

Chapter 1

Introduction

1.1 From Raw Materials to Methanol, Chemicals and Fuels

Heribert Offermanns, Ludolf Plass and Martin Bertau

The planet Earth is a sphere with a limited surface of $5 \times 10^{13} \text{ m}^2$, of which 71 % is water and only 29 % is land. A total of 27.5 % of the landmass (i.e. 11 % of earth's surface) is used as arable acreage, 20.8 % as pasture and 9.4 % is used to grow timber. The remaining surface, which mainly is made up of deserts and mountains, is unused: 10.1 % is a frozen surface and 2.0 % is inland water. Meanwhile, the human population requires not less than 7 % of the land—a number that is constantly growing at the expense of the arable landmass. In fact, the usable area has been diminishing for years.

Carbon is the 13th most common element. It is found in nature in the form of diamonds and graphite and it is chemically bound as CO_2 , carbonate, natural gas, crude oil, coal, or biomass. However, carbon is highly unequally distributed in the earth's upper crust. Approximately 50,000,000 Gt (99.92 %) of carbon is fixed in the earth's crust, chiefly as carbonate rock. Only approximately 40,000 Gt

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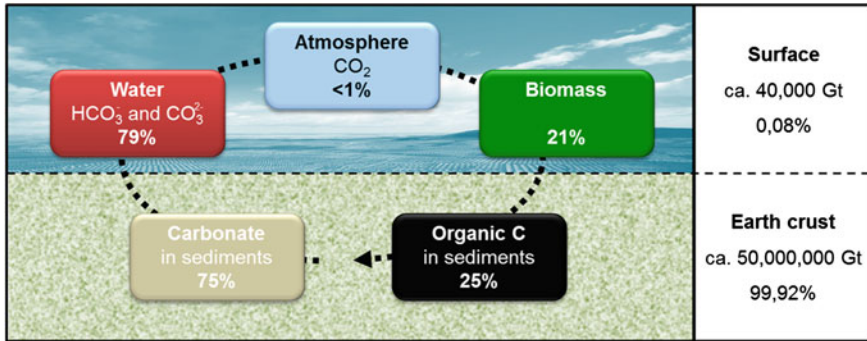


Fig. 1.1 Carbon distribution in the earth's crust. (Adapted from [3])

—a meager 0.08 %—is near the surface. The fact that 79 % of this latter amount is abundant as hydrogen carbonate and carbonate in water underscores the scarcity of economically exploitable carbon [1, 2]. Taking all this into account, one will inevitably come to the conclusion that the fraction of technically recoverable carbon is exceedingly rare but enriched in large-scale deposits (Fig. 1.1).

All natural carbon sources are exhaustible, but nature produces gargantuan amounts of renewable primary resources. By means of photosynthesis, plants produce carbohydrates from atmospheric CO_2 , sunlight and water. To a smaller extent, proteins and vegetable oils are also produced. The yearly production of biomass is estimated according to the U.S. Department of Energy (2005) to be approximately 150 Mt. Humans stand admiring this incredible performance while trying to understand how nature works. According to Primo Levi (see Fig. 1.2), the chemical leaf—technical photosynthesis—is the goal.

We use only small quantities of the long-existing and continuously accrued biomass (~ 4 %) for the production of food/fuel or as chemical or energy raw material. This usage (only 4 % human consumption) is not expected to substantially increase in the future.

Unlike the global population (currently 7 billion, estimated to be 9 billion in 2050), there will be no increase in the size of the earth. Therefore, every available acre of farmland should be prioritised for the production of food. However, there is a concerning downward trend in arable acreage because the growing population is consuming land for settling and concomitantly inappropriately using agricultural land. It should be common practice to use only the biomass that cannot serve as human nutrition as feedstock for energy and fuel, be it directly or indirectly.

Since the invention of fire, man has used biomass (wood) for heating. Wood used to play a considerable role in methanol production (wood alcohol), acetic acid (wood vinegar) and acetone. Also, hard coal and lignite have been (and are still) in use as feedstock for chemicals and energy. For instance, aromatics from tar distillation—a byproduct of coke production—served as raw materials for the production of dyes (I.G. Farben).

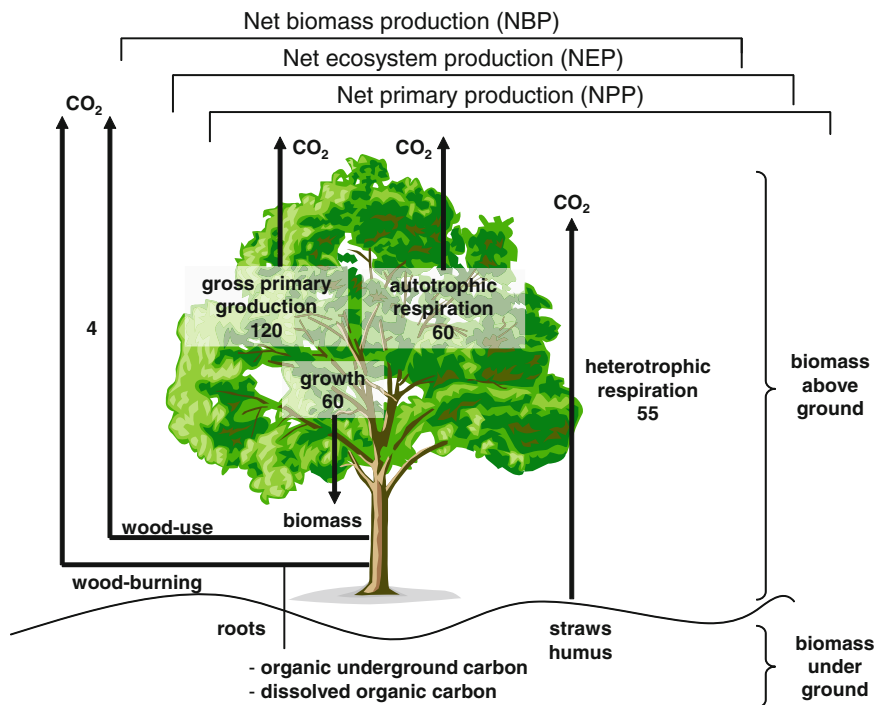


Fig. 1.2 Carbon loop in biomass production (numbers are in Gt). (Adapted from [4])

Crude oil (bitumen), which in some regions comes up to the surface, has been used for ages as cart grease and as an ingredient for ointment, among others. Until the middle of the 19th century, however, both natural gas and (especially) crude oil did not play any role as feedstock for chemicals or energy.

In 1853, the sleeping giant crude oil was woken up by the Galician pharmacist and chemist Ignazy Lukasiewicz (together with his associate Jan Zeh), as well as the physician, physicist and geologist Abraham P. Gessner, independently from each another. They tried to clean and distill crude oil to use it for oil lamps. The visions of the naturalist Benjamin Silliman of Yale University about the possible uses of the distillate were even surpassed. However, it still took decades until the era of crude oil began in the wake of inventions by Carl Benz and Rudolf Diesel, as well as Henry Ford's pioneering work.

The share of crude oil distillates for lamps decreased from 75 % in 1880 to 13 % in 1920, and the first refineries were built in Cleveland, Ohio in 1898. The driving force of crude oil processing was the production of gasoline and diesel fuel. Petrochemistry developed slowly, while natural gas and oil to a high degree began to replace hard coal and lignite as feedstock for power generation. The selection of carbon sources is broad, but the exhaustible fossil raw materials oil and gas—the consumption of which is an irreversible process—carry the greatest

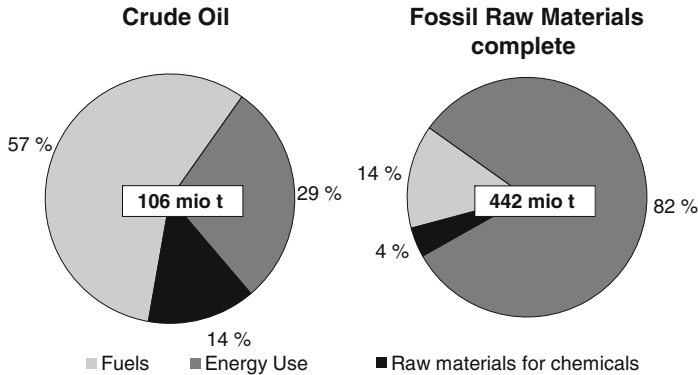


Fig. 1.3 Distribution of consumption of fossil raw materials and crude oil in Germany [6]

share of fulfilling the demand for energy, fuel and chemicals. For example in Germany, 80 % of all fossil raw materials (gas, oil and coal) are used for energy, 14 % for fuel, and only 4 % for chemicals (Fig. 1.3) [5].

The remaining static lifetimes of fossil raw materials are estimated as follows [6, 7]:

- Natural gas (reserves): 63 years
- Natural gas (resources): 74 years
- Crude oil (conventional reserves): 42 years
- Heavy oil, shale oil (nonconventional): 17 years
- Crude oil (conventional resources): 21 years
- Heavy oil, shale oil (nonconventional): 66 years

Brown coal (lignite) reserves are estimated to last for 227 years and hard coal reserves for 169 years, whereas the resources may last up to 1028 and 874 years, respectively. Reserves are proven deposits that can be economically exploited with known technology. Resources are deposits that cannot be exploited yet economically or are not proven for sure. The technical feasibility of their extraction requires improved technology; frequently, it is increasing world market prices that render resources into reserves [7].

Approximately 10 % of the world population consumes 90 % of the energy. With increasing qualities of life, the demands for showers/baths, heating and air conditioning will increase. There are many options to use carbon sources as feedstock for energy, fuel and basic chemicals, but carbon-rich fossil raw materials such as gas and oil have been preferred because their production is easier, logistics are simpler, and therefore the economics are better. It looks like predatory exploitation.

In the 1970s, critical voices were heard. In 1972, the Club of Rome published the book *The Limits to Growth* [8]. The Italian organic chemist, author and survivor of the Auschwitz concentration camp, Primo Levi, wrote the following in his book *Il Sistema Periodico*:

The human being has not yet tried consciously or unconsciously to compete with nature on this subject. That means, he has not yet taken the effort to withdraw the carbon from the air, that carbon which he needs badly for food, clothing, heating and to satisfy the hundreds of other requirements of modern life. He has not done anything, because there was no need to do so. He has found gigantic reserves of carbon easy to be used. But there is a vital question: for how many decades further? [9]

In the late 1950s, Friedrich Asinger—professor of Technical Chemistry and Petrochemistry at the Aachen RWTH, a pioneer in petrochemistry in research and teaching, and a commendable advisor of big chemical companies—called for a responsible handling of fossil raw materials. Although sometimes smiled at by students and colleagues, he taught that the crude oil—with its carbon chains formed over millions of years—should predominantly be used for the synthesis of chemicals, because the building of carbon chains is complicated and expensive.

After his retirement, Asinger dedicated special attention to the question of what comes after fossil raw materials, and methanol became the focus of his interest. He also expressed visions: “Once the fossil raw materials will become scarcer and more expensive or will dry out completely, there will remain as raw material, except for biomass, carbon dioxide only” [10]. However, Asinger ascribed special importance to coal for the time after the fossil raw materials with the shortest range (oil and gas) were exhausted, as indicated in the subtitle of his book “The Mobilisation of Coal”.

Asinger and his Aachen colleague Rudolf Schulten developed a concept for the use of nuclear power that used coal as the carbon source. The nuclear heat of the pebble-bed reactor (developed by Schulten) served to split water, while the oxygen was used to combust coal in order to supply energy and pure carbon dioxide. The hydrogen obtained from nuclear thermal water splitting was envisaged to reduce the carbon dioxide to methanol. Although the fate of the pebble reactor is sealed, these early “Aachen visions” have lost none of their topicality and importance. Asinger and Schulten could not foresee that power generation by means of wind and solar energy would one day become of the great importance we witness today. The technical progress of wind mills and solar power, based on exceptionally high governmental subsidies, rendered this development possible—in particular in Germany, where in 2012, a total of 8.2 % of power was generated from renewables [11].

Instead of nuclear energy, wind and solar energy can be used to produce hydrogen via electrolysis, which is then either used for repowering or further converted to methanol or methane (“power to gas”)—a topic that is dealt with in detail in [Chap. 8](#). In fact, there are many options to reasonably combine water electrolysis, power generation and production of CO₂, as well as using the latter as a raw material. When Asinger published his book “Methanol - Chemie- und Energierohstoff” [10], the time for his visions had not come yet, and decision makers were not prepared to recognise the significance and consequences of what he proposed. The book was not translated into English and has been out of print for a long time. Meanwhile, the situation worsened, and now there is great public awareness for power generation based on fossil raw materials, as well as a

continued vigilance for the CO₂ issue. Thus, the time may have come to publish a second, revised edition of Asinger's book in English.

Methanol is the focal point of this book, in an attempt to address the question, "What comes next?".

The intensity of the discussion about the future supply of raw materials for the requirements of power generation, fuel and chemical industry, as well as the discussions about the greenhouse effect, have increased.

Many scientific and technical organisations, science academies, industry organisations and government commissions have demonstrated their point of view. For example, the nuclear power phaseout by the German government gave rise to further questions such as energy storage, for which methanol can play an important role (see [Chaps. 7, 8](#)) [12].

Around the world, South Africa is pursuing the further development of the Fischer–Tropsch process. China has established huge plants for the production of methanol on the basis of hard coal, with the aim of producing consecutive products. The Chinese production capacity for propylene on the basis of methanol (MTP), for instance, totaled up to 1 million tonnes in 2013 and will further increase substantially. One can see from this single example that Asinger's vision—the mobilisation of coal via methanol—has become reality indeed.

With the world's population approaching 9 billion people, the demand for energy, fuel and raw materials for chemistry and food production will increase rapidly. The same holds true for CO₂ emissions, which will also increase. Hence, the development of alternative technologies for producing energy is mandatory. In light of this strong increase in energy demand, special attention must be paid to reasonably utilising fossil carbon feedstock. Fossil raw materials with short "static ranges"—that is, the quotient of current reserves to annual output, such as with oil and gas—make easily convertible feedstock for chemical industry. Fossil raw materials with long ranges, such as hard coal, lignite and shale oil, will require additional efforts prior to use as chemical feedstock. In fact, methanol production from both CO₂ and long-range fossil raw materials may offer a solution to this dilemma. This approach may also provide new perspectives on biomass utilisation, which for the reasons outlined previously has to be prioritised for food production.

This book will not discuss all the advantages and disadvantages of future energy supplies. However, it goes without saying that methanol clearly has the potential to play a key role in the time beyond oil, gas and nuclear power. This book will therefore thoroughly discuss the following subjects:

- Raw materials for the synthesis of methanol and their conditioning
- Methods to produce methanol and their economics
- Properties of methanol (physical data, toxicology)
- Use of methanol as fuel, for the energy sector, and as chemical feedstock

Because methanol is a liquid with a boiling point of 65 °C, it can be distributed through pipeline grids and transported with big tankers. It is miscible with water so it is not as dangerous as crude oil. Likewise, storage in fuel depots does not cause any problems. With an energy density of 22.7 MJ/kg, methanol is well suited as

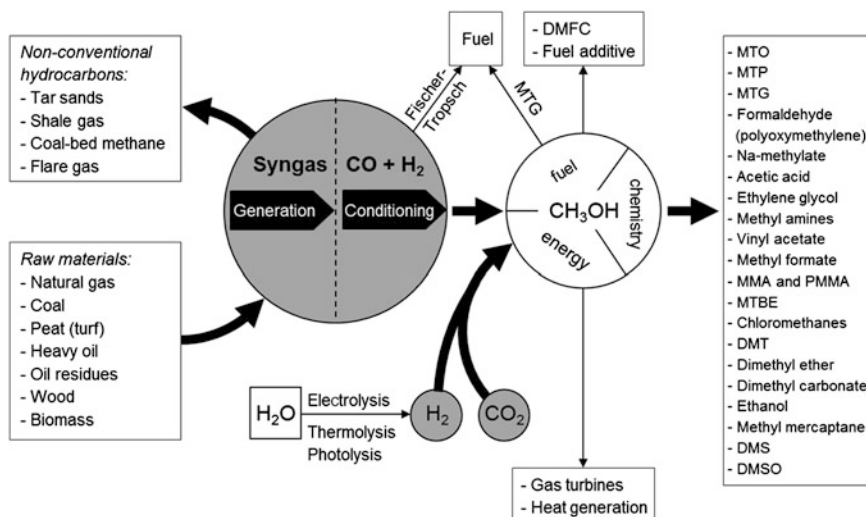


Fig. 1.4 From raw materials to synthesis gas (*syngas*), methanol, chemicals and fuels. Abbreviations: *DMFC* direct methanol fuel cell, *MTO* methanol-to-olefins, *MTP* methanol-to-propylene; *MTG* methanol-to-gasoline. (Adapted from [12])

energy storage compound. [Chapter 8](#) provides a comparison of methanol versus methane in chemical storage for excess power from renewable resources, using Germany as an example.

It has been widely accepted that no energy store is superior to methanol's chemical bond. For comparison, the lead accumulator is 0.11 MJ/kg; in Li-ion batteries, it is 0.5–3.6 MJ/kg. Methanol has been recognised as a basis chemical for a long time. The first large scale plant for methanol production starting from synthesis gas (according to Pier and Mittasch) was put into operation in 1923 in Leuna, Germany. Not later than 1930, methanol production reached 100,000 tonnes/year. By means of zeolite catalysis, the whole range of second-generation petrochemicals is accessible starting from methanol. The compound is also a useful feedstock for specialty chemicals. For wood gasification, it is well known that methanol can be used as fuel, either in pure form or as an additive to gasoline. In direct methanol fuel cells, methanol is used to transform chemical energy directly into electrical energy (without the detour via reforming). Therefore, there are a number of reasons why Asinger should once again be given the opportunity to be heard when stating: “Should hydrogen be economically available, pure sulphur free carbon dioxide could serve as feedstock for the methanol synthesis.” [Chapters 7](#) and [8](#) provide analyses and data to enable the reader to develop a fact-based opinion on the possibilities of a methanol-driven economy.

The essential elements of methanol utilisation in chemistry and energy feedstock are summarised in [Fig. 1.4](#).

Fig. 1.5 Friedrich Asinger, a pioneer in petrochemistry and mediator between basic and applied research



1.2 Friedrich Asinger

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Friedrich Asinger was an internationally respected researcher in the chemical and petrochemical industries. The name of Friedrich Asinger [13, 14] is not only linked to the Asinger reaction [15–18], which is a reaction of carbonyl compounds with elementary sulphur and ammonia to form nitrogen- and sulphur-containing heterocycles. He was also well known for teaching and research in petrochemistry at the Universities of Halle-Wittenberg, Dresden and Aachen, mainly thanks to his many textbooks [19–25]. It is no exaggeration to say that Asinger greatly influenced petrochemistry. Indeed, he considerably helped to shape the transition from the chemical raw material of coal to natural gas and oil (Fig. 1.5).

Asinger also was concerned about the overexploitation of the valuable raw materials gas and oil for energy production, and he became an advocate of nuclear energy and C_1 -chemistry [12, 26]. As early as the 1960s, he advocated for the future use of methanol as an energy and chemical feedstock. His book *Methanol - Chemie- und Energierohstoff*, which he wrote after his retirement, has unfortunately not been translated into the English language. Twenty years before the currently much-debated book, *Beyond Oil and Gas: The Methanol Economy*, by Olah et al. [27] was published, in 1986. Asinger pointed out the usefulness of pure, sulphur-free

carbonic acid; together with cheaply available hydrogen, it could serve as a starting material for methanol synthesis. Furthermore, he said: “When raw material sources one day will become increasingly short in supply and more expensive or are even totally exhausted ... there remains, apart from biomass, only carbonic acid as the source of raw materials for the organic chemical industry.”

Born in Freiland, Austria, Friedrich (“Fritz”) Asinger studied chemistry at Wien University of Technology and was granted his doctorate in 1932. For financial reasons, he had to turn down offers for a habilitation and for postdoctoral work at Columbia University in New York. He started his industrial career as chemist in a medium-sized chemical company in Vienna. In 1937, he took a position as research chemist at Leuna-Werke, founded in 1916 as Ammonia Works Merseburg by BASF; there, Asinger was promoted to group leader and later to head of research. Asinger was a successful inventor and innovator in the fields of sulphochlorination and sulphoxidation of paraffin, coal chemistry and new detergents.

Concurrent with his industrial activities, he received his habilitation from Graz University of Technology (Austria) and became an honorary lecturer at the Institute of Organic Chemistry at the University of Halle-Wittenberg under the directorship of the later Nobel Prize winner Karl Ziegler. In 1946, as part of the Operation Ossawakim—the forced deportation of skilled scientists from the Soviet-occupied eastern part of Germany—Asinger was displaced to the territory of the Soviet Union. Apart from his experimental work, which consisted of an order to develop rocket fuel, he wrote the manuscripts for the books *Chemie und Technologie der Paraffinkohlenwasserstoffe*, *Chemie und Technologie der Monoolefine* and *Einführung in die Petrolchemie*. In 1954, after 7 years in the Soviet Union, Asinger was released and allowed to return to the German Democratic Republic, where he resumed work at the Leuna company.

The Asinger books were published by the Akademie-Verlag Berlin in the years 1956–1959. English translations were published in 1967 for *Paraffins* and 1968 for *Monoolefins* by Pergamon Press Oxford, UK. In 1958, Asinger was appointed Professor of Organic Chemistry at the University of Halle-Wittenberg; also in 1958, he moved to Dresden University of Technology, where he became Professor and Director of the Institute of Organic Chemistry. In 1959, Asinger was appointed to a professorship at the Aachen RWTH and directorship at the Institute of Technical Chemistry and Petrochemistry.

As a citizen of Austria, Asinger had the chance to leave the German Democratic Republic, which was at that time separated by the “iron curtain” from the Federal Republic of Germany. It was for this reason why none of his coworkers could follow him. Therefore, Asinger had to establish a completely new research team. More than 150 students finished their studies with a doctoral degree under *Doktorvater* (Doctoral thesis supervisor) Friedrich Asinger. Students from 12 nations were members of the Institute, and more than 10 of the Asinger students took up an academic career. At Aachen, he wrote the books *Die Petrolchemische Industrie I + II* (Akademie-Verlag, Berlin, 1971) and *Methanol - Chemie- und Energierohstoff* (Springer-Verlag, Heidelberg, 1986). These books have never been

translated into the English language and therefore received no international recognition, particularly in the United States. Highlights of the Asinger books were the citations; for instance, there were more than 1,400 in his *Methanol* book, with most of them annotated with a commentary from the author.

1.3 The History of Methanol in the Chemical Industry

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For many decades, inorganic chemistry (e.g. Haber–Bosch process) and the chemistry of aromatics on the basis of coal tar dominated the chemical industry. F. F. Runge (1795–1867) isolated phenol and aniline from tar, which were cornerstones in the development of artificial dyestuffs. Fundamental research work by A. W. von Hofmann and A. Kekulé von Stradonitz and applied research of J. P. Gries, C. A. Martius, A. von Baeyer, H. Caro, C. Graebe, V. von Weinberg, C. Hagemann and others built the foundation of the most important dyestuff companies, which were joined stepwise to eventually form the IG Farbenindustrie AG, Frankfurt, in 1925–26. Similar developments occurred in Great Britain (W. A. Perkin) and in the United States [28–33].

The chemistry of aliphatic compounds lived in the shadows, with methanol (wood alcohol) and, less importantly, ethanol as raw materials. Today's most important polymers, such as polyolefins (more than 50 %) and polyamides with an overall yearly production of approximately 240 million t (according to Plastic Europe 2011) were not available because of the lack of basic petrochemical feedstock.

The growing importance of gold production (especially in South Africa) by means of the cyanide lixiviation process, which was developed by MacArthur and the Forrest brothers (1887), increased the demand for sodium cyanide so rapidly that the old production process (vinasse) could no longer cover the demand. Around the turn of the 20th century, H. Y. Castner and C. Kellner invented a process that was improved and finally was lead to technical maturity by chemists of the Deutsche Gold und Silberscheideanstalt (Degussa, later Degussa AG), and this new process replaced the old one.

In the Castner-Kellner process, charcoal reacts with ammonia and sodium metal. In order to secure the supply of the raw material charcoal, Degussa took part in the creation of the Holzverkohlungs-Industrie Konstanz (Hiag AG) in 1902. Hiag merged with its most important competitor, the Verein für Chemische Industrie AG (Frankfurt), in 1930. The companies were combined under the name HiagVerein GmbH and were absorbed 100 % by the Deutsche Gold und Silberscheideanstalt to become the department Hiag.

For logistical reasons and because of the forestry structure, many small manufactories for carbonising wood were established all over the beech woods in Germany. After the shutdown of smaller production facilities, 11 plants were still in operation in 1931. The carbonisation in retorts replaced the outdated technology of carbonising in heaps and made possible the production of organic chemicals in addition to the main product of charcoal. The first retorts had a capacity of 2.5 solid measures of timber, later ones had capacities of 10.0 solid measures of timber, and eventually the modern Reichert retorts reached a capacity of 40.0 solid measures of timber.

The byproducts of wood carbonisation in the bigger plants lead to the start of the organic chemistry business for Deutsche Gold und Silberscheideanstalt [34–36].

The carbonisation of natural seasoned beech wood yields the following:

- 26.7 % charcoal
- 4.4 % wood vinegar, mainly acetic acid
- 1.8 % wood alcohol, mainly methanol
- 7.1 % wood tar
- 16.2 % wood gas
- Residual water

At the beginning of the 20th century, the wood carbonisation industry in Germany was a monopoly [33]. The situation in Great Britain and the United States was similar. Wood gas and wood vinegar were important raw materials for major organic chemicals. There was no other access to formaldehyde (Paraform, Ultraform, Bakelit, urotropine, hexamethylenetetramine, pentaerythritol, etc.). Also, acrolein can be synthesised by condensation of acetaldehyde (from ethyl alcohol) and formaldehyde; it is one of the raw materials for the production of D,L-methionine, an amino acid important for animal feed.

A secondary product of wood vinegar was acetone, a raw material for methyl methacrylate and therefore for Plexiglas.

From wood tar, guaiacol and creosote were extracted.

Wood chemistry lost its importance after the introduction of coke-based C₁-chemistry with the development of the first technical synthesis of methanol in 1923 (Ammoniakwerk Merseburg of BASF; M. Pier, A. Mittasch) and with the advent of the chemistry of acetylene in the 1930s (W. Reppe); it was eventually supplanted by petrochemistry. During the first half of the 20th century, the chemistry of the aliphatics experienced an enormous boom (Fig. 1.6) (Table 1.1).

The first rail tank car of methanol left the Ammoniakwerk on September 26, 1923. It was at this plant where methanol production reached 100,000 tonnes per year in 1936 and 200,000 tonnes per year during World War II (Fig. 1.7) [37].

The Deutsche Gold und Silberscheideanstalt built a new chemistry complex in Fürstenberg/Oder and switched to a new route for methanol, acetylene and ethylene. However, this venture was abruptly stopped by the war. The plant was dismantled in 1945 and the apparatus were transported to the Soviet Union [34].

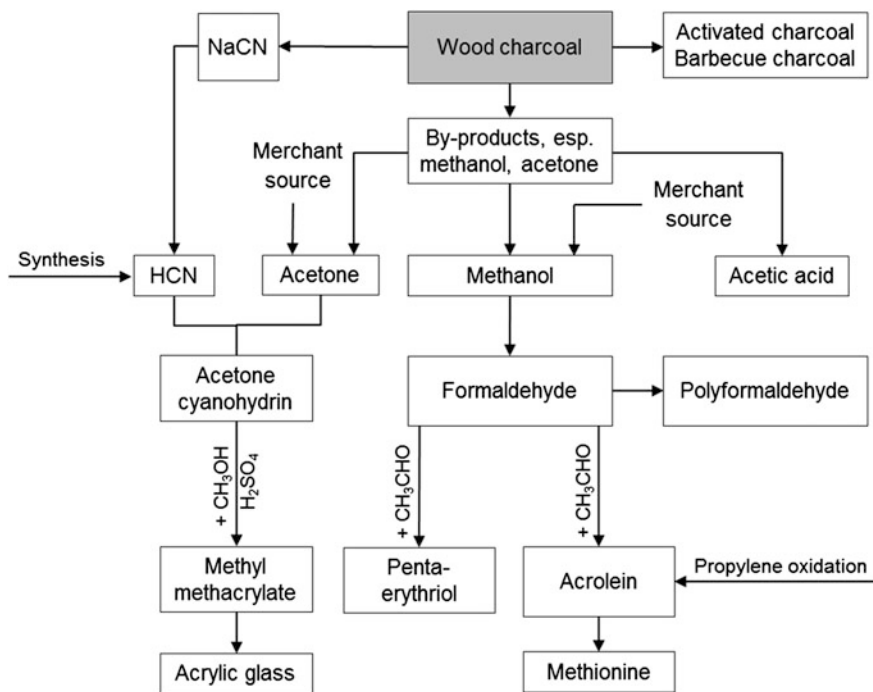


Fig. 1.6 Degussa's wood charcoal chemistry [36]

Table 1.1 Development of wood/charcoal based chemistry in Germany, 1933–1943 [36]

Wood-based products in metric tonnes (Hiag plants in post-war West Germany) ^a	1933	1938	1943
Charcoal	32,120	72,980	72,510
Activated charcoal	80	250	610
Wood tar	7,630	19,600	19,960
Tar oils	640	1,370	9,120
Guaiacol	0	20	60
Creosote	280	60	20
Flotation oils	0	50	810
Denatured wood alcohol	740	790	560
Solvent	600	890	600
Methanol	1,370	2,190	1,770
Formaldehyde	1,620	3,180	7,120
Paraformaldehyde	0	0	10
Acetates	3,100	6,940	9,770
Acetone	1,120	1,510	1,400
Acetone cyanohydrin	0	430	1,600

^a Bodenfelde, Brilon-Wald, Bruchhausen, Brücken, Konstanz, Kredenbach, Lorch, Mombach, Oeventrop, Schleiden and Züschen. The figures include the totals for both charcoal and wood tar and the end products derived from them, but only the end products of wood vinegar and wood alcohol, which were entirely distilled into these by the plants



Fig. 1.7 The first tankwagon with methanol leaves Leuna on 26th September 1923 [38]

After the end of the war, petrochemicals became the dominating feedstock for organic chemicals and consequently also for typical Degussa products such as formaldehyde, pentaerythritol, acrolein, acetone, acetonyanhydrin, methyl methacrylates (MMA) and polymethylmethacrylates (PMMA).

1.4 Methanol in Industrial Chemistry (General)

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Methanol (CH₃OH)—also named methyl alcohol, carbinol, or wood alcohol—is the first representative of the homologous series of alcohols that are correctly named by adding the syllable *-ol* to the corresponding paraffin. Methanol (molar mass 32.0429 g mol⁻¹) is a colourless, neutral, but polar liquid. It boils at 64.6 °C and freezes at -97.6 °C. For physical properties, see Sect. 5.1 for toxicology, see Sect. 5.2.

With a global annual consumption of 53 million tonnes in 2011 [39], methanol is one of the most important commodities of the chemical industry.

Figure 1.8 gives an overview of the value chain from methanol via its derivatives to a large variety of products or end uses in many sectors [41]. The three major products produced from methanol are formaldehyde (36 %), methyl tertiary-butyl ether/tertiary-amylmethylether (MTBE/TAME; 13 %) and acetic acid (9 %; Fig. 1.9). Formaldehyde production remains the largest single consumer of methanol.

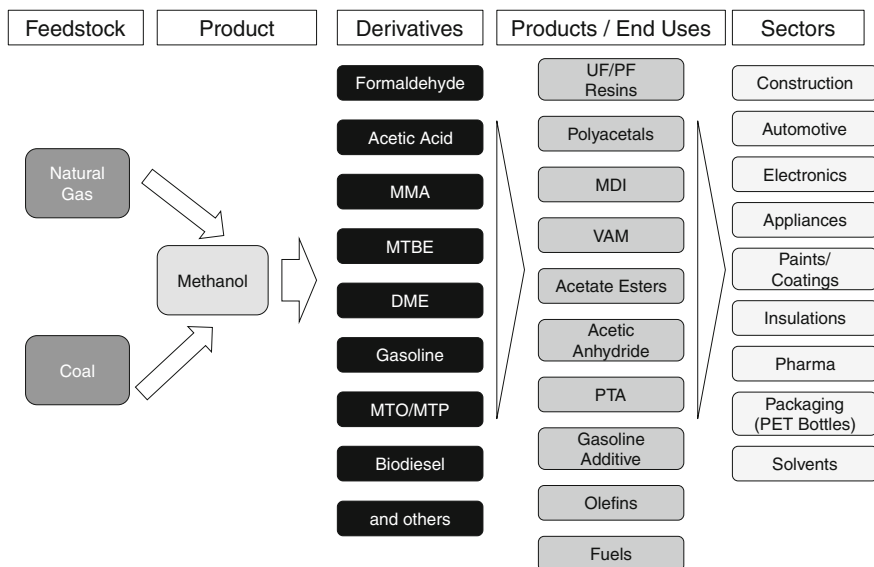


Fig. 1.8 Value chain of methanol [40]. A detailed description of methanol chemistry is given in chapter Chap. 6. Abbreviations: *MTO* methanol-to-olefins; *MTP* methanol-to-propylene

It is, among others, used for the production of plastics and resins, pharmaceuticals, chemical fibres, paint and pesticides. The production of MTBE/TAME is mainly used as an octane booster in gasoline, accounting for 16 % of the global annual consumption. However, the share of MTBE has decreased since 2003, when MTBE was replaced by ethanol as an antiknocking agent for fuels in California and 15 other U.S. states due to the contamination of water resources by MTBE from spilled fuels [41]. A large part of the acetic acid, which consumes approximately 9 % of global methanol production, is converted into vinyl acetate monomer (VAM).

The remaining 48 % of global methanol consumption is divided into the production of a large variety of chemical intermediates such as chloromethane, methylamine, methylmethacrylate and methylmercaptane, as well as the use of methanol or methanol derivatives such as dimethyl ether (DME) as a fuel or fuel blend (see Sects. 6.2 and 6.3). Overall, approximately one third of global methanol production is consumed in the fuel sector [42]. The chemicals produced from methanol stayed at approximately the same or slightly decreased levels on a percentage basis between 2009 and 2013 (Fig. 1.9). However, the fuel sector (MTBE/TAME/gasoline/DME) was estimated to increase from 30 % in 2009 to 40 % in 2013.

The so-called methanol-to-olefins (MTO) process, which allows for the production of feedstock for consumer plastics such as polyethylene and polypropylene, is starting to be a large-scale methanol consumer, increasing its share from 0 % in 2009 to 11 % in 2013. Ethylene and propylene are by far the two largest volume chemicals produced by the chemical industry. Approximately 120 Mio tonnes of

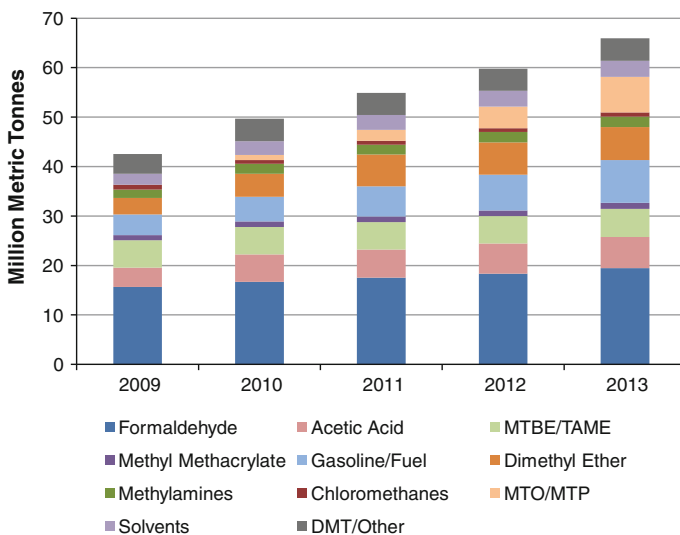
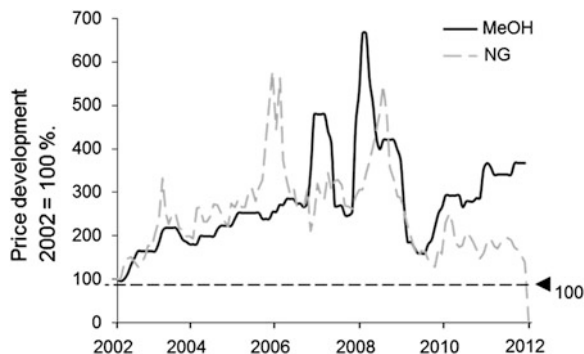


Fig. 1.9 Development of global methanol demand by sector (2013 forecast) [40]. Abbreviations: *MTBE/TAME* methyl tertiary-butyl ether/tertiary-amylmethylether; *MTO* methanol-to-olefins, *MTP* methanol-to-propylene

ethylene and 80 Mio tonnes of propylene were consumed worldwide in 2011. The demand for propylene is growing at a faster rate (approximately 4.5–5 % per annum; in China, approximately 6 % per annum) compared with that of ethylene (approximately 3–4 % per annum). Because the majority of both chemicals are still produced by steam cracking and fluid catalytic cracking, resulting in a given ratio of both chemicals, the increasing imbalance will need to be compensated for by the intentional production of propylene. Technologies used for intentional production are mainly propane dehydrogenation, metathesis, olefin cracking and to a growing extent methanol-to-propylene (MTP) technology, as further described in Sect. 6.4.3. The market price at which methanol is available for these processes is a decisive factor for the technology diffusion of these emerging applications [43]. Therefore, cost-efficient methanol production is a key objective for methanol producers and technology providers to maintain or improve profit margins in an increasingly competitive market (see chapter Chap. 7) (Fig. 1.10).

A study by Masih and coworkers conducted from 1998 to 2007 suggests that increasing natural gas prices are the driving force for methanol prices in Europe and the United States. In contrast, in the Asia–Pacific region, the surging demand for chemicals from growing consumer industries such as electronics, textiles, construction, leather and plastics processing was identified as the key driver for methanol prices [45]. Since 2006, the price of methanol has been extremely volatile. The steep increases in methanol prices in the second half of 2006 and in the last quarter of 2007 were caused by the shutdown of significant production

Fig. 1.10 Development of methanol *MeOH* [44] and natural gas *NG* prices [45] in the United States as a percentage of the reference price in January 2002



capacity due to technical problems and maintenance. High prices of natural gas have supported the high pricing level of methanol through 2008. In 2009, the methanol price dropped dramatically due to decreased demand because of the global economic crisis that followed the financial crisis. The methanol price increased to more than 350–400 € per tonnes in 2011, despite a relatively low natural gas cost in the United States, which is owed to the increasing availability of unconventional resources (shale gas).

Additionally, a regional shift has occurred in the production of methanol. Countries with large reserves of low-cost natural gas have invested into large-scale production facilities in order to monetise their “stranded gas” reserves, a byproduct from oil production. For example, because of the cost competition for products downstream of the methanol value chain, disfavoured plants in the United States were shut down. The Middle East and Asia, which have large reserves of natural gas and hard coal, have become the major methanol-producing regions [46]. With the increasing availability of shale gas in the United States, the price of natural gas has significantly dropped, leading to a higher profitability for the domestic production of base chemicals such as methanol. In recent years, China has become the world’s largest consumer of methanol, with approximately 30 % of the global annual consumption (Fig. 1.11).

The expected annual growth rates in the range of 10–20 % are resulting from the plans of the Chinese government to reduce the dependency of China from costly crude oil, such as by blending gasoline with coal-based methanol [47]. The percentage of methanol used as gasoline/fuel is supposed to grow from 11 % in 2011 to 16 % 2016 (Figs. 1.12 and 1.13). As already indicated in Fig. 1.9, the MTO/MTP technology sector continues to show the strongest increase (from 6 % in 2011, to 11 % in 2013, and to 22 % in 2016). Such developments are even further enhanced by the low natural/shale gas prices in North America (Fig. 1.10), where a substantial number of projects, including MTO/MTP processes, are in the planning phase. In addition, methanol plants that had been shut down for raw material cost reasons may be put back into operation.

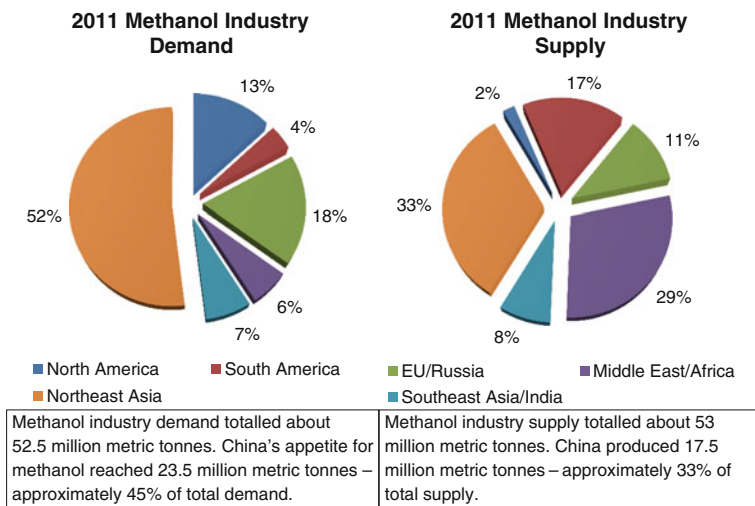


Fig. 1.11 Worldwide methanol supply and demand in 2011 [39]

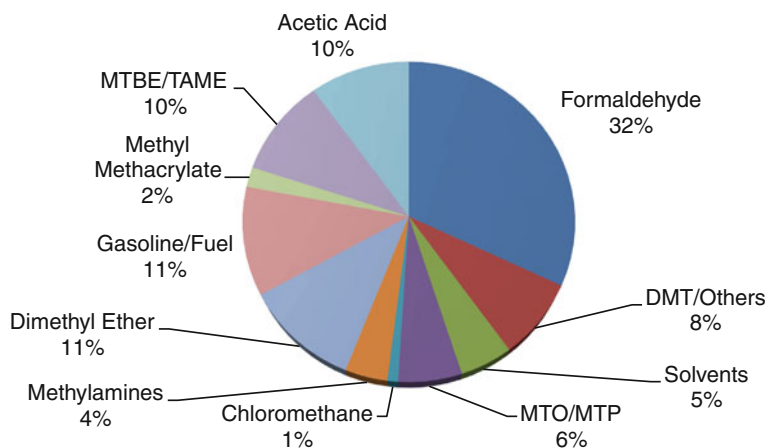


Fig. 1.12 Methanol demand by end use for 2011 [40]. Abbreviations: *MTBE/TAME* methyl tertiary-butyl ether/tertiary-amylnethylether; *MTO* methanol-to-olefins, *MTP* methanol-to-propylene

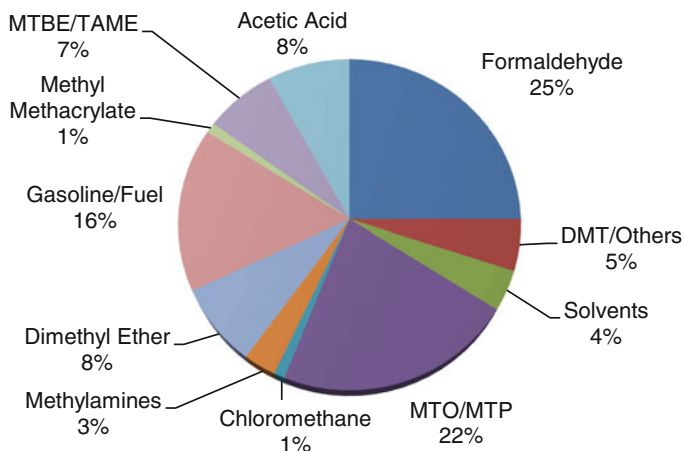


Fig. 1.13 Methanol demand and end use in 2016 [40]. Abbreviations: *MTBE/TAME* methyl tertiary-butyl ether/tertiary-amyl methylether, *MTO* methanol-to-olefins, *MTP* methanol-to-propylene

1.5 Methanol in Energy Storage and Carbon Recycling

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Changing from a fossil/nuclear-based energy supply system to a renewable-based energy supply system poses substantial challenges regarding the necessary technological, economic and also social transformation processes. They all have to be synchronised within the limited timescale from today to the year 2050. As a forerunner in this process, Germany has to describe and compare the energy storage and carbon recycling processes, which are an essential element of this transformation process.

Some key parameters of the energy transformation are:

- Reduction of CO₂ emissions by >80 % in 2050
- Production of >90 % of electrical power via renewable resources by 2050
- Meeting stringent economic parameters
 - Securing a safe power supply at all times
 - Securing an affordable energy supply

For an increasingly renewable and strongly fluctuating power supply, the existing power storage capacities in Germany, as in most other countries, are far

underdeveloped. The only storage system for longer seasonal periods (4 weeks–3 months) is a chemical storage system. This means that electric power has to be converted via electrolysis to hydrogen as a first step.

Thereafter, essentially three chemical storage options are available, as discussed further in [Chap. 8](#):

- Hydrogen storage:
Results in the least conversion loss, but poses difficulties for longer-term storage and has high costs associated with a completely new infrastructure.
- Conversion from hydrogen to methane (SNG):
Results in additional conversion losses, including in transport and storage. However, the existing infrastructure via the natural gas pipeline and power production system are attractive.
- Conversion from hydrogen to methanol:
Again results in higher conversion losses. However, its lower storage and transport losses, higher repowering efficiency and most importantly, the potential to use “green” methanol in the chemical and fuel markets are attractive.

Important issues for chemical storage include the necessary capacity for grid stability and the necessary capacity to store “surplus power.” Analysis has shown that the amount of surplus power far exceeds the amount of storage power for grid support from 2040 on. To avoid the shutdown of the power supply at certain times (and thus paying EEG compensation to the suppliers) or to export substantial power to other countries at marginal—sometimes even negative—prices (while again paying EEG compensation—a German scheme according to the Renewables Energy Sources Act—to the suppliers), a chemical storage system has to be designed for a foreseeable amount of surplus power.

The important question for the choice of the storage chemical is the question of what to do with the difference between surplus power and grid support power. In fact, there are two options:

Variant 1: Methane

Feeding the difference in energy as methane into the natural gas pipeline system.

Variant 2: Methanol

Feeding the difference in energy as methanol into the chemical/fuel market.

The “green methane” option implies that methane feed-in remuneration will be in accordance with the natural gas price, thus rendering this approach uneconomical for the foreseeable future until 2050. One has to bear in mind that natural gas prices have experienced a considerable drop due to the availability of shale gas. Because this amount will further increase, “green methane” will hardly have the potential to compete with shale gas prices.

The use of “green methanol,” which has been produced from surplus power charged at 1 ct/kWh, as a chemical or in the fuel market provides the potential for an economical solution for the longer-term chemical storage of energy because the price levels for fossil resources will foreseeably further increase. In addition,

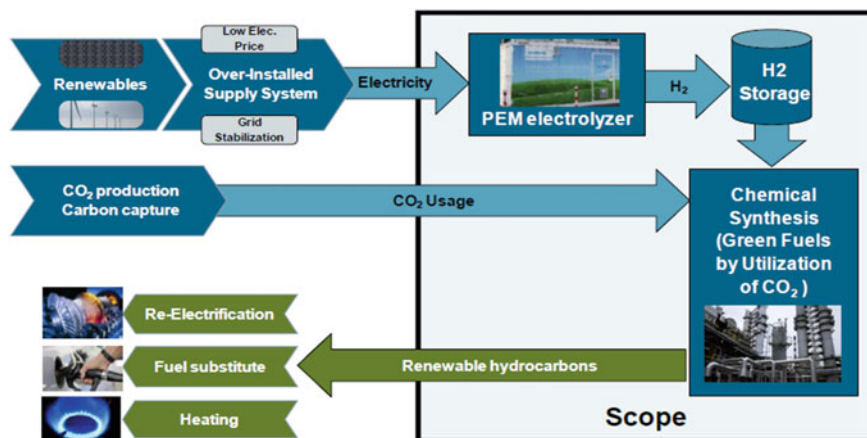


Fig. 1.14 Production of renewable hydrocarbons from surplus energy. (Courtesy of the authors) [48]

methanol has greater potential to recycle CO_2 obtained from combusting fossil or renewable resources than methane.

The “dualism” of methanol—that is, its property to be utilisable in both the chemistry and energy sectors—implies that chemical feedstock as well as combustibles for power generation and transportation/mobility purposes can be produced economically on a large scale from one source. Clearly, SNG can be used for mobility purposes, too; the same applies even for chemical feedstock. However, the overall efficiencies of (1) methane generation from renewables and (2) methane conversion to chemicals via synthesis gas or methanol are by far lower. For that reason, it is economically not competitive with methanol generation and utilisation.

The availability of “green methanol,” a chemical entity that has been produced from CO_2 , sunlight and water, will be an important contribution to the decarbonisation discussion. In addition to living things, the majority of consumer goods and combustibles are based on carbon. However, the decarbonisation discussion has been held in only in a few countries. For the benefit of their respective national economies, a switch to a methanol-based (i.e., “carbonised” economy) offers many more opportunities for more sustainable chemical production and power generation. The combustion of end-of-life products to CO_2 allows for the closing of the carbon loop for both green chemicals and biomass. This approach can be applied anywhere for the benefit of everyone.

Figure 1.14 shows how surplus electricity can be converted into hydrogen, then stored in the required quantity, allowing for the production of methanol in continuously operated chemical synthesis plants.

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