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CHAPTER 9

ENERGY TRANSFORMATIONS and FOSSIL FUELS

Our industrial society is based on the instant availability of relatively large amounts of energy, whether it be for heating or air conditioning our homes, transporting us by car, rail, or jet, or manufacturing products for our consumer society. In the late twentieth century and early twenty first century, it became obvious that there were limitations being placed on the availability of this energy. In addition, it became apparent that each of the common energy sources had unwanted environmental impacts.

In this chapter we explore the various energy sources and energy transformations. We then focus on the prime current energy source for electrical power, home heating, and transportation - fossil fuels. The following chapter deals with nuclear energy, and Chapter 11 discusses alternative and renewable sources of energy.

Questions Addressed in This Chapter:

1. What is energy?
2. What are the different types of energy?
3. What are the various sources of energy?
4. Are there any limitations on our ability to obtain energy?
5. What are the chemical structures of fossil fuels?
6. What is the chemistry of fossil fuels?
7. How can we maximize output from fossil fuel utilization while minimizing pollution?
8. What is the origin of petroleum and where is it found?
9. How are gasoline and other products obtained from petroleum refining?
10. What are the sources of natural gas? What is fracking?
11. How large are our fossil fuel reserves?

Introduction

The weather and terrain found in different parts of the world determine both the energy needs and the manner in which energy is supplied to its inhabitants. Mountainous Switzerland and Norway rely heavily on waterpower, as do residents who obtain power from dams on great river systems, such as the Nile River in Egypt. Flat desert regions that include Israel and Arab countries rely increasingly on solar power. The small, densely populated islands of Japan and Great Britain have relied heavily on nuclear power because of their lack of other energy resources. Residents of the North Sea countries such as Germany, Denmark and Scotland and some developing countries are increasingly utilizing wind power that is abundant in their countries. China has extensive coal and gas deposits and is paying the air pollution price for burning large amounts of high sulfur coal, especially in large cities.

*Sources
of
energy*

The United States relies heavily on fossil fuels, coal, petroleum and natural gas. Greater than half of its petroleum is imported, causing large trade imbalances and, in part, causing it to become the world's largest debtor. Oil and natural gas are favorite fuels because of their ease of use and transport. Recent computer-based exploration tools have aided in the discovery of deep natural gas deposits in the United States and have suggested this fossil fuel may be an indigenous alternative to imported oil. Coal is abundant in the United States but has both transportation and pollution costs associated with it. Nuclear energy is responsible for 20% of the electrical energy produced in the United States, but reactors are aging and relatively few new nuclear reactors are planned, especially after the nuclear accident from the Fukushima earthquake and sunami in March, 2011. Growth in world electrical generating capacity of nuclear power plants slowed significantly after 1990.



There are two types of energy, nonrenewable (like fossil fuels) and renewable (continuously supplied in relative abundance, like sunlight or wind power). World supplies of nonrenewable fossil fuels are predicted to be exhausted in one to two centuries, although some are claiming that these reserves are much more extensive than have been forecast. Two trends will undoubtedly increase the amount of world energy consumed in the future, the rate of increase in world population and the rising expectations of developing countries.

Our studies of air and water pollution demonstrate that a significant portion of this pollution originates from the sources of energy used to power industry, heat and air condition homes and offices, power electrical appliances, and provide transportation. These sources of energy are primarily fossil fuels such as natural gas, petroleum, and coal. If we wish to diminish pollution from these sources, it is necessary to burn less fossil fuel and to find substitute energy sources that pollute less. This chapter and the next will explore the various sources of energy, the ways in which we use energy to generate electrical power by transformation from one form of energy to another, and the scientific limitations on and problems associated with energy transformations. Chapter 10 will cover nuclear energy and associated topics. Chapter 11 will explore alternative

non-fossil fuel sources of energy and ways in which fossil fuel use can be diminished through conservation measures.

Types of Energy

Energy can be defined as the capacity to do work. **Work** is defined as the transfer of energy when a mass is moved through a distance with a force applied in the direction of the mass's movement.

All types of energy fit into one of the two major categories, **potential energy** ("energy-in-waiting") and **energy-in-motion** (often called "kinetic" energy). These categories and their subcategories are illustrated in Figure 9-1 and by scrolling over the figures opened by clicking the following buttons:

Potential energy

Gasoline and dynamite have the potential chemical energy to move automobiles and huge chunks of rocks, respectively. Water behind a dam contains gravitational potential energy that can be tapped to generate electrical energy or used in destructive ways to wash away villages downstream if the dam suddenly gives way. Uranium in a nuclear bomb has the capacity to release nuclear energy suddenly to perform work to move mountains. Two magnets held apart with opposite poles facing each other (north pole against south pole) have a potential magnetic energy of attraction. Just before a lightning strike, electrostatic charges are built up in clouds. All of these sources of energy (above the line in Figure 9-1) are poised and have the capacity to do work, but are not in the process of doing any work. In order to accomplish work, each of these sources of potential energy must be converted into one of the energy-in-motion forms (below the line, Figure 9-1).

*Potential
energy*

*The energy
wheel*

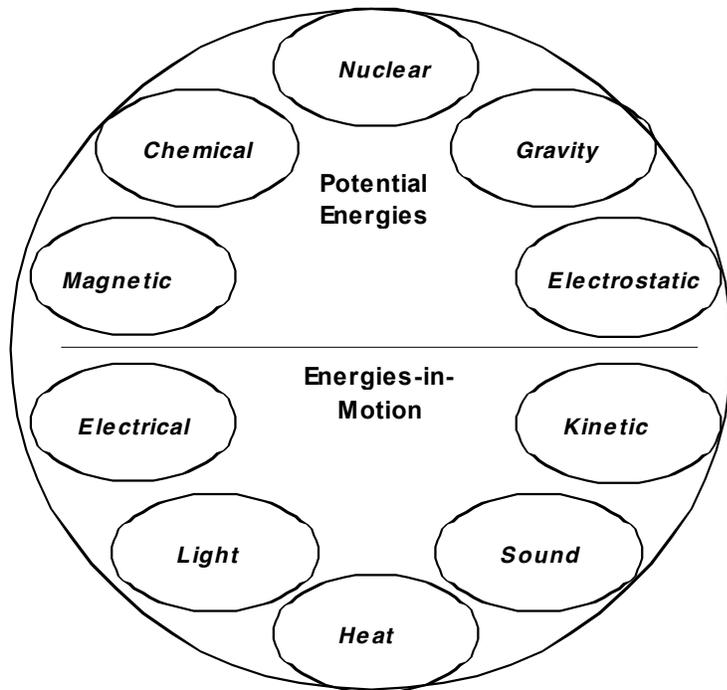


Figure 9-1 The energy wheel showing the interrelationships among the different forms of energy. Above the line are the four types of potential energies, energies in storage, and below the line are the "energies-in-motion", energies that are not easily stored for later use. Conversions among all of these types of energies are possible but some are more difficult than others. Only energy conversions between or among those listed on this wheel are allowed in any energy transformation.

Energies-in-motion

We choose to call the five types of energy below the line in Figure 9-1 "energies-in-motion," energy that is associated with some sort of dynamic activity. When coal or oil is burned in combination with oxygen in the air, chemical potential energy is converted into heat energy, an energy associated with the translational, rotational and vibrational motion of atoms and molecules. Electrical energy consists of electrons moving rapidly through chemical compounds such as wires or transistors. Consumers use electrical energy to turn motors, resulting in the conversion of electrical into magnetic and then into kinetic energy of the revolving motor drive. In an explosion resulting from dynamite or a nuclear bomb, the resulting damage arises from the conversion of potential chemical or nuclear energy into light (movement of photons), heat, sound (sound waves transmitted through air causing the movement of air against the eardrum) and the kinetic energy of fast moving debris. In the above processes, we see illustrations of transformations of types of potential energy into different types of energy-in motion.

Energies-in-motion

Energy Transformations

The performance of work or the extraction of heat from a fuel can only be accomplished through an energy transformation. ***The only types of energy transformations that are possible are between and among the energies listed in the energy wheel (Figure 9-1) and the listed energies are the only known energies for***

this use, as far as we know. Of the many possible combinations, only a limited number of energy transformation provide us with the energy we need to power our houses, cars, etc. For example, we transform solar (light) energy coming from the sun into electrical energy using solar cells and store the solar energy as chemical energy in batteries. We dam rivers to create potential gravitational energy for later use in generating electrical energy. Electrical power is generated by transforming the kinetic energy of movement of vast quantities of air moving as wind into magnetic and then electrical energy. At present, however, we mostly utilize the chemical energy available in fossil fuels such as petroleum, natural gas, and coal for their stored chemical energy and convert it into heat and kinetic energy.

We are confined to promoting energy transformations among only those energies contained within the energy wheel in Figure 9-1; these are the only known sources of energy, except for cosmological dark energy (Chapter 2 link), which is still not understood. Any time an observed event occurs on our Earth, there is an energy change representing a change from one kind of energy to another. Our lives represent one continuous chain of energy conversions. For example, our food is stored chemical energy that is transformed into heat, mechanical, electrical, and different forms of stored chemical energy (molecules other than food). These energy transformations power life processes as well as those that make life possible, such as muscle and brain activity and those that support life processes, such as energy for transportation.

*Energy
transformations*

Currently, our primary sources of energy are potential energy, such as fossil fuels (chemical), nuclear reactors (nuclear), and hydroelectric power (gravitational). Each of these potential energy sources remains available as long as we are able to store them. All other sources of energy from the "energy-in-motion" category must be employed before they vanish or they degrade into other energy forms. Solar energy is perhaps the most familiar example. The sun delivers photons continuously, whether we use them or not. The solar photon cannot be saved for use at a later date - unless it is converted into another form of energy. An electrical current flows or it doesn't; it cannot be stored somewhere. In a battery, chemical energy is stored and, upon demand, is converted into electrical current. This current ceases when the energy transformation ceases. A car sitting on top of a hill has potential energy. The same car, with released brakes, motor off, and out of gear, converts its potential energy as it rolls down the hill into kinetic energy as it accelerates (gravity to kinetic energy in Figure 9-1). A moving car has considerable kinetic energy of motion and can do a lot of damage, if stopped suddenly in a crash, converting mechanical into the chemical energy of breaking many chemical bonds, a process that absorbs most of the kinetic energy. Sound energy represents energetic atmospheric disturbances that cause eardrums to oscillate. Heat is a special case and represents energy stored in the movement of molecules and atoms in those molecules in matter of all kinds. Heat energy can be stored but can spread rapidly and is usually employed as a transient means of storing energy, for example as the heat of burned gases in the cylinder of an automobile engine.

Let's demonstrate this by using the energy wheel in Figure 9-2 with a specific example, that of the conversion of the chemical energy of coal into electrical energy which is used to light a lamp. First the coal (chemical) is burned, converting chemical

energy into heat energy (heat). The heat energy liberated by the chemical reaction is used to convert water into steam (heat), which is used to turn a turbine (kinetic), which turns a generator (magnetic) that creates electrical energy (electrical), which is transmitted to the home to light the lamp (light). The light energy is ultimately converted into heat.

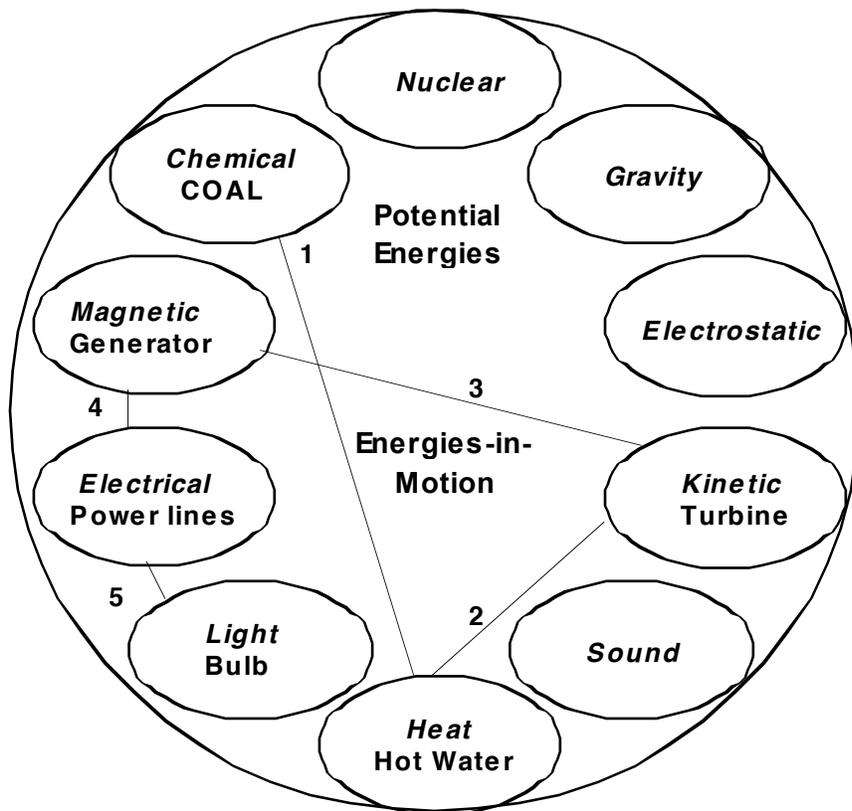


Figure 9-2 An illustration of energy conversions in the energy wheel shown in Figure 9-1. The chemical energy in coal is converted into heat (1) that is used to heat water into steam that turns a turbine (2) that generates electricity (3) that travels over power lines (4) causes a lamp to give off light (5). All of the light energy is ultimately converted to heat. In each of the steps there is heat formed in addition to the energy conversion identified. Therefore the net result of all of these steps is the conversion of chemical energy (coal) into heat. During these processes, energy is converted from one form to another, but there is no change in the total energy of the world.

We cannot create any kind of energy from anything except another type of energy. Careful measurements by scientists have demonstrated that the total energy before and after every energy transformation is exactly the same. For example, the energy contained in the light bulb is exactly equal to the electrical energy that went into the lighting of the bulb. Every careful measurement that has ever been taken has confirmed this same conclusion. These observations lead to one of the fundamental laws dealing with energy - the First Law of Thermodynamics.

Thermodynamics

First Law of Thermodynamics

The generalized statement of our discussions above is the first law of thermodynamics: *The total energy of the universe remains constant.* This is sometimes called the law of *conservation of energy*. In all chemical reactions, energy is neither created nor destroyed, merely transformed from one form into one or more other forms, one of these likely being heat. In nuclear reactions, such as those found in the sun or in nuclear power plants, this previous statement must be modified to include the fact that, if mass is destroyed during the nuclear reaction, energy must be created, and vice versa. This relationship is recognized quantitatively in the Einstein relationship, $E = mc^2$, where “E” is the energy created by the amount of mass “m” destroyed (really converted into energy), and “c” is the speed of light. It also represents the amount of mass that can be created in those situations where energy can be converted into mass (high energy gamma rays can also create matter when they are absorbed). So, the most comprehensive statement of the first law of thermodynamics is that *the total amount of matter-energy in the universe is constant.*

*First
Law
of
Thermo-
dynamics*

The first law of thermodynamics is not legislated by a vote of the majority of an assembly of scientists. It is based upon countless observations and quantitative measurements of the transformation of one form of energy into another. In all known instances, this law has been obeyed. Scientists cannot give any reasoned discourse as to why this law should be valid; they merely observe that it is a universal law that has never been violated. The first law is one of three laws that are the foundation for the subject of **thermodynamics**, the study of the relationship of heat and energy in matter.

Chemical thermodynamics is the study of heat and energy changes during chemical reactions. Chemical bonds are usually broken in reactants and formed in products during chemical reactions, resulting in an increase or decrease in chemical energy. Generally this extra energy is either provided by or released as heat. As an example of this, we examine the burning of natural gas (predominantly CH_4) in air.



Before the burning takes place, we have the mixed cold gas and air. After the burning, we have the hot combustion products, the hot gases carbon dioxide and water. We write a balanced chemical equation representing these changes in the following manner:

*Chemical
thermo-
dynamics*

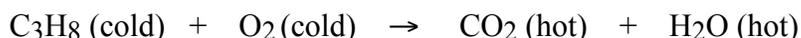


Equation (9-1) claims that one mole of methane molecules (6.02×10^{23} molecules) reacts with **two** moles of water molecules to yield one mole of higher temperature carbon dioxide and two moles of higher temperature water molecules.

This equation is balanced in two ways. First, the number of atoms before and after the reaction are balanced. There are the same number of hydrogen atoms (4 moles of hydrogen atoms) and the same number of oxygen atoms (4 moles), and the same number of carbon atoms (one mole) on both sides of the arrow (both sides of the equation). This must be true since there must be conservation of mass (and atoms) in any chemical reaction. There is also a conservation of energy in any chemical reaction, including this one.

Example 9-1 Balancing chemical equations (Combustion of propane gas)

Balance the chemical reaction for the burning of propane gas (C₃H₈):



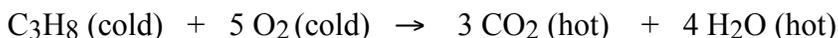
We first note that we have three carbon atoms in the propane and only one in CO₂, so we multiply the carbon dioxide molecule by three.



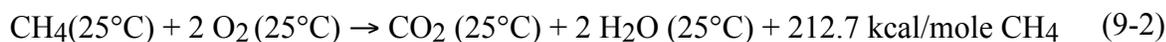
We now examine the number of hydrogens on both sides of the equation and see that there are 8 on the left side and only 2 on the right. We therefore multiply the number of water molecules on the right by 4 to equalize the number of hydrogen atoms



Now carbon and hydrogen atoms are balanced, but oxygen atoms are not. We see that there are six in carbon dioxide and four in water, a total of ten, with only two on the left side of the equation. We therefore multiply the oxygen molecule by 5, balancing the equation.



Equation (9-1) is also balanced in terms of energy, but only in a qualitative sense. Thermal energy (heat) has been released and is present as "hot" carbon dioxide and H₂O molecules and N₂ and remaining O₂ molecules, if air was burned. We can be much more specific if we cool down the hot gases to the same temperature as that of the methane and oxygen mixture before burning and measure how many calories of heat are delivered to the surroundings. For example, we could heat up water with these hot gases, as we do on the top of a gas stove burner, and measure the increase in the temperature of the water. From this increase in temperature and the known values of the heat capacity of water (1 calorie per degree per gram of water, see Chapter 4), we can calculate the total amount of energy liberated in this combustion. This experiment has been carried out under rigidly controlled laboratory conditions and the results are given in equation (9-2).



Equation (9-2) indicates that 212.7 kilocalories (thousand calories) per mole of burned methane are released to the surrounding atmosphere when the gases before and after burning are all at exactly 25°C. That is, all of the excess energy of the hot gases is extracted to bring the temperature of the hot combustion gases down to 25°C. This equation is an example of a more general class of chemical reactions, all of which give off varying amounts of energy. Such reactions are called **exothermic reactions**, i.e., chemical reactions that give off heat. All combustion reactions are exothermic reactions. In searching for potential fuels, the goal is to provide the maximum number of calories per gram or mole of fuel possible in an exothermic chemical reaction. Plastic heating packs for warming food utilize the mixing of two or more chemical ingredients in a plastic container, causing an exothermic chemical reaction, which provides the liberated heat to warm the food. Most, but not all, chemical reactions are exothermic. In order to initiate most exothermic reactions, energy must be provided to initiate these reactions. This energy is called activation energy. (Click following button for details) [A-9-10](#)

*Exothermic
chemical
reactions*

Another group of chemical reactions, called **endothermic reactions**, absorb, rather than give off, energy. The heating of water from a lower to a higher temperature is an endothermic process. When Epsom salts ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) are added to water, they cool the water in an endothermic process.

Second law of thermodynamics

There are a number of ways of stating this law, which is much more subtle than the first law. One implication of the **second law of thermodynamics** is that *heat tends to flow spontaneously in only one direction, from hot objects to cold objects*. This always happens. No case has ever been observed where heat has *spontaneously* flowed from a cold substance to a warm substance. There is no violation of the **first** law of thermodynamics if heat were to flow spontaneously from a cold object to a hot object. There is something in the nature of heat that drives it in only one direction only. Consider a hot cup of coffee and the natural flow of heat from the hot liquid to its surroundings. Coffee lovers go to great lengths to keep hot coffee hot, including using thermos bottles that merely delay the inevitable - cold coffee. However, there has never been an observation of a cold cup of coffee extracting heat from the surroundings and becoming hot. If there were, and it could be repeated by many scientists, this would violate the second law of thermodynamics and therefore invalidate the law! Another way of thinking of the second law is using the concept of disorder. Spontaneous processes usually lead to greater disorder. For example, a highly ordered piece of ice at room temperature absorbs energy and melts, yielding more molecularly disordered liquid water, which then evaporates to give even more disordered water vapor.

*Second
law of
thermo-
dynamics*

Click the following button for detailed discussion of the second law and entropy: [B-9-10](#)

Third law of thermodynamics

The **third law of thermodynamics** states there is a state of perfect order for perfect crystals at 0 degrees Kelvin. This Kelvin temperature scale has the minimum value of zero K, which is equal to negative (–) 273°C. Numerically, the relationship between Celsius and Kelvin is: degrees K = degrees C + 273. At absolute zero Kelvin (0 K - by convention, the ° symbol is omitted), there is a myth that all motion would cease if it were possible to achieve this temperature (it is not!). All translational and rotational motion does cease at absolute zero. However, according to quantum theory, there is still residual vibrational motion even at this lowest of all possible temperatures.

[If you clicked button [B-9-10](#) on the previous page, the third law of thermodynamics states that the value of the entropy of the most stable crystalline state of a substance is zero at absolute zero degrees Kelvin.]

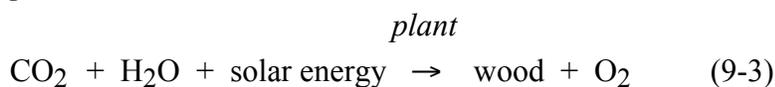
Third Law of Thermodynamics

Energy, disorder and molecules

The number and the type of atoms, and the manner in which these atoms are bonded together in a molecule, determine the total energy of that molecule. Armed with a knowledge of energies and entropies [Button [B-9-10](#)] of various molecules, the study of thermodynamics aids in the search for chemical fuels that release large quantities of energy.

When molecules undergo exothermic chemical transformations by rearrangement of their atoms to form lower energy molecules, the energy released goes into molecular motions such as rotation and vibration of the chemical products—that is, it is transformed into heat in the products. Looking at this process in terms of the reverse reaction, if we add the right kind of energy to low energy molecules in just the right manner, we can facilitate bond breaking and rearrangements to create high-energy molecules that can be used as fuels.

Let's write a simplistic equation representing the formation of wood in a tree from the reactants, sunlight, carbon dioxide, and water (plus small amounts of minerals), and examine it from a thermodynamic point of view:



Read from left to right, this is called an **endothermic** (energy absorbing) reaction, called **photosynthesis**, because it requires sunlight as an energy source, carbon dioxide, and water molecules and a plant supplying small amounts of other elements to produce the wood and oxygen products.

The energy stored in the products on the right side of the equation are now higher in energy than the chemical reactants carbon dioxide and water on the left. Wood is of course a fuel and the reverse of equation (9-3), read from right to left, demonstrates that the same amount of energy should be *liberated* in burning that wood as that





which was used to synthesize the wood. Of course, the energy released upon burning will be released as both visible and infrared light from the flames and wood as well as the heat of the products.

Energy Resources

Either directly or indirectly, we obtain almost all of our energy from our sun. Except for nuclear and geothermal energy taken from hot spots in the Earth, all other sources of energy are ultimately derived from the sun. Fig. 9-4 shows that petroleum, natural gas, and coal provided about 80% of the U.S. energy needs in 2009, all originating from stored photosynthesis energy. Nearly all of the renewables also have their origins in solar energy.

Fuel sources

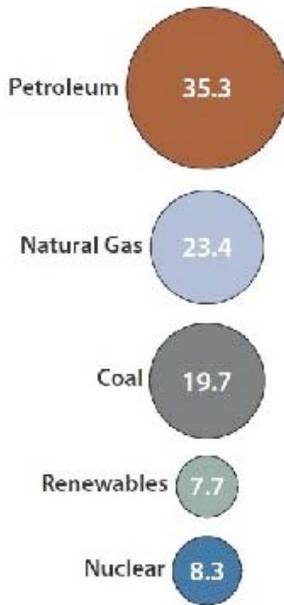


Fig 9-4. Approximate percentages of energy resources that are obtained from each of the above listed sources for all energy needs in the US in 2009.

The sun provides the driving energy for photosynthetic processes that create wood and other plant materials. Many centuries ago, plant materials were buried underground and subjected to very high temperatures and pressures, converting them to the various fossil fuels that are in widespread use today. Figure 9-5 shows the variety of these hydrocarbon fuels available for processes that convert chemical energy stored in these fuels into electrical, mechanical, and other useful forms of energy.

We can categorize the various fossil fuels according to the ratio of hydrogen to carbon atoms (Figure 9-5). For example methane has a ratio of 4 hydrogen atoms per carbon atom, whereas, at the other end of the spectrum, various types of coals have an average ratio of one hydrogen or less per carbon atom. Between these two extremes are peat, tar sands and petroleum. High H/C ratio products are desirable liquid and gaseous fuels, whereas the low H/C ratio products

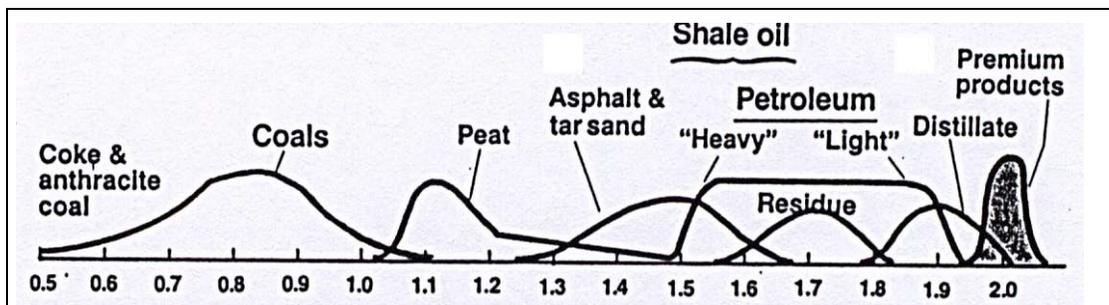


Figure 9-5 Ratio of numbers of hydrogen / carbon atoms in various fuels (C&E News, May 21,'95,33)

are primarily more difficult-to-handle solid fuels. Let's examine the chemistry of each of these categories, starting with natural gas.

Natural gas

Introduction and current status

The extraction of easily mined natural gas “peaked” in the 1970s and was predicted to fall continuously. Most of the relatively shallow, large trapped pockets of natural gas have been mined. The use of natural gas as a bridge fuel to a carbon-free energy future was in doubt because of probable future shortages.

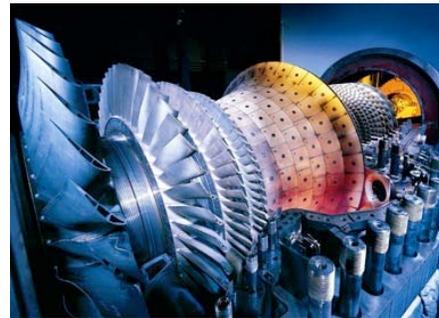
However, within the past decade, there has been a technological revolution in the mining of natural gas that has placed this fuel at the top of the list of critically important and abundant fossil fuels, especially in the United States. A relatively new horizontal drilling and hydraulic rock-fracturing technique (“**fracking**”) has been developed to extract natural gas from the vast deposits of natural gas-bearing shale found in the US and elsewhere in the world. This technique has suddenly changed the energy dynamics and fuel economy because of its relatively low cost. US natural gas reserves are now considerably expanded and production of natural gas is predicted to exceed the previous peak volume.

Natural gas is important in all sectors of the modern economy. It is used for electricity generation, industrial heating, chemical feedstock, and for water and space heating in residential and commercial buildings. The role of natural gas is expected to expand during the short term while the need to reduce CO₂ emissions increases. Natural gas is now widely considered to be *the* bridge fossil fuel for use while alternative non-carbon energy sources are researched and developed on a large scale. That is, of course, if the economics of this new technique work out as advertised by its proponents.

Advantages and risks

Natural gas is a high-energy fuel and one of the most valuable of the natural resources taken from the Earth. It is easily transportable through pipelines, and burns cleanly if there is sufficient oxygen. Methane can be burned at a relatively low temperature in comparison with other fossil fuels and therefore emits less of the air pollutant NO_x. Of course, one of the combustion products of methane is the greenhouse gas CO₂. However, methane emits the least amount of CO₂ per unit of energy delivered when compared with any of the other carbon-based fuels. That is, for the same amount of energy obtained from coal, oil or natural gas, there will be less carbon dioxide produced by methane than by either of the other two fossil fuels. This is one of the reasons there is a concerted effort to convert fossil fuels into methane.

Unlike oil, natural gas requires minimal processing once it has been extracted. New gas burning equipment is available with greatly improved efficiencies for energy recovery during the burning of the natural gas, further lowering the amount of CO₂ produced per calorie of heat energy gained. In this method, the hot gases from a burning methane-oxygen mixture are used to power a jet engine, which is used to generate electricity. The hot gas exhaust from the jet engine is then passed through a heat exchanger to produce steam that drives a steam turbine. In this process, 60% of the energy from natural gas can be extracted as electrical energy, in comparison with a maximum of around 50% to an average of around 33% efficiency for the average coal fired plants. Natural gas fired electrical generators respond more quickly to demand than coal fired generators. Thus, natural gas is an ideal fuel for supplementing much more variable and less reliable solar and wind electrical generation capability. Even higher efficiencies can be obtained if methane is used in a fuel cell (Chapter 11). However, all of the above advantages depend on an appropriate regulatory environment because of some problems with the extraction, storage, and transport of natural gas.



Cutaway of steam electrical turbine

Counterbalancing some of the advantages of natural gas, methane is a far more powerful greenhouse gas than carbon dioxide. Thus, should there be even small leaks in natural gas pipelines, the environmental advantages of methane could be significantly reduced. One way to utilize the heat released from the burning of methane is to heat water to make steam and then use the steam to turn a turbine to generate electricity.

At this time, it appears that shale drilling will be the primary source of natural gas in the future. The main risks associated with shale gas drilling are fivefold:

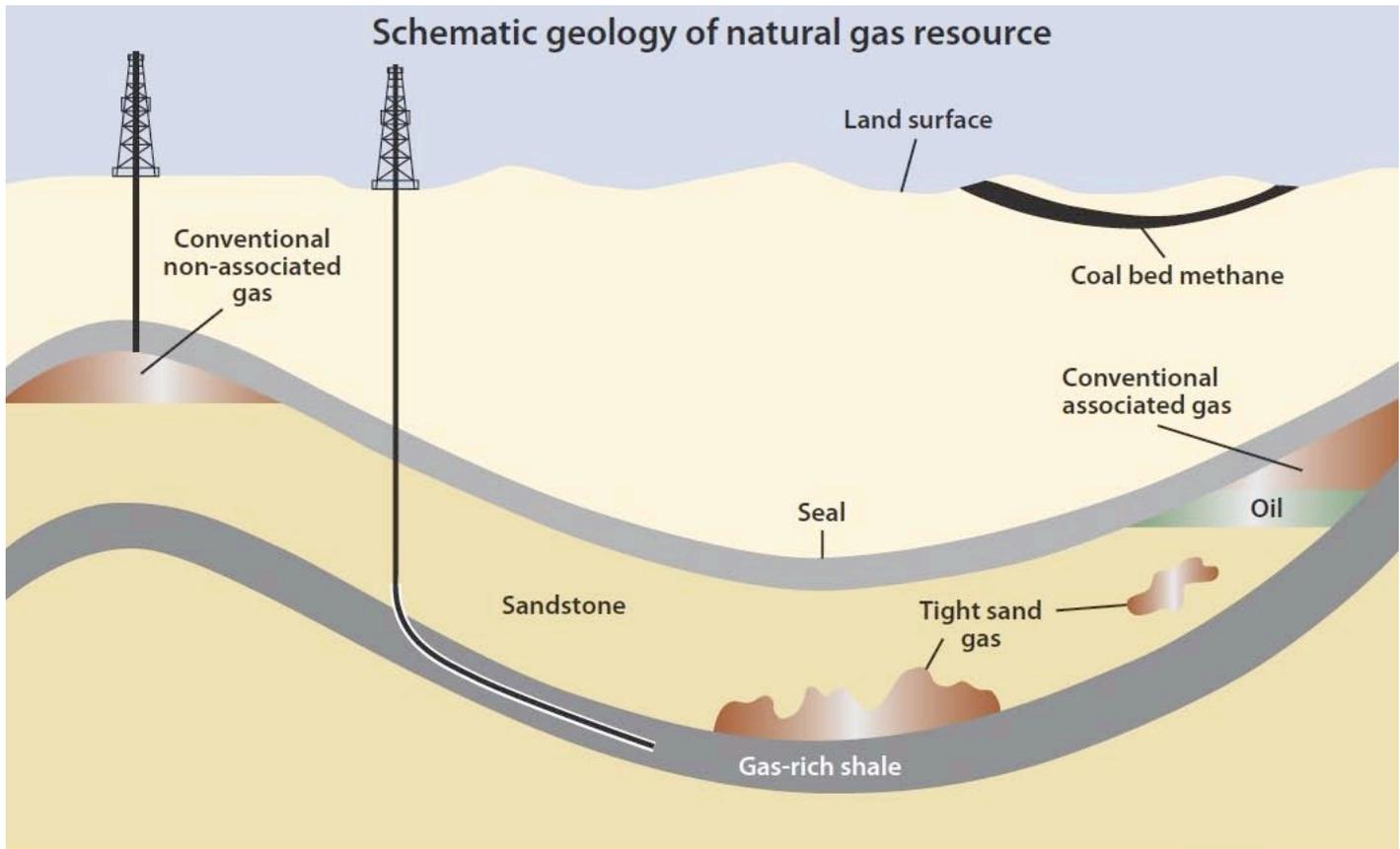
1. Contamination of groundwater aquifers with drilling and fracking fluids or natural gas while drilling and during well construction and fracking.
2. On-site surface spills of drilling fluids, hydraulic fracking fluids, and wastewater that is recovered from the fractured rock region.
3. Contamination as a result of inappropriate off-site wastewater disposal.
4. Excessive water withdrawals for use in high-volume fracturing.
5. Excessive road traffic and impact on air quality.

There have been a number of accidental spills and numerous anecdotal reports of unusual illnesses in individuals living near drilling pads. These illnesses have been attributed to accidental spills and poor quality workmanship at the drill sites. Industrial representatives claim that there have been no proven instances of water contamination from the fracking operation when carried out according to generally accepted safety standards. While the “Halliburton” loophole exempts some aspects of fracking operations from the Federal Safe Drinking Water Act, fracking is still supposed to be regulated by state agencies. Claims have been made that in many rural areas, there is poor state and local oversight of shale fracking operations leading to some notable, well publicized, engineering problem-caused well drilling accidents.

Composition, occurrence, and extraction of natural gas

Natural gas composition depends upon its source. In all oil well samples of natural gas, methane (CH_4) is the principal component. Smaller amounts of ethane (CH_3CH_3), propane ($\text{CH}_3\text{CH}_2\text{CH}_3$), butane ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$), carbon dioxide, nitrogen, hydrogen sulfide (H_2S) and noble gases are found in natural gas. Propane and butane are separated and sold as bottled LPG (liquefied petroleum gas). Noble gases such as helium are separated and used to prepare ultra low temperature liquid helium and for non-scientific purposes such as in buoyant balloons. H_2S is removed to prevent the formation of SO_2 during combustion.

There are two general types of natural gas sources illustrated in Fig. 9-6. The first type is where the gas is found in relatively large pockets, one above oil pools (labeled as “Conventional associated gas”) and the other where the gas containing rock is very porous, and the natural gas flows out of the origin rock readily but migrates up and is trapped in a geological formation (labeled as “Conventional non-associated gas”). The second type is where is gas is trapped within poorly permeable or impermeable rock much deeper than conventional natural gas. Although more difficult to extract, there is much more non-conventional natural gas stored deeper than the shallow conventional gas. However, the technology required to extract this deep trapped gas is more complex and expensive than used for conventional gas.



Source: U.S. Energy Information Administration

Fig. 9-6 Various sources of natural gas

Conventional type gas is usually under higher than atmospheric pressure and flows out of the well readily as soon as the drill bit breaks through to the trapped gas. After treatment for minor contaminants, the gas is ready for storage or transport through a complex pipeline network. Non-conventional gas sources require special treatment to be able to release and extract the trapped natural gas. Of this second type of non-conventional gas there are three subcategories designated in Figure 9-6 as “Coal bed methane,” “Tight sand gas,” and “Gas-rich shale.”

Coal bed methane and water are adsorbed to coal particles in coal seams. After drilling a well into a coal seam, water is pumped out of the coal bed. Further pumping desorbs natural gas that is adsorbed to the coal fragments, allowing the adsorbed natural gas to be pumped up the well for treatment. This same methane is one of the prime safety hazards of coal mining because of its explosive properties when mixed with air. Many miners have lost their lives because of natural gas explosions because of improper ventilation of the mines in which they were working.

Tight sand gas is trapped underground at some depth in impermeable hard rock or in non-porous sandstone or limestone formations. Techniques such as fracturing or acid treatment are needed to release the natural gas from these deposits. Strong acids such as HCl dissolve the rock, releasing the gas.

Gas-rich shale deposits are ancient sea beds, containing large amounts of organic matter that can be over a mile deep, crushed at high pressure and temperature underneath many other layers of impermeable rock. The pores in these rocks are not well connected. Thus the methane is trapped within the rock. These deposits can be quite extensive, but are relatively thin in comparison with their sea-bottom breadth. For example, the Marcellus shales cover around half the area of the state of Pennsylvania. It is only in the early 21st century that, in addition to the conventional vertical drilling, there has been the technology developed to “turn the corner” and accomplish horizontal drilling at great depths. Much of this technology was developed for drilling in the Gulf of Mexico and was widely publicized in the 2010 Gulf oil spill.

The same hydraulic fracking procedure is employed in the shale drilling, except that the well is drilled from 3,000 to 8,000 feet deep through many solid rock layers and then turned at a steep angle to drill into and through the mostly horizontal ~100 foot thick gas-rich shale deposit, sometimes drilling horizontally as much as an additional mile. Metal casings are sealed in cement to prevent drilling and fracking fluids from entering shallow aquifers or anywhere else along the long drilling path. This process is critical to preventing contamination of wells near the drilling site. Before fracking, these sealed pipes within pipes are tested for leaks at high pressures. Up to 12 horizontal bores can be drilled from a single vertical well. Ten bores, each with five 1,000-foot fracking segments, would require 50 million gallons of water and 250,000 gallons of chemicals. Explosive charges shoot holes in the fracking segments and create primary cracks in the surrounding shale.

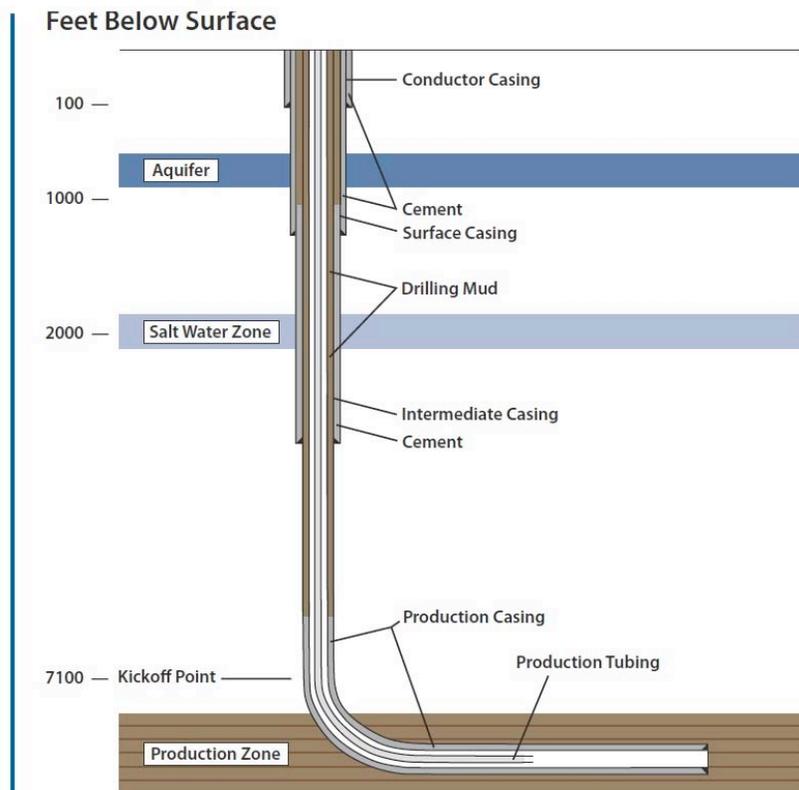
Shale gas, which now accounts for 50% of all extracted natural gas, is extracted with the aid of hydraulic fracturing. **Hydraulic fracturing (fracking)** is a process in which a water-based liquid is pumped into the preliminarily punctured rock along the fracking segments. Although water and fine sand make up 99.5% of this fracking fluid, added chemicals are critical to the success of the fracking. Hydraulic pressure is applied to the fracking fluid at a rate and pressure so high that it causes extensive fracturing of the layered rock. Sand suspended in the fracking liquid keeps the fractured shale rock layers separated and exposed. This provides a very large surface area which allows the natural gas to escape after the fracking liquid is allowed to move back up and out of the well pipe. Because of the high pressures involved, there can be blowouts in which this fracking liquid can cause large spills that ultimately contaminate streams, groundwater, and wells near the drilling site. Following drilling and fracking, the well is capped and the fracking equipment and associated trucks with all of the drilling equipment is moved out. The natural gas is then allowed to flow out into storage tanks or pipelines. The flow rate of the gas falls off continuously and the well can be productive for a number of years.

With over 20,000 shale wells drilled over the last 10 years, the environmental record, for the most part, has been a good one. However, it is important to recognize the inherent risks and the damage that can be caused by just one poor operation. In studies of accidents with shale drilling, almost half have been related to contamination of shallow water zone primarily with natural gas. Another third of reported incidents pertain to on-site surface spills. In the studies surveyed by a recent Massachusetts Institute of Technology report, no incidents are reported which conclusively demonstrate contamination of shallow water sources with fracking fluids.

Because of the recent extensive use of fracking, it is worth examining the composition and chemistry of the fracking fluids.

Click button for further details. [C-9-17](#)

Figure 2.18 Typical Shale Well Construction (Not to Scale)



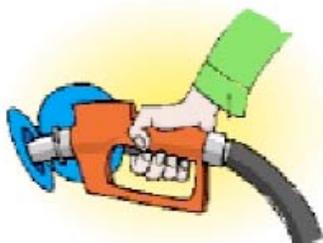
Source: Based on Modern Shale Gas Development in the United States – a Primer

Methane hydrates

Another potentially very large source of methane can be found at the bottom of many seas around the world. Methane hydrates are compounds formed between methane and water at high undersea pressures in which the methane molecules are trapped in water cages. Originally discovered in Arctic waters, they have since been found elsewhere in the world in varying forms. Preliminary estimates claim that there is more energy stored in methane hydrates than in all of the other extant fossil fuel reserves put together. Methane hydrates are found in marine sand reservoirs, non-sand marine reservoirs, massive seafloor/shallow hydrates at seeps and marine shales. Estimates are that methane hydrates are unlikely to reach commercial viability for global markets for at least 15 to 20 years. Depressurization of the hydrate formation should yield a relatively sustainable and well-controlled flow of methane gas.

Petroleum

Current imports of petroleum by the top economic powers of the world indicate their great desire for this liquid fossil fuel. So much in demand is this commodity that, for example, the United States imports about two thirds of its crude oil from other countries. Oil is a blend of products obtainable from one relatively cheap, easily transportable source, crude oil. The fact that the major source of this oil is the Middle East, with its fragile political structure, is of great concern. In part, because of this major import, the US has become a major debtor nation.



Petroleum

As discussed earlier, petroleum and natural gas are formed from organic matter residues trapped in buried sediments. Bacteria acting to decompose the organic matter removed nitrogen and oxygen atoms, enhancing the carbon and hydrogen content. As new layers of sediment accumulated, high pressures and temperatures caused the conversion of the remaining carbon-containing material into **hydrocarbons** (compounds containing primarily carbon and hydrogen) as diverse as methane and asphalt. Eventually these layered sediments solidified into rock, mainly fine grained shales and, after being buried under many other different layers of rock, were subject to high temperature and pressure, causing the formation of hydrocarbons which accumulated in porous rock formations, generally sandstone or limestone.

This reservoir rock also contained salt water from the former seas. Research has demonstrated that water under high temperatures and pressures has characteristics that are markedly different from those at normal pressure and room temperature. These altered solvent properties are now thought to play an important role in the formation of petroleum and coal and are under investigation for their usefulness in the mining and refinement of both oil and coal. A new chemical research field has opened the study the interactions of high pressure hot water with organic compounds whose structures are related to those found in coal and oil.

Of all the petroleum that has ever existed, according to geologists, most has come to the surface of the Earth and been destroyed in the atmosphere throughout the history of the Earth. The reservoirs that remain are rare occurrences in the history of petroleum development. Reservoirs are often located at geological faults where there has been a vertical thrust in the Earth's crust. In addition, there are natural domes that are formed that house reservoirs. The key to reservoir formation is the impermeability of the cap rock. Keep in mind, however, that these fossil fuels are contained in rock. The reservoir is not an empty pocket in the Earth containing crude oil, as many diagrams seem to imply!

How much oil and gas is there? How long will it last?

The answer to both of these questions is, we don't really know. Estimates for both of these quantities have been continually changing, especially during the past several decades with the development of new oil and gas extraction technology. Estimated oil and gas reserves have been increasing significantly. All the oil and gas that has been recovered and is believed to be recoverable is between 3 and 5 trillion barrels of oil equivalent (6,000 cu ft gas = 1 barrel = 42 U.S. gallons). Seven hundred billion barrels have been produced and consumed. There are 600 known or mapped sedimentary basins. Of these, 160 are known to be productive or capable of producing oil and gas. Six of these basins have accounted for two thirds of all oil and gas ever found. The Persian Gulf region alone has an estimated 40% of the world oil reserves.

*Long term
supplies
of fossil
fuels*

As indicated in our discussions of natural gas, oil and gas occur together. While the largest known oil deposits in the world are in the Middle East, vast quantities are also found in Russia and Mexico. The US deposits, estimated as 1.1 trillion barrels, while significant, are not as extensive as those from abroad, estimated as 7-8 trillion barrels. The largest in the US are in Prudhoe Bay under Alaska's North Slope. These have produced one fifth of US domestic petroleum. There is much debate over the amount of oil contained in the Alaskan Arctic National Wildlife Refuge. The US has 5 percent of the world's population, but consumes nearly 25 percent of world oil supplies. Recent explorations of very deep regions (30,000 feet) of the Gulf of Mexico and other locations under water, salt, and shale have shown possible large oil deposits. Estimates are of some 30 different areas that have potential for development and test drills have promising yields. As the cost of imported oil escalates above \$100 per barrel, the high cost of recovery of this deep Gulf of Mexico oil allows for profitable drilling of domestic oil.

“Peak oil” is defined as the point at which oil production from new wells or other petroleum sources equals the falloff of production from existing depleted wells and other sources. Some experts say we have reached this peak, whereas others are estimating that it is at least several decades ahead. All of these estimates have a wide range of uncertainties, primarily because of: (a) the uncertainties in the future price of oil;

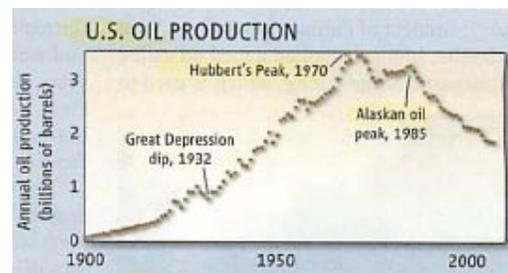


Fig. 9-8 Graph illustrating the concept of “peak oil” production.

(b) the current production status of existing oil fields; (c) the capacity of potential new oil fields; (d) the capacity of current and new (unlikely) refineries; (e) responses to climate change initiatives. There seems to be unanimity on the finite extent of the world's oil reserves and that we must find substitute energy sources soon. The shape of the oil production curve in Fig. 9-8 has been studied as a means of predicting the total amount of oil available.

How is the oil and gas recovered ?

By drilling into the ground, sometimes straight down, but more recently by drilling vertically next to the reservoir and then curving the drill shaft and drilling horizontally into the oil-containing area, this allows the driller to selectively remove only oil, rather than having to first deal with the natural gas and then oil that normally come in succession from the completely vertical drilling method. When wells "run dry," the primary phase of recovery is over. At this point, only about 15% of the well's total fossil fuel has been extracted. It is more difficult and expensive to recover the remainder of the well's petroleum.



In order to recover a greater fraction of a reservoir's oil, *secondary recovery* methods are employed. These are methods in which displacement fluids are injected at points around the original drill site to force the oil into and up the drill shaft. These replacement fluids can be water or ocean water (as in Prudhoe Bay), carbon dioxide bearing water, propane or ethane from natural gas, and steam. Only about 20-40% of the total amount of oil in a reservoir is recovered by primary and secondary methods.

Tertiary treatment methods of oil recovery involve using water containing chemical additives. The chemicals are various types of polymer solutions designed to thicken water, which then is able to more effectively sweep the crude oil out of the porous oil-containing rocks. Chemists have synthesized surfactants, which are specially designed detergents, to add to these polymer solutions in tertiary oil recovery. By lowering the surface tension between the water and the oil, these surfactants are able to remove stubborn oil from small pockets in the rock. "Fire-flooding" is a method where some of the oil is set on fire and the heat and gases from the burning increases the pressure and lowers the oil viscosity, allowing the oil to move through rock more easily.

*Drilling
for oil
and
natural
gas*

New techniques using natural bacterial decomposition of oil in subsurface petroleum reservoirs that release clean burning methane have been proposed. Petroleum serves as a food source for certain bacteria under anaerobic conditions, with methane produced as a byproduct. Thus, if conditions can be enhanced for this otherwise slow petroleum degradation, methane may be able to be captured from oil deposits that are difficult to mine by conventional methods or are considered uneconomic candidates for the various treatments described above. Some injected bacteria together with nutrients grow on the mineral surface, releasing the oil from the

surface and allowing it to be extracted. Experiments are possible with genetically altered bacteria designed to further aid in the release of oil from rock pores.

Land-based sources of oil other than drilling

Oil or tar sands and oil shale deposits contain a large amount of the world's oil reserve. One of the largest **tar sand** deposits, covering an area as large as England, is found in northern Alberta, Canada. An estimated 1.7 trillion barrels of “heavy oil” (high molecular weight hydrocarbons) is contained in these sands.

The terrain is largely covered by a peat bog and boreal forests and the temperatures in the region vary from -46°C to 32°C . The sands are first encountered at 60 meters depth. The surface of the sand grains are jacketed by bitumen, a highly viscous form of petroleum having the consistency and chemical characteristics of tar. The consistency of this unusual oil reservoir can be described as taking thick axle grease and mixing it with sand. Steam generated usually with natural gas is used to heat and thin the thick coating material. Following the heating, the liquid **bitumen** (the resulting material containing carbon and hydrogen) is pumped to the surface. Large amounts of energy must be expended to extract this oil. In order to be able to extract this hydrocarbon product, the sands must either be heated with steam, or



diluted with light hydrocarbon solvents. The product must be refined to reduce its molecular weight. Strip mining techniques are used with removal of the top layers of earth, scooping out the sands, transporting them to be treated, returning the treated sands. Finally, responding to Canadian law to restore back to “nature,” attempts to recreate natural surroundings. Many are skeptical how successful this restoration will be.

Concerns have been expressed about the overall efficiency and carbon footprint of such operations, in addition to the disposal of the waste and the amount of water needed for the operation of this process. Two tons of oil sand need to be treated to extract one barrel of crude oil product. The extraction and refinement process produces from two to four times the amount of greenhouse gas per barrel as conventional oil. For this reason, there is resistance to building long pipelines crossing the continental U. S. from northern Canada to Texas delivering the crude Canadian tar sand product for refinement. Vast lakes contaminated with bitumen from the tailings from tar sand processing exist in Canada. Attempts are being made to reclaim these lakes, but low level contamination of very large water volumes is posing a major challenge.

Oil shale is contained in sedimentary rock in the form of a precursor of oil called **kerogen**. Deposits of oil shale are found in Colorado, Utah and Wyoming and are thought to contain the equivalent of over one hundred billion barrels of oil. However, because the oil must be extracted by heating the crushed stone to 500°C (930°F), recovery of oil by this process is slow, expensive and environmentally a problem because of the waste crushed shale. It takes about 1.5 tons of shale to extract one barrel of oil. The energy content of shale oil per ton is lower than any other substance used for commercial fuel. Large amounts of water are also needed in the mining process in an area that is already short of water.

Molecules that are found in petroleum

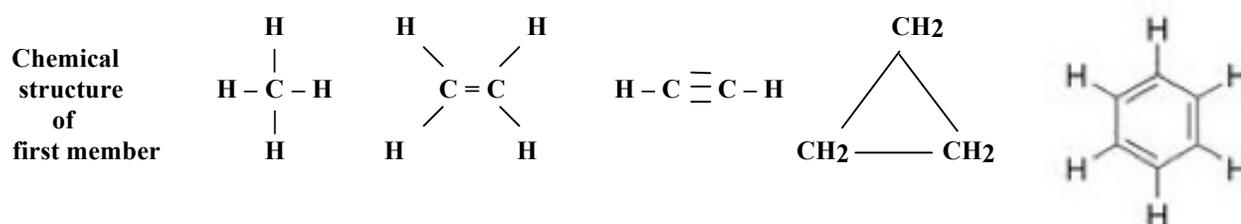
The composition of crude oil, which contains literally many hundreds of compounds, varies with its source. Oil from ocean oil spills can be tracked to a particular tanker because the petroleum composition is generally unique for each tanker load. Petroleum is a very complex mixture of **hydrocarbons** (molecules containing hydrogen and carbon atoms). Petroleum from the ground usually consists of large quantities of dissolved methane and other gaseous and liquid hydrocarbons such as those illustrated in Table 9-1. These molecules are commonly **straight chain hydrocarbons**, or **alkanes**. The 3-dimensional structure of these molecules can be understood on the basis of connected, tetrahedral carbon atom. Alkanes are usually depicted in illustrations as being straight, but can take up configurations that are twisted and contorted and far from straight because of the flexibility of the carbon-carbon single bond. In addition to alkanes, there is a class of cyclic hydrocarbons contained in petroleum (Table 9-2). These consist of rings of carbon atoms attached to each other, with several hydrogen atoms attached to each carbon atom.

Table 9-1 Types of hydrocarbon compounds found in petroleum

Name	Formula	Boiling Point °C	Structural Formula	Use
Methane	CH ₄	-162	$\begin{array}{c} \text{H} \\ \\ \text{H} - \text{C} - \text{H} \end{array}$	Natural gas
Ethane	C ₂ H ₆	-89	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H} - \text{C} - \text{C} - \text{H} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	Minor component of natural gas
Propane component	C ₃ H ₈	-42	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \\ \text{H} - \text{C} - \text{C} - \text{C} - \text{H} \\ \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$	Bottled gas
n-Butane	C ₄ H ₁₀	0	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \\ \text{H} - \text{C} - \text{C} - \text{C} - \text{C} - \text{H} \\ \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	Bottled gas
n-Pentane	C ₅ H ₁₂	36	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \quad \\ \text{H} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{H} \\ \quad \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	Used in gasoline
n-Hexane	C ₆ H ₁₄	69	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \quad \quad \\ \text{H} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{H} \\ \quad \quad \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	Used in gasoline
n-Heptane	C ₇ H ₁₆	98	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \quad \quad \quad \quad \quad \quad \\ \text{H} - \text{C} - \text{H} \\ \quad \quad \quad \quad \quad \quad \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$	
n-Octane	C ₈ H ₁₈	126	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \quad \quad \quad \quad \quad \quad \\ \text{H} - \text{C} - \text{H} \\ \quad \quad \quad \quad \quad \quad \quad \\ \text{H} \quad \text{H} \end{array}$	
n-Nonane	C ₉ H ₂₀	151	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \quad \quad \quad \quad \quad \quad \quad \\ \text{H} - \text{C} - \text{H} \\ \quad \quad \quad \quad \quad \quad \quad \quad \\ \text{H} \quad \text{H} \end{array}$	
n-Decane	C ₁₀ H ₂₂	174	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \quad \quad \quad \quad \quad \quad \quad \quad \\ \text{H} - \text{C} - \text{H} \\ \quad \quad \quad \quad \quad \quad \quad \quad \quad \\ \text{H} \quad \text{H} \end{array}$	

Table 9-2 Types of hydrocarbon compounds found in petroleum

	Alkane	Alkene	Alkyne	Cycloalkane	Aromatic
Common family name	Paraffins	Olefins	Acetylenes	–	–
General formula	C_nH_{2n+2}	C_nH_{2n}	C_nH_{2n-2}	C_nH_{2n}	–
First member	Methane	Ethylene	Acetylene	Cyclopropane	Benzene
Formula	CH ₄	C ₂ H ₄	C ₂ H ₂	C ₃ H ₆	C ₆ H ₆



Gasoline from petroleum

Gasoline consists of compounds having 6-12 carbon atoms mixed with a number of additives designed to enhance combustion efficiency and engine performance.

Gasoline contains only a small subset of the complex mixture of compounds found in liquid crude oil. To create gasoline, chemists must first separate the lower molecular weight compounds they desire and, in some cases modify their chemical structure, create the additives, and blend the gasoline.

Petroleum refining

The many different compounds of liquid crude oil have a wide range of molecular masses and boiling points. **Distillation**, a technique used by chemists for separating such liquids into different boiling point ranges, is a process in which the components of a liquid mixture are removed at different times after condensing the exiting vapors from a tall column in which the boiling liquid components have many chances within the column to condense from the vapor state back to the liquid state and be heated back into the vapor state. A commercial equivalent of this distillation column is a multiple story steel column (Fig. 9-9). Thus, a separation by distillation into classes of compounds with different boiling point ranges gives rise to gasoline, kerosene, heating oil, lubricating oil, etc. in order of increasing boiling points. In dealing with the many volatile compounds contained in petroleum, it is inevitable that there are losses during the refining process. An estimated 5% of the volatile compounds in petroleum refining are lost to the atmosphere. However, to put these losses in perspective, losses from motor vehicles to the atmosphere are far greater than those from the refining process.

Each of the above classes of compounds is further **refined** to enhance its commercial value. The petroleum constituents most in demand are the lower molecular weight gasoline fractions. Over 500 million road vehicles consume half of the world's oil supply. Much of a modern refinery is devoted to lowering the average molecular mass and altering chemical properties of higher molecular weight compounds to make motor gasoline, jet fuel, and heating and lubricating oils. The keys to most of these processes are the use of solid **catalysts**, special chemical compounds used to enhance or make possible (**catalyze**) desired chemical transformations. Solid catalysts are present in these processes as fine powders that behave much like fluids when gases are forced through them.

Because some of the high molecular weight fractions that are subject to cracking are in the heating oil range, there is sometimes an imbalance between supply and demand. If the winter is severe, heating oil is in great demand and there is a shortage of supplies of gasoline, industries have to do a balancing act to satisfy both customers, if possible. In addition to cat cracking, there is another refining technique called **alkylation** in which small three and four carbon atom compounds are fused, again with the aid of a catalyst, into a higher molecular weight compound that is useful as a gasoline additive.

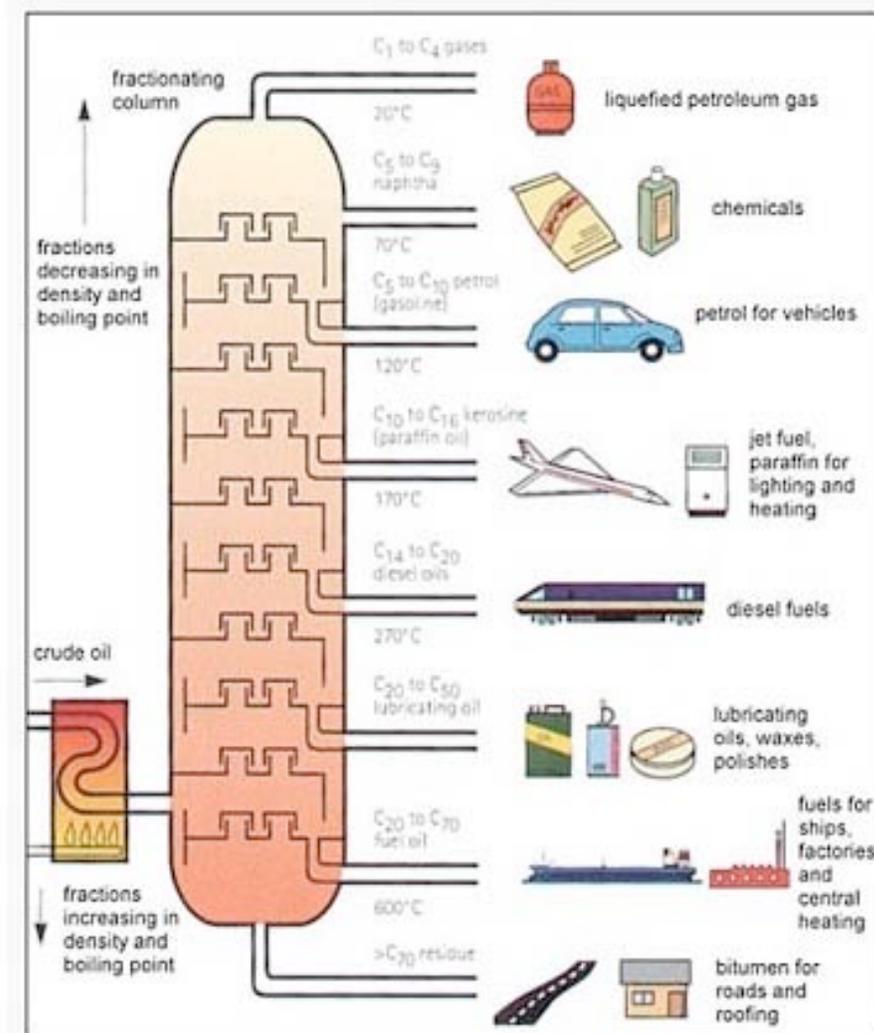


Fig. 9-9 Distillation column used in the separation of different components of crude oil.

Engine knock and octane rating

Without additives, gasoline spontaneously ignites in the engine by the spark plug before it is supposed to and causes a ping or **engine knock**. In order to prevent this, one or more compounds must be added to the straight gasoline fraction of mainly seven- and eight-carbon hydrocarbons from the refinery. Tetraethyllead $[Pb(C_2H_5)_4]$ used to be a significant gasoline antiknock additive in the United States, but was phased out when concern was expressed regarding the possibility of lead poisoning,

Octane ratings

especially in children. Other compounds have been substituted as antiknock agents. Let's take a look at the structures of some of the lighter components of petroleum in the gasoline fraction and see the structural difference between the additives and the straight petroleum product.

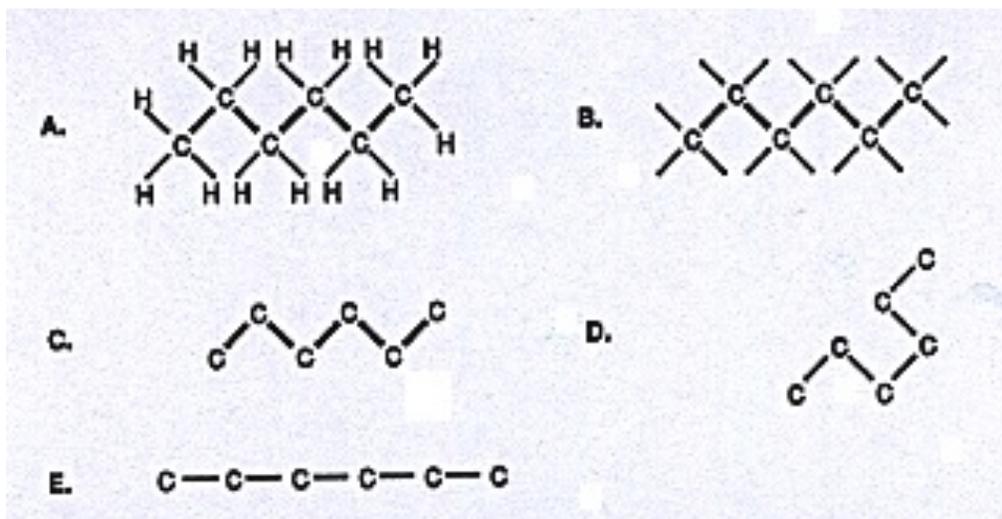
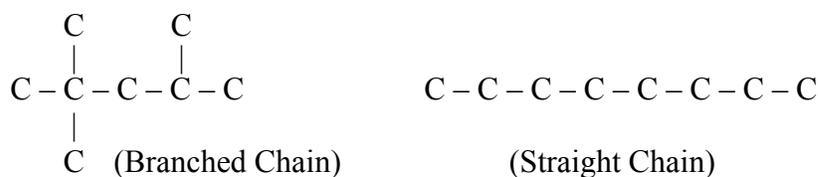


Figure 9-10 Five different representations of C_6H_{14} : (A) containing all atoms; (B) containing only carbon atoms and all bonds; (C) containing only carbon atoms and carbon-carbon bonds ("carbon skeleton"); (D) another of the many different conformations of this same molecule; (E) the misleading "straight chain" representation. [Jmole representation will be added below this in the final presentation]

Alkanes, also called saturated **aliphatic hydrocarbons**, have a formula C_nH_{2n+2} , where n is the number of carbon atoms. The lightest of the members of this family are: methane, CH_4 , ethane, CH_3CH_3 , propane $CH_3CH_2CH_3$, and butane $CH_3CH_2CH_2CH_3$. Each successive member of this family merely inserts a CH_2 group into the middle of the carbon chain of the previous member. Although they are called "straight chain" hydrocarbons and are generally written on the page in that manner (Figure 9-5), they are quite flexible molecules and are able to take up many different conformations: the ones illustrated in Figure 9-10 are only some of many for the "linear" hexane (C_6H_{14}) molecule. Note that the "shorthand" way of illustrating the structures in B through D of Figure 9-10 shows only carbon-carbon bonds, not the hydrogen atoms bonded to the carbon atoms.

The **octane rating**, a measure of the anti-knock quality of a gasoline blend, does not indicate how much n-octane ($C_8H_{18} = CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$) is present, but how much "branched" alkane, or its equivalent, is present in the fuel. To understand the concept of a **branched alkane**, we need to focus on a carbon atom "skeleton," which shows only the carbon atoms, and their carbon atom to carbon atom bonding pattern:



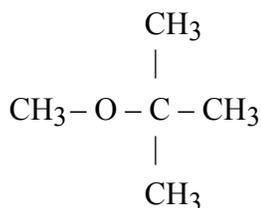
*Branched
alkanes*

Each of the above two compounds has the same number of carbon atoms. In the straight chain alkane on the right, each inner carbon is attached to two other carbon atoms and the two end carbon atoms are attached to only one other carbon atom. There is nothing forbidden about having more than two carbon atoms attached to a single carbon atom via covalent bonds. In the example above, the branched chain octane molecule on the left (also containing eight carbon atoms) has one carbon atom that is attached to four other carbon atoms and another carbon atom that is attached to three other carbon atoms. The branched compound on the left, isooctane (2,2,4 trimethylpentane, the numbers indicating the number of the carbon to which the methyl groups are attached, numbering carbon atoms from the left in the straight chain), is the standard for the octane rating scale, with an arbitrary value of 100 to represent their anti-knock effectiveness. In general, branched chain compounds have higher octane ratings than straight chain compounds.

In the above figure, we see there are at least two different ways (there are others) in which the carbon chain can be arranged in eight-carbon compounds with the formula C_8H_{18} . These two compounds, *which contain exactly the same number of carbon and hydrogen atoms* and has the same molecular mass, are, nevertheless different compounds and are called **isomers**. Isomers have different melting and boiling points, as well as other differing physical and chemical properties. For example, for a given number of carbon atoms, the larger the degree of branching, the lower is the boiling point. Most important, the two compounds have different ignition temperatures in an automobile engine cylinder. The straight chain compound is prone to igniting before the spark plug fires, thereby causing knocking. The branched chain compound ignites during the firing of the spark plug and causes smooth, efficient operation of the engine.

Isomers

Additives to gasoline other than branched hydrocarbons are used as anti-knock agents. Among these are derivatives of benzene such as toluene and xylene, benzene rings with one and two methyl groups (CH_3-) substituting for one and two hydrogen atoms, respectively, in benzene. Oxygen-containing compounds are also added to gasoline. The two simplest alcohols, methanol (CH_3H) and ethanol ($\text{C}_2\text{H}_5\text{OH}$), have been used as gasoline additives and MTBE, methyl tertiary butyl ether,



is a gasoline additive that boosts antiknock rating and supplies additional oxygen atoms to more fully oxidize the hydrocarbons in gasoline and to reduce carbon monoxide emissions. An ether is a compound with the general formula ROR', where R and R' are alkyl groups, derivatives of alkanes with one hydrogen missing.

There are few branched hydrocarbons found in nature, so part of the mission of the gasoline refiners (besides separating the various fractions of petroleum into gasoline, kerosene, heating oil, etc.) is to convert or **reform** the straight chain compounds into branched chain and cyclic hydrocarbons (ring compounds with no end methyl groups) such as cyclohexane (C₆H₁₂).

This process is accomplished with catalysts made of metals and is technically very complex and somewhat expensive. Gasoline is a very complicated mixture of as many as nearly a hundred different compounds, some of which are in trace quantities. Additives and blends of different hydrocarbons help to make the gasoline meet a particular need in a particular location during a certain set of climate conditions.

While 90 percent of a barrel of crude oil goes into making gasoline, diesel fuel, heating oil, and jet fuel, a number of other specialty products are also made from crude oil: lubricating oils, paraffins, petrolatum, specialty lubricants, transmission and brake fluids, drilling oils, cosmetics, baby oil, lotions, hydraulic oils, and transformer oil.

Deep water drilling



April, May and June, 2010. When will they be able to cap the well in the Gulf of Mexico? The long wait, with television coverage of the massive amounts of crude oil and natural gas gushing for months from the out-of-control BP well head, introduced the world to the risks associated with deep water drilling for fossil fuels. This event has been described by a White House adviser as “the worst environmental disaster the US has faced.”

The **Deepwater Horizon** mobile offshore drilling unit was designed to operate in waters up to 8,000 feet deep and drill down to 30,000 feet. The drilling rig, owned by

Transocean, was leased to BP Oil. Production casing was being installed and cemented by Halliburton Energy Services for an exploratory well, when, on April 20th, methane gas shot





up through the drill column, exploded, and caught fire on the platform of the Deepwater Horizon, killing 11 workers. A blowout preventer failed to stem the outflow of crude oil and gas, and many attempts to cap the well failed until finally, on July 15, 2010 when it was finally capped. It is estimated that 4.9 million barrels of oil escaped the well in the largest oil spill in U.S.-controlled waters.

About a million gallons of chemical dispersants were applied at the well head in an effort to disperse the oil into tiny droplets with a much larger surface area and make it more easily digested naturally by resident bacteria. Because there are many natural seeps of oil from the Gulf seafloor, there are relatively large populations of oil-digesting bacteria in the sea water. However, the toxicity of these dispersants has been questioned, with some claims that there was more damage to marine life from the dispersants than from the oil. Dispersants were also applied to surface oil slicks. While tar balls littered Gulf beaches, visible oil slicks did not last for an excessive period, but large amounts of oil remained for long periods on the bottom of the sea because of the effects of the dispersant, presumably.

Short term effects on marine and bird life were evident and numerous, with many thousands of deaths of shorebirds and other marine wildlife. Long term effects are being studied. It is too early to summarize what the overall biological effects will be but they will undoubtedly be quite significant and possibly even cause major changes in the ecology of wide areas of the Gulf of Mexico. The full economic and psychological effects are yet unknown, but are and will be undoubtedly massive. The economic losses to the fisheries and tourism industries are still mounting.



Despite this, undersea oil explorations continue not only in the Gulf of Mexico, but around the world, because of the anticipated demand for oil especially from emerging economies of China, India, and other developing nations. For example, the Brazilian oil firm Petrobras, is currently exploring an area offshore from Sao Paulo, Brazil, where the oil is contained under a deeply buried layer of prehistoric rock salt. This “pre-salt” oil deposit is thought comparable in volume to that under Saudi Arabia and Kuwait spread below an expanse of the Atlantic Ocean half the size of Italy. The only problem is that this deposit is over four miles below the ocean surface and much further from shore than the Deepwater Horizon rig. The pressure at these depths is 200 times that at the ocean surface and such that the thick salt cap over the oil behaves more like taffy when drilling through it. Even though challenging, risky, and exceedingly expensive, this drilling operation is driven by the huge oil potential below the salt.

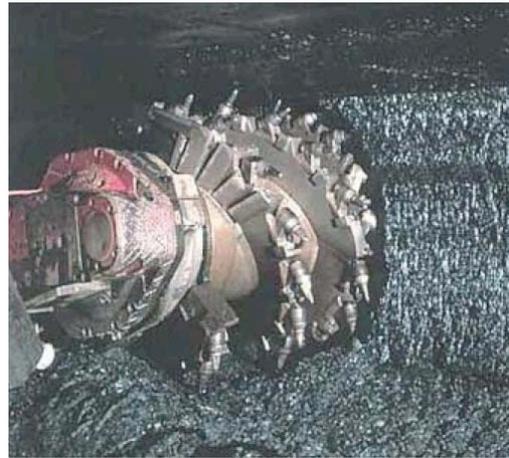
All of these deep drilling projects are not only expensive and pose large potential safety risks, they are economically risky. This is because they depend on the

price of oil, which fluctuates wildly in an uncertain economic climate. Often they are abandoned temporarily as the price of oil drops and resumed when it increases to an acceptable level. When the price of renting an oil rig can be as much as a million dollars a day, there can be a cash flow problem if the rig is not producing any oil or encounters a technical problem that shuts down or delays oil production.

Coal

Coal is the fuel used to generate about 40% of the world's electricity. The US has far more coal than petroleum. An estimated 270 billion tons of coal constitute about 85% of the US fossil fuel reserves, although this is decreasing with the increased natural gas accessibility and reserves. These reserves are predicted to last well into the 21st century, perhaps beyond. Nearly half of the US electrical generating capacity is fueled by coal. However, coal provides only about 20% of the total energy "consumed" (really converted to another form) in the US economy. This is because of the many economic and environmental problems with the burning of coal, for example, due to the problem of the production of acid rain, hazardous particulates, and carbon dioxide. It is especially important that these problems be solved because developing countries will be utilizing increasing quantities of coal to supply their energy needs. Technology developed by the more advanced countries will be made available to the developing countries to help keep down the otherwise inevitable pollution. Western Europe's problems with acid rain were discovered to be at least partly due to air pollution in Eastern Europe. Acid rain, particulate, and carbon dioxide pollution are no respecters of national borders.

Coal



Cutting machine for faster coal mining

In addition to the pollution problems associated with coal are the effects of mining process on the miners and on the land itself. Coal deposits occur in a variety of geologic formations. Some are located deep in the ground and require elaborate tunnels with air exhaust systems, and all the dangers associated with deep underground mining. Coal dust and associated environmental conditions in the mines are noted for causing lung disease in miners. Most of the mined coal deposits located near the surface of the Earth are "strip mined." That is, the earth overlayer is removed and the coal is mined in the open by very large power shovels. Problems are encountered when mining is completed in returning the layers of earth to their original condition and disposing of the waste rock generated by the mining process. Often the waste from such mining practices as mountain top removal is merely stored in the nearby valleys, where it causes stream pollution and disturbing waste storage dams that can break.

The origin of coal

According to current theories, some 50 to 300 million years ago, the remains of a variety of plants accumulated in swamps and inland seas, and were buried in such a manner that the organic matter didn't decay, that is, it was not oxidized by the atmosphere. Subsequent aerobic and anaerobic digestion by microorganisms removed protein from



the plant material and converted the plant cellulose to carbon dioxide and water, leaving a lignite residue similar to that present in humus (Chapter 8). Many fused aromatic rings are contained in this complex substance. Then slow changes in the waterlogged swamps led to the formation of a dark brown or black residue produced by the decomposition of marsh plants called **peat**. The remains of the microorganisms and organic polymers were then buried under deep layers of sediment and subjected to very high temperatures and pressures. In this process, more carbon dioxide and water were lost. The remaining material contained primarily carbon with small quantities of hydrogen, oxygen, nitrogen, iron, and sulfur. **Lignite** is the youngest form of coal. After millions of years of heat and pressure, lignite was gradually transformed into a number of different forms of “**soft**” or **bituminous coal**. Further geological changes, such as uplifting and mountain formation, increased pressure and temperature, causing the formation of **anthracite (“hard”) coal**. With each of these changes in coal structure, there was a loss of hydrogen and oxygen, increasing the percent carbon content of the coal and resulting in harder coal.

The different types of coal are ranked by the number of calories or joules of heat released per gram. The lowest ranked coal is lignite (brown coal), with various types of sub bituminous and bituminous or “soft” coals at intermediate rankings, and anthracite coal ranking highest. The higher the rank, the higher the carbon content, and the lower the moisture and volatile compound content. The higher ranking coals approach, but do not achieve, the structure of graphite (Figure 9-11).

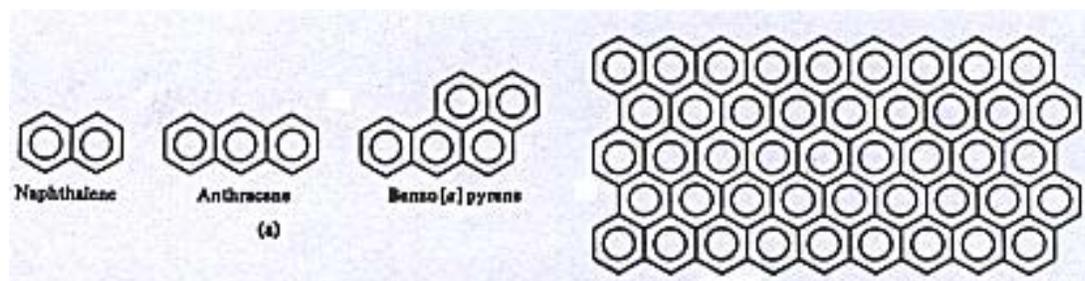


Figure 9-11 Fused ring aromatic molecules, some of which are the decomposition products from partially combusted coal (a); a small section of one part of a sheet of pure graphite (far right); a single layer of an extended form of this structure is called “graphene” and has unusual electrical and other properties.

What is the chemical structure of coal?

Coal has a highly complex structure, with many fused benzene rings characteristic of graphite and a variety of other chemical subunits with hydrogen, oxygen, nitrogen and sulfur atoms. Coal can be thought of as “islands” of fused aromatic rings (which are represented much like chicken wire fence) containing certain groups of atoms held together by saturated carbon atom bridges to the next island. There are a number of oxygen-containing atomic groupings present, e.g., -OH, >C=O and -O-. These groups affect the chemical and physical properties of coal. For example, there is a correlation between the number of OH groups in coal and the caking characteristics of the coal. In low rank coal, most of the sulfur is in straight and branched chain hydrocarbons. As the coal ranking increases, there is more sulfur associated with aromatic molecules. The average number of carbon atoms in the fused ring clusters increases from about 9 in lignite to about 20 in sub-bituminous and bituminous coals. There are on average two to three rings per cluster. The way in which minerals, which are responsible for coal ash, are bound to the organic matter in coal is not understood.

*Chemical
structure
of
coal*

The efficient burning of coal leads to carbon dioxide, if sufficient oxygen is present, as well as oxides of sulfur, but this complete oxidation is difficult to achieve. If coal is heated or burned with an insufficient amount of oxygen, carbon monoxide and many other complex chemical substances such as creosote and coal tars that coat the chimney can be formed. In this case, the full energy content of the coal is not extracted unless the carbon monoxide and other carbon-containing compounds are further oxidized to carbon dioxide in an afterburner. One problem with coal is the disposal requirement for the large amount of ash or mineral content left following combustion.

Two types of sulfur-containing compounds are associated with coal, the organic type and inorganic sulfur, generally iron pyrite (FeS_2). This compound is found in cracks and fissures in coal and is thought to have seeped into the coal after its formation. This inorganic sulfur is relatively easily removed by crushing the coal to a fine powder and putting it in water, where the low density coal floats away and the heavier inorganic pyrite sinks and is separated. The covalently bound sulfur in the complex coal structure is not as easily removed. Low sulfur coal is most desirable, since it contributes less to the production of acid rain.

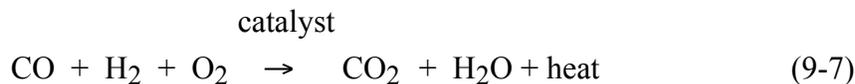
Conversion of coal into more useful fuels

Because the U.S. has abundant reserves of coal in comparison with petroleum reserves, there has been much research on transforming coal into other, more easily utilized, forms of chemical energy. One of these, "liquefaction" of coal, converts coal into liquid hydrocarbons, whereas the other, "gasification," supplies a product that can be transported through pipelines.

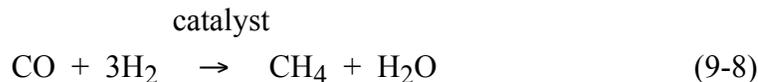
Gasification: Figure 9-5 shows that coal has the lowest hydrogen to carbon atom ratio of all the fossil fuels. The addition of hydrogen adds to its fuel value. When hydrogen-containing fuel reacts with molecular oxygen, the heat of formation of water contributes more energy than the carbon would alone when it was oxidized to carbon dioxide. Thus, attempts are being made to hydrogenate the coal to give hydrocarbons. If one heats coal to 500-800°C the coal is “devolatilized” to give methane (CH₄). The reaction of hot coal with steam gives rise to carbon monoxide and hydrogen.



In this process, some oxygen must be added to burn part of the coke to supply heat for the operation. The carbon monoxide and hydrogen mixture, called “**syngas**,” can be mixed with excess oxygen and burned to give heat, water and carbon dioxide:



However, it is also possible to convert this mixture of carbon monoxide and hydrogen, into methane by adding extra hydrogen:



Following removal of water, this methane can be transported through the normal methane pipeline system, or liquid organic compounds can be synthesized from the syngas. The products of the reaction of syngas depend upon the conditions and catalysts employed.

Research has demonstrated that a wide variety of organic compounds can be created by heating the coal at high temperatures and pressures. There are two different types of treatment; the total gasification process and the mild gasification process. In the former the goal is the maximum conversion of carbon to the gaseous state. In the latter, a more economical process creates a variety of gases and liquids.

Coal liquefaction: There are two general types of liquefaction processes. The first is to treat coal with solvents that can donate hydrogen atoms to the carbon atoms in the coal. The second is to utilize the syngas generated in equation (9-6) to make a number of different useful organic liquids, the goal being to increase the hydrogen content. Coal can be mixed with high-pressure hydrogen in the presence of metal catalysts. The liquids produced are similar to those obtained from petroleum, but have a different composition.

We have seen that natural gas and petroleum can be burned incompletely. The problems are even worse with coal, because it is a solid and it is not as easy to thoroughly mix the fuel with oxygen as it is with a liquid or gaseous fuel. For this reason, coal is often ground into a fine powder, formed into a bed, with air forced

through this powder. This makes the fine coal powder behave almost like a fluid, giving the name “fluidized bed” process. The efficiency of thermal energy production from coal is significantly improved using this process. Fine powdered coal can also be blown into a hot furnace and burned, exposing a maximum surface area to the hot oxygenated surroundings.

All fossil fuels are used as starting materials (called “**chemical feedstocks**”) of the petrochemical industry, which manufactures plastics, detergents, tires, paints, polymers for clothing, and medicines. If there is a future shortage of fossil fuels for utilization as energy sources, there will also be a shortage of raw materials that are the base of a large part of our industrial economy. Some chemists argue that the existing reserves of fossil fuels should be conserved for industrial feedstock and not be irreversibly converted to carbon dioxide and water. They argue that products manufactured from fossil fuels, such as plastic, can be recycled, whereas use for fuels is a one-way chemical reaction.

Carbon dioxide sequestration

Because of the anticipated global warming and climate change caused by the large amounts of CO₂ emitted by coal burning electrical generating plants, there is an urgent need to capture and store the CO₂ away from the atmosphere for long periods of time. At present there are many ideas as to how this might be accomplished, with only experimental tests of these schemes. One of the most promising is the pumping and storage of CO₂ into depleted oil wells. The technology is already in place for pumping CO₂ into these wells to flush out residual oil in tertiary treatment of existing wells. However, there are uncertainties in such techniques. Among them are how fast the CO₂ might leak and contaminate less shallow aquifers, and whether the acidity from large CO₂ concentrations will affect surrounding minerals in the cap that originally trapped the oil and natural gas. There is an urgent need for accelerated research in this area. For a new idea that is linked with carbon sequestration, click the following button: [D-9-34](#)

Health-related costs of fossil fuel production and use

According to a Congressionally-mandated 2009 National Research Council report, health and other non-climate-related damages from fossil-fuel-based energy production have been estimated at \$120 billion in the U.S. each year. These additional costs are primarily from estimated health impacts and ***premature deaths (estimated at 20,000 per year!)*** arising mostly from coal and oil fuel production and use and are not figured into the price of the energy delivered. The study used life-cycle analysis methods and focused on damages caused by SO₂, NO_x, and particulates. Most of the costs were from electricity generation (\$63 billion) and transportation fuel production (\$56 billion). These costs do not include any estimates from climate change



implications, which separately have a wide range estimated cost ranging from \$7 to \$700 billion due to the effects of greenhouse gas emissions. Electricity generated from coal was the largest cause of estimated damages from both health- and climate change-related effects. According to one of the investigators in this report says ““There are plants out there with a billion dollars in damages, and the relevant question becomes: What would it cost to install a scrubber” (\$100 million, far less than the damage done). The report concludes that the price of energy in the U.S. is artificially low and does not reflect its actual cost.

Water is often added to coal ash to transport it to its storage location as a slurry. The slurry is generally contained behind a dam, which in a number of instances, has broken and flooded surrounding homes. The ash contains residual environmental contaminants, one of which is arsenic, a group VA element in the periodic table, which is usually in its fully oxidized state (V oxidation state) as arsenate (AsO_4^{3-}). The ash settles into the bottom sediments of these ponds, which become anoxic and anaerobic bacteria reduce the arsenic to a toxic III oxidation state. Levels of arsenic in these slurry ponds have been measured at concentrations greater than 2,000 ppb (parts per billion), whereas EPA maximum allowable levels are 10 ppb.

The future of fossil fuels in the world economy

The rate of world consumption of fossil fuels continues has increased steadily over the last decades, with a leveling off in the latest world recession. However, it has been projected that in the next twenty years annual global energy demands will increase by around 50 percent and electrical power generation is predicted to increase by around 70 percent. These increases will be driven by population growth and increased energy demand by developing countries, in particular China and India. Most of this demand will be met through the conversion of the chemical energy of petroleum products, natural gas, and coal into heat and kinetic energy, water and oxidized carbon containing products, mainly carbon dioxide. Thus, the emission of the greenhouse gas CO_2 will steadily increase, according these estimates.

World reserves of liquid hydrocarbon fuels are predicted to decrease significantly within 20 to 25 years. There would appear to be a several decade window in which to convert to renewable energy sources. However, atmospheric scientists of the Intergovernmental Panel on Climate Change suggest that we need to lower the amount of atmospheric CO_2 by 70 percent over the next 100 years to stabilize atmospheric carbon dioxide concentrations at 450 ppm. Other groups are calling for a reduction to 350 ppm. Either of these limits would call for significant and rapid improvements in energy efficiency and a possible shift to nuclear energy, which is the subject of the Chapter 10, or renewable energy sources, which is the subject of Chapter 11.

SUMMARY

1. What is energy?

Energy can be defined as the capacity to do work. Work is the transfer of energy when a mass is moved through a distance with a force applied in the direction of movement.

2. What are the different types of energy?

There are two general types of energy, potential energy and “energy in motion.” Potential energies are: chemical, nuclear, gravitation, magnetic, and electrostatic. Energies-in motion are: electric, light, kinetic, heat, and sound.

3. What are the sources of energy on the Earth?

These are either potential energy: chemical (fossil fuels, wood), nuclear (uranium, deuterium) or gravitation (water in dams); or energy-in-motion: light (solar energy). Except for geothermal and nuclear energy, almost all other energy sources have their ultimate origin in solar energy.

4. Are there any limitations on our ability to obtain energy?

Only through energy transformations can we do work, provide heat, and accomplish goals that require “expenditure” of energy. Some energy transformations are very difficult to perform; the complete conversion of heat into other forms of energy without the involvement of some other form of energy is impossible. The first law of chemical thermodynamics says that the energy of the universe is constant and that one can only transform, not create or destroy, energy.

5. What are the chemical structures of fossil fuels?

Natural gas is primarily methane. Liquid fossil fuels are composed primarily of carbon and hydrogen atoms covalently bonded to form either straight chain hydrocarbons or cyclic structures. Coal is a complex structure with carbon and hydrogen as the primary constituents, with oxygen, nitrogen, and sulfur as minor constituents.

6. What is the chemistry of fossil fuels?

Fossil fuels are burned in the presence of oxygen and therefore are oxidized. The chemical reactions involved are highly complex exothermic reactions. They initially involve breaking carbon-hydrogen covalent bonds to form free radicals. If the oxygen is limited or the temperature is too low, complex organic compounds and carbon monoxide result in addition to water. The greatest amount of thermal energy is extracted from the fuel when the products are carbon dioxide and water.

7. How can we maximize output from fossil fuel burning while minimizing pollution?

Maximize the surface area of the fossil fuel so that oxygen is readily available and keep the burning temperature high enough to completely combust the carbon in the fuel to carbon dioxide. Unfortunately, carbon dioxide from complete combustion, which yields the maximum thermal energy, is also a

8. What is the origin of petroleum and where is it found?

Petroleum was formed when decaying organic matter was subjected to very high temperatures and pressures during geological processes. Some of this petroleum fills the spaces between underground rock and stone in certain geological features called shale and is often held in place by impermeable rock formations.

9. How is gasoline obtained from petroleum?

First the lower boiling, straight chain hydrocarbon liquids in petroleum are separated by distillation. Branched hydrocarbons and other additives are synthesized through petroleum processing involving solid catalysts. Then different types of gasoline are blended from these compounds.

10. What are the sources of natural gas? What is fracking?

Natural gas is formed in organic rich rocks under high temperatures and pressure and buried under layers of rock. Because it is a gas, it will migrate upward through porous rock and be trapped in geological domes, unless it is trapped in impermeable rock structures. If it is, this trapped gas can be recovered by drilling into shale rock, expose the rock to high pressure water containing special chemicals that allow the fracture of the rock and release of the trapped gas.

11. How large are our reserves of fossil fuels?

We are not certain. Liquid hydrocarbon fuels in the US have been predicted to run out in the twenty first century. Coal is probably more abundant and may last through the twenty first century. However, the use of coal as a primary fuel comes with significant environmental degradation and limitations will be placed on the use of these fuels because of their emission of the important greenhouse gas CO₂.

Review Questions

1. What is the difference between potential energy and “energies-in waiting.”
2. Which types of energy generate electricity, move motor vehicles, and heat homes?
3. Can the first law of thermodynamics be violated? Why/Why not?
4. In most nuclear reactions, a very small amount of mass is lost. Doesn't this violate the first law of thermodynamics?
5. When methane is burned in the presence of oxygen, is chemical energy transformed into heat energy or is heat energy transformed into chemical energy?
6. What is the difference between exothermic and endothermic chemical reactions?
7. In terms of the different types of energy, why are the methane combustion product gases at a higher temperature than the methane and oxygen gases.
8. In the burning of methane, demonstrate how the first law of thermodynamics is obeyed by examining the energies of the reactants and the products.
9. Why is gasoline considered a superior fuel to coal?
10. From an environmental point of view, why is methane a superior fuel in comparison with any other carbon based fuel?
11. Is an oil well a pocket deep underground containing only oil in it?
12. Discuss the differences among primary, secondary, and tertiary petroleum recovery methods used in the extraction of oil from an oil field.
13. What is the difference between tar sands and oil shale?
14. What is the difference between hydrocarbons and straight chain hydrocarbons?
15. What are branched hydrocarbons?
16. What is the difference between alkanes and cycloalkanes?
17. What is the function of petroleum refining?
18. What is the function of and the products produced by fractional distillation towers?

19. What is the function of solid catalysts in petroleum refining?
20. How is engine “knocking” prevented?
21. How is the octane rating of a gasoline improved?
22. What are the advantages and disadvantages of coal as a fuel?
23. From a chemical point of view, what are the differences among the various types of coal?
24. Contrast the chemical structure of coal with that of the components in gasoline.
25. What chemical treatments are used to overcome some of the disadvantages of coal as a fuel?

Problems

1. Are energy transformations possible between any two types of energy in the energy wheel (Figure 9-1)? Which transformations might be difficult or impossible? Think of concrete examples of each transformation.
2. Given: (A) a bulb containing one mole of methane and two moles of oxygen gas at 25°C; and (B) a bulb of the same size containing one mole of carbon dioxide and two moles of water vapor at 25°C. In which bulb would be the contents with the higher chemical potential energy?
3. Show why the spontaneous heating of a cold cup of coffee while sitting at room temperature is not a violation of the first law of thermodynamics, but is a violation of the second law of thermodynamics.
4. The spontaneous melting of a snowball to form a puddle of water that evaporates brings about what changes in the entropy of the universe?
5. Natural gas escaping into a room in a house only explodes when a match is lit or a spark is created. Explain in chemical terms what happens to initiate this explosion.
6. Draw structures of five different molecules that might be found in the effluent from a freshly drilled oil well.
7. What is an isomer? Draw structures of all the isomers you can think of for C₅H₁₂ and C₆H₁₄ using carbon skeleton drawings.

Discussion Questions

1. Discuss the advantages and disadvantages of the various fossil fuels in terms of economics, environmental damage, international politics and terrorism, and the laws of thermodynamics.
2. Give examples of applications of the first and second laws of thermodynamics that are not given in this text.

Group Projects

1. After doing research on the web and in the library, organize teams to debate the subject: “The United States should cease using petroleum products and switch to using coal for its energy needs.”
2. Search the internet and the library for the following topics: first law of thermodynamics, second law of thermodynamics, petroleum exploration, petroleum drilling, petroleum refining, and natural gas exploration.

Readings (to be updated)

Chemistry in Context, American Chemical Society, McGraw-Hill, 2000

Chemistry of the Environment, Thomas G. Spiro and William M. Stigliani, Prentice Hall, 1996.

Oil and Water, David Helvarg, Popular Science, August, 2001, p 45

Fueling the Future, Chemical & Engineering News, Jan. 20,2003