for domestic gas in the recent past, and the higher price of \$16/GJ HHV is near that of the price of gas delivered to Japan as LNG. Gas prices are likely to continue to fluctuate as new reserves that are somewhat more expensive to produce are added to the US supply. This figure shows why pulverized coal and NGCC (cheaper gas) plants are the present technologies of choice for power generation.

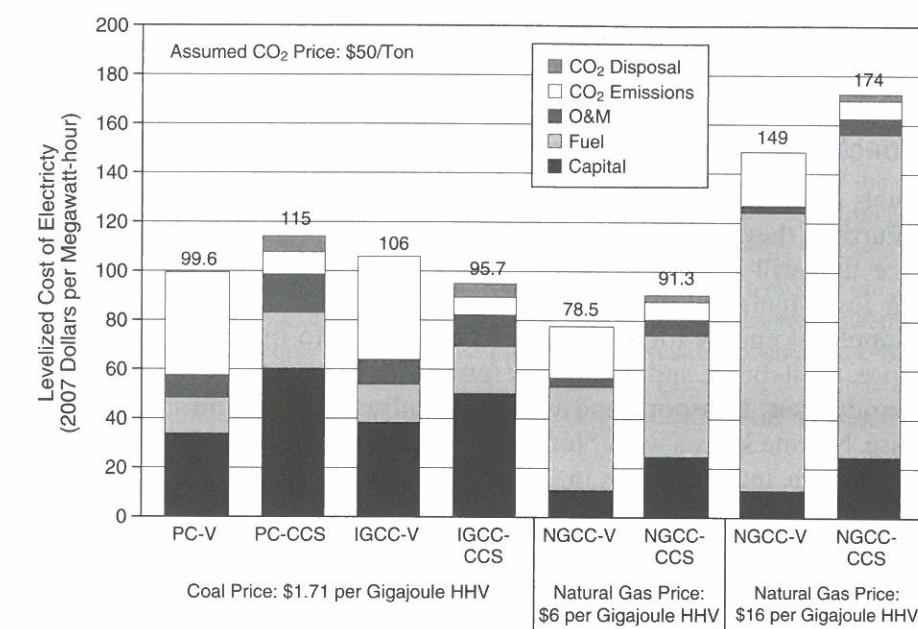


Figure 8.23

The effect of a \$50/tonne price of CO₂ on the LCOE of power plants. IGCC-CCS becomes the cheapest coal option, while the competitiveness of NGCC remains sensitive to fuel price. These estimates, like those for other technologies, do not necessarily include all of the site-specific costs of building a plant, nor all of the real-world contingencies that may be needed depending on economic conditions. Note: V refers to CO₂ vented. Source: NRC (2009). © 2009 National Academy of Sciences. Reprinted with permission of National Academies Press.

Finally, figure 8.23 shows the same comparisons assuming an additional charge of \$50/tonne of CO₂ released to the atmosphere. Under this scenario, the IGCC plants with CCS become economic, as do NGCC plants with CCS, if the price of gas is on the lower side of the gas price range. If gas prices rise substantially, coal will continue to be the economic fuel of choice for power generation, especially if there are no charges or only low charges for carbon emissions. It is interesting to note that while some nations are merely trying to estimate damages from the addition of a ton of CO₂ to the atmosphere (see table 4.12)—and estimate a range of climate damage costs between \$1 and \$100/ton of carbon dioxide (NRC, 2010)—others, like Norway, have set a carbon tax (in 1996, \$50/ton) at a level that would initiate technological change.

While new energy policies are being considered, investors in the fossil-fuel power business may be tempted to build conventional plants with the hope that they will be exempt from any future carbon emissions regulations and granted free CO₂

allowances. A recent report recommended that Congress close this “grandfathering” loophole before it becomes a problem (MIT, 2007).

8.9 Conclusion: Why Are Fossil Fuels Important to Sustainable Energy?

Fossil fuels are needed to sustain economic progress now and for the foreseeable future. Further, they must be used to enable the transition to nonfossil alternatives at a pace that will prevent economic disaster. Environmental concerns notwithstanding, fossil fuels will continue to play a significant and perhaps dominant role in the supply of energy for some time to come, due to the current economy; the abundance, availability, and proven performance of fossil fuels; their multitrillion-dollar production, transport, and utilization infrastructure; and their widespread global use. No one knows what “for some time” means. But we do know that fossil fuels have been indispensable in enabling social and economic progress in the developed world.

Developing countries with fossil-fuel reserves (i.e., almost all countries) will wish to use these sources for their own development or as a source of revenue for development. Under the international Agenda 21 framework (United Nations, 1992), developing countries define their own national clean development guidelines, following general guidelines that promote efficiency and environmental protection. Where cleaner technologies are significantly more expensive, international aid will be needed—but availability of such funding is limited. (See chapter 21.) If alternative technologies can compete with fossil fuels in the absence of existing infrastructures, there is the possibility of “leapfrog” technology (e.g., cell phones). However, such opportunities seem limited for bulk energy production today.

To sustain progress largely without fossil fuels will require a carefully crafted transition period. This transition period is needed to allow viable alternatives to be developed and tested at commercial scale and then to be deployed to the marketplace at a pace that will avoid untenable economic dislocations and the local, regional, and global political disruptions that would almost certainly accompany economic upheaval. The time scales for this transformation will be long enough that fossil fuels must play a significant buffering role throughout most of the transition. There can be no doubt that global use of fossil fuels will at some point decline, whether due to concerns over climate or other untenable environmental impacts, or to irreversible scarcity—scarcity that is permanent, not temporary (chapter 2). However, planners and decision makers cannot forecast when this will occur. Thus, we must forge ahead both with the development of nonfossil alternatives and with the improvement of fossil energy technologies to sustain the benefits fossil fuels currently provide and to assure that they can be used in an economically and environmentally sound manner.

Problems

- 8.1** Assuming capture and recovery efficiencies of 98% and 97% respectively, show that 1,000 tons/day of CO₂ would correspond to capturing most of the carbon emissions from a 50 MW_e plant fired with coal. State all your assumptions, including fuel H/C ratio and fuel-to-electricity conversion efficiency. How would your answer change if the electrical output of the plant remained the same but you switched from coal to natural gas as the fuel?
- 8.2** Estimate the rate at which energy flows from a gasoline pump to a motor vehicle during a “fill-up.” Express your answer in kW. If this rate of energy delivery were electric power, roughly how many people would it serve, assuming a typical US residential community? Make the following assumptions: the HHV of 1 gallon of gasoline is 145,000 Btu; it takes 5 minutes to fill up a 16-gallon auto tank; and a 1 GW_e electrical plant serves a residential community of 1 million people.
- 8.3** Our discussion of electricity costs in section 8.6 stated that coal costs of \$1.00–1.50 per million Btu are equivalent to about \$24–36 per ton, and that natural gas costs of \$2.00–5.00 per million Btu correspond on an equivalent energy basis to \$12–30 per barrel oil. Use the data on fuel properties in table 8.1 to confirm these equivalencies.
- 8.4** One measure of the scale of a process is its throughputs of fuel or other input raw materials, e.g., lbs of coal per hour. Compare the coal throughputs for a small-scale experiment that uses 10 mg of coal in 6 seconds, and a single boiler in a large commercial-scale central-station electric generating plant. Assume: the commercial facility has a total output of 1,020 MW_e supplied by three boilers of equal capacity; the boiler has a heat rate of (8,980 Btu_{th}/hr)/(kW_e) based on fuel HHV, and fires coal with a gross heating value (i.e., HHV) of 14,000 Btu_{th}/lb.
- 8.5** Your company is currently burning natural gas in air to provide high-temperature heat for an important process. You discover that to reduce adverse emissions of certain raw materials used in the process, you need to increase the process operating temperature. Discuss qualitatively how you could accomplish this. What if you had to *decrease* the temperature? What other factors would need to be considered if you chose to replace the fuel entirely, say with “intermediate Btu gas” manufactured from biomass? (Hint: see chapter 10.)

References

- Babir, F. 1999. PEM Fuel Cells: Basic Principles and Equations. White paper. West Palm Beach, FL: Energy Partners.
- Beér, J. M. 2000. Combustion Technology Developments in Power Generation in Response to Environmental Challenges. *Progress in Energy and Combustion Science* 26:301–327.
- Bjørseth, A., ed. 1983. *Handbook of Polycyclic Aromatic Hydrocarbons*. New York: Marcel Dekker.
- Chisholm, S. 2000. Stirring Times in the Southern Ocean. *Nature* 407:685–687.