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Introduction

Ever since our distant ancestors managed to light fire for providing heat, means for cooking and many essential purposes, humankind's life and survival has been inherently linked with an ever-increasing thirst for energy. From burning wood, vegetation, peat moss and other sources to the use of coal, followed by petroleum oil and natural gas (fossil fuels), we have thrived using Nature's resources [1]. Fossil fuels include coal, oil and gas – all composed of hydrocarbons with varying ratios of carbon and hydrogen.

Hydrocarbons derived from petroleum oil, natural gas or coal are essential in many ways to modern life and its quality. The bulk of the world's hydrocarbons are used as fuels for propulsion, electrical power generation and heating. The chemical, petrochemical, plastics and rubber industries also depend 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 is now close to 12 million metric tons per day [2]. An ever-increasing world population (presently nearing 7 billion and projected to increase to 8–11 billion by the middle of the twenty-first century [3]; 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 twenty-first century to sustain the standard of living to which the industrialized world has 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 twentieth century, is now approaching 7 billion. With an increasingly technological society, the world's resources have difficulty keeping up with 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. Man needs not only food, water, shelter, clothing and many other prerequisites but also increasingly huge amounts of energy. In 2004 the world used some 1.13×10^{20} calories per year (131 Petawatt-hours), equivalent to a continuous power consumption of about 15 terawatts (TW), which is comparable to the production of 15 000 nuclear power plants each of 1 GW output [4]. With increasing world population, development and higher standards of living, this demand for energy is expected to grow to 21 TW in 2025 (Figure 1.1). In 2050 the demand is expected to reach 30 TW.

Table 1.1 World population.

Year	1650	1750	1800	1850	1900	1920	1952	2000	2009	Projection 2050 ^a
Population (millions)	545	728	906	1171	1608	1813	2409	6200	6800	8000 to 11 000

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

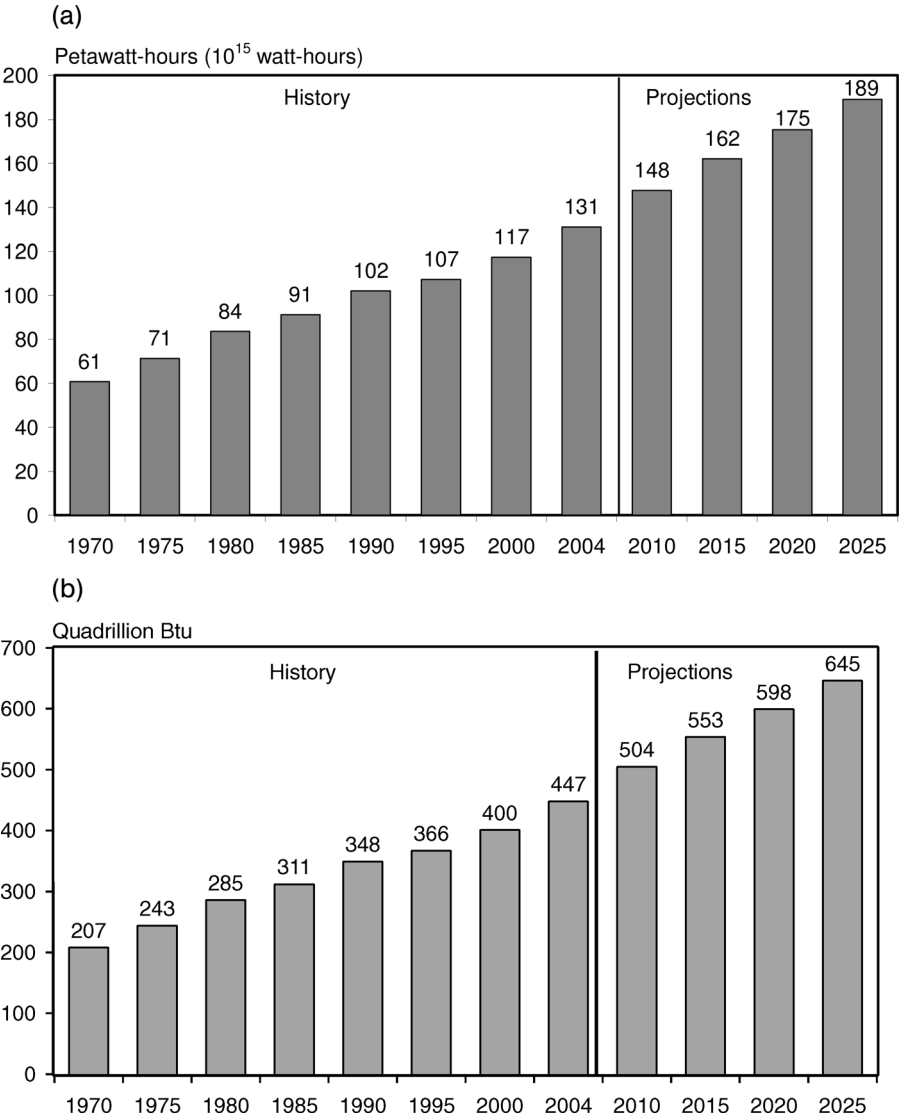


Figure 1.1 World primary energy consumption 1970–2025 in units of (a) petawatt hours; (b) Btu (British thermal units). (Based on data from: Energy Information Administration (EIA), International Energy Outlook 2007.)

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

When fossil fuels such as coal, oil or natural gas (i.e., hydrocarbons) are burnt 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 the combustion products. 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 timescale.

Nature has given us, in the form of oil and natural gas, a remarkable gift. 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 25 barrels of oil per year, this would amount to each of them having 300 people working all year long to power the industries and man their households to maintain their current standard of living. Considering the present cost of oil, this is truly a bargain. What was created over the ages, however, mankind is consuming rather rapidly. Petroleum and natural gas are used on a massive 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 twentieth 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% of the energy mix (Table 1.2) [6].

With regard to electricity generation, coal still represents about half of the fuel used, with some 19% for natural gas and 19% for nuclear energy (Table 1.3).

Other industrialized countries, in contrast, obtain between 20% and 90% of their electrical energy from non-fossil sources (Table 1.4) [7].

Oil use has grown to the point where the world consumption is around 85 million barrels (1 barrel equals 42 gallons, i.e., some 160 L) a day, or almost 12 million metric

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

Energy source	1960	1970	1980	1990	2000	2005
Oil	44.2	43.5	43.7	39.6	38.8	40.4
Natural gas	27.5	32.1	26.1	23.3	24.2	22.6
Coal	21.8	18.1	19.7	22.6	22.8	22.8
Nuclear energy	0.002	0.4	3.5	7.2	7.9	8.1
Hydro-, geothermal, solar, wind, and so on	6.5	6.0	7.0	7.2	6.2	6.1

Source: U.S. Census Bureau, *Statistical Abstract of the United States 2008*, Section 19, Energy and Utilities.

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

	1990	2000	2005
Coal	52.5	51.7	49.8
Petroleum	4.2	2.9	3.0
Natural gas	12.6	16.2	19.0
Nuclear	19.0	19.8	19.3
Hydroelectric	9.6	7.2	6.6
Geothermal	0.5	0.4	0.4
Wood	1.1	1.0	0.9
Waste	0.438	0.607	0.594
Wind	0.092	0.147	0.361
Solar	0.013	0.013	0.012

Source: U.S. Census Bureau, *Statistical Abstract of the United States 2008*, Section 19, Energy and Utilities.

tonnes [2]. Fortunately, we still have significant worldwide reserves left, 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 nearing 7 billion and still growing (as indicated earlier, it may reach 8–11 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) [2, 8]. Until fairly recently the reserves have been growing, but lately they seem to have leveled off.

The question is, however, what is meant by “depletion” and what is the real extent of our reserves? Proven oil reserves, instead of being depleted, have in fact almost

Table 1.4 Electricity generated in industrial countries by non-fossil fuels (%; 2004).

Country	Conventional thermal	Hydroelectric	Nuclear	Geothermal, solar, wind, wood and waste	Total non-fossil
France	9.4	10.9	78.6	1.1	90.6
Canada	25.7	58.0	14.7	1.6	74.3
Germany	61.9	3.6	27.5	6.9	38.1
Japan	62.2	9.2	26.4	2.2	37.8
Korea, South	62.8	1.2	35.9	0.1	37.2
United States	71.0	6.7	19.8	2.4	29.0
United Kingdom	75.5	1.3	20.0	3.2	24.5
Italy	81.1	14.1	0.0	4.8	18.9

Source: Energy Information Administration, *International Energy Annual 2007*, World Net Electricity Generation by Type, 2004.

Table 1.5 Proven oil and natural gas reserves (in billion tonnes oil equivalent).

Year	Oil	Natural gas
1960	43	15
1965	50	22
1970	78	33
1975	87	55
1980	91	70
1986	95	87
1987	121	91
1988	124	95
1989	137	96
1990	137	108
1995	140	130
2002	160	160
2003	162	162
2004	162	161
2005	164	162
2006	165	163

Source for 1995–2006: *BP Statistical Review of World Energy* [2].

doubled during the past 30 years and now exceed 150 billion tonnes (more than one trillion barrels) [2]. This seems so impressive that many people assume that there is no real oil shortage in sight. However, increasing consumption due to increasing standards of living, coupled with a growing world population, makes it more realistic to consider per-capita reserves. Based on this consideration, it becomes evident that our known accessible reserves will not last for much more than this century. 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 will not become exhausted overnight, but market forces of supply and demand will start to drive the prices up to levels that nobody even wants to presently contemplate. Therefore, if we do not find new solutions, we will face a real crisis.

Humankind wants the advantages that an industrial society can give to all of its citizens. We essentially rely on energy, but the level of consumption varies vastly in different parts of the world (industrialized versus developing and underdeveloped countries). At present for example, the annual oil consumption per capita in China is still only two to three barrels, whereas it is about ten-fold this level in the United States [2]. 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 from 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. Large price fluctuations, with temporary sharp drops, can be expected, but the upward long-term trend in oil prices is inevitable.

Even though the generation of energy by massive burning of non-renewable fossil fuels (including oil, gas and coal) is feasible only for a relatively short period in the future, it is generating serious environmental problems (*vide infra*). The advent of atomic energy opened up a fundamental new possibility, but also created dangers and concerns regarding the safety of radioactive by-products. Regrettably, these considerations brought any further development of atomic energy almost to a standstill, at least in most of the Western world. Whether we like it or not, we clearly have few alternatives and will rely on using 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, but solutions to overcome them are essential and certainly feasible.

As we continue to burn our hydrocarbon reserves to generate energy at an alarming rate, diminishing resources and sharp price increases will inevitably lead to the need to supplement or replace them by feasible alternatives. Alternative energy and fuel sources and synthetic oil products are, however, more costly. Nature's petroleum oil and natural gas are the greatest gifts we will ever have. However, with a barrel of oil presently priced between \$30 and \$150, within wide market fluctuations, some synthetic manufacturing processes are already becoming economically viable. Regardless, it is clear that 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 limited control.

Synthetic oil products are feasible. Their production was proven via synthesis-gas (syn-gas), a mixture of carbon monoxide and hydrogen obtained from the incomplete combustion of coal or natural gas, which, however, 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 [9]. 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. It thus can hardly be seen on its own as the technology of the future. To utilize still-existing large natural gas reserves, their conversion into liquid fuels through syn-gas is presently being developed; for example, on a large scale in Qatar, where Shell is spending over \$10 billion on the construction of gas-to-liquid (GTL) facilities, to produce about 140 000 barrels per day of liquid hydrocarbon products, mainly sulfur-free diesel fuel. Chevron in partnership with Sasol has already built a GTL unit in Qatar with a capacity of 34 000 barrels per day. However, even when running at full capacity, these plants will provide only a daily total of some 180 000 barrels, compared with present world use of transportation fuels alone in excess of 45 million barrels 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 already being developed. As will be discussed below, still abundant natural gas can be, for example, directly converted, without first producing syn-gas, into 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.) into ethanol is evolving. Whereas ethanol can be used as a gasoline additive or 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 developed as renewable equivalents of diesel fuel, although their role in the total energy picture is again limited. Biofuels have also started to affect food prices by competing for the same agricultural resources [10].

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 chemically produce, efficiently and economically, hydrocarbon fuels from CO_2 and H_2O . Nature, in its process of photosynthesis, recycles CO_2 with water into new plant life using the Sun's energy. While 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 non-renewable on the human timescale.

The “Methanol Economy®” [11] – the 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 even coal) reserves while mitigating global warming caused by the carbon dioxide released by their excessive combustion. The “Methanol Economy” is in part based on the more efficient direct conversion of still-existing natural gas resources into methanol or dimethyl ether, and most importantly on their production by chemical recycling of CO_2 from the exhaust gases of fossil fuel-burning power plants as well as other industrial and natural sources. Eventually, even atmospheric CO_2 itself can be captured and recycled using catalytic or electrochemical methods. This represents a chemical regenerative carbon cycle alternative to natural photosynthesis [12]. Methanol and dimethyl ether (DME) are both excellent transportation and industrial fuels on their own for internal combustion engines and household uses, replacing gasoline, diesel fuel and natural gas. Methanol is also a suitable fuel for fuel cells, being capable of producing electric energy by reaction with atmospheric oxygen contained in the air. It should, however, be emphasized that the “Methanol Economy” *per se* is not producing energy. In the form of methanol or DME it only stores energy more conveniently and safely compared to extremely difficult to handle and highly volatile alternative hydrogen gas, which is the basis of the so-called “hydrogen economy” [13, 14]. Besides being most convenient energy storage materials and suitable transportation fuels, methanol and DME can also be catalytically converted into ethylene and/or propylene, the building blocks of synthetic hydrocarbons and their products presently obtained from our diminishing oil and gas resources.

The far-reaching applications of the new “Methanol Economy” approach clearly have great implications and societal benefit for humankind. As mentioned, the world is presently consuming about 85 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 such as under desert areas, in the depths of the seas, the inhabitable reaches of the Polar Regions, and so on. In contrast, the recycling of CO₂ from industrial exhausts or natural sources, and eventually from the 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 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 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 from CO₂. Other means of cleaving water by thermal, biochemical (enzymatic) or photovoltaic (using energy from the Sun, our ultimate clean energy source) pathways are also evolving.

Initially, CO₂ will be recycled from high level industrial emissions to produce methanol and to derive synthetic hydrocarbons and their products. CO₂ accompanying natural gas, geothermal and other natural sources will also be used. The CO₂ content of these emissions is high and can be readily separated and captured. In contrast, the average CO₂ content of air is very low (0.038%) (Table 1.6). Atmospheric CO₂ 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. Humankind's ability to technologically recycle CO₂ to useful fuels and products will eventually provide an inexhaustible renewable carbon source.

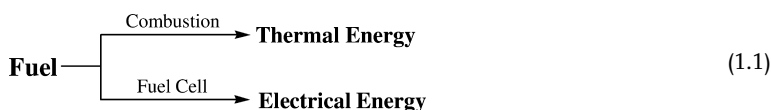
Carbon dioxide can readily be recovered from industrial sources, such as flue gas emissions of power plants burning carbonaceous fossil fuels (coal, oil and natural gas), fermentation processes, the calcination of limestone in cement production, production of steel and aluminum, and so on, as well as natural CO₂ accompanying natural gas, geothermal sources and others. As these plants and operations emit very large amounts of CO₂ they contribute to the increasing "greenhouse warming effect" of our planet, which is causing grave environmental concern. The relationship between the atmospheric CO₂ content and temperature was first studied scientifically by Arrhenius as early as 1895 [15]. 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 CO₂ content in the atmosphere and Earth's surface temperature.

Table 1.6 Composition of air.

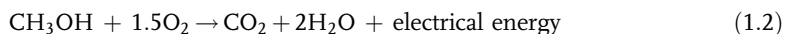
Nitrogen	78%
Oxygen	20.90%
Argon	0.90%
Carbon dioxide	0.038%
Water	Few % (variable)
Methane, nitrogen oxides, ozone	Trace amounts of each

Recycling excess CO_2 evolving from human activities into methanol and dimethyl ether, and further developing and transforming them into useful fuels and synthetic hydrocarbons and products, will thus not only help to alleviate the question of our diminishing fossil fuel resources but at the same time help to mitigate global warming caused by human-made greenhouse gases.

One highly efficient method of producing electricity directly from varied fuels is achieved in fuel cells via their catalytic electrochemical oxidation, primarily that of hydrogen (Equation 1.1).



The principle of fuel cells was first recognized by William Grove during the early 1800s, but their practical use was only recently developed. 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. The process is clean, giving only water as a by-product. Hydrogen itself, however, must be first produced in an energy-consuming process, using at present mainly fossil fuels and to a lesser extent the electrolysis of water. The handling of 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 reformers, which converts them into a mixture of hydrogen and carbon monoxide from which hydrogen is then separated. Although this process relies mostly 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, convenient liquid methanol, or its derivatives, in fuel cells without first converting it 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 Caltech-Jet Propulsion Laboratory of NASA, who for a long time developed fuel cells for the U.S. space programs [16, 17]. In such a fuel cell, methanol reacts with oxygen present in the air over a suitable metal catalyst, producing electricity while forming CO_2 and H_2O :

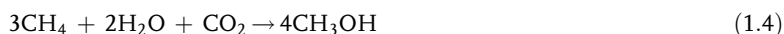


More recently, it was found that the process could also be reversed. Methanol and related oxygenates can be made from CO_2 via aqueous electrocatalytic reduction without prior electrolysis of water to produce hydrogen in what is termed a "regenerative fuel cell." This process can convert CO_2 and H_2O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

The reductive conversion of CO_2 into methanol is primarily carried out by catalytic hydrogenation using hydrogen produced by electrolysis of water (using any available energy sources such as atomic, solar, wind, geothermal, etc.) or other means of cleavage (photolytic, enzymatic, etc.):



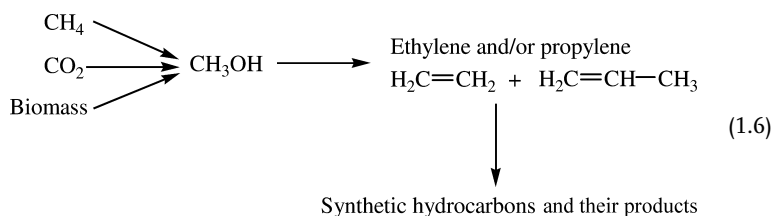
Natural gas, when available, can also be used for the CO_2 to methanol conversion, including improved processes such as our proposed bi-reforming (Chapter 10) [18]:



As mentioned, methanol is a convenient energy storage material and an excellent transportation fuel. It is a liquid, with a boiling point of 64.6°C , allowing it to be transported easily and stored using existing infrastructure. Methanol can also be readily converted into dimethyl ether, which has a higher calorific value and is an excellent diesel fuel and household gas substitute:



Methanol and DME produced directly from methane (natural gas) without going to syn-gas or by recycling of CO_2 can subsequently also be used to produce ethylene as well as propylene (Equation 1.6):



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.