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Introduction

Ever since our distant ancestors managed to light fire for providing heat, means for cooking and many other essential purposes, humankind's life and survival are inherently linked with an ever-increasing thirst for energy. From burning wood, vegetation, peat moss, and other sources to the use of fossil fuels such as coal, followed by petroleum oil and natural gas, humankind has thrived using Mother Nature's resources [1]. Fossil fuels are all composed of hydrocarbons with varying ratios of carbon and hydrogen. These hydrocarbons derived from petroleum, natural gas, or coal are essential in many ways to modern life and its quality. A large quantity of the world's hydrocarbons is used as fuel for propulsion, electrical power generation, and heating. The chemical, petrochemical, plastic, and rubber industries also depend on hydrocarbons as raw materials for their products. Indeed, most of the industrially significant synthetic chemicals are derived from petroleum sources. The overall use of oil in the world now exceeds 13 million metric tons per day (95 million barrels per day) [2]. The rapidly growing world population, which stood at 1.6 billion at the beginning of the twentieth century, has now exceeded 7 billion and is expected to reach 8–11 billion by the middle of the twenty-first century and up to 16 billion by 2100 [3] (Table 1.1 and Figure 1.1). This increase in world population and energy consumption, compared with our finite nonrenewable fossil fuel resources, which are being increasingly depleted, are clearly on a collision course. New solutions are needed for the twenty-first century and beyond to sustain the standard of living to which the industrialized world has become accustomed and the developing world is striving to achieve.

With an increasingly technological society, the world's resources have difficulty in keeping up with the demands. Satisfying our society's needs while safeguarding the environment and allowing future generations to continue to enjoy planet Earth as a hospitable home is one of the major challenges that we face today. Humans need not only food, water, shelter, clothing, and many other prerequisites but also huge and growing amounts of energy. In 2010, the world used about 1.33×10^{20} calories per year (154 PWh), equivalent to a continuous power consumption of about 18 TW, which is comparable to the production of 18 000 nuclear power plants each with a 1 GW output (Figure 1.2) [4]. With increasing world population, development, and higher standards of living, this demand for energy is expected to grow to 23 TW in 2025 and to about 30 TW in 2050.

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Table 1.1 World population (in millions).

1650	1750	1800	1850	1900	1920	1952	2000	2015	Projection 2050
545	728	906	1171	1608	1813	2409	6200	7400	8000–11 000

Source: United Nations, Department of Economic and Social Affairs, Population Division.

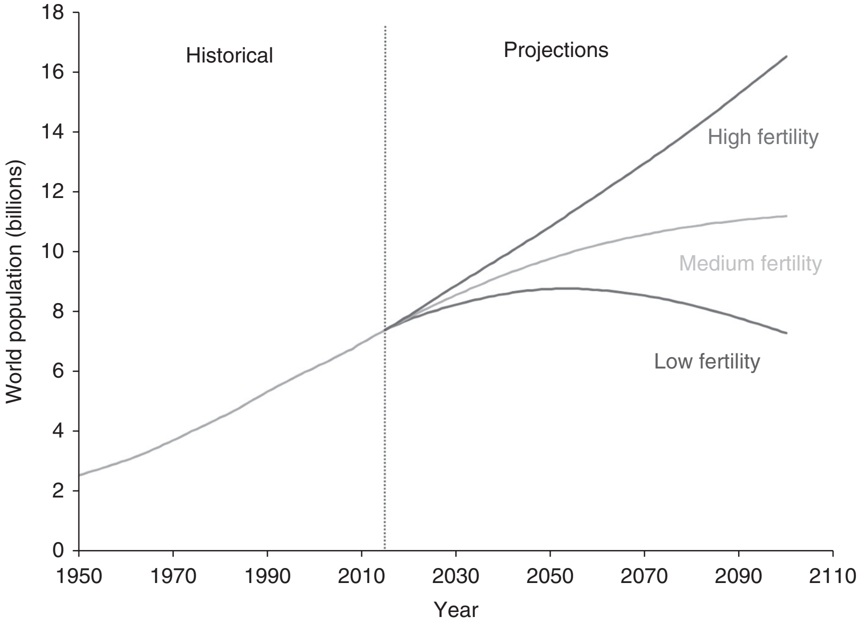


Figure 1.1 World population over time and in the future. *Source:* United Nations, Department of Economic and Social Affairs, Population Division.

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

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

Fossil Fuels: Petroleum oil, natural gas, shale gas, tar sand, shale bitumen, tight oil, and 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 are thus not renewable on the human timescale.

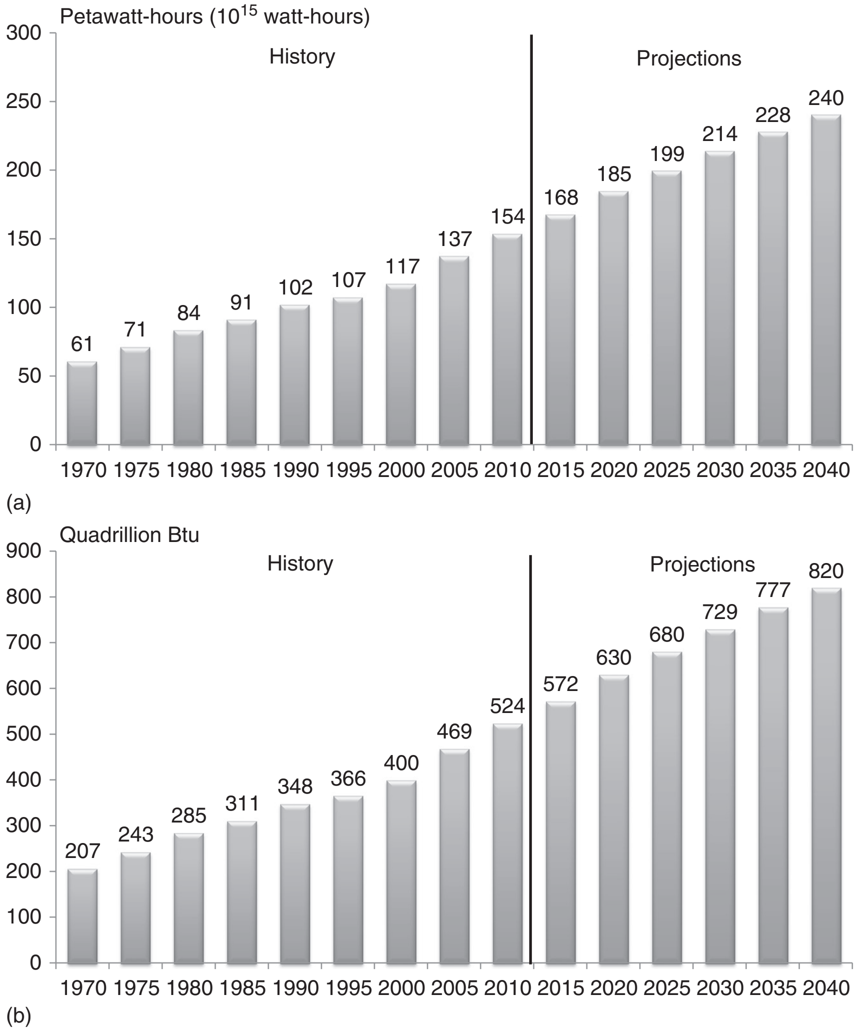


Figure 1.2 World primary energy consumption, 1970–2040 in units of (a) petawatt-hours; (b) Btu (British thermal units). *Source:* Based on data from: Energy Information Administration (EIA), International Energy Outlook 2013.

Nature has given us a remarkable gift in the form of oil and natural gas. It has been determined that a single barrel of oil has the energy equivalent of 12 people working all year, or 25 000 man hours [5]. With each American consuming on average about 23 barrels of oil per year, this would be equivalent to each of them having almost 300 people working all year long to power the industries and providing the household in order to maintain the current standard of living. Considering the present cost of oil, this is truly a bargain. The fossil fuels that were created over the ages are, however, being consumed rather rapidly by humankind. Petroleum and natural gas are used on a massive scale to generate energy and as raw materials for diverse man-made materials and products such as plastics, pharmaceuticals, and dyes that have been developed during the twentieth century. The United States' energy consumption, for example, is heavily based on fossil fuels, with atomic energy and other sources (hydro, geothermal, solar, wind, etc.) representing only a modest 18% of the energy mix (Table 1.2) [6].

With regard to electricity generation in the United States, coal, which represented for a long while the largest portion of the fuels used, is now almost at parity with natural gas at about 33% each, followed by nuclear energy around 20% (Table 1.3). Due to considerable environmental issues, availability of cheap domestic shale gas, and decreasing costs of electricity from renewable sources, the role of coal has been diminishing rapidly during the last decade.

Other industrialized countries obtain between 15% and 95% of their electrical energy from nonfossil sources (Table 1.4) [7].

Oil use has grown to the point, where the world in 2015 was consuming around 95 million barrels (1 barrel equals 42 gallons, i.e. some 160 l) a day, or about

Table 1.2 United States energy consumption by fuel (%).

Energy source	1960	1970	1980	1990	2000	2005	2010	2015
Oil	44.2	43.5	43.7	39.6	38.8	40.4	36.7	36.7
Natural gas	27.5	32.1	26.1	23.3	24.2	22.6	25.2	29.0
Coal	21.8	18.1	19.7	22.6	22.8	22.8	21.3	16.0
Nuclear energy	0.002	0.4	3.5	7.2	7.9	8.1	8.6	8.6
Hydro-, geothermal, solar, wind, etc. energy	6.5	6.0	7.0	7.2	6.2	6.1	8.2	9.7

Source: U.S. Census Bureau, Statistical Abstract of the United States and U.S. Energy Information Administration.

Table 1.3 Electricity generation in the United States by fuel (%).

Energy source	1990	2000	2005	2010	2015
Coal	52.5	51.7	49.8	45.1	33.3
Petroleum	4.2	2.9	3.0	0.9	0.7
Natural gas	12.6	16.2	19.0	23.9	32.9
Nuclear	19.0	19.8	19.3	19.7	19.7
Hydroelectric	9.6	7.2	6.6	6.3	6.1
Geothermal	0.5	0.4	0.4	0.4	0.4
Wood	1.1	1.0	0.9	0.9	1.0
Waste	0.438	0.607	0.594	0.453	0.535
Wind	0.092	0.147	0.361	2.306	4.703
Solar	0.013	0.013	0.012	0.032	0.614

Source: U.S. Census Bureau, Statistical Abstract of the United States and U.S. Energy Information Administration.

Table 1.4 Electricity generated in selected industrialized countries by type of fuel (%, 2015).

Country	Total electricity production (TWh)	Conventional thermal	Nuclear	Hydroelectric	Geothermal, solar, wind, biofuels and waste	Total nonfossil
France	568.2	6.0	77.0	10.5	6.5	94.0
Canada	631.6	17.9	16.5	60.1	5.6	82.1
United Kingdom	337.7	52.8	20.8	2.6	23.7	47.2
Germany	651.5	53.5	14.1	3.8	28.6	46.5
Italy	282.0	59.5	0.0	16.0	24.4	40.5
United States	4312.2	66.9	19.3	6.3	7.5	33.1
Korea	548.7	67.6	30.0	1.1	1.3	32.4
Japan	1014.9	81.7	0.9	9.0	8.4	18.3

Source: International Energy Agency, Electricity Information 2016.

13 million metric tons [2]. Fortunately, we still have significant worldwide reserves, including heavy oils, oil shale, tar sands, and even larger deposits of coal, a mixture of complex carbon compounds more deficient in hydrogen than in oil and gas. Our more plentiful coal reserves may last for 200 years or more, but at a higher socioeconomical 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 scarcer, more expensive, and will not last for very long. With a world population exceeding 7 billion and still growing, 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 proven incorrect (Figure 1.3). As a matter of fact, the proven reserves of oil and gas have been steadily growing over the years due to the discovery of new fields and the adoption of novel technologies allowing the extraction of fossil fuels from sources that could not be previously exploited economically. Proven oil reserves, instead of being depleted, have in fact almost quadrupled during the past 50 years and are now close to 250 billion tonnes (more than 1.5 trillion barrels) [2]. This seems so impressive that many people assume that there is no real oil shortage in sight.

The question is, however also, what is meant by “depletion.” Increasing consumption due to improving standards of living, coupled with a growing world population, makes it more realistic to consider reserves on a per-capita basis. If we do this, it becomes evident that our known reserves will last for a shorter period of time. Even if all other factors are taken into account (new findings, savings, alternate sources, etc.), our overall reserves will inevitably decrease and thus we will increasingly face a major shortage. Oil and gas are finite resources. Although they will not be depleted overnight, market forces of supply and demand will start to drive their prices up to levels that nobody even wants to contemplate presently. Therefore, if we do not find new solutions, we will eventually face a real crisis.

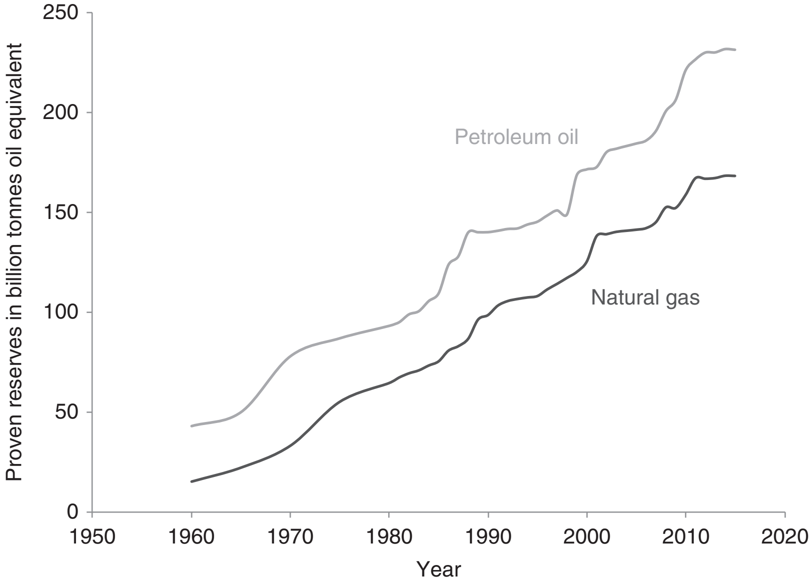


Figure 1.3 Proven oil and natural gas reserves (in billion tonnes oil equivalent). *Source:* For 1980–2016: BP statistical review of world energy 2016.

Humankind wants all the advantages that an industrial society can give to all its citizens. We 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 about 2.5 barrels, whereas it is about ten-fold this level in the United States (23 barrels per capita per year) [2]. Oil use in China is expected to at least double during the next decade, and this alone equals more than the consumption of the United States – reminding us of the magnitude of the problem that we will face. Not only world population growth but also the increasing energy demands from China, India, and other fast developing countries are already putting great pressure on the world's oil reserves, and this, in turn, will eventually contribute to price escalation. Large price fluctuations, with temporary sharp drops, can be expected, but the upward long-term trend of increasing oil prices seems inevitable. We will need to get used to higher prices, not as a matter of any government policy but as a fact of market forces over which free societies have very little control.

As we continue to burn our hydrocarbon reserves to generate energy at an alarming rate, diminishing resources and sharp price increases will increasingly lead to a need to supplement or replace them by feasible alternatives. Although petroleum oil is one of the greatest bargains nature has given us, alternative energy and fuel sources and synthetic substitutes are generally costlier. However, with a barrel of oil priced between $30 and $150, within wide market fluctuations, some of these are already becoming economically viable.

Synthetic oil product and substitutes are feasible. Their production has been proven on an industrial scale via synthesis-gas (syngas), a mixture of carbon monoxide and hydrogen obtained from the incomplete combustion of coal or natural gas, which, however, are themselves nonrenewable. Coal conversion was used in Germany during World War II and in South Africa during the boycott years of the Apartheid era [8]. Nevertheless, the size of these operations hardly amounted to 0.3% of the present United States consumption alone. This route – the so-called Fischer–Tropsch synthesis – is also highly energy consuming, giving complex product mixtures and generating large amounts of carbon dioxide, thereby contributing to global warming. Thus, it can hardly be seen as the technology of the future. Nevertheless, to utilize still-existing large coal and natural gas reserves, their conversion to liquid fuels through syngas is being applied on a large scale in China, the Middle East, and other locations. However, these plants can provide only a minor amount of the world's consumption of transportation fuels, which, by itself, is in excess of 58 million barrels per day. This figure demonstrates the enormity of the problem we face. New and more efficient processes are clearly needed. Some of the required essential new basic science and technology to produce synthetic oil more efficiently are already being developed. Still, abundant natural gas could, for example, be directly converted to liquid hydrocarbon fuels and products, without passing through syngas. The use of our even larger coal resources to produce synthetic oil could also extend their availability. However, these would not solve the associated global climate change problems. Thus, 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.) into bioethanol, is being pursued. Although ethanol can be used as a gasoline additive or alternative fuel, the enormous quantities of transportation fuel needed clearly limit the applicability to specific countries and situations. Plant-based substitutes are also being developed as renewable equivalents of diesel fuel, although their role is also limited and their environmental impact and benefits are questionable. In addition, biofuels can affect food prices by competing for the same agricultural resources [9].

The advent of atomic energy opened up a fundamental new possibility, but also created dangers and concerns related to the safety of radioactive by-products. It is regrettable that these considerations brought any further development of atomic energy almost to a standstill, at least in most parts of the Western world. On the other hand, concerns about the use of nuclear power especially after the accidents of Chernobyl and Fukushima are understandable. Nevertheless, if we want to be serious about the mitigation of carbon dioxide emission, atomic energy, albeit made safer and cleaner, is a leading alternative that does not produce CO_2. Problems including those of safe storage and disposal of radioactive waste products must be solved. Pointing out difficulties and hazards as well as regulating them is necessary, and solutions to overcome them are essential and certainly feasible.

Even though the generation of energy by burning nonrenewable fossil fuels will last only for a relatively limited period in the future, it is generating serious environmental problems. When hydrocarbons are burned, as pointed out, they produce harmful carbon dioxide (CO_2) and water (H_2O). The very large amounts of CO_2 released contribute to the so-called "greenhouse warming effect" of our planet, which is causing grave environmental concerns.

The relationship between the atmospheric CO_2 content and temperature was first studied scientifically by Arrhenius as early as 1895 [10]. The climate change and warming/cooling trends 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 global temperature. Human activities have increased CO_2 emissions, but the effect of these emissions is only superimposed on nature's own variable cycles.

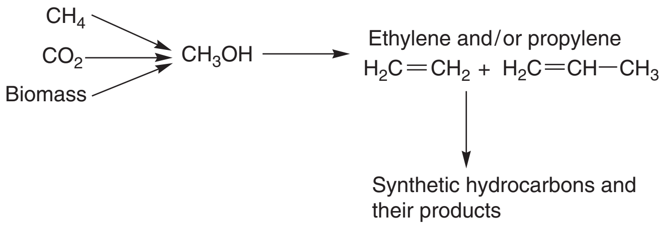
It is also a great challenge to reverse the combustion process and to chemically produce, both efficiently and economically, hydrocarbon fuels from CO_2 and H_2O. Nature, in its photosynthesis, achieves it by recycling CO_2 with water into new plant life using the Sun's energy. Although fermentation and other processes can convert plant life into biofuels and products, the natural formation of new fossil fuels takes a very long time, making them nonrenewable on the human timescale.

"The Methanol Economy®" – the specific subject of our book – elaborates a new approach of how humankind can decrease and eventually liberate itself from its dependence on diminishing oil and natural gas (and eventually coal) reserves while mitigating global warming caused by excessive carbon dioxide released from their combustion. The "Methanol Economy" is in part based on the more efficient conversion of still-existing fossil-fuel resources to methanol or dimethyl ether (DME) and, most importantly, on their production by chemical recycling of CO_2 emissions from fossil-fuel-burning power plants as well as other industrial and natural sources. Eventually, even atmospheric CO_2 itself will be captured and recycled by using catalytic or electrochemical methods. This represents a chemical regenerative carbon cycle alternative to natural photosynthesis [11–13].

Both methanol and DME are excellent transportation and industrial fuels on their own for internal combustion engines, electrical power generation, and household uses, replacing gasoline, diesel fuel, natural gas, etc. Methanol is also a suitable fuel for fuel cells, being capable of producing electric energy by reacting with atmospheric oxygen contained in the air. DME is readily obtained by dehydration of methanol.

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O$$

It should be emphasized that the "Methanol Economy" itself does not produce energy. Methanol or DME only stores energy more conveniently and safely compared, for example, with extremely difficult to handle and highly volatile hydrogen gas, which is the basis of the so-called "Hydrogen Economy" [14, 15]. Besides being most convenient energy storage materials and suitable transportation fuels, methanol and DME can also be easily converted into ethylene and/or propylene. These are essential 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. They are presently obtained from our diminishing oil and gas resources, on which we rely so much in our everyday life.



The far-reaching implications of the new “Methanol Economy” have great significance and societal benefit for humankind. As mentioned, the world is presently consuming about 95 million barrels of oil each day, and about two-thirds as much natural gas equivalent, both being derived from our declining and nonrenewable natural sources. Oil, natural gas, and coal were formed by nature over the eons in scattered and frequently increasingly difficult-to-access locations such as under deserts, in the depths of the seas, the inhabitable reaches of the polar regions, and so on. In contrast, recycling of CO_2 from human activities, industrial exhausts, or natural sources, and eventually from the air itself, which belongs to all of us, opens up a new vista. The energy needs of humankind, in the foreseeable future, will be fulfilled using any available source, including alternative sources and atomic energy. As we still cannot store energy efficiently on a large scale, new ways of storing energy are also needed. The production of methanol offers a convenient means of large-scale energy storage. Even now, existing nuclear and renewable energy power plants, during off-peak periods, could, by electrolysis of water, generate the hydrogen needed to produce methanol from CO_2. Other means of cleaving water by thermal, biochemical (enzymatic), or photovoltaic (using energy from the Sun, our ultimate clean energy source) pathways are also being developed.

Initially, CO_2 will be recycled from high-level industrial emissions to produce methanol and to derive synthetic hydrocarbons and their products. CO_2 is already recoverable from sources such as flue gases of power plants burning fossil fuels, fermentation processes, the calcination of limestone in cement production, production of steel and aluminum, and so on. CO_2 accompanying natural gas, geothermal energy, and other natural sources will also be used. The CO_2 content of these emissions is high and can be readily separated and captured. In contrast, the average CO_2 content in the air is very low (0.04%) (Table 1.5). Atmospheric CO_2 is therefore presently difficult to utilize on an economic basis. However, these difficulties can be overcome by ongoing developments using selective absorption or other separation technologies. Moisture, the by-product of CO_2 capture from the air, is a potentially important source of clean water. This could also help the economies of CO_2 capture. The ability of humankind to technologically recycle CO_2 to useful fuels and products will eventually provide an inexhaustible renewable carbon source.

Recycling excess CO_2 evolving from human (anthropogenic) activities into methanol and DME, and further developing and transforming them into useful fuels and synthetic hydrocarbons and products, will help alleviate the question of

Table 1.5 Composition of air.

Nitrogen	78%
Oxygen	20.90%
Argon	0.90%
Carbon dioxide	0.04%
Water (moisture)	up to ~8% (variable)
Methane	trace amounts
Nitrogen oxides	
Ozone	

our diminishing fossil-fuel resources and at the same time help mitigate global warming caused at least in part by human-made greenhouse gases. The conversion of the captured CO_2 to methanol can be achieved by catalytic hydrogenation with H_2 generated by electrolysis (or other cleavage technology including photolytic, enzymatic, etc.) of water using any available energy such as solar, wind, geothermal, and nuclear.

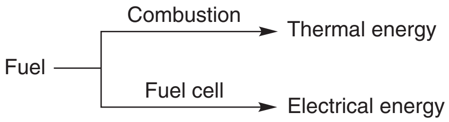
$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

Alternatively, natural gas, when available, can also be used for CO_2 to methanol conversion including improved processes such as our proposed bi-reforming (see Chapter 12) [16, 17].

$$3CH_4 + 2H_2O + CO_2 \rightarrow 4CH_3OH$$

One highly efficient method of producing electricity directly from varied fuels including methanol and DME is achieved in fuel cells via catalytic electrochemical oxidation.

A **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 William Grove during the early 1800s, but their practical use was only developed with the advent of space exploration. Most fuel cell technologies are still based on Grove's approach; that is, hydrogen and oxygen (air) are combined in an electrochemical-cell-like device, producing water and electricity. This process is clean, giving only water as a by-product. Hydrogen itself, however, must be first produced in an energy-consuming process. The handling of the highly volatile hydrogen gas is not only technically difficult but also dangerous. Nonetheless, the use of hydrogen-based 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 fossil-fuel sources using reforming, which converts them into a mixture of hydrogen and carbon monoxide. The carbon monoxide is further converted by reacting with water to carbon dioxide and hydrogen. These two gases are then separated. Although this process relies on our diminishing fossil-fuel sources, electrolysis or other processes to cleave water also provide hydrogen without any reliance on fossil fuels. Hydrogen-burning fuel cells are still limited in their applicability. In contrast, a new approach (discussed in Chapter 11) uses directly convenient liquid methanol, or its derivatives, in fuel cells without first converting them into hydrogen. The direct oxidation liquid-fed methanol fuel cell (DMFC) has been developed in a cooperative effort between our group at the University of Southern California and a research group at the Caltech – Jet Propulsion Laboratory of NASA, who, for a long time, has built fuel cells for the U.S. space programs [18, 19]. In such a fuel cell, methanol reacts with oxygen present in the air over a suitable metal catalyst, producing electricity directly while forming CO_2 and H_2O:

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

It was also found that this process can 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 methanol), depending on the electrode material and potential used in the fuel cell in the reverse operation.

Methanol is already one of the most important industrial chemicals and is now starting to be developed as the base material for the replacement of oil-based products from transportation fuels to heating (household) gas/oil, as well as various derived products and materials, for energy storage, and even synthetic proteins and carbohydrates for animal feed. Although methanol is still mainly produced from fossil fuels, the production of synthetic regenerative methanol from CO_2 and H_2O is a proven concept that will gain more ground as fossil-fuel-associated issues are mounting. Methanol can be essentially considered as a bridge fuel/feedstock between a fossil-fuel-dominated present and a sustainable tomorrow. The "Methanol Economy" thus has a broad and promising future.