Chapter 10

'SYNTHETIC' FUELS, OIL SHALE AND TAR SANDS

New clean coal technologies can substantially improve efficiency and reduce emissions from powerplants. Until they are proven at commercial scale, however, their use entails more risk for utilities than conventional technologies. This additional risk could make it difficult for these new technologies to enter the marketplace quickly, especially given the tight deadlines of the Clean Air Act Amendments of 1990. The Clean Coal Technology Program, the single largest technology development program in the Department of Energy, is designed to help overcome this risk by offering the Federal Government as a financial partner in demonstrating worthy projects.

(National Energy Strategy, Executive Summary, 1991/1992)

The long-term risk of investing in new technologies that have not been demonstrated in multiple commercial applications inhibits the new technology market to such an extent that Federal resources have been needed to help fund commercial demonstration efforts. The Department of Energy's cost-shared Clean Coal Technology Demonstration Program, to which industry has contributed \$2 for every \$1 of Federal money invested, has evolved from an early focus on emission control systems to an emphasis in its later rounds on highly efficient, environmentally superior advanced power systems.

(Sustainable Energy Strategy, 1995)

Coal, petroleum and natural gas are the traditional fossil fuels whose direct use today accounts for most of the world's energy consumption. These fuels are rich in carbon and hydrogen. A relatively large amount of energy is stored in them and they have a high calorific value. However, these are not the only fossil fuels found on our planet. As they are depleted, or as their price increases, other fossil fuels can become more attractive for commercial exploitation. Furthermore, the abundant coal can be converted into cleaner and more convenient gaseous and liquid fuels, similar to petroleum and natural gas. These non-traditional, or unconventional, fossil fuels are discussed in the present chapter.

Oil Shale

Oil shale is an inorganic, non-porous rock that contains some organic material in the form of kerogen. In some respects, oil shale is similar to the source rock that produced petroleum. One important difference between oil shale and oil source rock is that the former contains greater amounts of kerogen (as much as 40%) than the latter, which usually contains about 1%. A second major difference is that oil shale has never been exposed to sufficiently high temperatures to convert the kerogen to oil. In a sense, we can think of oil shale as being a 'hybrid' of oil and coal. Oil shale contains more kerogen than oil source rock, but less than coal. The composition of the oil derived from oil shale is much more similar to the composition of petroleum than to coal. Some oil shales can be ignited, like coal, and they burn with a very sooty, smoky flame much like a coal of very high volatile matter content. However, oil shales are of no interest as solid fuels. Their principal interest is in the possibility of conversion to liquid fuels.

Lean shale contains about 4% kerogen. When heated to 350-400 °C, it yields about 6 gallons of oil per ton of shale. Rich shale may contain up to 40% kerogen and typically yields about 50 gallons of oil per ton.

Two thirds of the world's oil shale reserves are located in the United States. The largest known reserves of hydrocarbons of any kind are the Green River shale deposits in Wyoming, Colorado and Utah. These reserves are estimated to be 270 billion tons. At 20 gallons per ton of shale, this translates into 130 billion barrels of oil. This is five times as much as the proven reserves of petroleum in the U.S. (see Figure 9-6). However, no commercial production of fuels from oil shale exists today, so their economic recoverability is not well known. It is probably safe to say, however, that oil from shale is not economically competitive with petroleum at current world petroleum prices.

The recovery of oil shale uses mining techniques similar to the methods used in coal mining. The room-and-pillar method is one such approach. Oil is then recovered from the shale by *retorting* the shale. Retorting involves heating the shale in the absence of air to temperatures of 500 °C or more. Typically, 75-80% of the kerogen is converted to oil. An alternative to mining is *in situ retorting*. In this process, holes are bored into the shale deposit underground. By injecting hot gases and air into the shale, the shale can become

hot enough for the kerogen to turn into oil underground. *In situ* retorting eliminates the mining cost, many of the costs for above-ground retorts and liquid handling equipment, and addresses the problem of disposing of the shale after the oil has been 'cooked' out of it. In this case, since the shale has never been removed from the ground, there is, in a sense, no disposal problem at all.

The industrial processing of oil shale began a century ago. During the 1920s, oil shale was an economically important energy source. With the greater availability of low-cost petroleum, the commercial exploitation of oil shale ceased. During the energy crisis of the 1970s several major oil companies made massive investments both in research and development and in possible commercial use of oil shale. The Exxon Corporation even began construction of entire new towns in the Green River region. When petroleum prices began falling in the early 1980s, these efforts were abandoned.

Several technical problems must be overcome for successful large-scale use of oil shale in the future. The composition of oil from oil shale is sufficiently different from that of petroleum that liquids derived from oil shale cannot be used as direct substitutes for petroleum. Oil derived from oil shale has less carbon and hydrogen and more nitrogen, oxygen and (sometimes) sulfur than petroleum. Petroleum refinery operations would have to be modified to accommodate oil shale liquids as a feedstock. Hydrogen must be added to the oil during processing. Furthermore, special care must be taken to remove the nitrogen and sulfur during processing, to avoid the formation of SO_x and fuel NO_x when the oil is eventually burned. When oil shale is retorted, the inorganic portion of the shale expands considerably. The spent shale remaining after retorting has no commercial value, but it must be disposed of in an environmentally acceptable manner. Ideally, the spent shale is placed back in the mine, refilling the mined-out cavity and helping to prepare the area for land reclamation. Because of the popcorn effect, the volume of spent shale is greater than the volume of the mine from which it was taken. Thus even if the mine were completely refilled, there would still exist some amount of spent shale for which alternative disposal methods must be sought. In spite of these problems, liquid fuels derived from oil shale can become important alternatives to petroleum, when the world economic situation – particularly the price of crude oil – becomes favorable.

Tar Sands

Tar sands are grains of sand or, in some cases, porous carbonate rocks that are intimately mixed with a very heavy, asphalt-like crude oil called *bitumen*. The bitumen is much too viscous to be recovered by traditional petroleum recovery techniques. Tar sands contain about 10-15% bitumen, the remainder being sand or other inorganic materials.

The estimated world-wide resources of tar sands are about three times the known petroleum reserves. The world's largest deposit of tar sands is near Athabasca, in Alberta,

Canada. Other large deposits exist in the former Soviet Union and in Venezuela. In the United States, small deposits of tar sands are found in Utah.

If tar sand is heated to about 80 °C, by injecting steam into the deposit in a manner analogous to that of enhanced oil recovery, the elevated temperature causes a decrease in the viscosity of the bitumen just enough to allow its pumping to the surface. Alternatively, it is sometimes easier to mine the tar sand as a solid material. When the mined tar sand is mixed with steam and hot water, the bitumen will float on the water while the sand sinks to the bottom of the container, allowing for easy separation. Heating the bitumen above 500 °C converts about 70% of it to a synthetic crude oil. Distilling this oil gives good yields of kerosene and other liquid products in the middle distillate range. The remainder of the bitumen either thermally cracks to form gaseous products or reacts to form petroleum coke.

'Synthetic' Fuels (Synfuels)

Current estimates of the lifetimes of domestic oil and gas reserves are about a decade or two, as shown in Figure 9-6. More detailed information, including that for coal, is summarized in Tables 10-1 and 10-2. The numbers shown are larger than those of proven reserves, as they should be (see Chapter 6), but by no more than a factor of two. Despite the subtle differences in the definition of "undiscovered recoverable resources" and "demonstrated reserve base" – which we do not need to discuss here – it is obvious that coal will be around for several more centuries. So what is to become of it?

Region	Crude oil 10 ⁹ barrels	Natural gas 10 ¹² cubic feet
Onshore and State Waters	33.3	254.0
Alaska	13.2	57.9
Rocky Mountains and Northern Great Plains	4.5	15.2
Gulf Coast	4.2	82.5
Pacific Coast	3.5	11.0
Federal Offshore	16.1	145.1
Alaska	3.4	16.8
Gulf of Mexico	8.6	103.3
Total	49.4	399.1

 TABLE 10-1

 Undiscovered recoverable resources of U.S. crude oil and natural gas

[Source: Energy Information Administration.]

As mentioned previously, a time lag of some 50 years between the introduction of a new energy source and its widespread commercial acceptance and use has been typical in recent

history. So it may take another 50 years for society to witness the use of renewable energy sources – such as solar and wind energy – on a large, world-wide scale. It seems likely that a gap will develop between the time when natural gas and petroleum become scarce, and thus expensive, and the time when alternative energy sources will provide a major portion of the world's energy needs (see Chapters 16 and 17). We have already seen that the renewable energies contribute today much less than 10% of U.S. and world supply (see Figures 5-13 and 5-14) while fossil fuels contribute 90% or so. The day when this situation will be reversed appears to be at least 50 years away.

Region/State	Anthracite	Bit/Subbit	Lignite	% surface	Total
Appalachian	7.4	101.2	1.1	26.6	109.7
Pennsylvania	7.2	21.7	0.0	_	_
West Virginia	0.0	36.0	0.0	_	_
Ohio	0.0	23.7	0.0	_	_
Interior	0.1	131.2	13.6	28.3	144.8
Illinois	0.0	90.0	0.0	_	_
Western	0.0	211.4	29.8	40.2	241.2
Montana	0.0	104.1	15.8	_	_
Wyoming	0.0	68.5	0.0	_	_
Total	7.5	443.8	44.5	33.7	495.7

TABLE 10-2

Demonstrated reserve base of coal in the U.S. (in 10^9 short tons)

[Source: Energy Information Administration.]

The energy source that may provide the means for bridging this gap is coal. But it will do so only if it can be used in an environmentally acceptable way. Technology has been developed to convert coal into 'synthetic' gaseous or liquid fuels - *synfuels*. There is really nothing synthetic about them, as there is in synthetic (vs. natural) rubber. But this term has taken root and we'll adopt it here as well.

Coal itself is of course well established as a fuel. The Industrial Revolution would not have been possible without it. But it pollutes the environment more than oil or gas. We must go then through the trouble of converting it into a cleaner and more convenient fuel. There are several ways and reasons to do that. Let's look at the reasons first.

There exists an enormous investment in equipment that burns gaseous or liquid fuels; cars and trucks, locomotives, airplanes, many home furnaces and some power plant boilers are familiar examples. Our society has neither the economic resources nor the manufacturing capacity to replace all of that liquid or gaseous fuel equipment in a short time span. Therefore, liquid fuels will continue to be needed until new energy strategies – such as solar homes and vehicles – are developed and become widely accepted.

Also, liquid and gaseous fuels are much easier to purify than are solid fuels. For example, the sweetening of a sour gas is a straightforward process that allows the removal

of essentially all sulfur; but the beneficiation of coal for sulfur removal can be a cumbersome process that never succeeds in completely removing all sulfur from coal. (A consequence is the significant investment needed for flue gas desulfurization systems in coal-fired power plants; see Chapter 11) The conversion of coal to liquid or gaseous fuels offers opportunities for removing undesired components at the same time.

Finally, there are many convenience factors associated with the use of fluids rather than solids. Fluids are often easier to transport than solids; they are usually much easier to handle, with pipes, valves and meters. They can provide an instant on/off capability in a heating system. Particularly in domestic applications, oil or gas are far more convenient for the average householder than is coal and, not surprisingly, there is an overwhelming preference for oil or gas, rather than coal, for home heating.

There are essentially two approaches to coal conversion. They are known as *coal gasification* or *coal liquefaction*, depending on the type of product desired. In either case, synfuels production involves some strategy for the addition of hydrogen to hydrogen-deficient solid coal to form the relatively hydrogen-rich liquid or gaseous fuels (see Illustrations 7-1, 8-1 and 9-1). The relationship between the hydrogen content and the physical state of the fuel is illustrated in Table 10-3.

Fuel	(Typical) C/H mass ratio	(Typical) C/H molar ratio	State
Bituminous coal	15	1.25	Solid
Crude oil	9	0.77	Liquid
Gasoline	6	0.50	Liquid
Natural gas	3	0.25	Gaseous

TABLE 10-3

Relationship between hydrogen content of typical fuels and their physical state

Coal Gasification. In coal gasification the principal source of hydrogen is high-temperature steam. Steam is easily generated from inexpensive, abundant water. (In coal liquefaction, on the other hand, hydrogen is usually added as molecular hydrogen, H_2 , which can be expensive to produce on a large scale.)

The objective of coal gasification is to convert coal to a combustible gas, suitable for use as a fuel. The simplest way to obtain a combustible gas from coal is to *carbonize* the coal, that is, to heat it in the absence of air. We have already seen that heating coal in this way will drive off a variety of volatile substances. After compounds that would be liquids at ordinary temperatures are allowed to condense, the remaining gas is mainly a mixture of methane and hydrogen, with a calorific value in the range 550-700 BTU/ft³. (Recall that the calorific value of natural gas is 1000 BTU/ft³.) This gaseous product is called *coal gas*.

Coal gas was first used in 1798 as a fuel for gas lamps that illuminated a factory owned by James Watt (better known to us as the inventor of the first practical steam engine; see Chapter 4). The first company established in the United States to manufacture and distribute coal gas was founded in Baltimore in 1817. During the 1920s, about 20% of all fuel gas burned in the United States was coal gas. Coal gasification has left its mark on our vocabulary. The 1890s are sometimes referred to as "the gaslight era" because, prior to the widespread availability of electricity after the turn of the century, domestic lighting and street lighting relied on gas manufactured from coal. In those days, there was not much concern for the environment, and the area around a coal gasification plant was polluted with by-product coal tars and unpleasant odors. The neighborhoods around the "gas house" were often populated by 'lower-class' people. In the 1930s, the outstanding St. Louis Cardinals baseball teams were noted for their rough, aggressive style of play. The Cardinals teams of that era are still referred to in sports lore as "The Gashouse Gang."

A significant problem attending the manufacture of coal gas is that only about 20% of the coal is actually converted to gas. Most of the rest remains as a solid char or coke. Unless there is a ready local market for this coal char, it simply goes to waste. An ideal coal gasification process would convert the coal completely to gas. The key chemical step for achieving this is the reaction

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

which takes place at temperatures above 800 °C. When the reaction of coal (which is, of course, the source of carbon in the equation above) with steam is carried out in practical, large-scale equipment, the product gas has a calorific value in the range 300-500 BTU/ft³. This gas is sometimes called *medium-BTU gas*. Since its calorific value is only about half that of natural gas (or *high-BTU gas*), the carbon monoxide/hydrogen mixture cannot be used as a direct replacement for methane. An additional process, *methanation*, is needed:

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

The methane produced in this way is sometimes called *substitute natural gas* or SNG. It would be easier, and possibly cheaper, to obtain SNG in a single processing step:

$$C + 2 H_2 \rightarrow CH_4$$

This process concept is called *hydrogasification*. It has not been used commercially, but has been the subject of much research and development effort.

Coal gasification processes have been, and continue to be, used commercially in many parts of the world for at least 50 years, especially in Europe and South Africa. It is estimated that before World War II over 20,000 coal gasification units were in use in the United States, producing various grades of fuel gases for domestic heating, cooking, lighting and industrial heating. (It is ironic that during the energy crisis of the 1970s many people in the United States thought that coal gasification was some marvelous new idea.) This industry was wiped out by the spread of the interstate natural gas pipeline in the years after the war. Today there is only one large-scale coal gasification plant in the United States, in Beulah, North Dakota. It is based on German technology and it produces SNG.

A promising new development in coal gasification is the integrated gasification combined cycle plant (IGCC). It is being advertised by the electric power industry as the "cleanest method available for making electricity from coal" (Electric Power Research Institute Journal, July/August 1994, p. 6). In this concept, coal is gasified and the hot gases are burned to drive a gas turbine. The combustion gases leaving the turbine are still very hot, and the heat is recovered by producing steam, which is used to drive a steam turbine. Both the gas and the steam turbine can be used to generate electricity (see Chapter 18). This highly efficient process concept has been successfully demonstrated (in a technical, though not economic, sense) at the Cool Water plant in the Mojave Desert, near Barstow, California. Such IGCC plants may become a major contributor to electricity generation early in the 21st century (see Chapter 18). Today, quite a few demonstration plants are already in operation. A 250-MW plant has been operating in the Netherlands since 1994 and a 300-MW one was just started in Spain. Some 3000 MW of electricity will be produced in Europe before the turn of the century. In the United States, a 160-MW plant has been in operation in Louisiana since 1987, a 250-MW plant started up in Indiana in 1995, while three other power plants will be operational by the year 2000 (see Investigation 10-2) and will generate another 4000 MW of electricity. Two additional IGCC plants will be started up soon in China and South Korea.

Coal Liquefaction. Two basic approaches are used for coal liquefaction. *Indirect liquefaction* involves the gasification of coal to produce a mixture of carbon monoxide and hydrogen, called *synthesis gas*. The synthesis gas is then converted into a variety of liquid hydrocarbons using German-developed technology, called the Fischer-Tropsch synthesis. Depending on the specific conditions (temperature, pressure and catalyst) used for the Fischer-Tropsch synthesis, many useful products can be made, including branched-chain paraffins (for high-octane gasoline), kerosene and diesel fuel, fuel oil, and oxygen-containing compounds that can in turn be converted to products such as synthetic detergents, synthetic margarine and cooking oil. During World War II, Germany produced 200,000,000 gallons of fuel per year by indirect liquefaction. More recently, South Africa has been meeting most of its liquid fuel needs in essentially the same way.

Direct liquefaction is the reaction of coal with hydrogen (usually in the presence of some liquid solvent) to produce a synthetic crude oil, or syncrude. No intermediate gasification step is needed. Direct liquefaction is a very difficult process to carry out, involving temperatures over 400°C, hydrogen pressures of over one hundred atmospheres and an appropriate catalyst. The syncrude can be refined to produce gasoline with 75-80 octane rating, as well as diesel fuel and fuel oils. German war-time production of synthetic liquid fuels by direct liquefaction peaked at a million gallons per year. Today even modern versions of direct liquefaction, beneficiaries of four decades of research, are not competitive when crude oil sells for \$25 per barrel. The economics of coal-derived liquids are generally thought to become attractive when the oil price exceeds \$35 per barrel.

After the expenditure of tens of billions of dollars and many lives in the Persian Gulf War to insure that oil supplies would not fall into the hands of a despot antagonistic to the United States, one might question why coal liquefaction is not already a commercial industry. Indeed, workable liquefaction technology exists. The main stumbling block is still one of economics. The investment in a commercial-scale coal liquefaction plant will probably be several billion dollars. It must be recognized, however, that the large-scale successes of coal liquefaction have been achieved in situations where economics was not the decisive factor – wartime Germany, fighting on two fronts, and South Africa, commercially isolated from much of the world because of its past apartheid policies. When Allied bombers began destroying the coal liquefaction plants in Germany in May 1944, Albert Speer, the German minister of production, realized that the war was inevitably lost.

Whether similar crisis situations will be necessary for the re-emergence of synfuels industries remains to be seen. Stay tuned!

REVIEW QUESTIONS

10-1. Using the information provided in the previous chapters, verify some of the key statements in the NYT advertisement of 11/1/96 by the Solv-Ex Corporation ("It's time to reduce dependence on Middle East oil"). For example, does it make sense that "300 billion barrels are enough to produce 10 million barrels of oil daily for 80 years?

10-2. Table 10-1 makes the point that most of the domestic onshore oil resources (more than 50%) are in Alaska and California. How many tons of coal would be needed to replace that much oil (16.7 billion barrels) if 3 barrels of oil can be produced from 1 ton of coal? Would the reserves of Illinois coal (see Table 10-2) be sufficient to produce this much oil?

10-3. Table 10-1 also makes the point that most of the readily accessible onshore gas resources are in the Gulf states (33%). How many tons of coal equivalent does this much gas represent? Is the demonstrated reserve base of Montana lignite (see Table 10-2) larger or smaller than this quantity of energy?

10-4. In an article in the prestigious *Science* magazine ("Resource Constraints in Petroleum Production Potential," 7/12/91, p. 146), a group of authors from the U. S. Geological Survey arrive at the following conclusion: "Geologic reasons indicate that the dominant position of the Middle East as a source of conventional petroleum will not be changed by new discoveries elsewhere. The share of world crude oil production coming from the Middle East could increase, within 10 to 20 years, to exceed 50 percent, under even modest increases in world consumption. Nonconventional resources of oil exist in large quantities, but because of their low production rates they can at best only mitigate extant trends. Increased production of natural gas outside the United States, however, offers an opportunity for geographically diversified energy supplies in the near future." They substantiate their conclusions with the information summarized below:

(a) How well does this information agree with the data provided in Chapters 7-10, and especially with Figures 7-1, 8-1 and 9-1?

	Cumulative production	Identified reserves	Undiscovered resources
		Petroleum	
North America	182.8	83.0	121
USA	152.7	48.5	49
Middle East	160.2	584.8	122
Soviet Union	103.6	80.0	101
World	610.1	922.1	547
	Natural gas		
North America	826.5	440.2	926
USA	731.5	272.0	399
Middle East	54.6	1247.2	1125
Soviet Union	332.2	1450.0	1582
World	1523.6	4042.2	5216

<u>Note:</u> The numbers for petroleum are in billions of barrels of oil and those for natural gas are in trillion cubic feet.

(b) Compare the fraction of world's petroleum reserves in the U.S. with that residing in the Middle East and ex-Soviet Union.

(c) Compare the fraction of world's gas reserves in the U.S. with that residing in the Middle East and ex-Soviet Union.

(d) Compare the fraction of world's petroleum resources in the U.S. with that residing in the Middle East and ex-Soviet Union.

(e) Compare the fraction of world's gas resources in the U.S. with that residing in the Middle East and ex-Soviet Union.

INVESTIGATIONS

10-1. In a NYT advertisement of 11/1/96 ("It's time to reduce dependence on Middle East oil"), the Solv-Ex Corporation (www.solvex.com) advocates the development of Alberta's tar sands or oil sands. Find out more about these reserves which, according to this ad, amount to "as much as the vast reserves of Saudi Arabia." Summarize the arguments used to support this initiative.

10-2. According to the U. S. Department of Energy, on January 10, 1997 the "U.S. electric utility industry took a major step into the next millenium of clean, high-efficiency electricity from coal with the dedication of one of the world's cleanest and most advanced coal power plants." Find out how this plant produces electricity from coal by visiting the following DOE Web site: http://www.fe.doe.gov.

10-3. Find out about Sasol, one of the very few synthetic fuels companies in the world. Visit its Web site at http://www.sasol.com/comprof.html. Briefly summarize its history.