1 Introduction

1.1 Energy

Energy is defined as the ability to do work and provide heat. There are different ways in which the abundance of energy around us can be stored, converted, and amplified for our use. Energy sources can be classified into three groups: fossil, renewable, and nuclear (fissile). Fossil fuels were formed in an earlier geological period and are not renewable. The fossil energy sources include petroleum, coal, bitumen, natural gas, oil shale, and tar sands. The renewable energy sources include biomass, hydro, wind, solar (both thermal and photovoltaic), geothermal, and marine. The main fissile energy sources are uranium and thorium. Despite adequate reserves, some classifications include fissile materials along with the nonrenewable sources.

For over ten thousand years, humans have used biomass for their energy needs. Wood was used for cooking, water, and space heating. The first renewable energy technologies were primarily simple mechanical applications and did not reach high energetic efficiencies. Renewable energies have been the primary energy source in the history of the human race. But in the last two hundred years, we have shifted our energy consumption toward fossil fuels. Industrialization changed the primary energy use from renewable resources to sources with a much higher energy density, such as coal or petroleum. During the last century, the promise of unlimited fossil fuels was much more attractive, and rapid technical progress made the industrial use of petroleum and coal economical.

Petroleum is the largest single source of energy consumed by the world's population (about 4.8 barrel/year/person), exceeding coal, natural gas, nuclear, or hydroelelctric, as shown in Figure 1.1. The United States' energy consumption and supply is shown in Figure 1.2. In fact, today, over 88% of the global energy used comes from three fossil fuels: petroleum, coal, and natural gas. Although fossil fuels are still being created today by underground heat and pressure, they are being consumed much more rapidly than they are created. Hence, fossil fuels are considered nonrenewable, that is, they are not replaced as fast as consumed. Unfortunately, petroleum oil is in danger of becoming short in supply. Hence, the future trend is

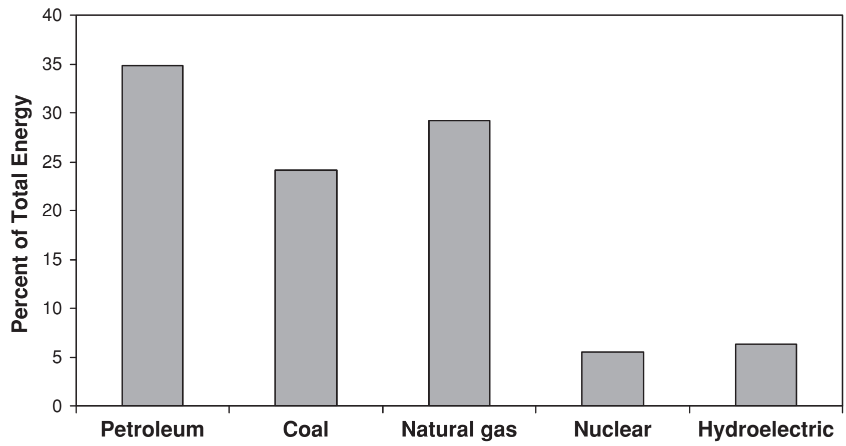

Figure 1.1. World consumption of various energies in 2008 out of the total consumption of 11.3 billion tons oil equivalent (BP, 2009).

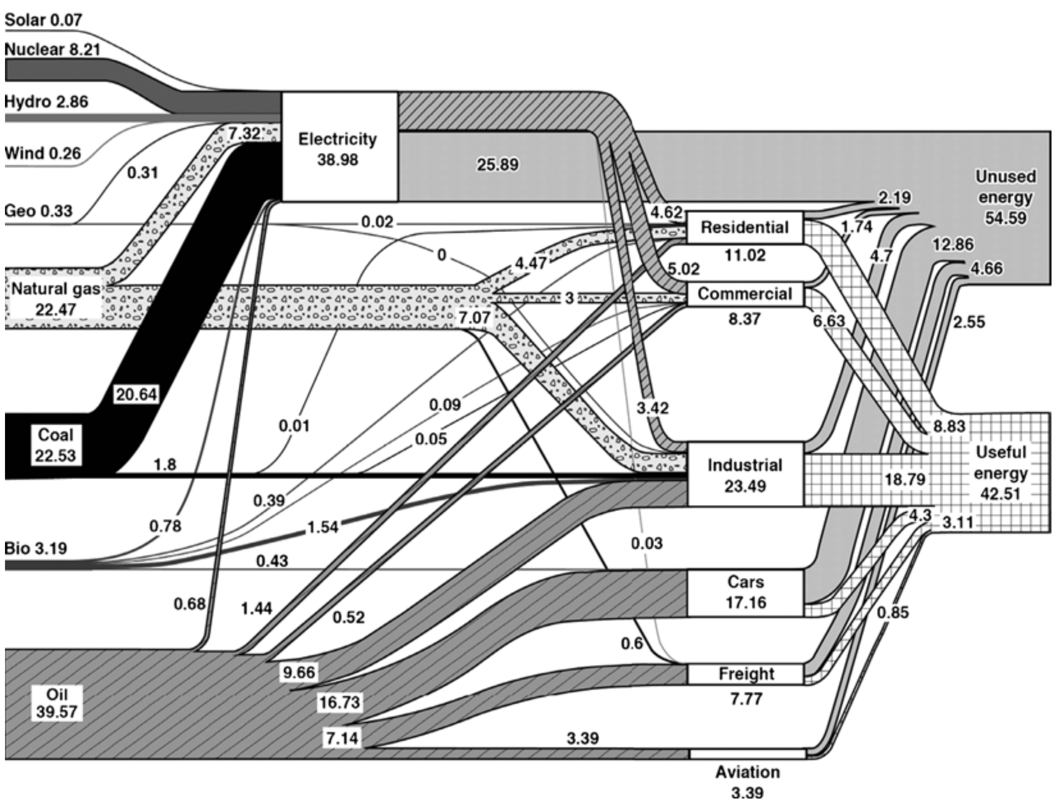

Figure 1.2. Energy consumption and supply in the United States for 2006 (U.S. DOE, 2008). Energies are shown in quad units (1 quad = 10^{15} BTU = 1.055×10^{15} J).

toward using alternate energy sources. Fortunately, technological development is making the transition possible.

A major problem with petroleum fuels is their uneven distribution in the world; for example, about 2% of the world population in the Middle East has 63% of the global reserves and is the dominant supplier of petroleum. This energy system is unsustainable because of equity issues as well as environmental, economic, and geopolitical concerns that have far-reaching implications. Interestingly, renewable energy resources are more evenly distributed than fossil or nuclear resources. Also, the energy flows from renewable resources are more than three orders of magnitude higher than current global energy need. Hence, renewable energy sources, such as biomass, hydro, wind, solar (both thermal and photovoltaic), geothermal, and marine, will play an important role in the world's future supply. For example, it is estimated that by year 2040 approximately half of the global energy supply will come from renewables (EREC, 2006), and the electricity generation from renewables will be more than 80% of the total global electricity production.

Another major problem with fossil fuel is the greenhouse gas emissions; about 98% of carbon emissions result from fossil fuel combustion. Reducing the use of fossil fuels would considerably reduce the amount of carbon dioxide and other pollutants produced. This can be achieved by either using less energy altogether or by replacing fossil fuels with renewable fuels. Hence, current efforts focus on advancing technologies that emit less carbon (e.g., high-efficiency combustion) or no carbon, such as nuclear, hydrogen, solar, wind, and geothermal, or on using energy more efficiently and sequestering carbon dioxide that is emitted during fossil fuel combustion.

Despite the above challenges, it is not easy to replace fossil fuels, as our modern way of life is intimately dependent on fossil fuels, specifically hydrocarbons, including petroleum, coal, and natural gas. For example, the majority of commodity products (e.g., plastics, fabrics, machine parts, chemicals, etc.) are made using crude oil or natural gas feedstock. And, more importantly, the major energy demand is fulfilled by fossil fuels, resulting in a major role for crude oil and natural gas in driving world economy.

1.2 Petroleum

Petroleum [word derived from Greek *petra* (rock) and *elaion* (oil) *or* Latin *oleum* (oil)] or crude oil, sometimes colloquially called black gold or "Texas Tea," is a thick, dark brown or greenish liquid. Petroleum consists of a complex mixture of various hydrocarbons, largely of the alkenes and aromatic compounds, but may vary much in appearance and composition. Petroleum is a fossil fuel because it was formed from the remains of tiny sea plants and animals that died millions of years ago and sank to the bottom of the oceans (Figure 1.3). This organic mixture was subjected to enormous hydraulic pressure and geothermal heat. Over time, the mixture changed, breaking down into compounds made of hydrocarbons by reduction

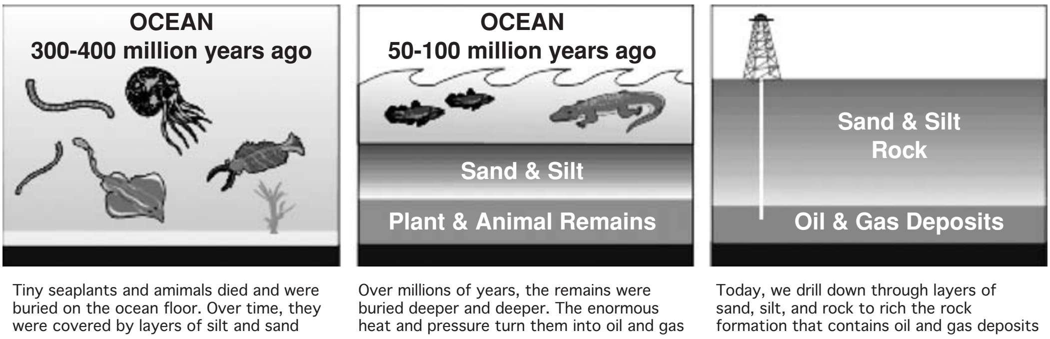

Figure 1.3. Cartoon showing formation of petroleum and natural gas (U.S. DOE, 2009).

reactions. This results in the formation of oil-saturated rocks. The crude oil rises and gets trapped under nonporous rocks that are sealed with salt or clay layers.

According to the well-accepted Biogenic theory (Walters, 2006), fossil fuels – crude oil, coal, and natural gas – are the product of compression and heating of ancient vegetation and animal remains over geological time scales. According to this theory, an organic matter is formed from the decayed remains of prehistoric marine animals and terrestrial plants. Over many centuries, this organic matter, mixed with mud, is buried under thick sedimentary layers. The resulting high pressure and heat transformed the organic matter first into a waxy material known as kerogen, and then into liquid and gaseous hydrocarbons. The fluids then migrate through adjacent rock layers until they become trapped underground in porous rocks called reservoirs, forming an oil field, from which the liquid can be removed by drilling and pumping. The reservoirs are at different depths in different parts of the world, but typical depth is 4–5 km. The thickness of the oil layer is about 150 meters, generally termed "oil window." Three important elements of an oil reservoir are a rich source rock, a migration conduit, and a trap (seal) that forms the reservoir.

According to not-well-accepted Abiogenic theory (Mehtiev, 1986), petroleum origin is natural hydrocarbons. This theory proposes that large amounts of carbon exist naturally in the planet, some in the form of hydrocarbons. Due to its lower density than aqueous pores fluids, hydrocarbons migrate upward through deep fracture networks. The two theories are reviewed by Mehtiev (1986).

1.2.1 History of Petroleum Exploration

According to historical accounts, the early oil wells were drilled in China before the fifth century (ACE, 2009). Wells, as deep as 243 meters, were drilled using bits attached to bamboo poles. The crude oil was burned to produce heat needed in the production of salt from brine evaporation. By the end of the tenth century, extensive bamboo pipelines connected oil wells with salt springs.

Separately, ancient Persian tablets indicate the medicinal and lighting uses of petroleum in the upper echelons of their society. Tar, the heavy component of the oil, was used in the paving of the street in Baghdad in the eighth century. In Baku

(Azerbaijan), oil fields were exploited to produce naphtha in the ninth century, as described by the geographer Masudi in the tenth century, and the output has increased to hundreds of shiploads by the thirteenth century as described by Marco Polo.

Modern petroleum refining began in 1846 when Abraham Gesner refined kerosene from coal. Six years later, Ignacy Łukasiewicz refined kerosene from "rock oil," which was more readily available. The successful process rapidly spread around the world. In 1861, Meerzoeff built the first Russian refinery in Baku (current capital of the Azerbaijan Republic), using the mature oil fields available. It is interesting to note that the battle of Stalingrad was fought over Baku, which produced 90% of the world's oil.

The first commercial oil well in North America was drilled by James Miller Williams in 1858 in Oil Springs (Ontario, Canada). In the following year, Edwin Drake discovered crude oil near Titusville, Pennsylvania and pioneered a new method for producing crude oil from the ground, in which the drilling was carried out using piping to prevent borehole collapse, allowing for a deeper drilling. The new method was significant advancement, as the previous methods for collecting crude oil were very limited. For example, the collection used to be performed where crude oil occurred naturally, such as oil seeps or shallow holes dug into the ground. Also, due to the collapse from water seepage, the digging of large shafts into the ground almost always failed. A notable advancement Drake achieved was to place a 10-meter iron pipe through the ground all the way to the bedrock below. This allowed Drake to do further drilling inside the pipe, avoiding the hole collapse from water seepage. Typical drilling below the pipe was to 13 meters, making a 23-meter well. The basic concept in Drake's technology is still being used by many petroleum companies, with the new wells being 1,000–4,000 meters deep. While searching for oil, many of the test wells turn up dry (i.e., do not contain any oil), which adds to the cost of petroleum exploration. Hence, some small investors still consider the exploration as a gamble. Despite the improvement in the technology since Drake's time, only about 33% of the exploration wells have oil; the remaining 67% come up dry.

In American homes and businesses, whale oil was used for lighting until 1850s and often experienced shortages. Starting in the 1860s, refined kerosene from crude oil became plentiful; hence, kerosene was used for lighting until the discovery of electric bulbs. Gasoline and other non-kerosene products from refining were simply discarded due to the lack of use. In 1882, the advent of gasoline engine-driven carriages (i.e., horseless carriages) solved this problem. There was heavy demand for gasoline; in fact, by 1920, there were 9 million motor vehicles in the United States alone for a population of 106 million.

1.2.2 Petroleum Refining and Shipping

A petroleum refinery separates crude oil into various byproducts and fuel components, including gasoline, diesel, heating oil, and jet fuel. Petroleum constituents

Table 1.1. *Petroleum constituents from oil refinery*

Fraction	Distillation range (°C)	Carbon number
Gas	<20	C_1–C_4
Petroleum ether	20–60	C_5–C_6
Ligroin (light naphtha)	60–100	C_6–C_7
Natural gasoline	40–205	C_5–C_{10}, and cycloalkanes
Jet fuel	105–265	C_8–C_{14}, and aromatics
Kerosene	175–315	C_{10}–C_{16}, and aromatics
No. 1 diesel fuel	170–325	C_9–C_{18}, and aromatics
No. 2 diesel fuel	175–365	C_{10}–C_{20}, and aromatics
No. 3 diesel fuel	185–390	C_{12}–C_{24}, and aromatics
Gas oil (No. 4 and 5 fuel oils)	>275	C_{12}–C_{70}, and aromatics
Gas oil (No. 6 fuel oils)	>365	C_{20}–C_{70}, and aromatics
Lubricating oil	Nonvolatile liquids	Long chains attached to cyclic structures
Asphalt or petroleum coke	Nonvolatile solids	Polycyclic structures

from oil refinery products are listed in Table 1.1. Because various components boil at different temperatures (or temperature ranges), refineries use a heating process called distillation to separate the components. For example, gasoline has a lower boiling temperature (i.e., gasoline is more volatile) than kerosene, allowing the two to be separated by heating to different temperatures. Another important job of the refineries is to remove contaminants from the oil, for example, sulfur from gasoline or diesel. If not removed, the sulfur will be emitted as sulfur dioxide from automobile exhaust, causing air pollution and acid rain.

An important nonfuel use of petroleum is to produce chemical raw materials. The two main classes of petrochemical raw materials are olefins (including ethylene and propylene) and aromatics (including benzene and xylene), both of which are produced in large quantities. The olefins are produced by chemical cracking by using steam and/or catalysts, and the aromatics are produced by catalytic reforming. These two basic types of chemicals serve as feedstock to produce a wide range of chemicals and materials, including monomers, solvents, and adhesives. The monomers are used to produce polymers and oligomers for use as plastics, resins, fibers, elastomers, lubricants, and gels. An important aspect of petrochemicals is their extremely large scale. For example, annual world production of ethylene is 110 million tons, propylene is 65 million tons, and aromatics are 70 million tons. Due to the economy of scale, each plant produces a large volume of petrochemicals, which are then distributed worldwide via interregional trade. The majority of the petrochemical industry is in the United States and Western Europe, although the production capacity in the Middle East and Asia is increasing due to the proximity of raw materials and end consumers.

Each day, Americans use about 21 million barrels of crude oil, out of which about one-third is produced domestically and two-thirds are imported. Most U.S. production is in Texas followed by Alaska, California, Louisiana, and Oklahoma, in that order. Gasoline and other liquid fuels from refineries are usually shipped out through pipelines to the major consumer centers, which is the safest and cheapest way to move large quantities of petroleum across land. The United States has an extensive network of underground pipelines measuring 384,000 km. Pump stations are installed at a spacing of 30–170 km to keep the petroleum liquids flowing at a speed of about 8 km/hour. For illustration purposes, it takes about 15 days to send a shipment of gasoline from Houston to New York.

Petroleum is the most important commodity in terms of international trade. Hence, it has been subjected to influence from the international groups. A notable group is the Organization of Petroleum Exporting Countries (OPEC), which is an intergovernmental organization of 13 nations: Iran, Iraq, Kuwait, Saudi Arabia, Venezuela, Qatar, Indonesia, Libya, United Arab Emirates, Algeria, Nigeria, Ecuador, and Gabon. OPEC members try to set production levels for petroleum to maximize their revenue by using supply/demand economics. For example, a decrease in the production level increases the price ($/barrel), and on the contrary, an increase in the production level lowers the price. But the total money a country receives is barrel of crude oil produced × price per barrel. Due to this complex dependence of revenue on production volume, member OPEC countries do not always agree with each other; as depending on the production levels for a member country, the optimum price may be different from another member. Hence, contrary to the group's vision, some OPEC countries want to produce less to raise prices, whereas the other OPEC countries want to flood the market to gain immediate revenue. In addition, the crude oil supply can be controlled for political reasons. For example, the 1973 OPEC oil embargo was a political statement against the United States for supporting Israel in the Yom Kippur war. Such embargo or cut in production caused a drastic increase in the price of petroleum. Today, a significant portion of U.S. crude oil import is from Canada and Mexico, which is more reliable and has a lower shipping cost. However, due to an internal law, Mexico can only export half of the petroleum it produces to the United States.

The United States is a member of the Organization for Economic Co-Operation and Development (OECD), which is an international organization of 30 countries that accept the principles of representative democracy and a free market economy. In 1970s, as a counterweight to OPEC, OECD founded the International Energy Agency (IEA), which is regarded as the "energy watchdog" of the Western world and is supposed to help avoid future petroleum crises. IEA provides demand and supply forecasts in its annual World Energy Outlook (WEO) report and current situation of crude oil market in its monthly publication. The WEO covers forecast for the next two decades and is highly regarded by people related to the energy industry.

1.2.3 Classification of Oils

The oil industry classifies "crude" by its production location (e.g., "West Texas Intermediate, WTI" or "Brent"), relative density (API gravity), viscosity ("light," "intermediate," or "heavy"), and sulfur content ("sweet" for low sulfur and "sour"

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Ram B. Gupta and Ayhan Demirbas
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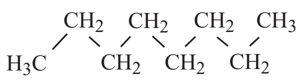
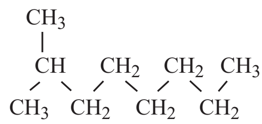
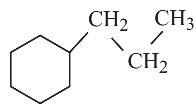
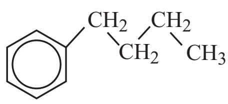
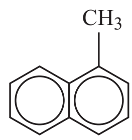
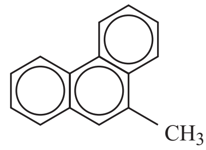
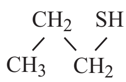
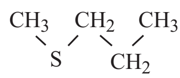
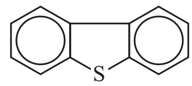
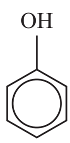
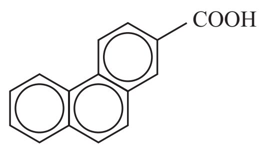
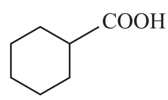
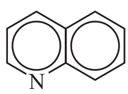
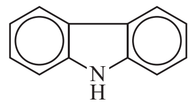
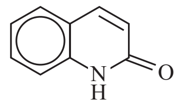
Table 1.2. *Class of compounds found in petroleum crude oils (Robins and Hsu, 2000)*

Compounds	Molecular structures		
Saturates			
Aromatics			
Sulfur compounds			
Oxygen compounds			
Nitrogen compounds			

for high sulfur). The density and viscosity of the crude oil depend on the composition of the oil, which varies greatly from one source to another, and the age of the producing well. Some of the class of compounds are listed in Table 1.2.

Tar sands are oil traps that are not deep enough in the earth to allow for geological conversion into conventional oil. This oil was not heated enough to complete the process of molecular breakage to reduce the viscosity. The oil has the characteristics of bitumen and is mixed with large amounts of sand due to the proximity to the earth's surface. The tar sand is mined, flooded with water in order to separate the heavier sand, and then processed in special refineries to reduce its high sulfur content (the original crude oil usually has 3–5% sulfur) and other components. This process needs huge amounts of energy and water. The deeper tar sands (below 75 meters) are mined in situ (COSO, 2007).

Natural gas liquids are liquid hydrocarbons produced along with natural gas (NG) from the oil wells. The chemical composition of NG is given in Table 1.3.

Oil shales contain kerogen, which is an intermediate stage on the way from biological carbohydrate to oil formation. The oil shale layer had not been subjected to enough heat in order to complete the conversion. For the final step, the kerogen must be heated to 500°C and molecularly combined with additional hydrogen to

Table 1.3. *Typical chemical composition of natural gas*

Component	Typical analysis (v/v%)	Range (v/v%)
Methane	94.9	87.0–96.0
Ethane	2.5	1.8–5.1
Propane	0.2	0.1–1.5
i-Butane	0.03	0.01–0.3
n-Butane	0.03	0.01–0.3
i-Pentane	0.01	trace–0.14
n-Pentane	0.01	trace–0.14
Hexanes plus	0.01	trace–0.06
Nitrogen	1.6	1.3–5.6
Carbon dioxide	0.7	0.1–1.0
Oxygen	0.02	0.01–0.1
Hydrogen	trace	trace–0.02

complete the oil formation. The final processing is done in the refinery and requires high amounts of energy (otherwise the energy would have come from the geological environment). The kerogen is still embedded in the source rock and did not concentrate as in the case of crude oil field. Often it is not attractive to mine the kerogen, due to the large amount of waste rock that comes along. However, the shale oil reserves in the world are greater than crude oil or NG, as shown in Table 1.4. Researchers are devising innovative ways to mine kerogen in situ by means of heat and steam.

1.2.4 Petroleum Reserves and Crude Oil Production

The petroleum reserves can be classified into three categories: proven, probable, and possible reserves. Proven reserves are those fields from which petroleum can be produced using current technology at the current prices. Probable reserves are those fields from which petroleum can be produced using the near-future technology at current prices. Possible reserves are those fields from which petroleum can be produced using future technology. Relying on our proven reserves, currently petroleum is the most important energy source, as 35% of the world's primary energy need is met by crude oil, 25% by coal, and 21% by NG, as shown in Table 1.5. The transport sector (i.e., automobiles, ships, and aircrafts) relies on well over 90% of crude oil. In fact, the economy and lifestyle of industrialized nations rely heavily on a sufficient supply of crude oil at low cost.

Table 1.6 shows crude oil production data for various regions. The Middle East produces 32% of the world's oil (Table 1.7), but more importantly, it has 64% of the total proven oil reserves in the world (Table 1.8). Also, the Middle East's reserves are depleting at a slower rate than any other region in the world. The Middle East provides more than half of OPEC's total oil exports and has a major influence on the worldwide crude oil prices, despite the fact that OPEC produces less than half of the oil in the world.

Table 1.4. *Energy reserves of the world (Demirbas, 2006a; Demirbas, 2006b)*[a]

Crude oil	Natural gas	Shale oil	Coal	Tar sands	Uranium	Deuterium
37.0	19.6	79.0	320.0	6.1	1.2×10^5	7.5×10^9

[a] Each unit = 1×10^{15} MJ = 1.67×10^{11} Bbl crude oil.

Table 1.5. *Year 1973 and 2005 fuel shares of total primary energy supply (excludes electricity and heat trade) (IEA, 2007)*

	World		OECD	
Energy sources	1973	2005	1973	2005
Oil	46.2	35.0	53.0	40.6
Coal	24.4	25.3	22.4	20.4
Natural gas	16.0	20.7	18.8	21.8
Combustible renewables and wastes	10.6	10.0	2.3	3.5
Nuclear	0.9	6.3	1.3	11.0
Hydro	1.8	2.2	2.1	2.0
Other (geothermal, solar, wind, heat, etc.)	0.1	0.5	0.1	0.7
Total (million tons oil equivalent)	6,128	11,435	3,762	5,546

Table 1.6. *Year 1973 and 2006 regional shares of crude oil production (IEA, 2007)*

Region	1973	2006
Middle East (%)	37.0	31.1
OECD (%)	23.6	23.2
Former USSR (%)	15.0	15.2
Africa (%)	10.0	12.1
Latin America (%)	8.6	9.0
Asia, excluding China (%)	3.2	4.5
China (%)	1.9	4.7
Non-OECD Europe (%)	0.7	0.2
Total (million tons)	2,867	3,936

Table 1.7. *Percentage of petroleum production by region (IEA, 2007)*

Middle East	Latin America	Eastern Europe	North America	Asia and Pacific	Africa	Western Europe
32	14	13	11	11	10	9

Table 1.8. *Percentage of total proven reserves by region (IEA, 2007)*

Middle East	Latin America	Eastern Europe	North America	Asia and Pacific	Africa	Western Europe
64	12	6	3	4	9	2