Future Energy: Opportunities and Challenges

Part II. Energy Sources

Chapter 4. Fossil Fuels

Originally published 2013 by the International Society of Automation (ISA)

Future Energy:
Opportunities and Challenges

Thomas W. Kerlin

4
Fossil Fuels

The Main Points

- **The fossil fuel resources are oil, oil shale, oil sands, natural gas, and coal.**

- **Fossil fuels consist of carbon and hydrocarbons (compounds composed entirely of carbon and hydrogen).**

- **Producing energy with fossil fuels releases carbon dioxide, a greenhouse gas.**

- **Light hydrocarbons (four carbon atoms per molecule or less) are gaseous at normal temperature and pressure. Heavier hydrocarbons are liquid or solid.**

- **Oil is used in transportation, as a chemical feedstock, and for heating.**

- **Natural gas is used for heating, as a chemical feedstock, for producing electricity, and as minor contributor to transportation energy.**

- **Coal is used for producing electricity and in steelmaking.**

- **U.S. oil production peaked around 1970.**

- **Many analysts provide estimates of future world oil availability. Hubbert's method is best known. Most predictions estimate a peak in world oil production anywhere from 2010 to 2040.**

- **Accessible natural gas reserves and production rate have increased significantly because of new acquisition technology called hydrofracturing (or fracking).**

- **Fracking is beginning to have an impact on accessible oil reserves and production rate. Previously inaccessible oil is now being extracted.**

4.1 Introduction

Fossil fuels are the result of the action of heat and pressure on dead plant and animal matter buried in the earth. The dead matter was initially composed mostly of carbon, hydrogen, and oxygen. Over millions of years, heat and pressure beneath the surface induced chemical reactions that eliminated the oxygen and resulted in carbon and hydrocarbons. Coal is a solid fossil fuel composed mostly of carbon.

Hydrocarbons found in the earth have a wide range of chemical compositions. Some hydrocarbons are gases, some are liquids, and some are solids at ordinary temperatures and pressures. The fossil fuel resources are oil, natural gas, coal, oil sands, and oil shale. Additional fuels are available as biomass and various fuels derived from biomass. Biofuels are discussed in Chapter 7.

Fossil fuels enabled the Industrial Revolution (approximately 1820-1870 in the United States), and their continued use enables the current high standard of living in developed countries. Fossil fuels are a finite resource that will be depleted someday, but huge reserves remain that could sustain civilization for at least a few more decades. However, environmental concerns may prevent using them to their full capacity. There is little doubt that fossil fuel acquisition and transport result in environmental, health, and safety issues, and that fossil fuel consumption impacts climate and the environment (see Chapter 19). If the problems related to fossil fuel acquisition, transport, and use grow as predicted by many analysts, it may be necessary to curtail their use even if they remain available.

Fossil fuels may be used directly to produce energy through combustion, or they may be chemically altered prior to their use as a fuel. The most widely useful form of fuel is liquid, followed by gas, and then solid. Chemical con-

version of fossil fuels includes liquid-to-liquid, solid-to-liquid, solid-to-gas, and gas-to-liquid processes. These conversions involve adding, subtracting, and/or rearranging atoms in the molecules of the source material.

Hydrocarbons are compounds comprised entirely of hydrogen and carbon. The simplest hydrocarbon is methane, CH_4. Methane, ethane, propane, butane, and isobutane are gases at ordinary temperatures and pressures (defined as conditions at or near usual ambient conditions). Hydrocarbons with larger molecules (more than four carbon atoms per molecule) are liquids or amorphous solids at ordinary temperatures and pressures.

Hydrocarbons exist in an enormous range of chemical species. Their chemistry depends on the number of carbon atoms per molecule, the number of hydrogen atoms per molecule, and the configuration of the molecule. Molecule shapes may be linear, branched, or ring-shaped. Even for a limited range of carbon atoms per molecule, many different hydrocarbon species are possible.

Hydrocarbons that are gaseous at room temperature and atmospheric pressure have the fewest carbon atoms and the largest ratios of hydrogen atoms to carbon atoms. The properties of the important gaseous hydrocarbons are shown in Table 4-1.

Table 4-1. Properties of Gaseous Hydrocarbons

Hydrocarbon	Formula	H/C Ratio	Boiling Point (at atmospheric pressure)
Methane	CH_4	4:1	-258.5°F (-161.4°C)
Ethane	C_2H_6	3:1	-127.5°F (-88.6°C)
Propane	C_3H_8	2.67:1	-43.8°F (-42.1°C)
Butane	C_4H_{10}	2.5:1	16°F (-0.5°C) for n-butane
			11.1°F (-11.6°C) for isobutane

Note: Butane has two isomers—compounds with the same chemical formula but different molecular structures and different properties.

All of the gaseous hydrocarbons listed in Table 4-1 can be liquefied at lower temperatures and/or higher pressures. The boiling point data show the boiling temperature increases as the number of carbon atoms per molecule increases. Hydrocarbons with more than four carbon atoms per molecule are liquid or solid at ambient temperatures.

Liquid hydrocarbons used for fuel have hydrogen-to-carbon ratios of 1.7 to 2.2. It is important to remember that a hydrogen-to-carbon ratio of around two is needed for liquid hydrocarbon fuels. Carbon atoms per molecule range from five to 17 for gasoline, kerosene, jet fuel, and Diesel fuel and up to 45 for heavy fuel oil.

Coal is a complex mixture of carbon and hydrocarbon compounds with a hydrogen-to-carbon ratio of about 0.8.

Processing organic chemicals to modify properties involves changing the number of carbon atoms per molecule and the hydrogen-to-carbon ratio. Oil refining, gas-to-liquid, coal-to-liquid, coal-to-gas, biomass-to-liquid, and biomass-to-gas processing all depend on such processes.

Liquid and gaseous hydrocarbons all have high heating values (HHV) of around 20,000 BTU per pound. Volumetric high heating values (such as BTU per cubic foot or BTU per gallon) vary widely because of density differences.

4.2 Oil

Oil is a mixture of liquid hydrocarbons. Oil properties depend on the relative amounts of the constituent hydrocarbons. Oil hydrocarbons with a preponderance of smaller molecules (fewer carbon and hydrogen atoms per molecule) are said to be light oils, and those with a preponderance of larger molecules are said to be heavy oils. Light oils are generally less viscous and have lower boiling points than heavy oils.

4.2.1 Importance of Oil

Oil plays a crucial role in modern civilization because of three factors:

1. Oil is a highly concentrated source of energy (around 20,000 BTU per pound).

2. Oil is readily transportable to where it is needed.

3. Oil is available in huge quantities worldwide at reasonable cost (at least for the present).

Because of these factors, oil supplies almost all of the world's energy for transportation. It is also heavily used for space heating and as a feedstock for many of the chemicals used in modern society. Without oil or a suitable substitute, modern civilization would crumble.

4.2.2 Origin of Oil

There are two theories about the origin of oil.

In the biogenic theory[1], dead matter, primarily dead microscopic aquatic animals, was buried long ago beneath the earth by accumulating sediment. The heat and pressure deep underground caused the transformation of the remains of the living matter into oil, some of which was trapped beneath impervious layers. The oil used by humans is the result of finding and tapping these reservoirs of underground oil.

In the abiogenic theory[2], carbon located deep in the earth undergoes chemical processes (and maybe biological processes involving microbes), and the result is oil. According to the abiogenic theory, oil is being produced continuously and is migrating toward the surface of the earth. The abiogenic theory discounts the role of dead organisms in oil production and refutes the conventional assumptions about formation, location, and amount of oil available for future exploitation.

The controversy about the origin of oil is scientifically interesting, but it has little practical relevance unless its resolution can help us find oil in previously ignored places or can demonstrate that oil is being replenished in accessible areas of the earth at a fast enough rate to replace the oil removed.

In this book, the biogenic vs. abiogenic controversy will be assumed to be irrelevant in considerations of energy issues facing America and the world in the twenty-first century. Pressing issues in the early twenty-first century do not allow the luxury of reliance on salvation by abiogenic oil. Maybe the abiogenic theory proponents and/or powerful new drilling technology will eventually lead oil exploration to new and productive discoveries of vast oil reservoirs, but relying on this serendipity is unwise.

4.2.3 Acquiring Oil

Oil acquisition activities include exploration, drilling, and extraction.

Exploration involves characterization of subsurface conditions in order to identify regions with the potential of yielding oil. The main tool used for finding oil is seismic testing. A shockwave is generated above the region being investigated. On land, special trucks use heavy mechanisms to impact the surface. Offshore seismic testing relies on pressure disturbances generated underwater with compressed air devices. In both cases, an array of sensors monitors the reflected sound waves, and computer analysis provides a sort of three-dimensional map of subsurface conditions. Geologists use this information to identify promising sites for subsequent drilling.

Drilling involves use of a rotating bit on the end of a shaft that is lengthened as drilling progresses. The average depth of oil and gas wells is about one mile. The deepest wells are about five miles deep. Well shafts can be vertical or slanted and can even be turned to the horizontal far below the surface. Slanted and horizontal drilling techniques enable the creation of multiple holes at one drilling site (as shown in Figure 4-1). This is very important for expensive off-shore sites. Also, since oil strata may exist in horizontal deposits beneath impervious rock, horizontal wells expose more well surface to the deposit and enhance oil flow to the surface.

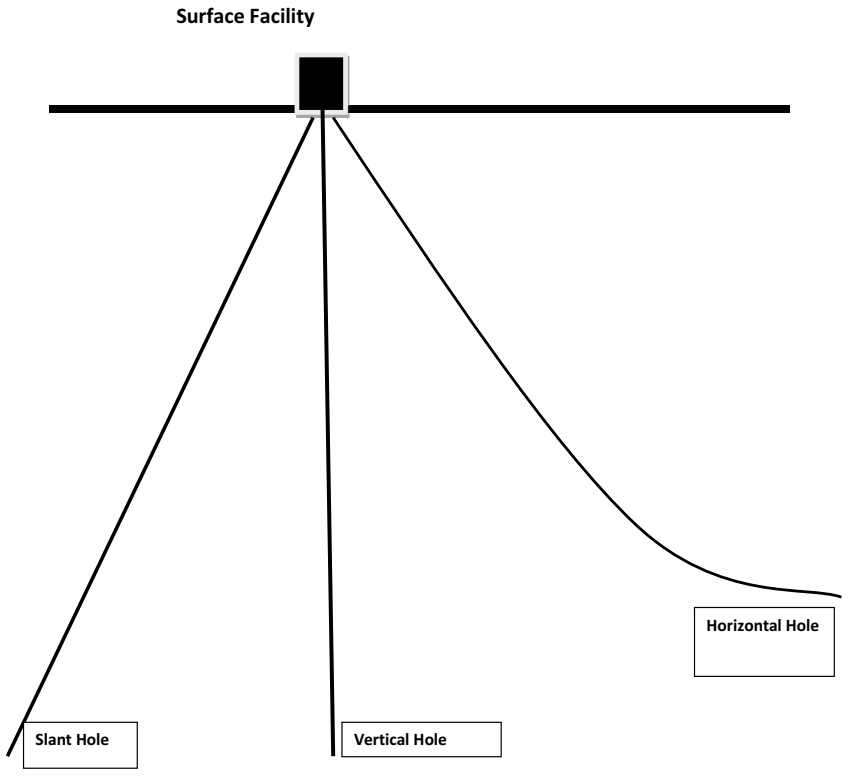

Figure 4-1. An Oil Well

A well is drilled through the region lying above the deep, oil-bearing formation. The well passes through any aquifers in the well's path, requiring a leak-tight casing to prevent water contamination.

Huge platforms, either resting on legs that sit on the sea floor or floating, provide sites for offshore drilling. Platforms that rest on legs are suitable for shallower sites. Floating platforms, essentially large barges that are held stationary by thrusters in the water, are needed for deep water applications. These platforms house all of the equipment used in drilling and facilities for large work crews. Because of the expense of building and operating an offshore facility, they are generally used to drill 30 or more holes.

When a well contacts an oil-bearing region, it provides a site with lower pressure than exists in the surrounding earth. The pressure difference is

often great enough to force oil and/or gas to the surface. Early oil wells sometimes experienced a "gusher," in which oil spurted high into the air. Modern well technology can prevent this uncontrolled flow.

Eventually, the flow of oil and gas out of a reservoir causes the pressure to drop. Further removal requires pumping, repressurization with injected gas or solvent extraction. Even with pumping, much of the oil remains trapped in the reservoir. This oil exists as small drops embedded in rock formations. Sometimes it is feasible and practical to inject fluids that free some of this trapped oil. These techniques are called secondary or tertiary extraction methods. Gas, usually carbon dioxide or natural gas, can be pumped into a nearby well to increase the underground pressure and release the oil. Steam may also be injected to reduce the viscosity of the oil and enable it to flow. Detergent solutions may be used to free the oil. Even downhole microwave heaters have been developed to heat trapped oil and enable it to flow.

Hydrofracturing, or fracking, may be used to acquire oil that is tightly bound in underground rock formations. Hydrofracturing involves high-pressure injection of a mixture of water, sand, and chemicals (usually of proprietary composition, but generally including toxic components) to fracture the underground formation around the well shaft and create flow paths to release the oil. The sand is a proppant, a material included to keep pathways open once they are created. The chemicals are included to increase pathway formation.

Generally, hydrofracturing involves injecting several million gallons of water under high pressure. After hydrofracturing is complete, pressurization ceases, and oil flows to the well bore and then to the surface. Much of the injected water and associated chemicals return to the surface along with the oil during extraction, and must be disposed of or used in other, subsequent hydrofracturing operations. This is called backflow water.

The impact on previously undisturbed environments and the possible release of harmful chemicals into the air or water has stimulated opposition to hydrofracturing. There is also some concern that alteration of underground rock formations will cause seismic activity.

Hydrofracturing is providing access to new, previously inaccessible oil. For example, the Bakken formation in North Dakota, Montana, and Saskatchewan has become a major producer because of hydrofracturing technology. Hydrofracturing technology certainly increases the reserves of accessible oil in the U.S. and the world, but the magnitude of this resource is still uncertain.

4.2.4 Oil Properties

Oil extracted at various sites varies in properties. It varies in color from black to brown, and even to yellowish or greenish, and it may include impurities such as sulfur. The smaller molecules are lighter and less viscous, and the larger molecules are heavier and more viscous.

4.2.5 Derivatives of Oil

Oil in the as-found state has limited usefulness. However, oil can be processed in refineries to yield a wide array of useful products[3]. The processes are designed for two main purposes: separation of desired components from undesired components and modification of undesired components to yield desired components.

Distillation is the principal separation process. Distillation occurs in a heated column designed to cause repeated evaporations and condensations of the input material. Components with lower boiling points are extracted at the top of the column, higher boiling point components are extracted at the bottom, and components with intermediate boiling points are extracted at intermediate points along the column.

Modification of oil components generally involves rearranging the atoms in the hydrocarbons that make up the oil. Cracking is the conversion of large hydrocarbon molecules into smaller molecules using heat and/or catalysts. Some of these smaller molecules are desired end products, and some are processed further to yield other desired compounds.

Refinery processes also include chemical reactions to alter the hydrogen-to-carbon ratio in the oil. Hydrogen (produced from natural gas as described in Section 4.7) is reacted with oil at elevated temperature and pressure and in the presence of a catalyst. The objective of this process, called catalytic hydrogenation, is to obtain a hydrogen-to-carbon ratio of around two as needed for liquid fuels.

The characteristics of the extracted oil have a large influence on the processing used to derive desired products. The most important characteristics are the relative amounts of light and heavy components and the concentrations of impurities, mainly sulfur. Low sulfur oil, called sweet oil, is strongly preferred over high sulfur oil, called sour oil.

In modern U.S. oil refineries, about half of the oil is converted into gasoline. The distribution of product yields can change with changing product demands and crude oil properties, but typical products from crude oil are shown in Table 3-6 of the previous chapter.

Liquid hydrocarbon fuels contain a mixture of many organic compounds. Suitability for the various uses as a fuel depends on the specific mix of compounds included. All liquid hydrocarbon fuels have approximately two hydrogen atoms per carbon atom. The number of carbon atoms (and the associated hydrogen atoms) in a molecule determine its suitability for different applications. Gasoline has five to 12 carbon atoms per molecule; kerosene and jet fuel have 11 to 13; diesel fuel and fuel oil have 13 to 17; and heavy fuel oil has up to 45.

No new refineries have been built in the U.S. since the mid-1970s. This fact is primarily due to environmental concerns and siting problems due to community opposition. The increased production needed to satisfy demand has been met by increasing the capacity of existing refineries and by importing finished products produced in refineries located outside of the U.S.

4.2.6 Oil Production, Reserves, and Forecasts

The 2007 world annual production of oil was about 26 billion barrels, and U.S. domestic production was about 2 billion barrels. The U.S. augmented 2007 domestic production with over 3 billion barrels of imported oil and oil products. U.S. production peaked around 1970. Figure 3-4 in the previous chapter shows histories of world and U.S. production. By 2007, cumulative production was about 1 trillion (1,000 billion) barrels for the world and 200 billion barrels for the U.S.

The only rational assumption is oil is a finite resource that is steadily being used up. There is no doubt that decreasing reserves will eventually slow production. Oil shortages are likely in years or decades, not centuries. Since the time required to develop and implement alternative fuels is long, action is needed now, whether the main beneficiaries will be us, our children, or our grandchildren.

Of course, estimating future oil production depends strongly on assumptions about the amount of oil in the earth that is available for recovery. This is the issue of oil reserve estimation. It is not a simple matter. "Experts" have been estimating oil reserves for decades, and most have been seriously wrong. Some forecasts predicted that oil would already be completely used up.

It is important to distinguish between "total reserves" and "remaining reserves." Total reserves are the recoverable reserves that were in the ground before extraction began, and remaining reserves are reserves still available for extraction. For the U.S., it is estimated about 230 billion barrels of recoverable oil were in the ground initially, and about 200 billion barrels have been extracted. The numbers for the rate of U.S. oil consumption are important in assessing the importance of any future oil discoveries. For example, how important would a new billion-barrel U.S. oil discovery be? One billion barrels sounds like a lot, but it would provide only 10 weeks of U.S. consumption at the current rate of use.

As indicated in Chapter 3, reserve estimates in some countries are less reliable than estimates for U.S. reserves. Nevertheless, analysts attempt to derive meaningful world oil reserve estimates. Most of these estimates say the remaining world reserves of recoverable oil lie between 1 and 2 trillion barrels. Since cumulative world production is around 1 trillion barrels, it appears that one-third to one-half of the recoverable oil that was in the ground initially has been extracted.

We must ask the question, "How long can the world satisfy oil production demands with the remaining resource?" The fact that 1 trillion barrels of oil were consumed in the last hundred years does not suggest that the remaining 1 to 2 trillion barrels will satisfy demand nearly as long, given current demand and expected increases in future demand.

We must turn to the uncertain art of quantitative forecasting to assess the range of possibilities for future oil availability. Because of the importance of future oil supplies, forecasting is treated in greater-than-usual detail in this section and in Appendix F.

Many future oil production forecasts have been published. Guy Caruso, Administer of the Energy Information Administration, documents 38 different forecasts made between 1972 and 2004. The estimates of the year of peak oil production for all but two of these forecasts range from 1989 to 2050. Most range from 2010 to 2040[4].

It should be noted that current oil extraction technology permits extraction of only about one-third of the oil in a reservoir. There is hope that new extraction technology will permit extraction of some of the remaining oil. Higher oil prices will make it economical to extract hard-to-get oil that was previously uneconomical.

The detail included in the published forecasting models varies enormously. Some are so simple that it is generous to call them a model[5]. Some are so involved that it is difficult to evaluate their plausibility[6]. The following sections describe two of the simpler approaches to forecasting. These were chosen because the link between underlying assumptions and predicted results

is transparent and because of the author's belief that quantitative estimation of the many factors that will determine future production and consumption is impossible.

Logistic Function Modeling

A technique called logistic function modeling[7] may be used in oil production forecasting. The premise of logistic function modeling for an exhaustible resource is as follows:

Premise of logistic function modeling: The fractional rate of cumulative production of an exhaustible resource is proportional to the fraction of that resource which remains.

If Q represents the cumulative production at some point in time, P represents the production rate at that time, and Q_t represents the cumulative production that will have occurred at the time of resource depletion (the total reserves), then application of the logistic function modeling premise results in the following:

$$P/Q = a(Q_t - Q)/Q_t \qquad (4\text{-}1)$$

where

a = a constant of proportionality

Equation 4-1 reveals that, according to the logistic premise, a plot of P/Q versus Q should be a straight line.

Figure 4-2 shows a plot of P/Q versus Q for the lower 48 states of the U.S. The latter part of the data approximates a straight line as predicted by the logistic premise.

There are various ways to solve Equation 4-1 for production, P. The most elegant method is based on recognition that Equation 4-1 is really a differential equation (P is the rate of change of Q or dQ/dt) with a known solution. The solution (details in Appendix F) is as follows:

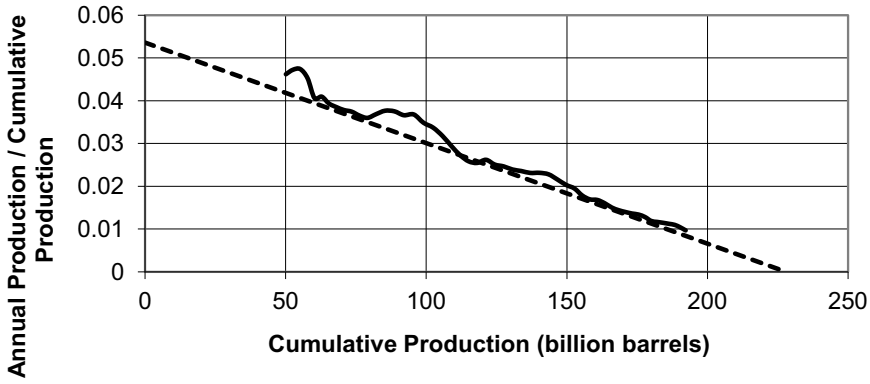

Figure 4-2. Hubbert Plot for U.S. Oil

$$Q = Q_t/[1+e^{-at}] \qquad (4\text{-}2)$$

where

t = time

A feature of the solution shown above is that time is measured from the instant when cumulative production is exactly half of the ultimate cumulative production (see Appendix F for details). Consequently, cumulative production values for times after the half production point are obtained by substituting positive values of t in Equation 4-2, and values for times before the half production point are obtained by substituting negative values of t.

M. King Hubbert[8,9] used a variant of this approach in 1956 to forecast future oil production in the lower 48 states of the U.S. He predicted a production peak in the mid-1970s. The peak actually occurred around 1970. Figure 4-3 shows the Hubbert forecast from 1956 and actual production data for the U.S.

Hubbert is regarded by many as the master prognosticator of future oil production. Many learned papers have verified his method, dissected the nuances, and applied his method to other problems, especially world oil production. There have also been publications that debunked the Hubbert

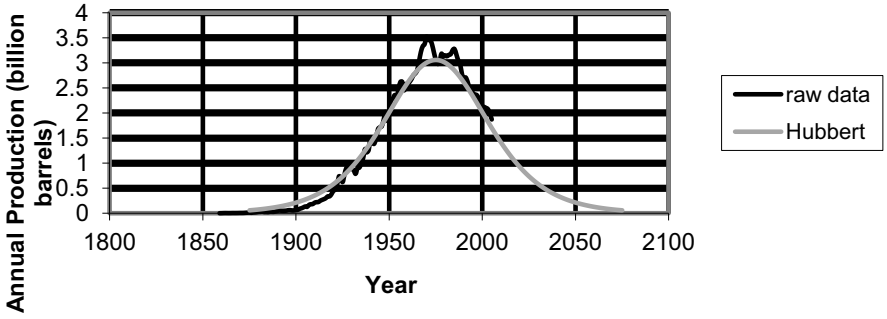

Figure 4-3. Hubbert Prediction and Actual U.S. Production

approach. Overall, Hubbert's method has gained widespread acceptance. The predicted and observed peak in U.S. oil production is now called Hubbert's peak, and he is honored with the formation of institutional centers devoted to the application and refinement of his method. One such center is the M. King Hubbert Center for Petroleum Supply Studies at The Colorado School of Mines. The importance of Hubbert's method is apparent if one does a web search on "Hubbert's peak" or "peak oil."

Hubbert was successful in forecasting U.S. production through its peak in his 1956 work. There is now great interest in predicting future world production.

A plot of P/Q vs. Q for world oil is shown in Figure 4-4. This plot may be used to check for linearity and, if linearity is observed, to give confidence in the validity of using the Hubbert method for world oil forecasting. The figure shows actual data (for cumulative production to about 1,000 billion barrels) and projections for total resource estimates of 2,000 and 3,000 billion barrels. The figure shows that a clearly defined linear region is absent, thereby reducing confidence in reliance on a Hubbert projection for world oil. Nevertheless, a Hubbert analysis was performed for two cases: total reserves = 2,000 billion barrels, and total reserves = 3,000 billion barrels. The results appear in Figure 4-5. For reserves of 2,000 billion barrels, the estimated peak production year is 2010. For reserves of 3,000 billion barrels, the estimated peak production year is 2022. Regardless of the doubts about

the applicability of Hubbert's method for forecasting future world oil production, these results suggest the peak in world oil production has occurred already or will occur in the near future. Figure 4-6 shows cumulative oil production by the Hubbert analysis method.

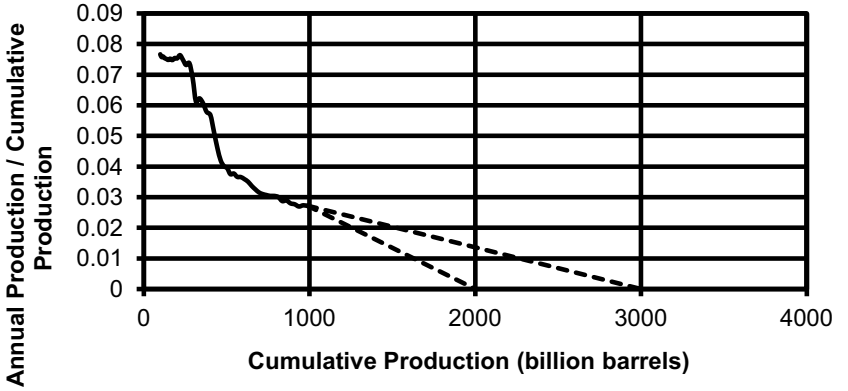

Figure 4-4. Hubbert Plot for World Oil

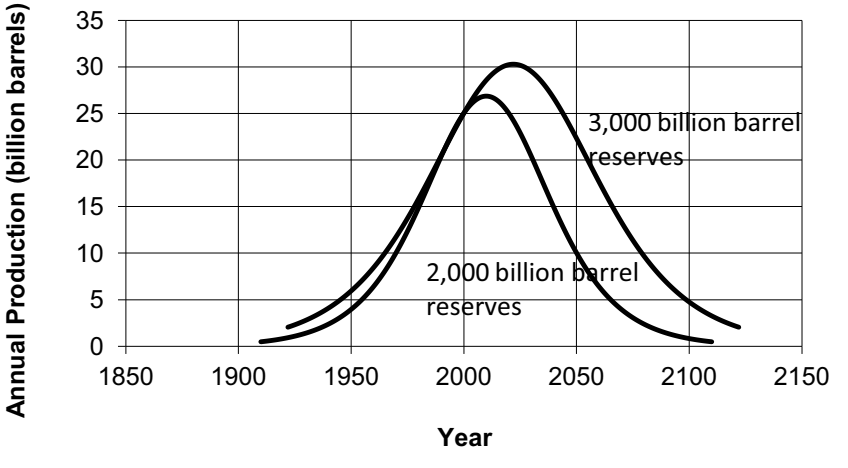

Figure 4-5. Effect of World Oil Reserve Estimate on Hubbert Annual Production Prediction

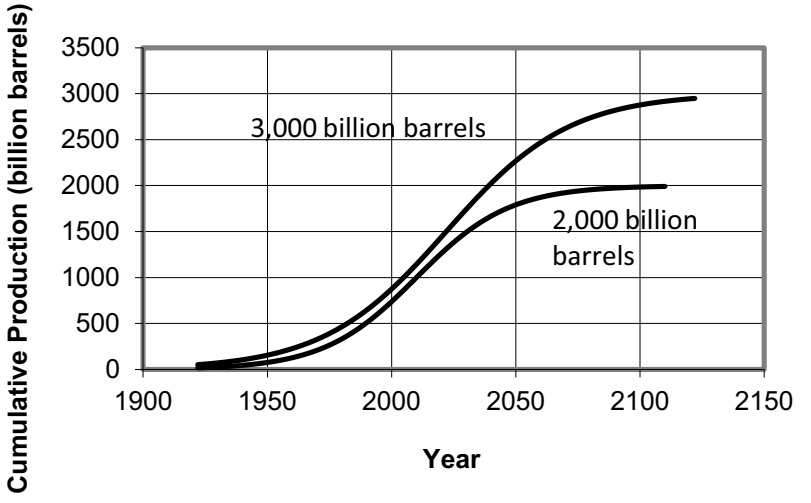

Figure 4-6. Effect of World Oil Reserve Estimate on Hubbert Cumulative Production Prediction

The EIA Model

A model was presented by Wood, Long, and Morehouse of the Energy Information Administration of the U.S. Department of Energy[5]. Their model is described here and is called the EIA model.

Forecasting by the EIA model is based on the assumption that annual production will continue into the future at a constant growth rate until annual production reaches some fraction of remaining reserves, then drops, with the continuing annual production rate equal to some assumed fraction of remaining reserves per year. Typical assumptions are a growth rate of 2 percent per year until annual production reaches 10 percent of remaining reserves, followed by production at 10 percent of remaining reserves per year. The EIA model assumes we will continue what we are doing until it is no longer possible to do so.

Figure 4-7 shows forecasts for annual production by the EIA model, and Figure 4-8 shows cumulative production for total reserve estimates of 2,000 and 3,000 billion barrels. The peak occurs in 2024 for reserves of 2,000 billion barrels, and in 2042 for reserves of 3,000 billion barrels.

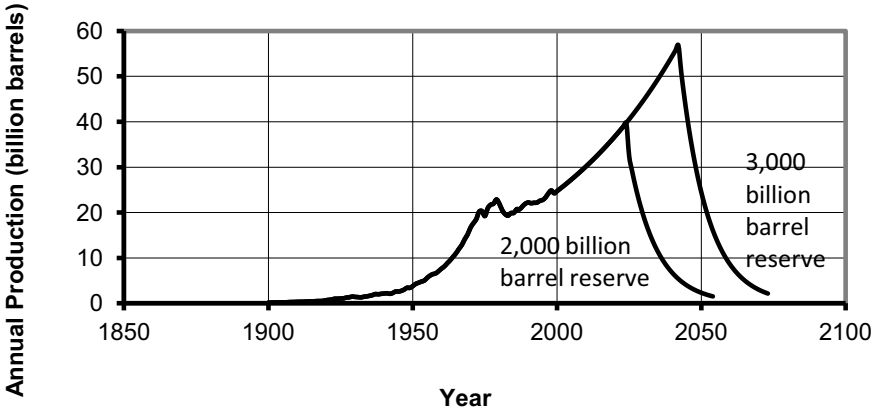

Figure 4-7. Effect of World Oil Reserve Estimate on EIA Annual Production Prediction

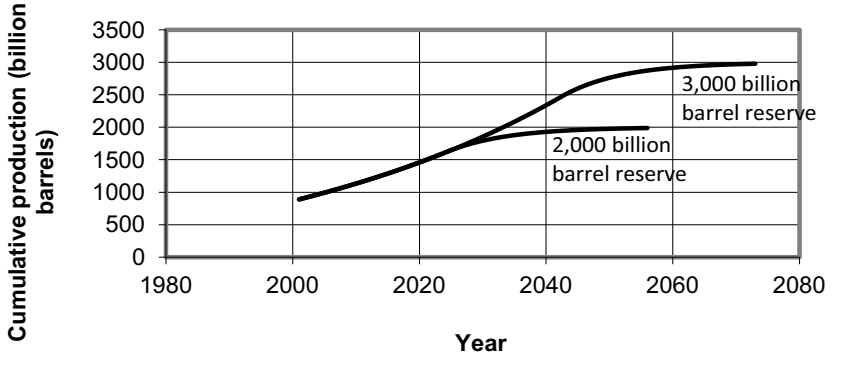

Figure 4-8. Effect of World Oil Reserve Estimate on EIA Cumulative Production Prediction

Assessment of World Forecasts

The models described above give estimates of future annual production and future cumulative production, but they differ in their treatment the underlying causes.

The Hubbert model predicts decreasing annual production as remaining reserves are depleted. It predicts production will start to decrease when exactly half of the reserves are depleted. This feature is consistent with the

logic that says that oil extraction will get more difficult as reservoirs are emptied. However, the perfect symmetry of the production curve is a simplification that is open to question. Hubbert's model is a "production constrained" model. The peak in annual production is the focus in a Hubbert analysis because predicted annual production subsequently decreases irrespective of the size of remaining reserves or the continuing demand. The peak in a Hubbert analysis signals the onset of inability to meet annual production requirements.

The Hubbert analysis predicted the peak of world oil production and the onset of supply shortfalls would occur in 2010 if the 2,000 billion barrel reserve estimate was correct and would occur in 2022 if the 3,000 billion barrel estimate is correct.

The EIA model assumes no natural constraints on annual production until depletion is almost complete. The EIA model is a "reserve constrained" model. Basically, the EIA model says oil will be extracted at the rate needed to satisfy demand. It assumes there are no limits on extraction rate due to geology or extraction technology. The peak in an EIA analysis is simply indicative of arrival at a point close to reserve depletion. The peak in an EIA analysis signals the end of business-as-usual and the onset of rapid reductions in annual production.

The EIA model predicts the onset of supply problems will occur in 2024 if the 2,000 billion barrel reserve is correct, and in 2042 if the 3,000 billion barrel estimate is correct.

The models predict nothing can be done to avoid world oil shortages after around 2020 or earlier if the total reserve estimate of 2,000 billion barrels is correct. If the 3,000 billion barrel estimate is correct, then the models predict shortages around 2040 or earlier.

There are major doubts about the validity of these models, but their results say total oil reserves, whether they total 2,000 or 3,000 billion barrels, will be unable to satisfy requirements after some time between 2010 and 2040 unless major and improbable consumption curtailments occur. 2040 may

seem far into the future for those who believe the 3,000 billion barrel estimate, but the long development and deployment time for alternative sources causes projected serious oil supply shortfalls to seem alarmingly close in time.

4.2.7 Oil Spills and the Environment

Experience has shown that oil spills can and do occur at well sites and during oil transport.

The largest accidental release at a well site occurred in the Gulf of Mexico in June 2010. The *Deepwater Horizon* operated in mile-deep water off the coast of Louisiana. An explosion destroyed the floating rig, broke the delivery pipe, and created a path at the sea floor for release of oil. Millions of barrels of oil were released. Major environmental and economic impacts resulted.

There have also been many spills resulting from accidents involving oil-carrying ships. The largest U.S. spill from an ocean tanker was from the *Exxon Valdez* incident in 1989. The ship ran onto a reef and spilled over 10 million gallons of oil into Prince William Sound, Alaska.

4.3 Oil Sand

Oils other than liquid crude oil are called unconventional oils[10]. Unconventional oils include kerogen, found in oil shale deposits, and bitumen, found in oil sand deposits. Kerogen and bitumen are complex mixtures of high molecular weight organic compounds. They are distinguished by their solubility in organic solvents and acids. Bitumen is soluble, and kerogen is not.

Unlike crude oil, natural gas, and coal, unconventional oils are mixed with large volumes of inorganic material that must be removed before the oil can be processed for ultimate use as a fuel. This unavoidably complicates extraction and processing operations and impacts the competitiveness of unconventional oils. However, they become increasingly competitive as

conventional energy sources become more expensive as they become scarce, and the cost of unconventional oil decreases as technology improves.

4.3.1 Importance of Oil Sands

Oil sands, also called tar sands or heavy oil, are a massive resource, containing a huge quantity of hydrocarbons. Oil sand can be mined and processed to yield gaseous and liquid hydrocarbons and an emulsion suitable as a coal replacement for power plants. If environmental and economic issues associated with oil sand mining and processing can be resolved, oil sand has the potential to extend world petroleum reserves significantly.

4.3.2 Origins of Oil Sand

The bitumen in oil sand is organic material that is one of the intermediate materials in the complex series of transformations of buried biomass into fossil fuel. Its precursor is kerogen (see below) and, if it were left at high temperature and pressure for a sufficient time, its decomposition would result in crude oil and natural gas.

4.3.3 Oil Sand Properties

Bitumen is a complex mixture of chemicals that typically contains (by weight) around 80 percent carbon, 10 percent hydrogen, and less than 10 percent oxygen, nitrogen, and various impurities, some of which, such as sulfur, create problems when they are burned.

The hydrogen-to-carbon atomic ratio for the hydrocarbons in oil sand is around 1.5. If the oil sand is to be processed into liquid hydrocarbon fuel, sufficient hydrogen must be added or carbon removed to yield hydrocarbons with hydrogen-to-carbon rations of around two.

4.3.4 Oil Sand Mining and In-situ Extraction

Oil sand may be mined by strip mining or in-situ liquefaction and extraction by pumping.

In strip mining, huge quantities of a mixture of bitumen, sand, and clay are extracted from deposits at–and near–the surface. After the bitumen is separated in processing facilities, large volumes of waste material remain. This material may be returned to the pits from which it was extracted to minimize permanent environmental effects.

In-situ extraction involves heating of the oil sand while it is still in the ground. This liquefies the bitumen, permitting it to be pumped to the surface. This heating can also modify the composition of the bitumen by breaking large molecules into smaller molecules.

4.3.5 Oil Sand Processing

The processing of strip-mined oil sand occurs in two steps: separation of the bitumen from the other materials in the ore and transformation of the bitumen hydrocarbons into other hydrocarbons with more useful properties.

The solid bitumen from strip-mined oil sand or the liquefied oil from in-situ extraction may be converted into lower molecular weight hydrocarbons by cracking, and the hydrogen-to-carbon ratio can be increased to around two by catalytic hydrogenation.

Large deposits of oil sand exist in the Orinoco Basin in Venezuela. The Venezuelans have developed a novel process for using their oil sands. After it has been separated from the inorganic matter, bitumen is mixed with water and an emulsifier to produce a material called Orimulsion that can be pumped. It is suitable for combustion in boilers, providing a fuel that can replace coal or heavy fuel oil in producing electricity.

4.3.6 Oil Sand Reserves

The largest known deposits of oil sand are in Alberta, Canada, and in Venezuela. The estimated recoverable reserves in these two areas are about 3.6 trillion barrels of oil equivalent. The main known U.S. oil sand deposit is in Utah, with estimated reserves of 12 to 20 billion barrels of oil equivalent.

4.3.7 Environmental Effects

The environmental consequence of mining and processing oil sand is a huge issue. The list of environmental concerns is:

- Ecosystem disruption
- Greenhouse gas released during mining and processing
- Air pollution
- Surface water pollution
- Ground water pollution
- Water consumption
- Alteration of surface features

Some environmental groups are mounting campaigns to restrict or prohibit oil sand mining and processing.

4.4 Oil Shale

4.4.1 Importance of Oil Shale

Like oil sand, oil shale deposits represent a huge potential energy resource[11]. Unlike oil sand, the oil shale deposits are mostly in the U.S. Pro-

cesses are available for converting oil shale into liquid transportation fuel, but there are major cost and environmental issues to be considered.

There have been several attempts in the past to exploit oil shale, especially when crude oil prices were high, but most efforts were subsequently abandoned in the face of high production costs and lower oil prices. Now, with higher crude oil prices, and with supply deficiencies approaching, interest in the oil shale resource is increasing. This increased activity has stimulated some environmental groups to speak out about the undesirable environmental effects related to oil shale extraction and processing.

4.4.2 Origin of Oil Shale

The kerogen in oil shale, like the bitumen in oil sand, is an intermediate compound in the series of chemical transformation involved in converting biomass into crude oil. In the geological process that results in crude oil, kerogen is formed, and then it is transformed into bitumen, which is a precursor to oil. Bitumen and kerogen exist because the conditions and time elapsed were insufficient for their transformation into oil.

4.4.3 Oil Shale Properties

Like the bitumen in oil sand, the kerogen in oil shale has a hydrogen-to-carbon atomic ratio of around 1.5. Hydrogen must be added or carbon removed to yield a hydrogen-to-carbon ratio of around two as needed for liquid hydrocarbon fuels.

4.4.4 Oil Shale Mining

Like oil sand, oil shale may be extracted by strip mining or by in-situ liquefaction and extraction by pumping. However, oil shale mining is more difficult than oil sand mining since the hydrocarbon is contained in rock rather than sand.

4.4.5 Oil Shale Processing

Like oil sand, oil shale is processed by cracking and catalytic hydrogenation after separation from the associated rock by crushing and washing.

4.4.6 Oil Shale Reserves

The estimated world reserve of oil shale is around 3 trillion barrels of oil equivalent. (Some prefer to call oil shale deposits "contingent resources" rather than reserves. This is to acknowledge that economical recovery methods are still unavailable[12].) The largest reserves are in the U.S., where the estimate is over 2 trillion barrels. The largest U.S. deposits are the Green River Formation in Colorado, Wyoming, and Utah.

4.4.7 Environmental Effects

Oil shale mining and processing have all of the environmental concerns previously listed for oil sand. In addition, in the surface heat treating of oil shale, the waste material undergoes expansion, creating more volume than was initially extracted and preventing restoration of the mined area to its original topography.

4.5 Gaseous Hydrocarbons

4.5.1 Properties

Natural gas, the current dominant gaseous fuel, is extracted from the earth, often along with crude oil. It is a mixture of gaseous hydrocarbons (typically 80 percent methane, CH_4; 7 percent ethane, C_2H_6; 6 percent propane, C_3H_8; 4 percent butane and isobutane, $C_4H_{10;}$ and 3 percent pentanes, C_5H_{12}). The gases with three or more carbon atoms are removed from natural gas before it is delivered for use as a commodity fuel. Consequently, the gases in consumed natural gas are methane and ethane. The propane and butanes are suitable for liquefaction under pressure. This facilitates their portability for use as a fuel.

Natural gas is compressible, so the specification of gas quantity requires specification of the temperature and pressure. The convention is to use the standard cubic foot, commonly defined in the U.S. as gas at 60°F and at atmospheric pressure, 14.7 pounds per square inch. The high heating value of natural gas varies for gas extracted from different wells, but typical values are around 1030 BTU per cubic foot for the high heating value and around 930 BTU per cubic foot for the low heating value.

Methane, the major component of natural gas, is a colorless, odorless gas. It has the formula CH_4. Combustion of methane yields carbon dioxide and water as follows:

$$CH_4+2O_2 \rightarrow CO_2+2H_2O+\text{energy}$$

Natural gas and oxygen can also be used to power a fuel cell, in which the energy produced is electricity. A fuel cell is basically a battery into which the reactants are fed continuously. Whether natural gas is used for combustion or for powering a fuel cell, the reaction products are carbon dioxide and water. Natural gas fuel cells are a candidate for widespread use as local electricity producers for homes and businesses, thereby eliminating the need for delivery of electricity by the grid.

Since methane occurs naturally as a component of natural gas and as a result of anaerobic digestion of biomass, it is appropriately considered to be both a non-renewable and a renewable energy source. In addition, methane can be manufactured from other hydrocarbons, from coal or from carbohydrates. Manufactured methane is an energy carrier.

Some methane-producing processes also result in the production of carbon monoxide. Carbon monoxide is a colorless, odorless, toxic gas. Its toxicity complicates the use of gases containing carbon monoxide. Carbon monoxide has the chemical formula CO. Combustion of carbon monoxide yields carbon dioxide as follows:

$$2CO+O_2 \rightarrow 2CO_2+\text{energy}.$$

Combustion of carbon monoxide yields 340 BTU per standard cubic foot. The distinction between high heating value and low heating value does not apply to carbon monoxide because no water is produced in combustion. The heat release from carbon monoxide combustion is around one-third the heat release from methane combustion.

Hydrogen is another gaseous fuel with huge potential importance. Since hydrogen is a highly reactive chemical, it readily forms compounds with other chemicals. Because of its tendency to form compounds, elemental hydrogen gas does not exist in nature. Hydrogen may be produced from hydrogen-bearing compounds by supplying the energy needed to break up the compounds. Consequently, hydrogen is an energy carrier rather than an energy source. Chapter 12 addresses hydrogen as a fuel.

4.5.2 Unconventional Gas

Conventional gas is that which requires only drilling a well into a gas-bearing underground formation. Conventional gas wells are typically no deeper than a few thousand feet. Conventional gas flows to the well through formations that have enough permeability to permit substantial flow.

"Unconventional" gas is that which is more difficult to access and extract, requiring application of technology as described below.

Exploitation of the huge U.S. reserves of unconventional gas has already begun. The size of the unconventional gas resource and the quantities that can be extracted economically are very uncertain. However, it is known that the U.S. reserves are large, possibly 10 times the reserves of proved gas or greater. If fully exploited, unconventional gas could satisfy consumption demand at the current rate for a century or longer.

There are several different types of unconventional gas. The unconventional gases that are receiving the bulk of current attention are shale gas, tight gas, coalbed gas, and methane hydrates. In addition, large quantities of two other types of unconventional gas, deep gas and geopressurized gas, are known to exist and may eventually become important.

The six types of unconventional gas are discussed below.

Shale Gas

Shale gas is gas contained in shale deposits. These lack the permeability needed to allow gas flow through the deposit to a well. Accessing shale gas requires intervention to fracture the shale. Shale gas is increasing in importance because of advances in hydrofracturing technology, horizontal drilling technology, and increased competitiveness with conventional gas.

Hydrofracturing enables extraction of large quantities of natural gas that is inaccessible by conventional drilling. Hydrofracturing for natural gas uses essentially the same technology as that used for extracting oil (see Section 4.2.3), but, since natural gas is less viscous than oil, it flows more easily through fracture zones. Natural gas extraction using hydrofracturing technology has grown rapidly and has become a major contributor to total gas production in the U.S. in the early twenty-first century.

The environmental concerns related to natural gas hydrofracturing are the release of gas and other chemicals into the groundwater, the release of gas into the air, the escape of gas into human habitats, and the improper handling of backflow water. There have been numerous well-publicized environmental, health, and safety incidents near gas hydrofracturing sites.

Tight Gas

Tight gas is gas contained in unusually low-permeability deposits, typically hard rock or non-porous limestone. Tight gas extraction depends on creation of porous pathways for gas flow. Pathways can be created by hydrofracturing or by injecting acid that dissolves part of the rock.

The environmental concerns are the same as with shale gas.

Coalbed Gas

Coalbed gas is methane that resides on seams or joints in coal deposits or is absorbed in pores in coal. Groundwater under elevated pressure holds the methane in place. Coalbed gas is a safety consideration in coal mining, and mines are vented to avoid gas explosions.

Groundwater and associated coalbed gas are released from the coal matrix when the pressure on the coal is reduced. When a well penetrates a coal seam, a low pressure region is created, permitting gas and the associated groundwater to flow to the well and then to the surface. The rate of flow depends on the permeability and porosity of the coal bed. Coal seams that are naturally fractured provide the best source of coalbed methane.

Methane Hydrate

Methane hydrate, also called methane calthrate, is a solid form of water that contains methane in its molecular structure[13]. Calthrates are substances in which a molecule resides in a cage made of other molecules. Methane hydrate is similar in appearance to normal water ice.

Methane hydrate occurs in oceans at depths of 1,000 to 6,000 feet and in some rocks on land. The quantity of methane hydrate in these deposits is uncertain, but potentially large.

Methane hydrate is considered an energy resource by some, but methods for acquiring it are not available and release to the atmosphere during collection is problematical because methane is a greenhouse gas with over 20 times the impact per molecule as carbon dioxide. Researchers are exploring ways to access this energy resource in safe and environmentally acceptable ways.

Deep Gas

As the name suggests, deep gas is gas located in deposits that are deeper than sources of conventional gas. Deep gas deposits are typically at depths of 15,000 feet or greater.

Geopressurized Gas

Geopressurized gas is gas in deep formations (10,000 to 25,000 feet) that are under very high pressure.

4.5.3 Methane Derivatives

Methane is currently the main source material for producing hydrogen. Methane also serves as a feedstock for production of various chemicals. As is discussed in Section 4.7, hydrocarbons can be produced by reactions involving methane, oxygen, and water. Hydrogen produced from methane may be used as a fuel or in the production of chemicals.

4.5.4 Natural Gas Reserves and Forecasts

As seen in Figures 3-3 and 3-4 in the previous chapter, U.S. natural gas production and consumption history is quite different than U.S. oil production and consumption history. There are no trends that would warrant a detailed forecast of future consumption. U.S consumption has fluctuated around 23 trillion cubic feet per year since the mid-1990s.

The proved reserves of domestic conventional and unconventional U.S. natural gas in 2011 were 284 trillion cubic feet. At the current consumption rate, 284 trillion cubic feet will last around 12 years. However, it is now believed that much more natural gas is economically recoverable in the U.S., primarily as unconventional gas. Unconventional gas is already a major part of U.S. gas production.

In recent years the rate of developing new proved reserves has essentially matched the rate of consumption. There are much larger reserves of natural gas in other countries, but using domestic resources rather than depending on foreign suppliers ensures security of supply and reduces foreign expenditures.

Natural gas is a versatile energy source. It is well-suited for heating applications in homes, industries, and businesses, and it is the cleanest-burning fossil fuel. It is used heavily as a feedstock for producing chemicals. It also sees limited use for transportation energy.

Some say natural gas is abundant. This statement is based on the likelihood that huge U.S. reserves of unconventional gas can be extracted at acceptable

cost and with acceptable environmental impact. Recent experience and steady advances in unconventional gas extraction technology provide a basis for confidence that gas will truly be abundant in the U.S. for many decades. However there are serious concerns about environmental, health, and safety impacts of gas extraction. Also, natural gas use produces carbon dioxide, though at a lower level than other hydrocarbons. These issues may constrain the future use of natural gas.

4.6 Coal

4.6.1 Importance of Coal

Coal is a huge and widely distributed energy resource. Before World War II, it was widely used for electricity production, heating, and transportation. As oil and natural gas grew in importance after World War II, electricity production became the dominant use for coal (about 90 percent of U.S. coal consumption is for electricity). Coal now provides about 75 percent of U.S. electricity.

Estimated remaining U.S. recoverable coal reserves are about 250 billion tons. The energy contained in these reserves is about 5,000 Quads. Estimated world recoverable coal reserves are about 1 trillion tons, with an energy content of about 20,000 Quads.

About 10 percent of coal in the U.S. is used as a feedstock to make coke (primarily used in steelmaking), to produce syngas (which consists mainly of hydrogen and carbon monoxide), or to produce synthetic liquid hydrocarbons.

4.6.2 Origin of Coal

Coal was formed from plants that grew in swampy areas millions of years ago. The natural process that formed coal is called coalification. Dead plants fell into oxygen-poor aquatic environments that inhibited decay. Eventually, sediment covered the dead plant material. The resulting heat

and pressure compacted the material, drove out water (including water driven out of the molecules of the plant matter), and drove out hydrogen and methane gases from the plant matter. These processes required millions of years. Various forms of coal were formed as a result of various levels of completion of the coalification process.

4.6.3 Coal Properties

The types of coal are usually ranked according to their state in the coalification process. Higher ranked coals contain less water, more carbon relative to hydrogen and oxygen, and more energy release per pound that is burned. The carbon content and energy rankings, from lowest to highest, are as follows:

Table 4-2. Coal Properties[14]

			Energy Content (million BTU/ton)	
Type of Coal	**Carbon (%)**	**Water (%)**	**World**	**U.S. Average**
Lignite	25–35	up to 45	9–17	13
Subbituminous	35–45	20–30	17–24	17–18
Bituminous	45–86	<20	21–30	24
Anthracite	86–97	<15	22–28	25

The carbon in coal, which amounts to the largest fraction of the components in mined coal, is made up of complex molecules comprised mostly of carbon. Coal is found along with varying amounts of other materials. These may be materials mixed with the coal or elements that are part of the complex coal molecules. Typical materials found mixed with coal are water, clay, sand, and rock. Many chemicals may be found in coal, but some of the most troublesome are sulfur, nitrogen, and heavy metals.

Coal energy content varies with coal type, but most coal used for electricity production (subbituminous and bituminous) releases around 20 million BTU per ton when burned.

4.6.4 Coal Mining

Coal is obtained from underground mines and surface mines. In the U.S., about two-thirds of the coal is obtained from surface mines and one-third from underground mines. Coal is mined in three main regions: the eastern Appalachian region, the midwestern region, and the western region. Huge surface mines in the western region produce low-sulfur, subbituminous coal that is hauled by train to electrical plants throughout the country.

4.6.5 Coal for Electricity Production

Coal is widely used to produce electricity. The environmental consequences of coal combustion affect the design and operation of modern coal-fired power plants (see Figure 4-9).

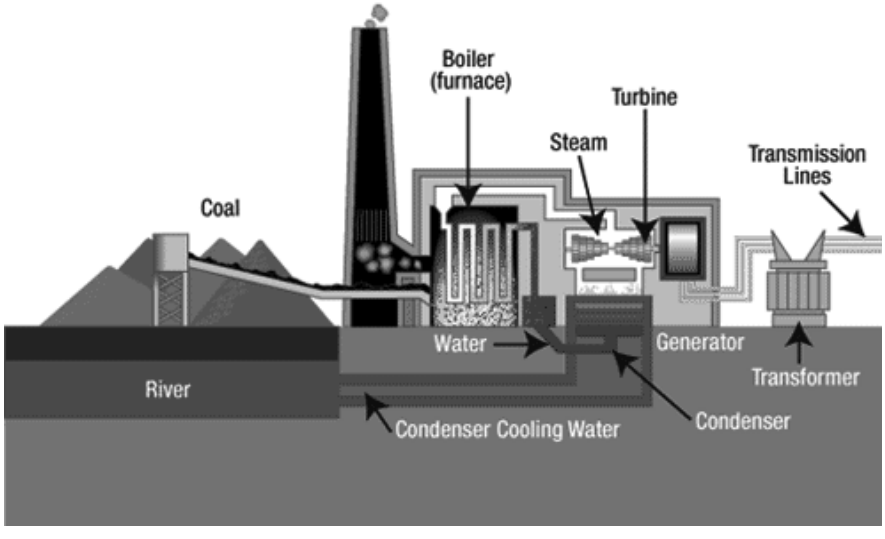

Figure 4-9. A Coal-Fueled Power Plant (courtesy of Tennessee Valley Authority)

Steps are taken before and after combustion in an electric power plant to reduce emissions associated with coal combustion. Coal with a significant content of sand, clay, and/or rock may be washed to remove these materials before use. Removal of these non-combustibles reduces subsequent ash pro-

duction. After combustion, filters and/or electrostatic precipitators may be used to reduce emissions of fly ash (small particulates in the exhaust gas), and scrubbers (alkaline wet slurry) may be used to reduce emissions of oxides of sulfur and nitrogen.

Large baghouse filters are sometimes used to remove particulates, but they cause pressure drops that reduce exhaust flow and plant efficiency, and they require cleaning and regular replacement. Electrostatic precipitators remove particulates without these adverse effects. They operate by inducing negative electric charges on the fly ash particles, then collecting the particles on positively-charged plates.

Before its introduction into the boiler, the coal is pulverized to the consistency of talcum powder. The boiler is a large box-like structure. Combustion occurs in the interior, and the resulting heat is transferred to water flowing through tubes located in the boiler walls and in the hot gas stream.

Coal combustion results in ash, unburned constituents of the coal. Deposits, called slag, also form on boiler tubes, requiring removal and disposition. Ash and slag contribute to the solid waste stream from the plant, which must be disposed of in an environmentally acceptable manner.

Even with the most efficient clean-up equipment, the combustion of coal releases carbon dioxide and pollutants into the environment. Fly ash in the air is an irritant to eyes and lungs. Oxides of sulfur and nitrogen interact with water in the atmosphere to produce acid rain. Heavy metals, including mercury, and radioactive materials, including uranium and thorium, are released. These problems have led to the development of new ways to use coal with less environmental impact (see Section 4.6.7).

4.6.6 Derivatives

The main products derived from coal are coke, syngas, and synthetic liquid hydrocarbons.

Coke is the result of baking low-sulfur, low-ash bituminous coal at temperatures as high as 2000°F. Volatile components are driven off, leaving a fused hard, gray porous residue of carbon and ash. Coke is used as a fuel and as a reducing agent for smelting iron ore in blast furnaces.

Syngas, a mixture of gases comprised mostly of hydrogen and carbon monoxide, is produced by reacting hot coal with steam. It may be converted into liquid hydrocarbons as described in Section 4.7.

4.6.7 Advanced Power Plant Designs

A large part of the environmental impact of coal combustion is the carbon dioxide and the pollutants in the gases released from the smokestack. Several new designs use coal to produce syngas. These designs minimize the carbon dioxide emissions.

One new concept uses coal to produce syngas followed by the water shift reaction to produce hydrogen and carbon dioxide. The hydrogen produced is subsequently used to fuel a gas turbine or a fuel cell. The idea is to use a reaction between coal and steam to make hydrogen (see Section 4.7).

The hydrogen is separated from the carbon dioxide and then fed as fuel to a gas turbine power plant or a fuel cell. Of course, carbon dioxide is still produced, but its isolation does not require separation from large quantities of nitrogen as would be needed following the combustion of coal in air. Designers envision pumping the carbon dioxide into underground reservoirs. This process is called carbon sequestration. Its practicality for large-scale carbon dioxide storage is unproved.

4.6.8 Coal Reserves, Production, and Forecasts

The estimated remaining reserve of recoverable coal in the U.S. is around 250 billion tons, out of the recoverable reserve of about 319 billion tons underground when coal mining began. Annual production is about 1.1 billion tons and, as of 2005, the cumulative production was about 69 billion

tons. Figures 3-5 and 3-6 in the previous chapter show U.S. annual production and cumulative production.

Forecasters often state, "At the current rate of consumption, coal will last for 250 years." This is true, but somewhat misleading. Consumption certainly will not continue at the current rate. Concerns about pollution, climate change, the growth of renewable fuel, and/or nuclear energy use may reduce coal consumption significantly. On the other hand, new clean coal technologies and/or the inadequacy of alternatives may increase coal use significantly.

4.6.9 Environmental, Health, and Safety Issues

Although carbon dioxide release is the major environmental concern related to coal use, there are also other concerns related to coal extraction and use.

Coal mining in Appalachia has resulted in major undesirable effects. Mountaintops have been stripped off to reach coal deposits. Tailings, the excess material removed during mining, have been left on the surface where rainwater reacts with constituents to form acids that run into streams, killing fish and aquatic plants.

Coal mining has also historically taken a toll on the mineworkers. Black lung disease has caused the illness and death of thousands of miners. Mine accidents have taken many lives. The National Institute of Occupational Safety and Health has documented over 600 accidents with five or more fatalities between 1839 and 2010[15]. The main cause, by a wide margin, was explosions.

Coal mining operations now must comply with restrictions that reduce or eliminate environmental damage and increase mine safety, but concerns about the adequacy of environmental protection and safety practices persist.

Power plant operation results in huge quantities of ash and slag. This solid waste is stored at on-site storage facilities. The possibility of environmental catastrophe was demonstrated by the ash spill at the Kingston Plant in Tennessee in December 2008. Ponds containing ash slurry failed, releasing 1.1 billion gallons into the environment. The slurry flowed onto surrounding land and into the nearby Emory River. Cleanup and restoration required a large and expensive effort.

4.7 Synthetic Liquid Fuels

Liquid fuels currently provide almost all of the energy used for transportation and will continue to be important in the future. The materials best suited for transportation applications are hydrocarbons with five to 17 carbon atoms per molecule, and certain alcohols. These compounds are liquid at normal temperatures and release significant quantities of energy upon combustion.

Some of the hydrocarbons in crude oil have the desired properties and are obtained by separation from the other components of crude oil. Obtaining desired liquid fuels from sources other than the suitable fraction of crude oil requires processing to alter the materials' chemical properties.

It has been said that it is possible to make almost any organic chemical from any other organic chemical. Certainly, a number of processes have been developed that can convert organic materials into different, more useful materials. The processing must begin with available compounds that contain carbon and/or hydrogen. Oxygen also plays a role, either in the feedstock, in intermediate steps in processing, or as a component of alcohol fuels. The four sources of carbon are oil, natural gas, coal, and biomass. (Some also say carbon in atmospheric carbon dioxide is a potential source material for producing fuel.) The four sources of hydrogen are oil, natural gas, water, and biomass. The oil source material is now predominantly crude oil, but it could be augmented or replaced by oil from oil sands or oil shale.

Processing generally involves breaking the source compounds apart and then reassembling the parts into new, desired products.

The breaking of source compounds usually requires high temperature, high pressure and/or catalyst-assisted processes. The processes are known by a variety of names, including pyrolysis, gasification, retorting, cracking, and thermal depolymerization.

Pyrolysis is the thermal disassembly of molecules in the absence of oxygen.

Gasification is the thermal disassembly of molecules in the presence of limited oxygen.

Retorting is the modification of chemical compounds through the application of heat.

Cracking is the conversion of large hydrocarbon molecules into an array of lower molecular weight hydrocarbons. The resulting lower molecular weight hydrocarbons are then processed further, including reacting with hydrogen to increase the hydrogen-to-carbon ratio as needed to provide suitable liquid fuels.

Thermal depolymerization is the disassembly of high molecular weight molecules through the application of heat.

Syngas, a mixture of hydrogen and carbon monoxide, is useful as a fuel and as a source material for producing liquid fuels. Syngas can be made from any fossil fuel and from biomass. Hydrocarbons and alcohols can be produced from syngas using thermochemical processes or by fermentation (though the fermentation process is in the developmental stage). Syngas is hugely important because of its role as an intermediate in many of the currently-envisioned processes for producing liquid synthetic fuels.

Syngas can be produced from methane and steam by the following reaction (called steam reforming):

$$CH_4+H_2O \rightarrow CO+3H_2$$

Heating methane in the presence of oxygen at levels inadequate to cause complete oxidation also yields syngas:

$$2CH_4+O_2 \rightarrow 2CO+4H_2$$

Syngas can also be produced from coal. The steam reforming reaction in the carbon in coal to produce syngas is:

$$C+H_2O \rightarrow CO+ H_2$$

It is also possible to maximize hydrogen production via a reaction between carbon monoxide and water, called the "water shift reaction," as shown below:

$$CO + H_2O \rightarrow CO_2 + H_2$$

For steam reforming of methane followed by the water shift reaction, the overall reaction is:

$$CH_4+2H_2O \rightarrow CO_2 +4 H_2$$

That is, reacting one atom of methane with two molecules of water yields four molecules of hydrogen.

For steam reforming of carbon followed by the water shift reaction, the overall reaction is:

$$C+2H_2O \rightarrow CO_2+2H_2$$

That is, reacting one atom of carbon with two molecules of water yields two molecules of hydrogen.

Most of the hydrogen currently produced comes from methane. Future hydrogen production will have to shift to other processes if hydrocarbon consumption is to be minimized.

A process for producing various compounds of carbon, hydrogen, and oxygen from syngas in the presence of iron or cobalt catalysts was invented by Franz Fischer and Hans Tropsch in Germany in the 1920s. From a fuel production standpoint, the most important Fischer-Tropsch products are hydrocarbons and alcohols. The basic chemical processes for producing hydrocarbons from carbon monoxide and hydrogen are as follows:

$$nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$$

and:

$$nCO+2nH_2 \rightarrow C_nH_{2n}+nH_2O$$

where n is an integer.

The chemical formula for producing alcohols from carbon monoxide and hydrogen is as follows:

$$nCO+2nH_2 \rightarrow C_nH_{2n+1}OH + (n-1)H_2O$$

The Fischer-Tropsch process results in heat release and a mixture of reaction products. The relative proportions of reaction products obtained depend on the catalyst used, the catalyst physical state, and process conditions. Many variations of the Fischer-Tropsch process optimize the production of desired products, but all Fischer-Tropsch processes produce a mixture of products.

Dimethyl ether can be produced from methanol obtained by Fischer-Tropsch synthesis of syngas. Dimethyl ether or DME (CH_3OCH_3) has the same chemical formula as ethanol, but a different molecular structure. DME can be used as a fuel. Since its boiling point at atmospheric pressure is -13°F (-25°C), DME is a gas at atmospheric pressure and ambient temperature. However, it can be liquefied at modestly elevated pressure. The heat-

ing values of liquid DME are around 12,400 BTU per pound (LHV) and 13,600 BTU per pound (HHV).

DME can be produced by the catalytic dehydration of methanol as shown below:

$$2CH_3OH \rightarrow CH_3OCH_3+H_2O$$

Therefore, the steps in dimethyl ether production are syngas production, methanol synthesis, and conversion of methanol to dimethyl ether.

The use of DME as a fuel for Diesel engines is under investigation and development.

Another possible use of syngas is the production of hydrocarbons by the Mobil Oil M-gas process. In this process, dimethyl ether is produced (as shown above) from Fischer-Tropsch methanol and then processed catalytically to accomplish further dehydration. The result is hydrocarbons of various carbon chain lengths. One such reaction is between dimethyl ether and methanol:

$$2CH_3OCH_3+2CH_3OH \rightarrow C_6H_{12}+4H_2O$$

The general purpose of the syngas to hydrocarbon reactions in the M-gas process is to eliminate oxygen and achieve a hydrogen-to-carbon ratio of about two in the resulting molecules.

Natural gas can serve as the source material for syngas to be used in Fischer-Tropsch synthesis of synthetic liquid fuels. Also, a newer process is based on cracking of methane to produce acetylene, followed by hydrogenation to produce ethylene. The ethylene is then processed to yield longer-chain hydrocarbons as needed for liquid fuels. Developers of this technology claim that it is superior to the Fisher-Tropsch processes for gas-to-liquid fuel synthesis[16].

Coal also may be converted directly to liquid hydrocarbons by pyrolysis or by catalytic hydrogenation of the carbon in the coal.

Pyrolysis of coal involves heating it to around 800°F in the absence of oxygen, then condensing the resulting gas. Oil was produced by pyrolysis of coal in the nineteenth century, before cheap petroleum became available. A process for coal pyrolysis, called the Karrick process, was patented in the early twentieth century.

Several processes have been developed for coal hydrogenation. The earliest process was the Bergius process. Hydrogen produced from coal and steam, or methane and oxygen, is reacted with the carbon in coal at high temperature and pressure to yield hydrocarbons.

Many different processes that use some variation of the technology described above have been developed and implemented.

4.8 Fossil Fuel Summary

An impressive body of technology exists for finding, extracting, modifying, and using fossil fuels. Oil provides our dominant transportation fuel. Natural gas provides a convenient heating fuel and serves as a feedstock for many chemicals. Coal provides most of our electricity. Oil sands and oil shale constitute large potential energy resources.

But the future for all of these energy sources is in question. Oil will become scarce in years or decades. Huge reserves of unconventional natural gas exist in the U.S., possibly extending adequate availability for up to a century, but environmental impacts may limit its use. Coal is also plentiful, but its use also causes environmental effects that may limit its use. Economical and environmentally acceptable acquisition of oil from oil sands and oil shale remains a challenge.

Transitioning from heavy reliance on fossil fuel to cleaner and more sustainable energy sources will take time and commitment. Fossil fuels will be a

significant part of our energy supply for at least decades into the future. The technologies described in this chapter, along with others that will surely appear, will be needed for providing needed fuel as cleanly and economically as possible.

References

1. Scripps Institute of Oceanography http://earthguide.ucsd.edu/fuels/oil.html

2. Glasby, G. P. "Abiogenic Origin of Hydrocarbons: An Historical Overview" *Resource Geology,* Vol. 56, No. 1, 2006 pp. 85-98.

3. Energy Information Administration report "Petroleum: An Energy Profile 1999" *DOE/EIA –0545(99)*, July 1999.

4. Caruso, G. "When Will World Oil Production Peak?" Tenth Annual Asia Oil and Gas Conference, Kuala Lumpur, Malaysia, June 2005. www.eia.doe.gov/neic/speeches/Caruso061305.pdf.

5. Wood, J. H., Long, G. R. and Morehouse, D. F. "Long-Term Oil Supply Scenarios," Energy Information Administration, August 18, 2000 available at http://www.eia.doe.gov.

6. Greene, D. L., Hopson, J. L. and Li, J. "Running Out of and Into Oil: Analyzing Global Oil Depletion and Transition Through 2050" *Oak Ridge National Laboratory Report ORNL/TM-2003/259*, October 2003.

7. Wikipedia *The Logistic Function* at http://en.wikipedia.org/wiki/Logistic_function.

8. De Sousa, L. "Hubbert's Peak Mathematics" http://wapd.wuthwering-heights.co.uk/subpages/hubbertmaths/hubbertmaths.

9. Deffeyes, K. S. "Beyond Oil" New York: Hill and Wang 2005.

10. U.S. Bureau of Land Management and Argonne National Laboratory "About Tar Sands" at http://ostseis.anl.gov/guide/tarsands.

11. U.S. Department of Energy, "America's Oil Shale" December 2004. http://fossil.energy.gov/programs/reserves/npr/publications/oil_shale_roadmap.pdf.

12. Andrews, A. "Oil Shale: History, Incentives and Policy" *Congressional Research Services Report Order Code RL33359*, April 2003.

13. U.S. Geological Survey "Gas (Methane) Hydrates-A New Frontier" at http://marine.usgs.gov/fact-sheets/gas-hydrates/title.html.

14. Energy Information Administration report "Coal Basics 101" at www.eia.doe.gov/basics/coal_basics.html.

15. National Institute for Occupational Health and Safety: http://www.cdc.gov/niosh/mining/statistics.

16. SynFuels: http://www.synfuels.com.

Exercises

4-1. All hydrocarbons produce around 20,000 BTU per pound when burned. Compare the carbon dioxide release for burning methane (CH_4 and 75 percent carbon by weight) and octane (C_8H_{18} and 84.2 percent carbon by weight) in pounds of carbon dioxide per pound consumed.

4-2. Use the Internet to learn how oil exploration is performed. Prepare a summary of methods used.

4-3. Use the Internet to find a current projection of world recoverable oil reserves. Discuss the plausibility of the projection and the implications for future society.

4-4. The Hubbert method worked well for U.S. oil production. Discuss the potential of the method for predicting world oil production.

4-5. Assume new discoveries raise the recoverable oil reserves in the ground at the onset of oil extraction to 4 trillion barrels. Perform a Hubbert analysis. When does the peak occur? Hint: Appendix F provides information related to this exercise.

4-6. The Hubbert model says production drops steadily after half of the reserves are used. The EIA model says oil production increases steadily until almost all of the reserves are exhausted. Discuss the

relative plausibility of the two models. Can you suggest an alternate model?

4-7. Use the Internet to discover the current status of oil sand use. Pretend you are a journalist for a newspaper and prepare an article on the status, prospects, and environmental consequences of the widespread use of oil sand.

4-8. Repeat problem 4.7 for oil shale.

4-9. New technology for extracting natural gas involves hydrofracturing gas-bearing rock formations. The process is often called "fracking." There have been reports of severe environmental problems associated with fracking, including gas in well water and pollution by the chemicals used in the fracking process. Use the Internet to discover the current status of fracking for gas and the environmental consequences. Pretend you are a journalist for a newspaper and prepare an article on the subject.

4-10. Use the Internet to discover the current status of methane hydrate as a practical energy source. Discuss your findings.

4-11. A problem with using coal is the release of carbon dioxide and various pollutants. Capturing and burying the released carbon dioxide is called *sequestration*.

A. Use the Internet to discover the new plant designs that facilitate sequestration. Discuss.

B. Use the Internet to discover the current status of sequestration technology, including predicted capacity, proximity of carbon dioxide sources, and permanence of isolation from the atmosphere.

4-12. Discuss the importance of syngas in the production of transportation fuel.

4-13. Oil shale has a hydrogen-to-carbon ratio of around 1.5. If it is hydrogenated with methane to achieve a hydrogen to-carbon-ratio of two, how much methane (in pounds and kilograms) is needed per ton of hydrogenated product?