

Chapter 2

Fossil Feedstocks—What Comes After?

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2.1 Fossil Raw Materials for Energy and Chemical Feedstocks

The abundant availability of fossil raw materials such as crude oil, natural gas, brown coal (lignite) and coal has given rise to our enormous prosperity. Fossil raw materials satisfy our energy needs and they provide a wide spectrum of chemicals that enrich our lives. This success is mainly based on the availability of fossil raw materials in vast amounts, energy density and transportability via pipelines. The so-called polymer age would have been impossible without the inexpensive wealth of oil and gas. Fossil raw materials make up approximately 80 % of world's energy supply (crude oil: 37 %, coal: 25 %, natural gas: 23 %). By 2035, the International Energy Agency expects a decline for fossil raw materials to 75 % while renewables increase, from today's 13 to 18 % of the world's energy supply [1]. China will be the world's largest energy consumer.

The worldwide material use for chemicals is approximately 10 %. To better understand the relationships and mutual dependences within the fossil raw material industry, a differentiation between use for energy and use for materials (chemicals) is helpful. For instance, naphtha produced in fuel refineries is used by the chemical industry for the manufacture of C_2 – C_4 olefins and aromatics, which are the basic chemicals for mass polymers such as polyethylene, polypropylene and polystyrene. However, they are also used to save heating energy in houses via insulation, thus reducing energy consumption.

Approximately one-third of fossil raw materials for energy are used for transportation, one third for generation of electricity, and one-third for heating purposes. In the United States, 97 % of all air, sea and land transportation systems are crude oil-based. It is obvious that the availability and price of chemical feedstocks

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for organic materials, using only 10 %, will be dictated by the crude oil manufacturing industry.

The rapidly growing world population, the increasing per capita consumption by industrialised countries, and the thriving economies of countries such as China and India give rise to concern and worry regarding the future availability of fossil raw materials. The biggest impact on future availability comes from the world population growth. The population grows every year by 80 million people, which is close to the population of Germany. If China, with its population of 1.3 billion people, begins to consume the same amount of crude oil as Germany (93 Mio tonnes in 2010), China alone would use more than half of the world's crude oil production. This raises some questions: Will we be in a position to cover all future demand? Where in the future will we obtain our fossil raw materials to meet world's energy and material need? Do we have alternatives to fossil raw materials?

In addition, the burning of fossil fuels to carbon dioxide is assumed to contribute significantly towards climate change, causing massive environmental problems (the greenhouse effect). The majority of experts agree that there are still sufficient fossil reserves and resources to satisfy the demand in the next decades. Oil companies have provided many energy scenarios, which easily can be found in internet or ordered directly [2, 3].

2.1.1 Availability of Crude Oil, Natural Gas and Coal

About 90 % of the crude oil reserves and 85 % of the natural gas reserves are state owned. A few producers, mainly in the Middle East, control more than 50 % of the oil and gas. Considering the recent unrest in Arabian countries, there is reason for concern regarding a secure supply. In addition, prices fluctuate and are volatile. Firm predictable prices and reliable supply form the basic conditions for planning and investment.

To attach a timeframe to the availability of fossil raw materials, experts refer to the depletion point, which is the number of years obtained by dividing the global reserves by global consumption [4]: crude oil: 42 years, natural gas: 63 years, hard coal: 159 years, and lignite: 227 years. The depletion points are based on reserves and not resources, which are much bigger but less reliable. Nevertheless, the fossil raw material reserves—formed by nature over eons and therefore not renewable in our timeframe—are finite at a time in the not-too-distant future.

There is growing understanding that we have to economise our energy consumption, search for alternatives and move toward energy conservation, such as the following:

- Better utilisation of energy: Improve efficiency, which could come from different areas, such as material science, bionics, engineering, biotechnology and natural sciences

- Improved technologies for using energy and exploitation of fossil raw materials
- Changes in mobility (going electric) and search for better/other transportation means (fuel cells, biofuels, hydrogen economy, methanol economy)
- Better transport and storage of energy (smart grids, smart houses and cities)
- Search for new energy resources, including nuclear
- Use of microbes, which produce underground methane
- CO₂ avoidance, storage and utilisation.

All of these items will change our lifestyles. Politicians, scientists, industry and citizens are challenged to make this change possible. Politicians must forward policies that are targeted at specific technologies, which often involve heavy initial subsidising. Many countries look at Germany, which has introduced an ambitious programme that moves away from nuclear energy to 35 % renewable electric energy by 2020.

Due to the vast complexity and scale (there are limits to the rate at which new technologies can be developed), there is no quick solution to move away from fossil raw materials and carbon energy [5]. If renewable electricity generated by the sun can be implemented soon, the depletion points for fossil raw materials will be extended. Most likely, however, we will have to deal with an energy mix for a long time to come.

The depletion point for crude oil is given as 42 years. How reliable is this number? Great uncertainties surround this question. We can hope to discover new oil fields (deep water, arctic). The recovery rate can be increased by improved recovery methods. Up from 20 to 30 % half a century ago, many fields are now targeting a 50 % recovery rate, with the best surpassing 70 %. More sophisticated enhanced oil recovery technologies will be developed and applied, such as seismic modelling, fracturing and stimulation of the reservoir. There are also vast amounts of unconventional oils, such as heavy oil (Venezuela), oil sand (Canada) and oil shale. The worldwide reserves, which by definition are exploitable with today's production technologies, are estimated to be 164 Gigatonnes. Adding the reserves of unconventional oil (66 Gigatonnes) means that the oil reserves are 230 Gigatonnes. The current annual global consumption amounts to approximately 4 Gigatonnes, suggesting a depletion point of 58 years [6].

Natural gas is found as pure gas, together with petroleum, as coal bed methane, as shale gas methane and as methane hydrates. Natural gas is mainly used as energy for heating buildings and for combustion in power plants. A small part is used directly as motor fuel. The worldwide chemical industry consumes about 8 % for material use. Natural gas, due to its hydrogen content, emits less CO₂ and therefore is considered to be an environmentally friendly energy source. The depletion point is said to be 63 years. Again, one has to consider reserves (6,954 exajoule or $183 \times 1,012 \text{ m}^3$) and resources. The resources embracing unconventional gas such as shale gas, coal bed methane and methane hydrates amount to 58,250 exajoule or $1,533 \times 1,012 \text{ m}^3$ [6]. Methane hydrates, present under the continental shelves of the seas and in the Siberian and Canadian tundra,

are thought to be the biggest source of unconventional gas. Currently, there are no technologies available to recover gas hydrates. Shale gas and coal bed methane can be freed from coal and shale by hydraulic fracturing using extremely high pressure and the addition of chemicals. Currently, the U.S. shale gas production amounts to 5–6 % of the consumption and is estimated to be 20 % by 2020 [7].

However, there is concern about the potential environmental impacts of hydraulic fracturing, including the contamination of groundwater by the chemicals added, as well as the migration of gases and hydraulic fracturing chemicals to the surface. For these reasons, hydraulic fracturing has come under scrutiny, with some countries suspending or banning it [8]. Many research efforts and developments are underway to carry out hydraulic fracturing without the use of chemicals.

When discussing the availability of methane gas, one must mention the biogas derived by the methanogenesis of biomass. Numerous plants worldwide are producing biogas, which mainly is used to produce electricity or heat; to a minor degree, it is used as transportation fuel. To avoid competition with food production, research and development are focusing on the use of “non-food-biomass”.

Historically, coal was the principal fossil raw material mined for heating purposes and for the production of coke for the steel industry. Coal was also the raw material used for establishing the chemical industry. Coal was supplanted by crude oil and natural gas. In 2004, the world’s coal production amounted to 5.5 billion tonnes. Its share of the total world primary energy market was 24 % (oil: 35 %, gas: 21 %, nuclear: 7 %, hydroelectric: 2 %, renewable: 11 %). Reserves are estimated at 1 trillion tonnes and resources at 6.2 trillion tonnes [6]. Coal is geographically widely dispersed, but five countries possess about 80 % of it.

Political and market forces favour the development of coal as a widely available, low-cost energy option. National security, shortage of foreign currency and local sources of employment are driving forces. Coal is mainly used for the generation of electricity in power plants and for heating. The chemical use is small and varies from country to country. In China, coal is gasified on a large scale to produce ammonia and methanol. Also, coal-based acetylene is still used by the Chinese Chemical Industry. In Germany, the material use of coal has shrunk to 2 %.

Based on its reserves, coal is generally seen as a major fossil fuel source for the longer term. However, the anthropogenic emission of CO₂ gives rise to great concern regarding climate change and ways to store CO₂ or use it are under consideration and development. There is also much room to improve the efficiency of coal-burning power plants, thus minimising CO₂ emissions. Many experts believe that the sequential supply responses to the increasing energy demand will start with coal, then move to biofuels, followed by renewable energy.

Figure 2.1 elucidates the techniques for producing energy (fuel) and chemicals from coal.

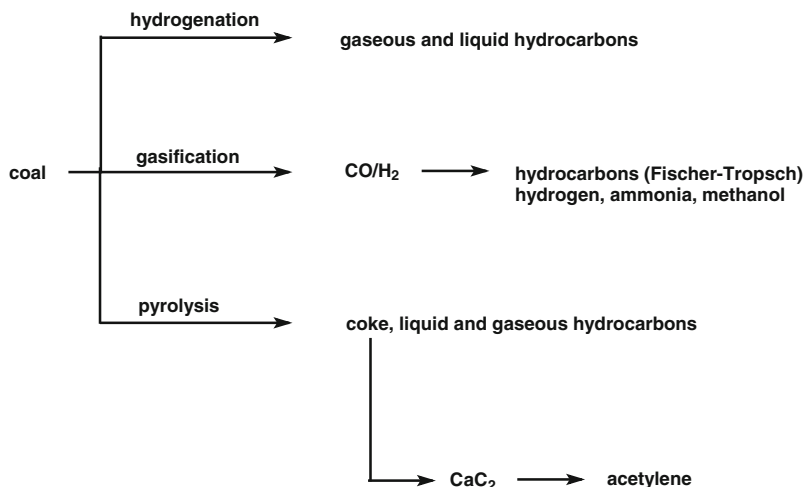


Fig. 2.1 Conversion technologies of coal for yielding energy (fuels) and chemicals

2.2 Alternatives for Replacing Fossil Raw Materials

The decline of fossil raw materials can entail serious economic and social implications. In addition to the concern about the future availability of raw materials for energy and material use, there is the threat of global warming caused by CO₂ emissions. Several options are available to mitigate dwindling fossil resources and global warming:

Solar resources wind, hydropower, thermal, photovoltaic, biomass

Biomass energy and chemicals

Planet movements ocean tides, waves, currents

Geothermal energy

Nuclear energy fusion and fission

Carbon dioxide hydrogenation to hydrocarbons and oxygenates

2.2.1 Solar Resources-Biomass

Wind, hydropower, thermal, photovoltaic and biomass can be used to generate electricity, thus replacing and substituting oil, gas and coal in conventional power plants [9]. The electricity can be used for driving cars, heating homes, and fueling the industry, which are major customers for fossil raw materials.

Figure 2.2 outlines various approaches for using sunlight to replace fossil raw materials.

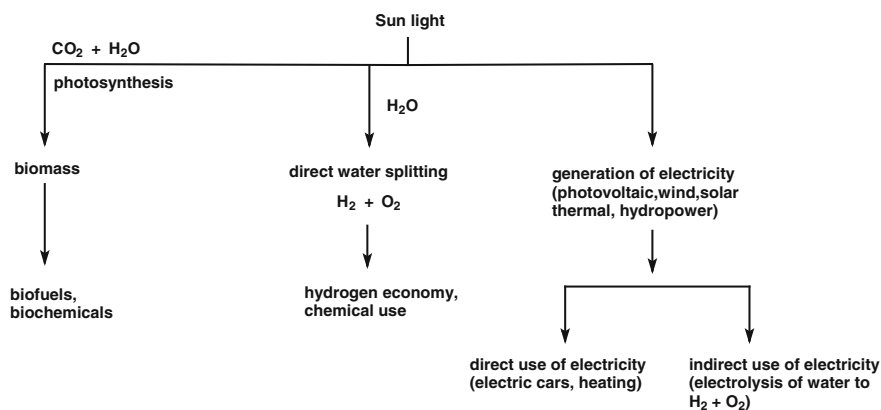


Fig. 2.2 Using sun light in replacing fossil raw materials

There are many options available to use the sun rays hitting the earth daily. The energy of the sun comes to us free of costs and represents a nearly unlimited resource, which we must learn to harvest to secure mankind's long-time survival. Numerous research and development efforts are underway worldwide to use sun's energy [10, 11].

As Fig. 2.2 shows, water or other liquids, when heated by the sun, can be used directly or via heat pumps. The direct use in solar power plants heats water via mirrors. The heated (400 °C) water can generate electricity via turbines and electrical generators. The electric energy can enter into existing or new electric grid structures and can be used for electric cars, heating of homes and industry uses.

Great potential exists for photovoltaics. Solar energy can be converted directly to electricity on the order of 20 % with silicon photovoltaic cells. By 2030, the European Photovoltaic Industry Association expects photovoltaics to have a 9 % share of world electricity consumption. However, photovoltaics are expensive and many doubts surround this expectation [12, 13].

Figure 2.2 also shows various other approaches that are under investigation, including direct water splitting to hydrogen and oxygen, thus enabling a hydrogen economy [14]. The hydrogen produced could also be used by the chemical industry, which is short of hydrogen and produces it from water and fossil carbon monoxide.

The most advanced method is the use of sun-derived wind energy, both onshore and offshore. Huge wind farms are in operation or are under construction. They are currently the best available technology for harvesting sunlight for electricity generation.

The direct storage of sun energy in reservoirs has been of interest for a long time [15]. Sun-derived renewable forms of energy, outside of biomass, involve mainly electric energy. It is very difficult to store electric energy as strategic reserve or for seasonal storage. When the sun is brightly shining or the wind is

powerfully blowing, more electricity is generated than the electric power grid can absorb. Various storage routes are under discussion: hydrogen, methane, liquid hydrocarbons, methanol and ethanol [16]. For sustainability, there are three requirements: accessibility, availability and acceptability. Methane meets all three requirements. With the availability of inexpensive hydrogen derived by water splitting through the sun (Fig. 2.2), CO₂ could be hydrogenated to methane. This route would provide an “eternal” feedstock, and at the same time would mitigate our CO₂ pollution problem. Methane can be stored and distributed safely within our existing, well-proven methane storage and distribution system. Another option is the hydrogenation of CO₂ to methanol (see later).

Biomass is an energy-rich carbon source derived by photosynthesis from CO₂, water and sunlight. In principle, biomass is inexhaustible and renewable. Biomass can substitute or replace fossil raw materials for many needs:

- **Bioenergy**

Heat (direct burning), electricity, fuels (bioethanol, biodiesel), biomethane

- **Materials**

Chemicals, biomaterials (biopolymers)

Biomass is widely used to provide energy. This can be achieved via direct burning, by wood-fired power plants yielding electricity, or by biofuels and biomethane. By 2035, the International Energy Agency expects the world's primary energy consumption to be composed of 29 % coal, 28 % oil, 22 % gas, 6 % nuclear, 2 % hydroelectric, 10 % biomass and waste and 3 % other [12].

The chemical industry is using biorenewable feedstocks such as plant oils, fats, sugar and starch for a wide spectrum of products (white biotechnology). World-wide, this share amounts to about 8 % and is increasing constantly. “Green polymers” such as polylactid and biopolyethylene are also rapidly increasing their market shares [6].

For bioenergy disposal on a large scale, which is an essential condition to replace fossil raw materials, vast areas of arable land are needed—land that often also can be used for food and animal feed production. In Germany, about 18 % of arable land is used for biofuels. Many consider it irresponsible to convert food into fuel and chemicals. Therefore, the first generation of biofuels, namely bioethanol and biodiesel, is discussed very controversially. In addition, the risks of excessive fertiliser use, costs, loss of carbon sinks, net energy use, high tax subsidies and the destruction of rainforests to cultivate sugar cane and palm oil are further objections [17]. Therefore, great hopes rest with the second generation of biomass—namely “non-food-biomass,” which will use lignocellulose derived from wood, agricultural and forestry remains. Non-food-biomass can be grown in areas that are unsuited to cultivate crops. Most Organisation for Economic Co-operation and Development countries, being in temperate regions, favour and support economic routes to second-generation biofuels and biochemicals [18], such as:

- Cellulosic ethanol (demonstration plants)
- Biomass conversion to synthetic gas (syngas) for biodiesel (demonstration plants)
- Biodiesel from microalgae and sugar-based hydrocarbons (research and development)
- Others, including methanol (commercial), biobutanol, dimethyl ether, pyrolysis-based fuels (demonstration plants) and novel fuels such as 2-methyltetrahydrofuran (research and development) [19]

In principle, there are three routes under investigation to convert non-food-biomass into energy and chemicals, as shown in Fig. 2.3: thermo-chemical-conversion, pyrolysis and biochemical conversion.

The biochemical conversion is based on a breakdown of lignocellulose into lignin, hemicellulose, cellulose and residues. The residues can be used for syngas or biogas manufacture. The intermediates lignin, hemicellulose and cellulose are further broken down by chemical or enzymatic processing techniques into chemicals such as furfurals, itaconic acid and levulinic acid (which are also called platform chemicals), thus opening up product routes to novel chemical feedstocks for the chemical industry and for novel fuels [20]. For instance, cellulosic ethanol can be converted to bioethene, which could replace or substitute fossil oil-derived ethylene.

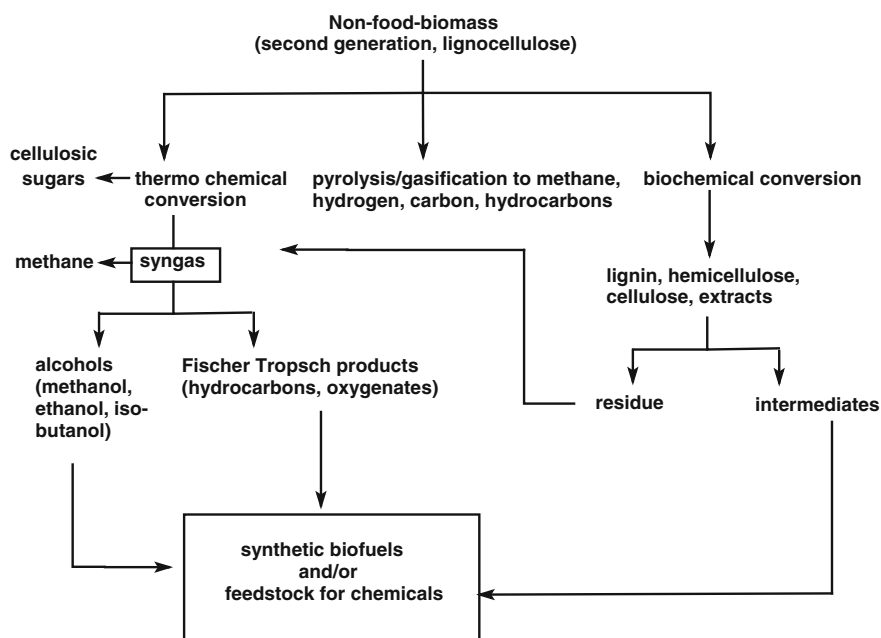


Fig. 2.3 Thermo- and biochemical conversion of non-food-biomass (lignocellulose)

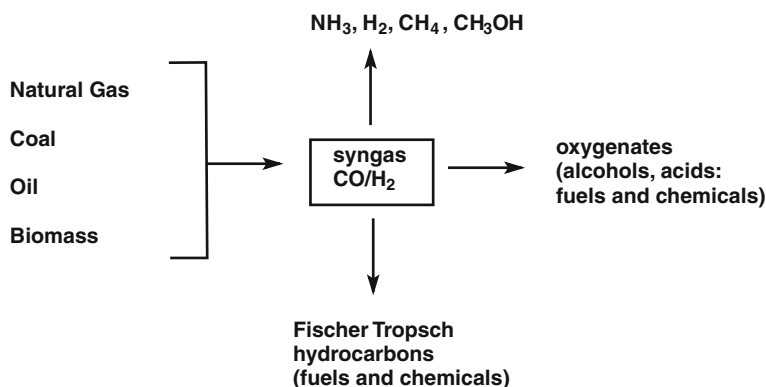


Fig. 2.4 Syngas C₁-chemistry

The thermo-chemical-conversion can follow two pathways: hydrolysis by water to sugars and conversion to syngas. The use of supercritical water (the Plantrose process by the company Remmatix) yields cellulosic sugars. Feedstock is wood or straw. Also, the use of acids and ionic liquids has been reported [21, 22].

The syngas route shown in Figs. 2.3 and 2.4, based on fossil raw materials gas, is a very old technology going back to the early 20th century that is still practiced today in many plants, such as coal (South Africa, China) and natural gas (Persian Gulf). This chemistry became known as the term C₁-chemistry [23, 24]. The synthesis of the oxygenate methanol and the Fischer–Tropsch process are state of the art. The application of biomass (Fig. 2.4) would integrate well into the existing fuel and chemical industry.

Biomass can also be pyrolysed/gasified to gas (methane, hydrogen), oil and residue/carbon (Fig. 2.4). The gasification/pyrolysis is still in the developmental stages [25, 26]. The Carbo-V-Process by Choren is an example of a semicommercial plant, although it was recently closed down.

The lignocellulose pathway in Fig. 2.3 embraces the concept of a biorefinery [27], which represents the key to an integrated production of energy and chemicals. A biorefinery, analogous to today's petroleum refinery, integrates biomass conversion processes to produce biofuels and biochemicals.

One chemical with great potential to substitute fossil raw materials is biomethane. Enzymes and microorganisms can convert biomass very efficiently into biogas—a mixture of methane and CO₂. With 10,000 L biogas, based on 1 hectare of arable land, biomethane ranks before biomass-to-liquid diesel (3,101 L), bioethanol (1,450 L) and biodiesel (1,183 L), respectively. Therefore, numerous economical biogas plants are in operation. In addition, biomethane can also be derived from synthesis gas (Fig. 2.4) via hydrogenation of carbon monoxide.

When discussing the availability and substitution potential of biomass, one must also consider the impacts of the “green revolution” based on plant breeding, genetic engineering and proper selection of plants. For instance, *Jatropha* seeds are

rich in oil (35 %) and are drought resistant. The oil can be used for biodiesel and represents a viable feedstock for the chemical industry.

2.2.2 Nuclear Power/Energy

The energy stemming from nuclear fission substitutes for fossil raw materials on a large scale. Also nuclear fusion, which is still in its infancy, represents a potential carbon-free energy source that is also free of CO₂ emissions. However, accidents in nuclear power plants and problems with storing the nuclear waste have made nuclear energy to a very controversial energy source, with many advantages and disadvantages. Although Germany has decided to abandon nuclear power, other countries continue. At a recent meeting, B. Bigot, chairman and chief executive officer of the French Alternative Energies and Atomic Commissions, stated [28]: “There is real need to develop sustainable low-carbon safe, environmentally benign and economically competitive technologies as nuclear and renewable energies to build a flexible energy mix adapted to the specific needs of each country.”

There is concern that biomass and solar energy cannot satisfy future energy demands. It is always dangerous to place all eggs in one basket. Therefore, the author of this chapter strongly believes that, at a minimum, research and development of nuclear power must continue to keep options open for nuclear energy (fission and fusion).

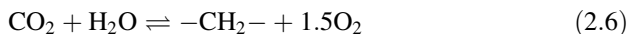
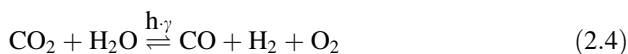
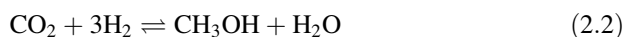
2.2.3 Carbon Dioxide

Carbon dioxide attracts many research efforts [6, 29–32]. The conversion of CO₂ into useful organic matter is pursued for two reasons: feedstock for fuels and chemicals [25, 33] and mitigation of CO₂ emission, which is held responsible for global warming. Here, it must be emphasised that there is a quantity problem. Even if we would base all chemicals on CO₂ as feedstock, the emissions of CO₂ would only be reduced by about 1 %. Application for fuels is 10 times greater.

Carbon dioxide is available in nearly unlimited amounts. It is the end product from all combustion processes using fossil raw materials. It is available as CO₂ gas in earth drilling operations, and it is present in carbonate rocks. One can expect unlimited reserves, as well as a secure and regional supply at stable prices.

To make use of the carbon atom in CO₂ for energy or chemicals, reduction routes are required in which one partner must contribute the necessary energy to overcome the thermodynamic and kinetic stability of CO₂. Quantitatively, great potential rests with the following reactions: hydrogenation to synthesis gas (Eq. 1),

hydrogenation to methanol (Eq. 2.2), reforming with methane (Eq. 2.3), photocatalytic/electrocatalytic reduction (Eq. 2.4) and hydrogenation to methane (Eq. 2.5):



These “dream reactions,” to be economical, require that the hydrogen or the energy come from inexpensive renewable energy resources that are sun derived (e.g. splitting of water) or based on nuclear energy. The dry reforming of methane with CO_2 (Eq. 2.3) needs high temperatures. The photocatalytic/electrocatalytic pathway (Eq. 2.4) is of great interest, but it is still in the stages of fundamental research and will not be a technically feasible option for the foreseeable future. The reaction of Eq. 2.6 can be regarded as technical photosynthesis and relates also to the Fischer–Tropsch synthesis [29].

2.3 Methanol Economy [34, 35]

Among all the discussions regarding the future availability of fossil raw materials and pollution by carbon dioxide, one of the oldest and versatile options—namely, a methanol economy—is not discussed with the same enthusiasm as a hydrogen economy or a ethanol economy [36]. However, methanol could fulfil nearly all requirements needed for raw materials, as is shown in Fig. 2.5.

The technical routes to methanol are based on synthesis gas, which can be produced from any carbon-containing source, such as fossil raw materials, CO_2 , or biomass. Today, mainly natural gas is used, followed by coal. Generally, the use of biomass as raw material feedstock for fuels and for the chemical industry is hampered by a lack of selectivities and yields in processing, because biomass consists of a wide range of organic compounds similar to crude oil and coal. Therefore, for crude oil and coal, a breakdown to basic chemicals is practiced. Will biomass, via its conversion to synthesis gas, parallel the development of crude oil and coal gas by creating one universal building block, namely synthesis gas?

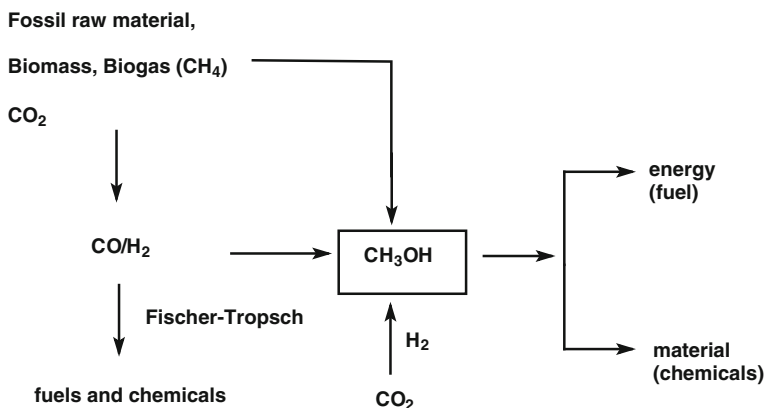
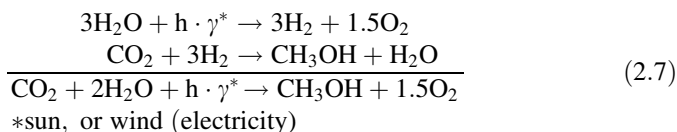


Fig. 2.5 A methanol economy

The old name for methanol is wood alcohol, pointing to its historical background. Enzymatic routes from biomass to methanol exist, but they are in their infancy for industrial usage. In this context, the missing link for a methanol economy, which is built on methane, is the direct chemical conversion of methane (e.g. biogas) into methanol—a reaction that is a great challenge for researchers.

Many gas fields exist, although they cannot be exploited due to their size. Portable methanol production units, which just appeared on the market, can be used for these stranded gas reserves. Also the transportation of coal out of arctic areas could be achieved applying methanol-coal slurry pipelines [37]. A part of the coal can be converted into methanol, which then together with coal can be pumped through a combined pipeline. Many concepts for a biorefinery also invoke methanol as one intermediate [26].

A fascinating alternative to fossil raw materials would be the direct conversion of CO_2 to methanol (Eq. 2.2). This would provide an “eternal” feedstock and at the same time would mitigate the CO_2 pollution problem. Nature uses photosynthesis from CO_2 and water to create biomass. Can we alter this process by converting CO_2 to methanol, whereby the hydrogen is derived from the sun or wind (electricity) (Eq. 2.7)?



Today, methanol is mainly used in single chemical applications, but methanol has the potential to provide the basic chemicals, C_2 – C_4 olefins, and aromatics by proven technologies. This is exemplified by the 500,000 t plant recently built in China to convert methanol into olefins (see Sect. 6.4.3).

Methanol can also be a feedstock to generate energy via fuel cells (see [Sect. 6.5.2](#)) or internal combustion and compression ignition engines (see [Sect. 6.3.1](#)). Here, proper performance has been established. Also, methanol derivatives such as dimethyl ether, dimethyl carbonate and methyl-tert-butyl ether are of interest in fuel applications (see [Sect. 6.3.2](#)). Methanol fuel cells are already in commercial use, especially for generating portable electric power used in mobile phones and laptop computers. Nearly every major electronic manufacturer is involved in the application of methanol fuel cells.

Methanol can be used to produce single-cell proteins for animal feed. The apocalyptic prophecies that mankind in the near future will suffer from a lack of energy, global warming and food shortages may turn out to have a solution via a methanol economy. Finally, the energy storage problem could be solved via a methanol economy, in which methanol is the storage molecule (see [Chap. 8](#)).

2.4 Conclusion

Presently, there is no practical and economical energy source available to replace fossil raw materials. In the past, the availability of huge fossil raw material reserves created the illusion of unlimited supply. However, increasing demands from population growth and per capita energy consumption made us aware that fossil raw materials are finite. The burning of fossil fuel also causes a climate problem that must be addressed. History teaches that human beings react to an important problem only when a crisis is already upon them. The energy system of the future will be very different from that of today.

Fossil raw materials will not run out overnight. We have many options available, such as energy conservation, a hydrogen economy, a biofuel economy, nuclear energy, sun-derived energy and a methanol economy—to name a few. In theory, there are many solutions and “dream pathways”; however, many will be unrealistic and will not be practical for reasons of economy, ecology, size of the market and so on. It will be a great challenge to find the most economical and ecological solution in an extremely complex system. There is a great deal of inertia present in developing alternatives to fossil raw materials considering the size of the market. Decades may pass before we are able to make these changes. There will be no easy path, but we must react now to have the technology available when it is needed. Governments and politicians will be asked to fund approaches; however, one should remember that in the 1970s the government advocated for an energy mix of 50 % fossil and 50 % nuclear, which today seems outdated. A methanol economy is one option with many advantages and disadvantages. Methanol, in which CO₂ is hydrogenated by sun-derived hydrogen from water splitting, looks enticing from a standpoint of energy and CO₂ avoidance. Methanol can help to integrate fossil raw materials and biomass value chains.

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