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Fossil Fuels

2.1 INTRODUCTION

Most fossil fuels, which include coal, oil, and natural gas, were formed from the remains of ancient life over the course of tens to hundreds of millions of years-hence the adjective fossil. The one exception to this rule is believed to be methane, the main component of natural gas, which has both abiogenic and biogenic origins and may form in much shorter time spans. Some ancient life decomposed in the presence of oxygen and would not have become fossil fuels, because the original stored chemical energy would be released during the oxidation process. The beginnings of the process by which fossil fuels are formed are still going on today in the oceans, and swampy areas, especially peat bogs—peat being the term for partially carbonized decomposed organic matter. While the beginnings of the process of future fossil fuel formation may be going on now, the rate of their formation is dwarfed by the rate at which humans have been using existing fossil fuels made over tens to hundreds of millions of years to power the industrialized society, and hence fossil fuels are a nonrenewable resource.

While no one can be certain exactly how much new coal, oil, and gas will be discovered in the future, reasonable estimates can be made about future discoveries. Thus, we can say that humanity's fossil fuel era that we now find ourselves in is a short blip on a very long timescale, meaning that the world consumption of fossil fuels looks qualitatively like that shown in Figure 2.1.

Clearly, the fossil fuel era is bound to end in a matter of at most a century or two, due to the finite amount of remaining reserves. However, as you might suspect, waiting until fossil fuels begin to run out before making the transition away from them would be an utter disaster for the planet for a host of reasons, climate change being only one among many. Today, fossil fuels account for totally 85% of the world's primary energy usage, with nuclear and hydropower comprising 8% and 3% and the renewable sources of geothermal, solar, tidal, wind, and wood waste amounting to a bit over 1% collectively. An obvious question is what has made fossil fuels so attractive as an energy source in the past as well as today and why is it so difficult to move away from them despite the mounting evidence of the environmental problems they pose. The answer has primarily to do with the enormous store of energy they contain (Figure 2.2). For example, coal, oil, and gas have at least 200 times the energy per kilogram that is stored in a lead acid car battery, and unlike the car battery, the energy was put there courtesy of Mother Nature. Fossil fuels represent highly concentrated stores of energy compared to the much more dilute concentrations typical of



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Figure 2.1 Annual consumption of fossil fuels by humans versus year AD. The decline from the peak is a consequence of the three fossil fuels running out in the future. The double peak reflects the fact that coal began to be utilized abundantly before oil.

renewable sources, such as wind and solar, and usually they can be more easily and cheaply collected, stored, shipped, and used where and when desired than most renewable energy sources. Of course, the low cost and high energy density of fossil fuels is not the whole story behind our addiction to them, with simple inertia and power politics also playing important roles. While there may be many similarities between oil and gas, e.g., their formation and extraction, coal is very different, which makes it logical to consider them separately.



Figure 2.2 Although coal is largely responsible for rising atmospheric CO_2 levels, there are also many negative impacts in the shorter term that are of much concern, as illustrated in this photo of the 1968 Farmington coal mine disaster that killed 78 miners in West Virginia. (From http://en.wikipedia.org/wiki/Coal_mining)

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BOX 2.1 HOW MUCH IS THERE?

A major issue about the three fossil fuels that affects greatly how long they will last is the estimates of the remaining amount in each case. Experts in this field classify mineral deposits into two categories, "reserves" and "resources," based on their geologic certainty and economic value. Thus, while "resources" are potentially valuable, and may eventually be economically extracted, reserves are known to be valuable and economically extractable using present technology. Reserves are often further subdivided into categories of proven, probable, and possible based on the degree of certainty that they can be economically extracted using existing technology—"proven" meaning >90% and "probable" meaning 50%, for example. One can obtain very different estimates for a particular fossil fuel depending on which word one uses. Thus, while the United States has been estimated to have 22 billion barrels of oil remaining as part of its proven reserves, it has more than 10 times this amount (274 billion barrels) as part of its resources, and there is a roughly comparable amount in the Canadian tar sands.

2.1.1 Carbon Cycle

The element carbon is an essential component of all fossil fuels and the ancient (and modern) life from which they arose. In fact, as any science fiction enthusiast is aware, we (and other life on Earth) are carbon-based life-forms, in case any extra-terrestrials (ETs) should inquire. In fact, roughly half the dry weight of most living organisms consists of carbon. The carbon cycle describes the host of biogeochemical processes by which carbon is exchanged between a multiplicity of reservoirs on and inside the Earth. These reservoirs on or near the Earth's surface include the atmosphere (where the carbon is mostly CO_2), the biosphere, the oceans, and sediments, which include fossil fuel deposits. The largest of these reservoirs by far is the oceans, and the greatest component there is the deep ocean part (38,000 Gton), which does not rapidly exchange carbon with the upper layers or the atmosphere. Of the reservoirs in the Earth's crust the fossil fuel deposits are the largest, while for aboveground terrestrial carbon the largest component (86%) is stored in forests. There are many pathways by which carbon can enter or leave the Earth's atmosphere. These include the decay of animal and plant matter, fossil fuel combustion, production of cement, and volcanic eruptions. As the planet warms due to increased atmospheric CO₂, even more CO₂ enters the atmosphere since the equilibrium concentration of dissolved CO_2 in the upper layers of the oceans becomes less.

2.2 COAL

The energy believed to be present in the world's coal supply dwarfs all other fossil fuels combined, and it has been estimated at 2.9×10^{20} kJ, most of which is not economically exploitable. Coal has been used by humans

as a heating fuel for at least 4000 years, but the earliest known European usage dates back only 1000 years. It was coal that powered the steam engines during the industrial revolution, beginning in the eighteenth century, which arguably would not have taken place without it. The extensive use of coal beginning with the industrial revolution left its imprint on the planet in terms of a significant increase in the atmospheric concentration of CO_2 (the primary greenhouse gas) whose rise started at that time. Prior to the industrial revolution, studies of bubbles trapped in Antarctic ice cores show that atmospheric CO_2 levels were around 260–280 ppm (parts per million), but the rise since then has been very rapid—especially during the last half century. In fact, present atmospheric CO_2 levels have risen to a higher point than has occurred during the last 400,000 years, and the rise since the industrial revolution began is almost entirely human caused—largely due to coal-burning power plants.

Humans are still more dependent on coal than ever—less so for heating than in the past, but more for electricity generation, and various industrial processes. Today, the roughly 41% of electricity worldwide is generated by coal-fired power plants, which together with automobiles using petroleum derivatives have been the main sources of rising atmospheric CO_2 levels. The problem of climate change associated with the greenhouse effect and the human contribution to it will be discussed at length in Chapter 9. Suffice it to say here that the basic physics behind the greenhouse effect is unquestionable, and the extent of the human contribution to climate change is considerable, if not preponderant.

2.2.1 Composition of Coal

Coal is a combustible sedimentary rock. It differs from other kinds of rocks, which are generally made of minerals, and hence inorganic by definition. Coal, however, is mostly carbon made primarily from plant material and is therefore organic. While carbon may be its primary component, it does contain minor amounts of hydrocarbons, like methane, and inorganic mineral material that are considered impurities. Coal does not have a specific chemical composition, because the precise mixture of sulfur, oxygen, hydrogen, nitrogen, and other elements comprising it varies according to the particular rank or grade of coal, and even within a grade. For example, for anthracite, the highest and hardest rank of coal, its composition includes 0%–3.75% hydrogen, 0%–2.5% oxygen, and up to around 1.6% sulfur. Although the number of coal ranks depends on the classification system, one system that is widely used is based on the four grades listed in Table 2.1.

The order of the rows (starting from the top) goes from the lowest rank of coal to the highest. As can be seen from Table 2.1, higher rank coals have both a higher percentage of carbon and higher energy content per unit mass. Higher ranks since they are more carbon-rich tend to have less hydrogen, oxygen, and sulfur, and they also tend to have lower percentages of "volatiles," which are substances that are driven

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Table 2.1Four Basic Ranks of Coal Based on the AmericanStandards Association					
Rank	% Carbon Content	Energy Content Btu per Ib			
Lignite	<46	5,500-8,300			
Sub-bituminous	46–60	8,300-11,000			
Bituminous	46-86	11,000-13,500			
Anthracite	86–98	13,500-15,600			

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Lignite, the lowest rank, is also known as brown coal.

off when the coal is heated to a high temperature in the absence of air. The percentage of volatiles for a given sample of coal is not calculated on the basis of its chemistry, but is found from direct measurements after the coal is subject to some standardized temperature over a period of time. Although there are some simple compounds in coal, most of the molecules in coal tend to be very massive and complex, since the plant fibers that they originated from are often long. These molecules, many of which even lack names, vary from one piece of coal to another, and within a piece. One such nameless molecule is depicted in Figure 2.3.

Figure 2.3 uses the symbols familiar to organic chemists. Thus, for example, the hexagons shown with single lines comprise rings of six carbon atoms, while those with double lines that strongly resemble a picture of a nut represent benzene rings (six linked carbons having hydrogen atoms always attached to the vertices).



Figure 2.3 Example of the complex molecules found in coal.

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2.2.2 Example 1: Energy Content of Coal

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An empirically determined formula for the energy content of coal based on the elemental abundances of carbon, hydrogen, oxygen, and sulfur is

$$E = 337C + 1442(H - O/8) + 93S$$
(2.1)

where *E* is in units of kJ/kg and the symbols stand for the mass percentages of the elements C, H, O, and S. Use Equation 2.1 and the information provided earlier about anthracite, i.e., H = 0%-3.75%, O = 0%-2.5%, and S = 1%, to estimate the highest value, lowest value, and average value of the energy content of anthracite assuming that no elements besides C, H, O, and S are present.

Solution

Based on the values of the constants in Equation 2.1, the maximum energy density requires H be as high as possible and O is as low as possible, and the minimum energy requires the opposite. Thus, using the data from Table 2.1, we have

 $E_{\text{max}} = 337(95.25) + 1,442(3.75 - 0/8) + 93(1) = 36,700 \text{ kJ/kg}$ = 15,800 Btu/lb

 $E_{\min} = 337(96.5) + 1,442(0 - 2.5/8) + 93(1) = 32,200 \text{ kJ/kg}$ = 13,800 Btu/lb

As a check, we note that these values are fairly close to those provided in Table 2.1 for anthracite.

2.2.3 Formation of Coal

According to geologists, all ranks or grades of coal were formed through the same process starting with dead plant matter. In most times and places, when plants die they decompose or are consumed by fire, i.e., the material is oxidized. However, on rare occasions and in specific places, especially in swampy areas, deposited plant matter can accumulate in a layer and be preserved from decay and fire by the absence of oxygen. Swamps are ideal places for such matter to gradually build up in the water, because of its anoxic nature (relative absence of oxygen). Actually, some decay may occur if small amounts of oxygen are present, but as long as the rate of decay is less than the rate of deposition, the debris layer will grow in thickness over time. Obviously, the growth in thickness will be extremely slow. Estimates are that to accumulate a 10 m thick layer (perhaps leading eventually to a 1 m thick coal seam) might take thousands of years.

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Although some coal has been reported as being found in rocks as old as 2 billion years, and some as young as 2 million years, the large majority of the world's coal began its formation during what is aptly known as the Carboniferous Period, which lasted during the period 359–299 million years ago. Conditions were especially suitable then because sea level was high and the forests tended to be in enormous tropical coastal swamps that were flooded by the seas. After a thick layer of organic debris has been laid down, the inflow of the sea over coastal swamps, or the retreat of the sea and the influx of stream deposits over the swamps, would cause a layer of sand and mud to be deposited over it. With the rise and fall of sea level, alternating layers of dead organic matter is sandwiched between the sand and mud. Over the course of time, the sediment would turn to rock, and the process of coal formation ("coalification") would occur with the application of pressure and heat causing volatiles to be driven off, the layer of organic material to become more compact, and its carbon concentration to increase. According to this scenario, the different ranks of coal, peat \rightarrow lignite \rightarrow sub-bituminous \rightarrow bituminous \rightarrow anthracite, form a time sequence, although in any given location the process might only have gone partway given insufficient time, pressure, or heat (Figure 2.4).

Thus, based on the sequence of steps just described, we see that the various ranks of coal from lowest to highest are not simply arbitrary types defined based on their carbon content, but rather steps in an evolutionary time sequence. The evidence for theory of coal formation is threefold: (1) coal is always found in "seams" or strata; (2) the seams sometimes contain actual plant fossils; and (3) successively higher grades of coal tend to (a) be found at greater depths, (b) be found in areas that have undergone higher temperature and pressure, (c) be denser, (d) contain less volatiles, and (e) have higher energy content. Incidentally, while anthracite was listed last, sometimes the sequence of increasingly pure carbon content can continue on to graphite—which is essentially pure carbon. Furthermore, it is even possible for pure graphite to become diamonds, but that requires pressures in excess of 14,500 atm = 1.45×10^9 Pa, which would only occur at very great depths.





BOX 2.2 WHERE DO DIAMONDS FORM?

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Given the known mass and radius of the Earth, we can easily calculate its average density to be 5500 kg/m³. Although the core of the Earth is made of iron and has a higher density than this, since the core occupies a small fraction of the total volume of the Earth, the average density will be quite typical of the Earth's rocky mantle. From the equation giving pressure as a function of depth beneath the surface $P = \rho gy$, we can calculate the depth *y* where pure graphite could be turned into diamonds as $y = P/\rho g = 1.45 \times 10^9/(5,500 \times 9.8) = 26,900 \text{ m} = 269 \text{ km}$. However, despite diamonds being the end of an evolutionary sequence involving carbon, geologists do not believe that they formed from coal that was carried downward to sufficient depth. Instead, the generally held belief is that diamond deposits were formed deep in the mantle and delivered to the surface by volcanic eruptions. The accepted value for their formation depth is between 150 and 200 km—a bit lower than our estimate.

2.2.4 Resource Base

Coal is the most abundant of the fossil fuels, and around 50 nations have commercially operating mines. Nevertheless, about 85% of the recoverable reserves of coal in the world can be found in these nine nations: the United States (22.6%), Russia (14.4%), China (12.6%), Australia (8.9%), India (7.0%), Germany (4.7%), Ukraine (3.9%), Kazhakstan (3.9%), and South Africa (3.5%). Given the special circumstances leading to coal formation described previously, it is not surprising that coal deposits are highly localized within a given country, and that different types of coal are found in different places (Figure 2.5).

The United States has about 240 years worth of coal remaining at its present rate of consumption. On a worldwide basis, the known reserves are sufficient to last about a century at the present rate of consumption. Regrettably that rate has been rising steadily, owing to the rapidly rising coal production rate in China, which now produces (and uses) roughly half the world's coal output. China's main use for coal is in connection with electricity generation, which fuels 69% of all its electric power, although coal has industrial uses, and is also sometimes used for home heating there. On average, the Chinese have been building several new coal-fired plants per week and will be doing so for years to come. As a result, in 2006 China has surpassed the United States as the nation emitting the most CO_2 annually. While America may welcome having relinquished the number one spot in this regard, it still far exceeds China in its per capita annual CO_2 emissions (Figure 2.6).

About 60% of the new plants China is building have advanced technology that is highly efficient and limit emissions other than CO_2 more effectively. To the extent that power companies retire an older, more polluting plant for each new one built, the net result would be a reduction in non-CO₂ emissions. Although introducing more efficient coal-fired

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Figure 2.5 Locations of U.S. coal deposits with color coding to designate ranks of deposits: light gray and dark gray being bituminous, light and dark yellow being lignite. (From http://en.wikipedia.org/wiki/Coal)



Figure 2.6 Dark-shade-coded indicator of per capita CO₂ emissions per country in units of tons of CO₂ per person per year. (From http://en.wikipedia.org/wiki/File:CO₂_per_cap-ita_per_country.png)

plants could also mean less CO_2 emitted per MW generated, any such gain is more than outweighed by the annual increase in Chinese coal consumption, which is rising at about 9% per year.

2.2.5 Electricity Generation from Coal

All three fossil fuels can be used for electricity generation, but petroleum is used mostly in other sectors (petrochemicals and transportation fuels), and coal tends to be the dominant fossil fuel source for electricity generation. There are many possible reasons, however, why a nation (such as Germany or Japan) might wish to use natural gas or even oil to generate

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Figure 2.7 Basic components of a coal-fired power plant.

electric power instead of coal, even though coal in the past has been the cheaper alternative—ignoring "external" (environmental) costs. These reasons include concern for the environment and human health, lack of abundant domestic coal reserves, and greater ease of transport of oil and gas through existing pipelines or nearby ports.

Figure 2.7 shows the basic process for converting the heat from burning coal into electricity. After coal has been pulverized and delivered to a combustion chamber, it is burned, and the heat boils water creating high pressure steam that drives a turbine connected to an electric generator. By the second law of thermodynamics, inevitably a fraction of the heat of combustion is rejected to the environment either up the chimney or in the cooling water that is used to condense the steam back to water, which is why coal plants, like all heat-generating plants, are often near lakes or rivers. Rivers can also serve for barge transport to bring the coal to the plant, although rail cars are also often used. A large coal-fired plant would typically require a train of about 100 cars (over a mile long) or 10,000 tons of coal to be delivered each day.

It would be desirable if the heat expelled to the environment were as small as possible, so that more heat could be converted to mechanical energy in the turbine, but there is the fundamental limit imposed by Carnot's theorem.

2.2.5.1 Example 2: Efficiency of a Coal-Fired Power Plant Given that coal ignites at around 450°C, how does the 33% efficiency of a coal-fired power plant compare with the highest possible efficiency dictated by the Carnot limit?

$$e_{\rm C} = 1 - \frac{T_a}{T_{\rm C}} \tag{2.2}$$

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Solution

Using Equation 2.2 with $T_{\rm C} = 450^{\circ}\text{C} = 723\text{K}$ and $T_a \approx 300\text{K}$, we find $e_{\rm C} = 1 - (300/723) = 0.59$, i.e., 59%, almost twice as great as the average coal plant efficiency.

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2.2.5.2 Rankine Cycle All fossil fuel power plants use heat engines to convert heat into mechanical work, and worldwide about 80% of them rely on the Rankine cycle to accomplish this. An example of a Rankine cycle is depicted in Figure 2.8 using the variables temperature (T) and entropy (S), instead of the usual P-V (pressure–volume) variables to which some readers may be more accustomed. One advantage of using a T-S plot rather than a P-V plot is that in this case the ideal Carnot cycle of two isothermal and two adiabatic curves can be represented as a simple rectangle. Another point to note is that the closed loop areas defined by $\oint T dS$ and $\oint P dV$ are



Figure 2.8 Two representations of the Rankine cycle (a) by function and (b) on a temperatureentropy diagram. Example of the Rankine cycle showing for which steps in the cycle $1 \rightarrow 2$, $2 \rightarrow 3$, $3 \rightarrow 4$, and $4 \rightarrow 1$ heat is added and removed, and positive or negative work is done.

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identical and represent the work W done in one cycle. Moreover, in both representations by conservation of energy; $W = Q_{in} - Q_{out}$.

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The working fluid in the Rankine cycle is water either in the liquid or vapor phase, with the concave down curve in Figure 2.8 showing the boundary between the two phases in the T-S plane. The point labeled the critical point at the maximum of the curve is the maximum temperature for which water could exist for the liquid phase. The steps in the cycle $1 \rightarrow 2, 2 \rightarrow 3$, $3 \rightarrow 4$, and $4 \rightarrow 1$, represent a time sequence of particular processes taking place in the steam boiler. In order to better understand how the steps in the cycle correspond to physical processes, consider step $2 \rightarrow 3$ as an example. Here we see in the figure that water under high pressure enters the boiler and has its temperature raised from about 60°C to 260°C (mostly following the part of the curve on the left) until it becomes high enough to boil at the start of the horizontal section of the path. As we traverse that section, more and more of the water is converted to steam at constant temperature. Once we reach point 3, all the liquid water has been converted to steam. For an ideal Rankine cycle, steps $1 \rightarrow 2$ and $3 \rightarrow 4$ would be vertical lines. and the cycle would approximate a Carnot cycle, the main difference being that the first part of the cycle bears no resemblance to a vertical straight line—an adiabatic path on a *T*–*S* diagram.

Given the formula for the Carnot efficiency for a heat engine (Equation 2.2), the two ways to raise the theoretical maximum efficiency are to lower the ambient temperature (unfeasible) or raise the maximum temperature of the working fluid. For plants operating on a Rankine cycle, this can be accomplished by adding an extra step to the cycle $3 \rightarrow 3'$ that goes up along the 50 bar isobar to a temperature above the critical temperature (generating "supercritical" steam) before the cycle is finally completed $(3' \rightarrow 4)$. This has the effect of increasing the area inside the curve and hence the efficiency of the process. The supercritical Rankine cycle was made possible in part by the advent of alloys that could tolerate the high temperatures and pressures needed. Supercritical plants around the world (still in the minority) operate at water temperatures 540°C and 3500 psi, and have efficiencies exceeding 45%.

2.2.6 Conversion of Coal to a Transportation Fuel

Apart from steam-powered locomotives powered by coal, transportation fuels are generally either liquids or gases. A gaseous fuel "syngas" (short for synthetic gas, which is a mixture of carbon monoxide and hydrogen) can be produced from coal by heating it under high pressure in the presence of water vapor. The syngas reaction known as coal gasification is

$$\operatorname{Coal} + \operatorname{O}_2 + \operatorname{H}_2 \operatorname{O} \to \operatorname{H}_2 + \operatorname{CO}$$
(2.3)

Although syngas can be used on its own as a transportation fuel, its energy content is only about half that of natural gas, so that normally it is

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converted instead into a more energy-rich liquid fuel similar to gasoline or else the hydrogen component is extracted and used to power fuel cells.

The conversion to a liquid akin to gasoline or diesel can be done through the Fischer–Tropsch (F–T) process, which involves a series of chemical reactions starting with syngas and resulting in the production of a variety of liquid hydrocarbons. The F-T process was invented by a pair of German scientists in the 1920s, and was used by Germany in World War II, when it lacked access to gasoline supplies. In fact, by 1944, Germany was producing 124,000 bbl of synthetic fuels per day. It was similarly used by the South Africans under apartheid when they were denied access to external supplies of gasoline. The process is still being used by South Africa today to make synthetic gasoline from coal—a process that accounts for 30% of their fuel needs. In most other nations, production of synthetic fuels usually starts from natural gas rather than coal-this currently being the more economical alternative. Nevertheless, should a technological breakthrough make the coal process more viable, it could become an attractive backup possibility in the event of petroleum shortages or price rises. In fact, one recent MIT study has projected that producing liquid fuels from coal could become economically viable in coal-rich nations as early as 2015 (MIT, 2011b).

2.2.7 Coal Mining

Coal is mined by one of two basic methods: surface (or strip) mining and underground mining. Surface mining is utilized in places where the depth of the coal seam is such that removing the overburden to expose the coal seam is economically preferable to the more difficult and dangerous method of underground mining. In the United States, if a coal seam is less than 50 m deep it will usually be surface mined, while depths below 100 m are usually underground mined. For depths between 50 and 100 m, the choice depends on the thickness of the coal seam. At one time, virtually all coal mining in the United States was done using underground mines, but today 60% are surface mined, sometimes using the highly controversial practice of mountaintop removal, which usually results in the complete disruption of natural ecosystems.

Coal mining historically has been a dirty and dangerous occupation. The two largest coal producing nations are China and the United States, which together produce 63% of the world's coal as of 2011, so it is worth-while to look at some statistics for these two nations. It is estimated that 100,000 coal miners were killed in accidents over the last century in the United States, with the annual death rate declining dramatically with improved technology and safety measures. Most other developed nations have also seen great improvements in mine safety in recent decades, so that mine deaths have dropped dramatically—on average, there are now only about 30 mine-related deaths per year in the United States. In China, the number one coal producer, the story is quite different. Among China's estimated 5 million coal industry workers, an estimated 20,000 die each year in accidents—about 700 times the U.S. number.

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Coal mining has been called the most dangerous occupation in China (China, 2004). Moreover, these fatality figures are deaths in the mine and do not include deaths from pneumoconiosis (black lung disease), which is still quite common among coal miners, even in developed nations. In the United States, for example, over 10,000 coal miners have died from it in the past decade. According to Chinese self-reporting, black lung disease has claimed 140,000 coal miner lives in the last half century, and close to half a million miners are now suffering from it (China, 2005). Given that China has around 50 times as many miners as the United States, these data imply surprisingly that the chances of a miner dying from black lung disease deaths are 20 times greater in the United States than in China. This comparison raises questions about the accuracy of self-reported data—particularly data that would prove embarrassing to a nation.

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BOX 2.3 ARE BLACK LUNG DISEASE DEATHS REALLY 20 TIMES GREATER IN THE UNITED STATES THAN IN CHINA?

As already noted, Chinese miners tend to work in deep underground mines far more often than their U.S. counterparts, which is where black lung disease is primarily contracted. Moreover, Chinese mines, especially smaller ones, tend to lack the kinds of high-tech safety measures that are common (required) in U.S. mines. Additional circumstantial evidence that the Chinese statistic is bogus is the "hidden" nature of black lung disease compared to coal mine deaths from cave-ins and other disasters, which are much harder to keep secret, and which are far less common in the United States than in China. Accurate statistics on black lung disease requires a proactive monitoring system that is mandated by the national government, and which results in penalties if it is not followed. The United States has just such a system in place. As a result of Federal Coal Mine Health and Safety Act of 1969 (amended in 1977), regular free chest x-rays are taken of all underground miners, with emphasis on early detection of the signs of black lung disease. There appears to be no such corresponding requirement in China. Even if there were, and even if it were complied with, workers if given the option of coming forward to have free exams, might well feel not-so-subtle pressures that keep them from actually having the exams if they understandably fear that their jobs might be in jeopardy. Given all the aforementioned points, it would seem more plausible that Chinese black lung disease were far more common in China than in the United States rather than the reverse. If Chinese black lung deaths per miner occurred at the same rate as in the United States, there would be 50,000 such deaths there each year, but the true figure is probably far more.

2.2.8 Environmental Impacts of Coal

Although coal miners may be the people having the greatest negative impact associated with coal, the health of everyone and the environment are both affected in a serious way when coal is mined, transported, stored, burned,

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and even long afterward. The environmental effects associated with coal mining and coal burning include air, water, and land pollution, resulting in very serious long-term consequences for both humans and ecosystems.

2.2.8.1 Atmospheric Emissions from Coal Power Plants Coal-fired power plants are prodigious emitters of pollution, although newer plants using "scrubbers" to filter the exhaust as it travels up the smoke stacks have significantly reduced some emissions. Nevertheless, as can be seen from Table 2.2, coal is still the dirtiest of the fossil fuels. For example, compared to gas-fired power plants, coal plants emit 1200 times more particulates and nearly double the CO₂.

Even apart from greenhouse gases contributing to climate change (considered at length in Chapter 9), air pollution due to coal-fired power plants has very serious consequences for humans. Just considering China alone, the world's largest coal producer, a report from scientists at the University of California at Berkeley puts the annual Chinese coalrelated death total at 420,000 (Zhang and Smith, 2007). The corresponding figure of annual coal-related deaths in the United States, the number two coal producer, is 24,000, many from air pollution (EPA, 2004). Moreover, an EPA-funded study also concluded that 90% of those deaths are preventable with currently available technology. In fact, EPA had been given the power to regulate such emissions as far back as the Clean Air Act of 1990, but lobbying by the coal industry has delayed new regulations limiting emissions of mercury and other toxic substances until 2011. Under the new rules, affecting an estimated 40% of U.S. coal plants, EPA estimates that 11,000 premature deaths will be avoided with a concurrent savings in health care costs of between \$37 and \$90 billion annually. The new rules are expected to cost the coal industry a one-time assessment of about \$10 billion, and will likely involve the closing of some older dirty coal plants that in many cases were slated for retirement anyway.

The author is old enough to remember a time when coal was burned to heat the home that his family shared with his grandmother. Shoveling the

Table 2.2 Emissions from Power Plants Using Various

Fuels in Units of kg/GJ for Actual Power Plants, as Reported by the European Environmental Agency							
Pollutant	Hard Coal	Brown Coal	Fuel Oil	Gas			
CO ₂	94.6	101.0	77.4	56.1			
SO ₂	0.765	1.36	0.228	0.00068			
N0 <i>x</i>	0.292	0.183	0.195	0.093			
C0	0.0891	0.0891	0.0157	0.0145			
Particulates	1.203	3.254	0.016	0.0001			

Source: EEA, European Environment Agency (EEA) gives fueldependent emission factors based on actual emissions from power plants in EU, *Air Pollution from Electricity-Generating Large Combustion Plants*, EEA, Copenhagen, Denmark, 2008.

coal to get it into the furnace was a dirty job that he occasionally had to do. Once burned, the smoke produced from the coal was quite appalling—even if most of the smoke was released up the chimney outside the home. Today, very few Americans use coal for home heating (outside of some rural areas of Pennsylvania), but this is not the case in China and much of the developing world. The Chinese situation is made even worse by the habit in many rural households of hanging vegetables to dry near the ceiling, which results in many cases of heavy metal poisoning when coal smoke is absorbed by the vegetables.

2.2.8.2 Other Atmospheric Emissions Including Radioactivity Although one normally associates radioactivity with emissions and wastes from nuclear power plants, in one sense the situation is significantly worse in the case of coal power plants. According to a University of California Berkeley study, even though nuclear wastes are much more radioactive than the fly ash wastes from coal burning, only the latter are routinely released to the environment in the many plants that lack the technology for capturing fly ash released in the flue gases after combustion. The study concluded that the fly ash from coal plants, therefore, releases 100 times more radiation to the environment than is the case for a normally operating nuclear plant per MW power generated (Hvistendahl, 2011). Of course, nuclear plants do not always operate normally, and the matter of nuclear accidents will be considered in Chapter 4.

In addition to atmospheric emissions during coal burning, significant emissions also occur during the mining of coal, including methane gas, which often occurs in coal deposits. Apart from the direct hazard to miners, methane released into the atmosphere is a particularly potent greenhouse gas. While methane stays in the atmosphere a far shorter time than CO_2 , it is considered the second leading contributor to the greenhouse effect, and has a "global warming potential" 21 times greater than CO_2 .

2.2.8.3 Waterborne Pollution and Acid Rain When coal is mined, water that comes into contact with coal surfaces leaches sulfuric acid, even after the mine has been shut down. The sulfuric acid pollutes streams, kills aquatic wildlife, and causes problems for the human water supply, which are especially serious for surface mining. Toxic trace elements dissolved in the water also contribute to the pollution, which in addition to causing environmental damage also cause serious economic losses by damaging agriculture and fishing both commercial and recreational. The geographical extent of the environmental damage can be greatly enhanced in the event of flooding.

Apart from water pollution resulting from mining, considerable amounts of water are needed during coal burning, but generally this does not result in any significant pollution with the important exception of acid rain, which occurs when carbon dioxide and especially sulfur dioxide in the flue gases react with rain water far from the plant to produce carbonic

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Figure 2.9 Trees killed by acid rain in Germany.

acid and sulfuric acid. We include these under "waterborne" pollution even though they leave the plant as gases, because they are deposited with rain. These corrosive substances (especially sulfuric acid) can kill trees and render lakes fish free. Since many power plant smokestacks are extremely tall such pollution is reduced locally, but the net effect is the creation of acid rain often many hundreds of miles from the source sometimes in another country. Through legislation, the acid rain problem has been considerably reduced in the United States and the European Union at a fairly modest cost (about a quarter of what had been predicted), but it remains a significant problem in Russia, China, and elsewhere (Figure 2.9).

The extra CO_2 put into the atmosphere by coal burning also has a significant impact on the world's oceans, making them more acidic (lower pH), as they absorb extra CO_2 from the atmosphere. For example, since the industrial revolution the average oceanic pH has decreased from 8.25 to 8.14. This change may sound insignificant, but it is actually a sizable change in acidity of nearly 30%. Moreover, by the year 2100, it is expected that as a result of rising levels of atmospheric CO_2 , the acidity is likely to rise to 227% of the preindustrial level, having profound effects on aquatic organisms.

2.2.8.4 Example 3: Connection between Acidity and pH Levels What pH change corresponds to a projected acidity increase of 127% by the year 2100?

Solution The definition of pH is

$$pH = -\log_{10} H^+ \tag{2.4}$$

where H⁺ is the hydrogen ion concentration in moles per liter. Based on the preindustrial pH level of the oceans of 8.25, we find using Equation 2.4 that the hydrogen ion concentration then was H⁺ = $10^{-pH} = 10^{-8.25} = 5.62 \times 10^{-9}$. If the acidity, i.e., the number of H⁺ ions, were to increase by 127%, the acidity would rise to $2.27 \times (5.62 \times 10^{-9}) = 1.27 \times 10^{-8}$ and the pH would then be $pH = -\log_{10} 1.28 \times 10^{-8} = -7.89$, a change of -0.36 from its pre-industrial value.

The greatest impact of increasing oceanic acidity is likely to be on the production rate of shells from calcium carbonate, since this calcification process is greatly inhibited by rising ocean acidity. Although the full range of the impact of reduced shell production remains unclear, it is likely to be highly detrimental to the biology and survival of a wide range of marine organisms, as indicated by lab experiments on some specific species (Hardt, 2010).

2.2.8.5 Impacts on the Land Surface coal mining has a severe impact on the landscape, and usually destroys the preexisting ecosystems and habitat—a disruption that is generally permanent. It is not unusual for hundreds of surrounding acres to be affected, and people living in the affected areas to be permanently displaced. Without rehabilitation efforts, the loss of topsoil and the toxic elements produced by mining may leave the land a vast infertile wasteland. With major rehabilitation efforts once a mine is shut down, some of the land may be reclaimed, but the result generally leaves the land unsuited to its original uses.

2.2.9 Carbon Sequestration and "Clean" Coal

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Is "clean coal" just a slogan promoted by coal companies, or does it hold the promise of making coal an environmentally benign energy source? Certainly the technology exists for significantly reducing pollutants other than CO₂. These technologies include "scrubbers" that remove gases (especially sulfur dioxide), toxic trace elements, and dust after combustion. They have been implemented for some coal-fired power plants, with the result that in many nations many newer coal plants are significantly cleaner than they used to be. Scrubbers, for example, have been implemented in about half the world's coal-fired plants, and the simple expedient of burning low-sulfur coal can, when possible, also further cut down on pollution. However, the real question concerns the possibility of eliminating or significantly reducing CO_2 emissions. This is a much more difficult challenge whose feasibility and cost-effectiveness remains to be demonstrated. Moreover, once the CO₂ has been removed, there is the technically difficult matter of disposing of it ("sequestering" it) at reasonable cost and in a manner that keeps it secure and does not allow it to enter the atmosphere at a later time.

Two of the disposal methods that have been investigated extensively include storing CO_2 in abandoned mines, and injecting it into old oil or

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2.2 Coal 47

gas fields that are no longer producing or in repositories under the deep ocean bottom. If the gas is injected at depths in excess of 2700 m its density would exceed that of seawater, so that it presumably would not rise to the surface. Nevertheless, despite the claims of industry spokesmen, there is no indication that carbon capture and sequestration (CCS) technology is anywhere close to fruition economically. Those technologies that have been developed could, if implemented, double the cost of generating electricity from coal, making their widespread implementation entirely dependent on subsidization or equivalently on setting a price on CO_2 emissions—either through a "cap and trade" system or, alternatively, a carbon tax. Given that many renewable energy technologies, especially wind power, are already approaching cost parity with coal and getting cheaper over time, the whole idea of promoting coal use (given all its other environmental problems besides climate change) is difficult to understand unless one's individual livelihood depends on the coal industry.

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BOX 2.4 U.S. CCS PROGRAM

The largest U.S. CCS effort by a major utility was indefinitely shelved in 2011. The company did not know if regulators would permit it to charge customers to recover the costs of the project, and it also believed, probably correctly, that the likelihood of the U.S. Congress to enact any climate legislation relating to global warming—including cap and trade or a carbon tax were negligible in the near-term future.

The most promising possibility, which might be a realistic, economically viable solution, would be carbon capture and utilization (CCU) rather than carbon capture and sequestration (CCS). A variety of ways captured CO_2 might be used include

- As a feedstock to synthesizing various chemicals
- As a way to produce construction materials through mineral carbonation
- As a nutrient to promote algae growth for biofuel production

It has even been suggested to turn the CO_2 into an energy source itself through a variety of methods. One of these would involve injecting it at sufficient underground depth, where the temperature and pressure would convert the gas into a supercritical state giving the gas some liquid properties, and then allowing it (when pulled up to the surface) to drive turbines. Of course, the question remains whether any of these schemes can be made cost effective, and whether the harmful environmental and health impacts of coal unrelated to climate change can be reduced greatly to the point where "clean coal" becomes more than an industry slogan (Figure 2.10).



Figure 2.10 Various options for carbon sequestration.

2.3 PETROLEUM AND NATURAL GAS

Petroleum or crude oil is a liquid hydrocarbon consisting of many kinds of complex molecules. Its elemental composition includes 83%-87%carbon, 10%-14% hydrogen, 0%-6% sulfur, and under 2% nitrogen and oxygen. Natural gas is a gaseous hydrocarbon, primarily methane, CH₄, with up to 20% higher hydrocarbons, primarily ethane. Recall that the complex molecules found in coal tend to have many strings of carbon atoms arranged in hexagons—see Figure 2.2. Oil, on the other hand, arose from the remnants of decaying microorganisms, mainly marine plants and animals, rather than long plant fibers. The microorganisms produce hydrocarbons with chains of various lengths. The shorter chain hydrocarbons exist as a gas (natural gas) and the longer chains as a liquid (oil or petroleum). As with coal, petroleum or crude oil contains various amounts of impurities, such as sulfur.

2.3.1 History of Petroleum Use

In one form or another petroleum was known going back around 4000 years, but it was not until the 1850s when a process was invented to extract kerosene from it as an alternative to whale oil used for lighting lamps that the first commercial oil well was drilled in Poland. Initially, the natural gas that often accompanies petroleum was simply burned off and wasted, because there was no easy way to store and transport it, since gas pipelines came much later. In the United States, oil drilling got its start in 1859 when a black fluid was found oozing from the ground in Titusville, Pennsylvania. Oil usage really began to take off when cars powered by an internal combustion engine began to be mass produced during the early years of the twentieth century—see Figure 2.11.

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Figure 2.11 World oil production since 1940. Projections from various indicated sources mostly show the peak production year within a few years of 2010, although some do show it to be decades in the future. (From http://en.wikipedia.org/wiki/Peak oil)

On a worldwide basis, oil production has shown considerable growth since the early years of the twentieth century. One cannot know exactly how oil production will vary in the future, but projections can give estimates that take into account such factors as known proven reserves, the increasing costs of extraction (as less accessible locations are drilled), the costs of alternatives, environmental concerns and regulations, and market forces.

2.3.2 Resource Base of Oil and Gas

As in the case of coal, the world's petroleum reserves are quite unevenly distributed around the globe. While the nations of the Middle East have a majority of the proven reserves (56%), as seen in Figure 2.12, there are also very significant deposits in North America (16%), Africa (9%), South America (mainly Venezuela, 8%), and Eurasia (7%). The United States at one time did have a much larger fraction of the world's proven reserves, but the nation has been consuming them at a prodigious rate, so the peak year for U.S. oil production (1970) has long since passed. Not surprisingly, an increasingly large fraction of oil consumed by the United States (the world's largest consumer) depends on imports, despite exhortations by seven U.S. presidents (beginning with Nixon) on the need for greater energy independence. U.S. oil imports steadily rose in recent decades. For example, they grew from 27% of oil consumed to 67% over the two



Figure 2.12 Proven oil reserves by country in billions of barrels, as reported in the U.S. Central Intelligence Agency Factbook, 2010. (From http://en.wikipedia.org/wiki/File:Oil_Reserves.png)

decades prior to 2007; only since 2007 has this fraction dropped—less because of U.S. domestic oil production than economic conditions. Oil imports represent a major contributor to the nation's trade deficit. In fact, the U.S. half-trillion trade deficit (in 2011) would be roughly halved were it not for imported oil. For any finite resource a point in time is always reached when the extraction rate reaches a maximum, which is then followed by an inevitable decline. For oil there is reason to believe that within a few years one way or the other that peak time is now—a topic discussed at greater length in Section 2.3.5.

Natural gas deposits can be found on their own, but it is often found in conjunction with oil. Thus, with some exceptions, some of the same nations that have large oil reserves also have large gas reserves as well. As of 2010, the world's proven natural gas reserves are 188 trillion m³, and the top six nations have the percentages as listed in Table 2.3.

Among the exceptions, we see that Russia has greater gas reserves than any other nation, even though its oil reserves are dwarfed by some Middle East nations; likewise, the United States has virtually the same gas reserves as Saudi Arabia, even though its oil reserves are less than a tenth those of the Saudi's. One of the major energy developments for the United States in the last decade has been a near doubling in the nation's reserves of natural gas owing to new technologies that make it possible to extract gas from deposits (mainly in natural gas shale) that was previously considered unreachable. The technology known as horizontal drilling hydraulic fracturing is discussed in Section 2.3.6.1.

2.3.3 Formation and Location of Oil and Gas

Oil and gas have been formed primarily from decaying microscopic marine organic matter (plankton) including algae. Another difference from coal is that oil and gas can seep upward through porous rock layers. Thus, usually oil and gas form within a source bed and then migrate

Table 2.3	Percentage of the Proven
Reserves	of Natural Gas in the
World, as	of 2010

Country	% World Gas Reserves		
Russia	25.0		
Iran	15.6		
Qatar	13.4		
Turkmenistan	3.95		
Saudi Arabia	3.92		
United States	3.64		

Source: https://www.cia.gov/library/ publications/the-world-factbook/ rankorder/2179rank.html

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Figure 2.13 Depiction of oil and gas deposits formed under heat and pressure from source rocks and migrating upward through porous rocks and faults until they are trapped below a layer of nonporous rock. (Courtesy of U.S.G.S., http://teeic.anl.gov/er/oilgas/restech/dist/index.cfm)

up into a porous reservoir bed. For the deposits to survive, it is further necessary to have a nonporous cap rock above the reservoir formation to trap them, or the gas and oil would not be concentrated and the oil field would not exist. This requirement, of course, is not necessary for coal, which is a solid. Unlike the implication of Figure 2.13, the oil and gas may not be present in literal pools, but instead be present in the tiny pores of the porous rocks.

Oil shales or gas shales accumulate differently. In this case, the hydrocarbon accumulates in the nonporous shale and is trapped there, dispersed throughout the rock. Hydrofracturing creates porosity and the fluids can be extracted.

Given the very specific arrangement of rock layers necessary for oil and gas deposits, geologists can explore for them by discerning the stratigraphy and structure of rock layers in different locations using seismic studies, and then drilling test holes. Drilling can be an expensive process, depending on the well depth. Many promising locations can be undersea, which of course makes the oil drilling and extraction process even much more expensive and risky if any is found.

Undersea locations are also the place where large repositories of methane can be found in the form of "clathrates," or methane hydrates, which are crystalline water-based solids similar to ice that can trap methane. In fact, estimates are that 6.4 trillion tons of methane is trapped in

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deposits of methane clathrate on the ocean floor, but extraction is far from being economically feasible. Petroleum formation requires certain temperature and pressure conditions. If the temperature is too low, gas may form, but not oil. At higher temperatures (the oil window), both oil and gas may form. Higher temperatures than this will destroy the oil, converting it back to methane. Many of the world's older oil and gas provinces, like those in the United States and Russia, have experienced temperatures beyond the oil window, so that many of their fields are now gas fields.

Unlike oil, natural gas, in addition to being formed biogenically, can also have an abiogenic origin. According to theory, at very great depths in the Earth the high temperature and pressure can convert buried organic matter into natural gas "thermogenically." Without such an alternate nonbiogenic formation process it would be difficult to understand how abundant quantities of methane ever arose on the "gas giant" planets (including Jupiter) and their moons, where no one believes that life had ever existed.

2.3.4 Are Coal, Oil, and Gas Really Fossil Fuels?

The notion of being a fossil fuel implies that it was mainly formed from what originally was living material that over the course of time was transformed through the application of heat and pressure. We need, however, remind ourselves that this commonly accepted belief is simply a theory of the formation of coal, oil, and gas and that the evidence for this theory needs to be weighed against possible competing theories. One alternative possibility is that the dominant process for producing hydrocarbons was abiogenic, with the organic material from which they were formed being part of the original composition of the planet. In this view championed by the late Cornell University physicist, Thomas Gold, and many others, hydrocarbons are formed deep in the Earth and seep upward through the Earth's crust, and either reached the surface or formed underground deposits—some of which later solidified to become coal (Gold, 1999).

As noted at the end of the last section, geologists readily admit that this scenario can and does occur for methane, and even solid carbonaceous material (diamonds), but they are loathe to extend it to liquid petroleum, and most especially to coal. Elsewhere I have examined the "crazy" idea that coal, oil, and gas are in fact primarily not fossil fuels, as part of an effort to consider a variety of controversial scientific theories and assess the evidence for and against them (Ehrlich, 2001). My finding that Gold's hypothesis of a largely abiogenic origin is reasonably plausible was not to the liking of a number of geologists who subsequently contacted me to express their strong disapproval. Nevertheless, the author continues to believe that the hypothesis, while unproven,

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2.3 Petroleum and Natural Gas 53

continues to be plausible. Apparently, the abiogenic hypothesis was actually quite widely believed in the past among geologists, but it was abandoned at the end of the last century after it failed to be useful in predicting where oil deposits could be found (Glasby and Geoffrey, 2006). However, while utilitarian thinking is understandable among energy company scientists, it seems irrelevant in regard to the validity of scientific theories.

These are some of the arguments in its favor of the abiogenic theory:

- Lab experiments show that hydrocarbons can be synthesized under the temperature and pressures found in the Earth's upper mantle.
- Porosity in rocks provides migration pathways upwards for liquids and gases, but not for coal, which is solid.
- If methane is known to have an abiogenic origin, why not petroleum as well, since the same basic mechanism is used (in the biogenic theory) to account for them.
- So-called biomarkers found in petroleum, supposedly giving evidence for its biogenic origin, have been found in some meteorites.
- Petroleum tends to be found in large patterns related to deep large-scale structural features of the crust rather than a patch-work of sedimentary deposits.
- There are indications that gas and oil deposits refill spontaneously over time—presumably from below.

There are, of course, many arguments against the theory. For example, geologists note that the spontaneous refilling of oil deposits need not imply upwelling from deep inside the Earth, but could indicate seepage upwards from another layer below the deposit. Moreover, chemists note that when they analyze crude oil they always find steroid molecules and there is no known way to create such molecules other than from living creatures.

BOX 2.5 WHY SHOULD WE CARE IF COAL, OIL, AND GAS ARE REALLY FOSSIL FUELS?

Whether or not the abiogenic origin theory of petroleum can serve as a guide to locating new promising locations for finding oil, it still has important real-world implications if true. First, as the last point in the arguments given earlier indicates, future petroleum sources might simply hinge on leaving wells fallow for a while. Second, if the total amount of petroleum and other fossil fuels is vastly greater than we now imagine (as the abiogenic theory suggests), the potential impact on climate change is also vastly greater without a shift away from them. Third, if the supply of fossil fuels is indeed "near infinite" (i.e., with a many 1000 year supply), the problem discussed in the next section becomes moot.

2.3.5 Peak Oil

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The concept of peak oil was first raised by geologist M. King Hubbert in 1956. His basic idea was quite simple, namely, that as long as the quantity of oil is finite, then for any given location, or a nation, or even the planet as a whole, the rate of oil production will tend to follow a bellshaped curve. Consider, for example, a single oil field-how would we expect the annual production from it to vary in time? Following its initial discovery, efforts are ramped up to exploit it, and as more and more wells are drilled the production rate will rise rapidly. At some point, extraction becomes increasingly difficult, the rate of increase in production tapers off, and a maximum production rate is reached, to be followed by an inevitable decline, as the field begins to become exhausted. Although Hubbert initially did not suggest a specific mathematical function to describe the bell-shaped curve of production from a particular oil field versus time, he later suggested the derivative of the logistic function $Q = Q_0(1 + ae^{-bt})$, which agrees better with observations than the more familiar Gaussian curve. Applying Hubbert's function to an entire nation rather than one oil field still gives good agreement with his theory, provided the nation's oil or gas supply tends to be not too diverse geographically—see Figure 2.14a for the nation of Norway. On the other hand, a large nation like the United States, whose oil exploration efforts are in geographically different regions, might be expected to agree less well with his theory—see Figure 2.14b. It is noteworthy that Hubbert's theory of peak oil was made at a time when the climb up the bell curve in many nations was in its early stages, i.e., well before the peak. Moreover, Hubbert applied his theory to the world as a whole for which he predicted a maximum oil production around the year 2000, although he did not foresee that a simple bell-shaped curve would apply



Figure 2.14 Oil production for (a) Norway and (b) the United States versus time with fitted Hubbert curves. (From http://en.wikipedia.org/wiki/File:Hubbert_US_high.svg)

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in this case. If anything, one might expect a sum of bell-shaped curves displaced in time, as new more challenging sources are exploited.

Additionally, for the world as a whole, one needs to take into account many factors that do not apply to a single oil field, given the very long timescale involved. These factors include supply and demand issues as well as the cost of competing alternatives to oil-factors Hubbert could only guess about in 1956. In other words, as oil becomes increasingly scarce, its price will rise due to both market forces and the need to drill in more challenging deposits (such as under the sea floor). At some point, the rising oil price will make alternative fuels more desirable, which will further depress the rate of oil extraction. Not surprisingly, Hubbert's 1956 prediction for world peak oil was imperfect, since the peak of world oil production did not occur around the year 2000 as he suggested 44 years earlier, but rather at least a decade later. Nevertheless, the essentials of his prediction would seem to be correct. Today, many geologists believe that there is around a 40 year supply of oil at the present rate of consumption (production), which is quite consistent with a 2011 peak, given a bell-shaped curve having Hubbert's predicted width. There are, of course, many dissenters, and some analysts put the peak at around 2040 when taking into account oil from unconventional (and more expensive) sources (Feasta, 2007). Figure 2.11 shows a variety of predictions regarding when peak production will be reached.

The domestic and international socioeconomic implications of peak oil are extremely important, because it suggests that moving away from fossil fuels (petroleum in particular) is not just a matter of choice but of necessity. It also implies that if the world does not make the transition very soon, the result could mean profound societal disruption, as oil supplies become increasingly scarce relative to demand, with ever-increasing potential for international conflict arising from competition for access to oil. The pressures are likely to be aggravated by the rapid economic rise of China and India, and by having so much of the world's petroleum reserves in the politically unstable Middle East. It will be especially acute for nations such as Japan, which is entirely dependent on imported energy, and to a lesser extent for the United States, a nation that depends heavily on imported oil. The potential for conflict is further exacerbated by the impact of climate change on food availability and access to water in many developing countries, even if they have little need for oil themselves. In fact, the quartet of food, energy, water, and climate (to which might be added economic and political turmoil) has been referred to as "a perfect storm for global events" (Beddington, 2009).

2.3.5.1 Example 4: How Many Years Are Left? Show that if the present world consumption of a resource is now at its absolute peak and consumption follows a Gaussian curve, then *T* defined as the number of years left at the present rate of consumption R_0 is roughly equal to half of the full width of the Gaussian at half max (FWHM). Note that it can easily be shown that the FWHM and standard deviation are related by *FWHM* = 2.35 σ .

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Solution

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If we are now at the peak (mean zero), the future annual consumption can be written as the following function of time *t*, where σ is the standard deviation:

$$R = R_0 \exp\left(-\frac{t^2}{2\sigma^2}\right) \tag{2.5}$$

Integrating Equation 2.5 over all future time gives us the amount of the resource remaining A:

$$A = \frac{1}{2}\sigma R_0 \sqrt{2\pi} = \frac{1}{2.35} (FWHM) R_0 \sqrt{\pi/2} = R_0 T$$
(2.6)

where the last equality follows from the definition of *T*. Solving Equation 2.6 yields $T = 0.53 \times FWHM$. Thus, if the peak is occurring about now, the number of years left at the current rate of usage is (within 7%) equal to half the FWHM, or about 40 years. This, of course, is only a mathematical exercise not a prediction, since various observers have very different estimates of when the peak of oil production will occur.

2.3.6 Petroleum and Natural Gas Processing

Starting from the original petroleum or natural gas deposit that has been located based on its geology and confirmed by test wells, there are many steps before the products of the crude oil or gas can be utilized, and we shall here discuss these three: extraction, transport, and refining.

2.3.6.1 Extraction of Oil and Gas In its initial stages after drilling an oil well, the pressure is usually sufficient to force the oil to the surface spontaneously. Typically, this primary recovery stage lasts up to 5%-15% of the capacity of the reservoir. Once the pressure drops and the extraction reaches its second stage, pumps must be used or water must be injected into the well to bring oil to the surface. At some point even these methods fail, and it is necessary to use enhanced recovery methods to make the oil easier to extract, which include injecting steam heat (to reduce the oil viscosity), or surfactants (detergents) to lower its surface tension. One enhanced recovery method around since the 1940s is known as hydraulic fracturing, hydrofracking, or simply fracking. In this method, fluids are injected into rock formations in order to induce fractures in them and to provide a pathway for oil trapped in the pores of the rock to reach the surface. Thus, the injected fluid (usually a mixture of water, chemicals, and suspended sand-like particles) has the dual purposes of opening and extending fractures, and aiding in the transport of suspended particles in the fluid so as to keep the pathways open. Fracking is used with natural gas as well as oil, and it can greatly enhance the size of the recoverable reserves by making it possible to extract oil and gas from rock formations very deep in the Earth up to 20,000 ft, and in formations not previously considered economically feasible, such as shale, which has very low

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natural permeability. The greater economy comes about when fracking is combined with the new technique of horizontal drilling. This combination has allowed extraction over an extended area using only one vertically drilled well instead of 10. As was noted earlier, owing to these new technologies, the extent of the proven reserves in the United States has approximately doubled within the span of a decade. Nevertheless, the practice of fracking remains a highly controversial one due to environmental considerations—see Section 2.3.8.

2.3.6.2 Refining of Gas and Oil Generally, crude oil and natural gas needs to be processed or refined before they are useful. Refineries are sprawling extremely complex chemical plants with miles of piping connecting various processing units. Natural gas processing is designed to clean raw natural gas by separating impurities and various non-methane hydrocarbons so as to produce "pipeline quality" dry natural gas, but the complex processes will not be described here. Oil refineries typically can process several hundred thousand barrels of crude oil per day, and usually operate on a continuous process, rather than in batches. The basic process in an oil refinery involves separating out the various useful components of crude oil according to their degree of volatility through a process known as fractional distillation. The different useful components of crude oil include many components including, among others, gasoline, kerosene, diesel oil, fuel oil, lubricating oil, wax, and asphalt. Each of the crude oil components consists of many different molecules whose structure give the substance its desirable properties, which may make it suitable as a fuel, lubricant, tar, or feedstock for producing petrochemicals, among other purposes. Unlike a pure substance consisting of a single molecule with a single boiling point, the distillates of crude oil are each defined in terms of a range of boiling points. Thus, kerosene is that distillate whose boiling point lies in the interval 150°C–200°C. The fractional distillation process in cartoon version is shown in Figure 2.15.

The petroleum distillates having low boiling points tend to be lighter, and commonly they are grouped into the three categories: light, middle, and heavy or residium (what is left after the lighter distillates are driven off). For example, the light petroleum distillates include liquefied petroleum gas (LPG), gasoline, and naphtha, and the middle distillates include kerosene (and related jet fuels) and diesel oil. Among those distillates intended as fuels it is important to remove non-hydrocarbon components such as sulfur, which can be a useful by-product for other purposes (such as making sulfuric acid). Fuels are also further processed in other ways, including blending them to achieve the desired octane rating, which measures the self-ignition temperature.

There are 148 oil refineries in the United States, and nearly half of them are in three states (Louisiana, Texas, and California), all near coastal areas—making them highly vulnerable to hurricane damage in the event of a landfall. Owing largely to environmental concerns, no new refinery has been built in the United States since 1976, although many existing refineries have been

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Figure 2.15 Fractional distillation process in an oil refinery in the case of "straight run" refining. Most gasoline today is made by "catalytic cracking" of large molecules to small molecules and then reforming them into gasoline.

expanded. In terms of economic damage, disruption of the economy, and danger to surrounding communities, oil refineries also may represent a more desirable target for terrorists than a better protected nuclear plant—even if they lack the psychological "dread factor" associated with all things nuclear. Such vulnerability is even more acute for nations such as India that have their oil refineries even more highly concentrated—with India's Reliance Petroleum refinery handling half the capacity in the entire nation.

2.3.7 Gas and Oil Power Plants

Electric power from generating plants that use natural gas as the fuel is environmentally less damaging than coal, and these plants have been especially useful in supplying power during peak times. The ability to supply peaking power arises because unlike coal plants their power output can be varied on a short timescale by adjusting the gas flow. Newer gas turbine power plants rely on a combined cycle using several turbines in series. In a combined cycle plant some of the heat expelled from the first cycle is converted into work (driving a second generator). Since more work is produced for the same input of heat, the combined cycle has significantly higher efficiency than a single cycle, and they are, therefore, much more economical. A combined cycle plant works best when the firing temperature in the first turbine (the gas turbine) is relatively high, so that the exhaust flue gas temperature is still quite high $(450^{\circ}\text{C}-650^{\circ}\text{C})$ and it is able to supply sufficient heat to provide the heat to the second stage; often, the second stage uses steam as the working fluid and operates on a Rankin cycle—see Section 2.2.5.2. A schematic representation of a binary cycle plant is shown in Figure 2.16. Triple cycle plants having a high, medium, and low pressure turbine also exist and they are still

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Figure 2.16 Schematic representation of a combined cycle (binary) power plant.

more efficient. From the input and output of each cycle in Figure 2.16 it is easy to see that the efficiency of a binary cycle plant can be expressed in terms of the efficiencies for each cycle as

$$e_{\rm CC} = \frac{Work}{Heat_{in}} = \frac{e_1 Q + e_2 (1 - e_1) Q}{Q} = e_1 + e_2 - e_1 e_2$$
(2.7)

The much higher efficiency of combined cycle gas-fired power plants also translates into both greater economy and lower CO_2 emissions per MW generated. For example, while conventional coal-fired plants are less expensive than conventional (single cycle) gas-fired plants, this is not the case when conventional combined cycle gas-fired plants are considered. The cost comparison is even less favorable to coal if CCS were required. It should, therefore, not be surprising that a number of nations, including the United States, Germany, and the United Kingdom, plan to shift increasingly toward gas-fired combined cycle plants, and much less heavily on coal plants in the future.

2.3.7.1 Example 5: A Binary Cycle Plant Suppose that the first stage of a binary cycle power plant has an efficiency of 35%. What is the maximum possible overall efficiency if the second stage operates at a temperature of $227^{\circ}C = 500$ K and expels heat to the environment at $27^{\circ}C = 300$ K?

Solution

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The maximum efficiency for the second stage is found from the Carnot efficiency, which gives $e_2 = 1 - (300/500) = 0.4$. Thus, using Equation 2.7, we find for the overall efficiency $e_{CC} = e_1 + e_2 - e_1e_2 = 0.35 + 0.40 - (0.35)(0.4) = 0.61\%$ or 61%.

2.3.8 Environmental Impacts of Oil and Gas

The environmental impacts of oil and natural gas are considerable, and they occur at various points including their extraction, transport, refining, and eventual usage, mainly as transportation fuels or in electric **((()**

power generation. In considering the environmental impacts from coal, we have seen earlier that its atmospheric emissions are significantly greater than those for oil and gas. For the transportation sector, it is possible to fuel cars and trucks using liquefied natural gas (LNG) or compressed natural gas (CNG) instead of gasoline with some engine modification. Studies of such vehicles show reductions in pollution levels of typically 49% for nitrogen oxides, and 90% for particulates. Although natural gas CO₂ emissions are significantly less for natural gas than coal (see Table 2.2), the reduction for natural gas compared to gasoline is more modest though still significant—up to 25% depending on the natural gas source. Thus, proposals to convert part of the transportation sector (such as all heavy trucks) to natural gas make sense in terms of some reduction in oil imports, as well as resulting in less air pollution—both CO_2 and, especially, non- CO_2 . Although CO_2 emissions from the use of natural gas are certainly less than those of coal, a sometimes overlooked source of emissions occurs due to gas leaks that can release prodigious amounts of methane into the atmosphere. Like CO_2 , methane is a greenhouse gas and, in fact, has 25 times the global warming impact on a per kg basis. According to the EPA's estimate, the leakage rate for natural gas is about 2.4%. This is below the critical value 3.2% above which natural gas would actually be a more potent source of global warming than coal!

The chief environmental concern regarding natural gas probably involves the practice of "fracking," and the resultant contamination of groundwater by chemical additives to the fluid injected into the oil or gas wells. Quite apart from chemical additives, wastewater from fracking is also often laced with highly corrosive salts, carcinogens like benzene, and other naturally occurring radioactive elements, like radium, that can occur naturally deep underground. One 2010 study by the EPA discovered toxic contamination of drinking water adjacent to wells, although the study was not able to exclude other sources of contamination such as agriculture (EPA, 2010). Another recent study by the Massachusetts Institute of Technology came to a similarly mixed conclusion, namely that "The environmental impacts of shale development (by fracking) are challenging but manageable." It further concluded that "There has been concern that these fractures can also penetrate shallow freshwater zones and contaminate them with fracturing fluid, but there is no evidence that this is occurring" (MIT, 2011a). Other university studies of the problems associated with water contamination are more ominous. For example, according to one 2011 study the methane concentration in water samples from 68 wells near shale gas drilling were found to be at a dangerous level, based on U.S. Department of Interior standards. In some cases the levels are high enough for homeowners to ignite the methane contained in the water coming out of their faucets by putting a match near the water stream. A final report on fracking was prepared by the U.S. Department of Energy in 2011. Essentially, that report supports using hydraulic fracturing ("fracking") but with a variety of safeguards and continuous

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monitoring of wells for emissions (DOE, 2011). Other specific measures cited in the DOE report include disclosure of the composition of fracking fluids, and the prohibition of specific fluids (diesel fuel). Drilling gas or oil wells is an expensive proposition, and some drilling companies have resorted to shoddy practices in their haste to begin extracting gas in the shortest possible time.

BOX 2.6 RECONCILING CONFLICTING CLAIMS ABOUT FRACKING

The natural gas industry claims that no case of groundwater contamination caused by fracking has ever been documented, and yet some environmentalists maintain that thousands of cases of groundwater contamination due to oil and gas drilling have been documented. Surprisingly, both of these claims could be true. There are many ways that groundwater can become contaminated as a result of drilling, including surface spills followed by percolation down to an aquifer—a much more likely route of contamination than fracking for which the induced fractures occur at depths of thousands of feet. Since fracking results in less vertical wells drilled than previously, its net impact actually could be less groundwater contamination.

Another area of significant environmental impact associated with oil and gas is that of oil spills.

Many small oil spills occur on a regular basis and fail to be reported in the media, but when a large spectacular one occurs, it can absorb the public attention for a considerable time, as was the case in the 2010 BP Deepwater Horizon disaster. Large oil spills can devastate the wildlife in the affected area. For example, even after cleaning, probably less than 1% of oil-soaked birds survive, so the effort would appear to be done primarily for public relations purposes. The restoration of the ecosystem by cleanup efforts can be difficult and lengthy and may depend as much on human remediation efforts as on nature, including the weather, ocean currents, and the presence of oil-consuming bacteria in the water. While the economic damage of a large oil spill may be relatively easy to assess, the full long-term impact on the ecosystem and to human health (especially among cleanup workers) may be much less so. While oil spills will remain a fact of life as long as the world relies on petroleum, it is however worth noting that while small oil spills occur on a daily basis, large spills have become less frequent with each passing decade since the 1970s (ITOPF, 2011).

The health and fatality costs associated with oil and gas pipelines can also be considerable. In 2011, for example, a gasoline pipeline exploded in Nairobi Kenya killing nearly 100 people. All things considered, while oil and natural gas are very far from environmentally benign, their impact on the environment is probably not nearly as bad as coal's, particularly in the case of natural gas. This judgment should not be interpreted as a reason to

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stick with fossil fuels, since they all do have serious negative impacts on the environment—it is only a judgment regarding which impacts are worse.

BOX 2.7 NATURAL GAS—FRIEND OR FOE TO RENEWABLE ENERGY SOURCES?

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There are two schools of thought concerning the relationship between natural gas and renewable energy sources such as wind and solar. Some observers (including the author) see natural gas as an important "bridge fuel" that can replace coal, and to some extent oil as well, as a much cleaner alternative during the decades necessary for a complete switch to renewable sources. Other observers take the contrary view that abundant cheap natural gas will impede the transition to renewable sources. However, given the rate at which the costs of renewable sources are decreasing, and the rate at which they are penetrating the marketplace, this concern may be unwarranted. Moreover, natural gas can be a power source that fills in the gaps left by variable renewable sources in order to provide steady electrical output to the grid. Thus, it offsets the variability of renewable sources, which will become increasingly important as the clean energy portfolio expands. One argument that some environmentalists give against the notion of natural gas as a "bridge fuel" is that it will probably stand in the way of limiting the global temperature rise to at most 2°C by the year 2100, which they view as a maximum level that will not be catastrophic. The merits of this argument will be discussed after the matter of climate change is fully considered in Chapters 9 and 14.

2.4 SUMMARY

This chapter considers the three fossil fuels, coal, oil, and gas, their formation, uses, and especially their environmental consequences, which can be very detrimental—especially in the case of coal. It also considers a variety of controversial questions including whether coal, oil, and gas are really fossil fuels at all, whether there can be such a thing as "clean" coal, and whether natural gas, which may be cleaner than coal or oil, can really serve as a "bridge" fuel while we move toward renewable energy sources.

PROBLEMS

- 1. Starting from the definition for a small change in entropy dS = dQ/T, show that $W = \oint PdV = \oint TdS$.
- 2. Explain why the Carnot cycle is described by a rectangle in a T-S plot. Hint: Based on the definition of entropy, why must adiabatic processes be represented by vertical lines?
- 3. Explain physically what is happening for step $3 \rightarrow 4$ in Figure 2.8.
- 4. Explain this sentence: "Based on the values of the constants in Equation 2.1 the maximum energy density requires H be as high as possible, and O is as low as possible, and the minimum energy requires the opposite."

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5. Suppose that a coal-fired power plant burns lignite coal. Based on the energy content of lignite (see Table 2.1), which is one type of "brown coal," estimate the CO_2 emissions in kg/GJ and compare your result with the emissions data of Table 2.2. Assume that all the carbon in the coal goes into CO_2 , with only a negligible amount creating CO.

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- 6. In Section 2.2.8, it was noted that since the industrial revolution the average oceanic pH has decreased from 8.25 to 8.14. Show that this corresponds to an increase in oceanic acidity of nearly 30%. Note that based on its definition pH is 7.0 for neutral distilled water, and that percentage increases in acidity are relative to this neutral point.
- 7. It has been suggested that one way to sequester CO₂ removed during coal burning would be to store it on the deep ocean floor at depths greater than 2700 m. (a) Find the pressure in atmospheres at that depth, assuming a density of seawater of 1020 kg/m³; and (b) determine the state of the CO₂ (solid, liquid, or gas) under such pressure from some searching on the web, assuming a temperature of 280 K; and (c) find a density–pressure phase diagram on the web that allows you to estimate the density at that depth, so you can verify whether the density exceeds that of seawater.
- 8. The world's proven natural gas reserves are estimated to be 1.9×10^{14} m³. Given that a ton of natural gas occupies a volume of 48,700 ft³ at atmospheric pressure, how does the amount trapped in hydrates (estimated at 6.4 trillion tons) compare to the proven reserves?
- 9. Explain these two sentences from the text: "Today many geologists also believe that there is around a 40 year supply of oil at the present rate of consumption (production). This expectation is actually quite consistent with a 2011 peak, given a Gaussian shape having Hubbert's predicted width."
- 10. In a combined cycle gas-fired plant does it matter which cycle has the higher efficiency? Which cycle might you expect in fact has the higher efficiency? What would be the analogous formula for overall efficiency for a triple cycle plant, in terms of the three efficiencies, e_1 , e_2 , and e_3 ?
- 11. Consider a power plant having a fixed electrical power output of 1000 MW. Show that if the efficiency of the plant were to increase from 33% to 50%, the amount of rejected heat per MW generated is halved.
- 12. For a combined cycle (binary) power plant show that if it is assumed that each cycle were a Carnot cycle, the overall efficiency is identical to what it would be for a single cycle having the same combustion and ambient temperatures.
- 13. The United States consumes about 400 million gallons of gasoline per day. Suppose that the nation's entire fleet of 2 million 18-wheeler tractor trailer trucks were converted to natural gas, by what amount would the fraction of U.S. oil imports decrease? Assume that the United States imports are 50% of all the oil it consumes and that the average 18-wheeler gets 6 mpg, and drives 60,000 miles per year.

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- 14. If your view of "fracking" (hydraulic fracturing) is that it is too risky to be pursued, look up some sources that support this view and, in a one-page description, see if you can find any flaws in the arguments. Do the same if your view happens to be that fracking should be pursued.
- 15. Write a one-page analysis on the relative importance of political and economic factors behind our addiction to fossil fuels versus strictly technical issues, such as their rich energy density.

REFERENCES

Beddington, J. (2009) Food energy water and the climate: A perfect storm of global events? http:// www.guardian.co.uk/science/2009/mar/18/perfect-storm-john-beddington-energy-foodclimate

China (2004) Shanghai Star Newspaper. November 18, 2004 http://app1.chinadaily.com.cn/ star/2004/1118/bz9-3.html

China (2005) People's Daily Online. March 18, 2005 http://english.peopledaily.com.cn/200503/18/ eng20050318_177365.html

China (2009) http://www.nytimes.com/2009/05/11/world/asia/11coal.html

DOE (2011) http://www.shalegas.energy.gov/resources/111811_final_report.pdf

EEA (2008) European Environment Agency (EEA) gives fuel-dependent emission factors based on actual emissions from power plants in EU. *Air Pollution from Electricity-Generating Large Combustion Plants*, EEA, Copenhagen, Denmark, ISBN 978-92-9167-355-1.

Ehrlich, R. (2001) Nine Crazy Ideas in Science, Princeton University Press, Princeton, NJ.

EPA (2004) http://www.msnbc.msn.com/id/5174391/

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EPA (2010) EPA: Natural gas drilling may contaminate drinking water-science news, redOrbit, June 25, 2011.

Feasta (2007) http://www.feasta.org/2007/01/12/why-confusion-exists-over-when-the-oilpeak-will-occur/

Glasby, G.P. (2006) A biogenic origin of hydrocarbons: An historical overview, *Resour. Geol.*, 56(1), 83–96.

Gold, T. (1999) *The Deep, Hot Biosphere: The Myth of Fossil Fuels*, Copernicus Books, New York. Hardt, M.J. (2010) http://www.scientificamerican.com/article.cfm?id=threatening-ocean-life

Hvistendahl, M. (2011) Coal ash is more radioactive than nuclear waste: Scientific American, Scientific American, Nature America, Inc., December 13, 2007. Web: March 18, 2011.

ITOPF (2011) http://www.itopf.com/information-services/data-and-statistics/statistics/

- MIT (2011a) MIT Energy Initiative (2011). The future of natural gas: An interdisciplinary MIT study, MIT Energy Initiative, 7, 8, http://web.mit.edu/mitei/research/studies/documents/natural-gas-2011/NaturalGas_Chapter%201_Context.pdf, accessed July 29, 2011.
- MIT (2011b) http://blog.cleantechies.com/2011/06/22/liquefied-coal-may-become-aneconomically-viable-fuel-option/
- Spill (2011) Expert recommends killing oil-soaked birds, *Spiegel Online*, May 6, 2010, http://www.spiegel.de/international/world/0,1518,693359,00.html, accessed August 1, 2011.
- Zhang, J. and K. Smith (2007) Household air pollution from coal and biomass fuels in China: Measurements, health impacts, and interventions, *Environ. Health Perspect.*, June 2007, 115(6), 848–855.