Chapter 1
Introduction

Ever since our distant forerunners managed to light fire for providing heat, means for cooking and many essential purposes, humankind's life and survival is inherently linked with our ever-increasing thirst for energy. From burning wood, vegetation, peat moss and other sources, to the use of coal, followed by that of petroleum oil and natural gas (fossil fuels), we have thrived using Nature's resources. Fossil fuels include coal, oil and gas, all composed of hydrocarbons with varying ratios of carbon and hydrogen.

Hydrocarbons derived from petroleum, natural gas or coal are essential in many ways to modern life and its quality. The bulk of the world's hydrocarbons is used as fuels for propulsion, electrical power generation, and heating. The chemical, petrochemical, plastics and rubber industries are also dependent upon hydrocarbons as raw materials for their products. Indeed, most industrially significant synthetic chemicals are derived from petroleum sources. The overall use of oil in the world now exceeds 11 million metric tons per day. An ever-increasing world population (presently exceeding 6 billion, projected to increase to 8–10 billion by the middle of the 21st century; Table 1.1) and energy consumption, compared with our finite non-renewable fossil fuel resources, which will be increasingly depleted, are clearly on a collision course. New solutions will be needed for the 21st century to sustain the standard of living to which the industrialized world become accustomed and to which the developing world is striving to achieve.

The rapidly growing world population, which stood at 1.6 billion at the beginning of the 20th century, has now exceeded 6 billion. With an increasingly technological society, the world's per capita resources have difficulty keeping up with demands. Satisfying our society's needs while safeguarding the environment and

Table 1.1 World population (in millions).

1650	1750	1800	1850	1900	1920	1952	2000	Projection 2050*
545	728	906	1171	1608	1813	2409	6200	8000 to 10000

* Medium estimate. Source: United Nations, Population Division.

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allowing future generations to continue to enjoy planet Earth as a hospitable home is one of the major challenges that we face today. Man needs not only food, water, shelter, clothing and many other prerequisites, but also increasingly huge amounts of energy. Today, the world uses some 1.05×10^{18} calories per year (120 Petawatt-hours), equivalent to a continuous power consumption of about 13 terawatts (TW), comparable to the production of 13 000 nuclear power plants each of 1 GW output. With increasing world population, development and higher standards of living, this demand for energy is expected to grow to 21 TW in 2025 and to about 30 TW in 2050 (Fig. 1.1).

Our early ancestors discovered fire and started to burn wood. The industrial revolution was fueled by coal, and the 20th century added oil, natural gas and introduced atomic energy.

When fossil fuels such as coal, oil or natural gas (i.e., hydrocarbons) are burned in power plants to generate electricity or to heat our houses, propel our cars, airplanes, etc., they form carbon dioxide and water. They are thus used up, and are non-renewable on the human timescale.

Fossil Fuels
Petroleum Oil, Natural Gas, Tar-Sand, Shale Bitumen, Coals

They are mixtures of hydrocarbons (i.e., compounds of the elements carbon and hydrogen). When oxidized (combusted) they form carbon dioxide (CO_2) *and water* (H_2O) *and thus are not renewable on the human scale.*

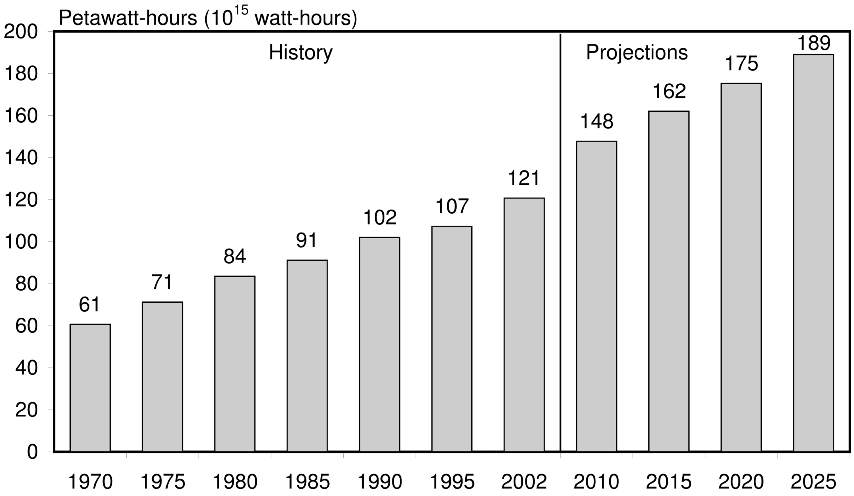


Figure 1.1 World primary energy consumption, 1970 to 2025. Based on data from: Energy Information Administration (EIA), International Energy Outlook 2005.

Nature has given us, in the form of oil and natural gas, a remarkable gift. What was created over the ages, however, mankind is consuming rather rapidly. Petroleum and natural gas are used on a large scale to generate energy, and also as raw materials for diverse man-made materials and products such as the plastics, pharmaceuticals and dyes that have been developed during the 20th century. The United States energy consumption is heavily based on fossil fuels, with atomic energy and other sources (hydro, geothermal, solar, wind, etc.) representing only a modest 15% (Table 1.2).

With regard to electricity generation, coal still represents more than half of the fuel used, with about 16% for natural gas and 20% for nuclear energy (Table 1.3).

Other industrial countries, in contrast, obtain between 25% and 85% of their electrical energy from non-fossil sources (Table 1.4).

Table 1.2 United States Energy Consumption (%).

Energy source	1960	1970	1980	1990	2000
Oil	44.1	43.5	43.6	39.8	38.5
Natural gas	27.5	32.1	26.0	22.9	23.7
Coal	21.8	18.1	19.6	22.8	22.7
Nuclear energy	0.002	0.35	3.5	7.3	8.1
Hydro-, Geothermal, Solar, Wind, etc. energy	6.6	6.0	7.2	7.4	6.9

Source: US Census Bureau, Statistical Abstract of the US 2002, Section 19, Energy and Utilities.

Table 1.3 Electricity Generation in the United States (%).

	1990	2000
Coal	52.6	51.8
Petroleum	4.1	2.9
Natural gas	12.5	15.7
Nuclear	19.1	19.9
Hydroelectric	9.7	7.2
Geothermal	0.5	0.4
Wood	1.0	1.0
Waste	0.4	0.6
Other waste	0.076	0.090
Wind	0.099	0.129
Solar	0.020	0.021

Source: US Census Bureau, Statistical Abstract of the US 2002, Section 19, Energy and Utilities.

Table 1.4 Electricity generated in Industrial countries by non-fossil fuels (%, 2001).

Country	Conventional thermal	Hydro-electric	Nuclear	Geothermal, Solar, Wind, Wood and Waste	Total non-fossil
France	8.4	14.1	76.8	0.7	91.6
Canada	28.1	57.8	12.8	1.3	71.9
Korea, South	58.2	1.5	40.1	0.2	41.8
Japan	58.9	8.5	31.0	1.6	41.1
Germany	62.5	3.7	29.7	4.1	37.5
United States	71.6	5.6	20.6	2.2	28.4
United Kingdom	73.6	1.1	23.7	1.6	26.4
Italy	78.7	18.0	0.0	3.4	21.3

Source: Energy Information Administration, International Energy Annual 2002, World Net Electricity Generation by Type, 2001.

Oil use has grown to the point where the world consumption is around 82 million barrels (1 barrel equals 42 gallons, i.e. some 160 L) a day, or 11 million metric tonnes. Fortunately, we still have significant worldwide reserves, including heavy oils, oil shale and tar-sands and even larger deposits of coal (a mixture of complex carbon compounds more deficient in hydrogen than oil and gas). Our more plentiful coal reserves may last for 200–300 years, but at a higher socio-economical and environmental cost. It is not suggested that our resources will run out in the near future, but it is clear that they will become even scarcer, much more expensive, and will not last for very long. With a world population exceeding 6 billion and still growing (as indicated earlier, it may reach 8–10 billion), the demand for oil and gas will only increase. It is also true that in the past, dire predictions of rapidly disappearing oil and gas reserves have always been incorrect (Table 1.5). As a matter of fact, until recently the reserves have been growing, but lately they have begun to level off.

The question is, however, what is meant by “rapid depletion” and what is the real extent of our reserves? Proven oil reserves, instead of being depleted, have in fact almost doubled during the past 30 years and now exceed 150 billion tonnes (more than one trillion barrels). This seems so impressive that many people assume that there is no real oil shortage in sight. However, increasing consumption (due also to increasing standards of living), coupled with a growing world population makes it more realistic to consider per-capita reserves. If we do this, it becomes evident that our known reserves will last for not much more than half a century. Even if all other factors are considered (new findings, savings, alternate sources, etc.), we will increasingly face a major problem. Oil and gas will not become ex-

Table 1.5 Proven Oil and Natural Gas Reserves (in billion tonnes oil equivalent).

Year	Oil	Natural Gas
1960	43	15.3
1965	50	22.4
1970	77.7	33.3
1975	87.4	55
1980	90.6	69.8
1986	95.2	86.9
1987	121.2	91.4
1988	123.8	95.2
1989	136.8	96.2
1990	136.5	107.5
1993	139.6	127
2002	156.4	157.6
2003	156.7	158.2

Source for 1993–2003: BP Statistical review of world energy, June 2004.

hausted overnight, but market forces of supply and demand will inevitably start to drive the prices up to levels that nobody even wants to contemplate presently. Therefore, if we don't find new solutions, we will inevitably face a real crisis.

Mankind wants all the advantages that an industrial society can give to all of its citizens. We all essentially rely on energy, but the level of consumption varies vastly in different parts of the world (industrialized versus developing countries). At present, the annual oil consumption per capita in China is still only five to six barrels, whereas it is more than ten-fold this level in the United States. China's oil use is expected to at least double during the next decade, and this alone equals roughly the United States consumption – reminding us of the size of the problem that we will face. Not only the world population growth but also the increasing energy demands of China, India and other developing countries is already putting great pressure on the world's oil reserves, and this in turn contributes to price escalation.

Even though the generation of energy by burning non-renewable fossil fuels (including oil, gas and coal) is feasible only for a relatively short period in the future, it is also generating serious environmental problems (*vide infra*). The advent of atomic energy opened up a fundamental new possibility, but also created dangers and concerns of safety of radioactive byproducts. It is regrettable that these considerations brought any further development of atomic energy almost to a stand still, at least in most of the Western world. Whether we like it or not, it is clear that we will have no alternative but to rely increasingly on nuclear energy, albeit making it safer and cleaner. Problems including those of the storage and disposal of radioactive waste products must be solved. Pointing out difficulties and hazards as well as regulating them, within reason, is necessary and solutions to overcome them is essential and certainly feasible.

If we continue to burn our hydrocarbon reserves to generate energy, and to use them at the present alarming rate, then diminishing resources and sharp price increases by the mid-21st century will lead eventually to a need to supplement these reserves, or generate them by synthetic manufacturing. Synthetic gasoline or oil products will, however, be costlier. Nature's petroleum oil and natural gas are the greatest gifts we will ever have. A barrel of oil still costs only around $50–75, within market fluctuations. It will be difficult for synthetic manufacturing process to come close to this price. We will need to get used to higher prices, not as a matter of any government policy, but as a fact of free market forces over which free societies have very little control.

Synthetic oil is feasible, its production having been proven feasible from coal or natural gas via synthesis-gas, a mixture of carbon monoxide and hydrogen obtained from the incomplete combustion of coal or natural gas (which are themselves non-renewable). Coal conversion was used in Germany during World War II and in South Africa during the boycott years of the Apartheid era. Nevertheless, the size of these operations hardly amounted to 0.3% of the present United States consumption. This route – the so-called Fischer–Tropsch synthesis – is also highly energy consuming, giving complex, unsatisfactory product mixtures, and can hardly be seen as the technology of the future. To utilize still-existing large natural gas reserves, their conversion to liquid fuels through syn-gas is presently developed for example on a large scale in Qatar, where major oil companies including ExxonMobil, Shell or ChevronTexaco, have recently committed over $20 billion to the construction of gas-to-liquid (GTL) facilities, mainly to produce sulfur-free diesel fuel. However, when completed, this will provide a daily total of some 100 000 t compared with present world use of transportation fuels in excess of 6 Mt per day. These figures demonstrate the enormity of the problem that we face. New and more efficient processes are clearly needed. Some of the required basic science and technology is evolving. As will be discussed (*vide infra*), still abundant natural gas can be, for example, directly converted, without first producing syn-gas, to gasoline or hydrocarbon products. Using our even larger coal resources to produce synthetic oil could extend its availability, but new approaches based on renewable resources are essential for the future. The development of biofuels, primarily by the fermentative conversion of agricultural products (derived from sugar cane, corn, etc.) to ethanol is evolving. Whereas ethanol can be used as a gasoline additive or even alternative fuel, the enormous amounts of transportation fuel needed clearly limits the applicability to specific countries and situations. Other plant-based oils are also being touted as renewable equivalents of diesel fuel, although their role in the total energy picture is minuscule.

When hydrocarbons are burned, as pointed out, they produce carbon dioxide (CO_2) and water (H_2O). It is a great challenge to reverse this process and to produce efficiently and economically hydrocarbon fuels from CO_2 and H_2O. Nature, in its process of photosynthesis, of course recycles CO_2 with water into new plant life. The natural formation of new fossil fuels form CO_2, however, takes a very long time, making them non-renewable on the human time scale.

The "Methanol Economy®" [1] – the subject of our book – elaborates an approach of how humankind can decrease and eventually liberate itself from its dependence on diminishing oil and natural gas (and even coal) reserves while mitigating global warming caused by their excess combustion giving carbon dioxide. The "Methanol Economy" is based in the interim on the efficient direct conversion of still-existing natural gas resources to methanol or dimethyl ether, or their production by chemical recycling of CO_2 from the exhaust gases of fossil fuel-burning power plants and other industrial sources. Eventually, atmospheric CO_2 itself can be recycled using catalytic or electrochemical methods. Methanol and dimethyl ether are both excellent transportation fuels on their own for internal combustion engines. Methanol is also an adequate fuel for fuel cells, being capable of producing electric energy by reaction with atmospheric oxygen (air). Fuel cells provide a convenient, efficient source for electric power. It should be emphasized that the "Methanol Economy" is not producing energy. In the form of liquid methanol, it only stores energy more conveniently and safely compared to extremely difficult to handle and highly volatile hydrogen gas, the basis of the "hydrogen economy". Besides being a most convenient energy storage material and a suitable transportation fuel, methanol can also be catalytically converted to ethylene and/or propylene, the building blocks of synthetic hydrocarbons and their products, which are currently obtained from our diminishing oil and gas resources.

The far-reaching implications of the new "Methanol Economy" approach clearly have great potential and societal benefit for mankind. As mentioned earlier, the world is presently consuming more than 80 million barrels of oil each day, and about two-thirds as much natural gas equivalent, both being derived from our declining and non-renewable natural sources. Oil and natural gas (as well as coal) were formed by Nature over the eons in scattered and frequently increasingly difficult-to-access locations (under desert areas, in the depths of the seas, the inhabitable reaches of the polar regions, etc.). In contrast, the recycling of CO_2 from industrial exhausts and eventually from air itself (which belongs to everybody) opens up an entirely new vista. The energy needs of humankind will, in the foreseeable future, come from any available source, including alternate sources of fossil fuels and atomic energy. As we still cannot store energy efficiently on a large scale, new ways are needed. The production of methanol offers a convenient means of energy storage. Even now, our existing power plants, during off-peak periods, could, by the electrolysis of water, generate the hydrogen needed to produce methanol. Other means of cleaving water by either biochemical (enzymatic) or photovoltaic (using energy from the Sun, our ultimate clean energy source) pathways are also evolving.

Initially, CO_2 will be recycled from industrial emissions (fossil fuel-burning power plants, cement factories, etc.) to produce methanol and to derive synthetic

Table 1.6 Composition of air.

Nitrogen	78%
Oxygen	20.90%
Argon	0.90%
Cabon dioxide	0.037%
Water	few % (variable)
Methane	trace amounts
Nitrogen oxides	
Ozone	

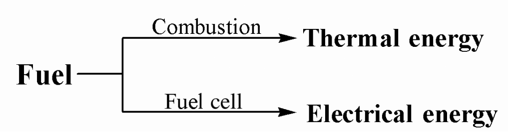
hydrocarbons and their products. The CO_2 content of these emissions is high and can be readily separated. In contrast, the average CO_2 content of air is very low (0.037%) (Table 1.6), and atmospheric CO_2 is therefore presently difficult to separate on an economic basis. However, these difficulties can be overcome by future developments using selective absorption or other separation technologies. Mankind's ability to chemically recycle CO_2 to useful fuels and products will eventually provide an inexhaustible renewable carbon source.

CO_2 can, as mentioned earlier, even now be readily recovered from flue gas emissions of power plants burning carbonaceous fuels (coal, oil, and natural gas), from fermentation processes, and from the calcination of limestone (cement production), production of steel, or other industrial sources. As these plants emit very large amounts of CO_2 they contribute to the so-called "greenhouse warming effect" of our planet, which is causing grave environmental concern. The relationship between the atmospheric CO_2 content and temperature was first studied scientifically by Arrhenius as early as 1898. The warming trend of our Earth can be evaluated only over longer time periods, but there is clearly a relationship between the CO_2 content in the atmosphere and Earth's temperature.

Recycling CO_2 into methanol (or dimethyl ether) and, through this into useful fuels and synthetic hydrocarbons and products, will not only help to alleviate the question of our diminishing fossil fuel resources, but at the same time help to mitigate global warming caused at least in part by man-made greenhouse gases.

One highly efficient method of producing electricity directly from fuels is achieved in fuel cells via their catalytic electrochemical oxidation, primarily that of hydrogen.

Fuel cell is an electrochemical device that converts free chemical energy of a fuel directly into electrical energy



The principle of fuel cells was first recognized by Sir William Grove during the early 1800s, but their practical use was only recently developed. The basis of most fuel cell technologies is still based on Grove's principle – that is, hydrogen and oxygen (air) are combined in an electrochemical cell-like device, producing water and electricity.

The process is clean, giving only water as a byproduct, but hydrogen itself must be first produced in an energy-consuming process, using (at present) mainly fossil fuels. The handling of hydrogen gas itself is not only technically difficult, but also dangerous. Nonetheless, the use of fuel cells is gaining application in static installations or in specific cases, such as space vehicles. Currently, hydrogen gas is produced mainly from still-available hydrocarbon (fossil fuel) sources using reformers, which converts them to a mixture of hydrogen and carbon monoxide. These two gases are then separated. Although this process relies on our diminishing fossil fuel sources, electrolysis or other processes to cleave water can also provide hydrogen without any reliance on fossil fuels. Hydrogen-burning fuel cells, by necessity, are still limited in their applicability. In contrast, a new approach (discussed in Chapter 11) uses directly liquid methanol (or its derivatives) in a fuel cell without first converting it to hydrogen. The direct oxidation liquid-fed methanol fuel cell (DMFC) has been developed in a cooperative effort between the University of Southern California and Caltech-Jet Propulsion Laboratory of NASA (who for a long time worked on fuel cells for the US space programs). In such a fuel cell, methanol reacts with oxygen of the air over a suitable metal catalyst, producing electricity while forming CO_2 and H_2O:

$$CH_3OH + 1.5O_2 \longrightarrow CO_2 + 2H_2O + \text{electrical energy}$$

More recently, it was found that the process could be reversed. Methanol (and related oxygenates) can be made from CO_2 via aqueous electrocatalytic reduction without prior electrolysis of water to produce hydrogen in what is termed a "regenerative fuel cell". This process can convert CO_2 and H_2O electrocatalytically into oxygenated fuels (i.e., formic acid, formaldehyde and methyl alcohol), depending on the electrode potential used in the fuel cell in its reverse operation.

The reductive conversion of CO_2 to methanol can also be carried out by catalytic hydrogenation using hydrogen. Hydrogen can be obtained by electrolysis of water (using all kinds of energy sources such as atomic, solar, wind, geothermal, etc.) or other means of cleavage (photolytic, enzymatic, etc.). Methanol is a convenient medium to store energy, and is an excellent transportation fuel. It is a liquid (with a boiling point of 64.6 °C) that can be easily transported using the existing infrastructure. Methanol can also be readily converted to dimethyl ether. Dimethylether has a relatively higher calorific value and is an excellent diesel substitute.

Methanol produced directly from methane (natural gas) without going to syngas or by recycling of CO_2 into CH_3OH or dimethyl ether can subsequently also be used to produce ethylene as well as propylene. These are the building blocks in the petrochemical industry for the ready preparation of synthetic aliphatic and aromatic hydrocarbons, and for the wide variety of derived products and materials, obtained presently from oil and gas, on which we rely so much in our everyday life.