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Chemical Recycling of Carbon Dioxide to Methanol and Dimethyl Ether: From Greenhouse Gas to Renewable, Environmentally Carbon Neutral Fuels and Synthetic Hydrocarbons

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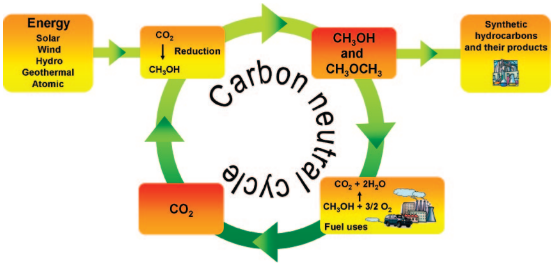

Nature's photosynthesis uses the sun's energy with chlorophyll in plants as a catalyst to recycle carbon dioxide and water into new plant life. Only given sufficient geological time can new fossil fuels be formed naturally. In contrast, chemical recycling of carbon dioxide from natural and industrial sources as well as varied human activities or even from the air itself to methanol or dimethyl ether (DME) and their varied products can be achieved via its capture and subsequent reductive hydrogenative conversion. The present Perspective reviews this new approach and our research in the field over the last 15 years. Carbon recycling represents a significant aspect of our proposed Methanol Economy. Any available energy source (alternative energies such as solar, wind, geothermal, and atomic energy) can be used for the production of needed hydrogen and chemical conversion of CO_2. Improved new methods for the efficient reductive conversion of CO_2 to methanol and/or DME that we have developed include bireforming with methane and ways of catalytic or electrochemical conversions. Liquid methanol is preferable to highly volatile and potentially explosive hydrogen for energy storage and transportation. Together with the derived DME, they are excellent transportation fuels for internal combustion engines (ICE) and fuel cells as well as convenient starting materials for synthetic hydrocarbons and their varied products. Carbon dioxide thus can be chemically transformed from a detrimental greenhouse gas causing global warming into a valuable, renewable and inexhaustible carbon source of the future allowing environmentally neutral use of carbon fuels and derived hydrocarbon products.

Prologue

A perspective article on the chemical recycling of carbon dioxide may not be a usual topic for the *Journal of Organic Chemistry*. It may be even questioned whether CO_2 recycling would qualify as a topic for an organic chemistry journal. However, CO_2 is an ubiquitous carbon source allowing the production of methanol and dimethyl ether, efficient alternative transportation fuels, as well as their varied derived products. The topic thus clearly falls into the scope of organic chemistry.

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Further, one of the major challenges of our time is to find efficient new solutions beyond our diminishing fossil fuels resources (oil, natural gas, coal) and the grave environmental consequences of excessive combustion of carbon-containing fuels and their products. The concept of the "Methanol Economy" that we have developed hinges on the chemical recycling of CO_2 to useful fuels. (i.e., methanol and DME) and other products.[1,2] At the same time, it renders carbon-containing fuels renewable (on the human time scale) and environmentally neutral. This not only allows us to mitigate a major human made cause of global warming but also provides us with an inexhaustible and generally available carbon source for ages to come.

Introduction and Concept

Starting with coal and subsequently petroleum oil and natural gas, fossil fuels allowed an unprecedented era of prosperity and advancement for human development in the past two centuries. The world still relies heavily today on fossil fuels to cover about 80% of its energy needs and to produce the vast multitude of derived fuels and essential products. The amounts of fossil fuels available to us are, however, finite and are rapidly depleting. Once consumed, they are not renewed on the human time scale. One of us (G.A.O.) has proposed some time ago the use of methanol as an alternative way to store, transport, and use energy (the so-called "Methanol Economy").[1,3−6] Methanol and derived dimethyl ether (DME) are also excellent fuels in internal combustion engines (ICE) and in a new generation of direct oxidation methanol fuel cells (DMFC), as well as convenient starting materials for producing light olefins (ethylene and propylene) and subsequently practically any derived hydrocarbon product. The "Methanol Economy", detailed in our recent monograph,[2] is capable of providing an environmentally carbon neutral, or in some cases even carbon negative, alternative to our diminishing oil and natural gas sources.[1−3,5] Methanol, as discussed subsequently, can be efficiently produced from a wide variety of sources including still available fossil fuels (coal, oil shale, tar sands, etc.) by improved methods, but also from agricultural products, municipal and industrial waste, wood, and varied biomass. More importantly, as discussed in the present perspective, methanol can also be produced in a new way from chemical recycling of carbon dioxide. Initially, this will be achieved from higher concentrations of CO_2-rich flue gases of fossil fuel burning power plants or exhausts of cement, fermentation, and other industrial plants, aluminum and iron ore smelters, etc. but also from major natural sources of CO_2 such as those accompanying natural gas or geothermal hot water and steam. In the future, however, even the low concentration of CO_2 from our air, presently around 380 ppm, can be captured and recycled to methanol, thus mimicking nature's own photosynthetic CO_2 cycle. Efficient new absorbents to capture atmospheric CO_2 are being developed. Chemical recycling of CO_2 to new fuels and materials is thus becoming possible, making them renewable on the human time scale. In contrast, nature's transformation of new plant life formed via photosynthesis into fossil fuels may take many millions of years[7] for which humankind cannot wait. Agricultural and natural product based biofuels are increasingly produced and used. This requires, however, at least in part shifting valuable food resources to fuel production and has already resulted in sharply increasing food prices[8] and increased pollution.[9,10]

Fossil fuels, as any carbon-containing materials, upon their combustion release carbon dioxide and water. The presently used conversion of fossil fuels (coal, natural gas) to liquid hydrocarbons and their products primarily by syngas-based chemistry (vide infra) itself generates large amounts of CO_2 and byproducts. CO_2 is a major greenhouse gas significantly contributing to global warming.[11] Mitigating its harmful effects is a well recognized major challenge for humankind. The Kyoto agreement and subsequent international efforts were directed to limit CO_2 emission into the atmosphere. Whereas econo-political approaches such as carbon quotas and trading were suggested and are increasingly put into effect in many countries, no new major technological solution has emerged. Our suggested Methanol Economy with the chemical recycling of carbon dioxide to methanol and/or dimethyl ether and subsequently to synthetic hydrocarbons and products offers such a new way to render fuels renewable and environmentally carbon neutral or even negative. It also offers humankind an inexhaustible carbon source in the form of recyclable CO_2, while at the same time mitigating human-caused climate change (i.e., global warming). Hydrogen needed for the chemical recycling of carbon dioxide can come from water (by electrolysis or other cleavage) or from still-existing significant hydrocarbon sources. Presently, available methane, primarily natural gas, but also other natural sources such as coalbed methane, methane hydrate, and methane from agricultural, domestic, and industrial sources can be effectively utilized to produce methanol using improved ways, including our new bireforming process (vide infra). We review here efficient new ways to achieve the chemical recycling of carbon dioxide including its capture, conversion to methanol and/or dimethyl ether combining chemical and hydrogenative reduction, or initial electrochemical reduction of CO_2 to CO. Of course, all ways to recycle carbon dioxide to methanol necessitate the use of significant energy. It should be emphasized that we are not dealing with energy generation but only its storage and use in a suitable form (i.e., methanol and/or dimethyl ether). At the same time, our carbon recycling chemistry and the Methanol Economy concept can utilize any form of energy; still existing fossil fuels and alternative sources such as solar, wind, hydro, geothermal, as well as atomic energy. They thus offer extensive versatility and practical applications. As essentially most of our energy in one form or another comes from the sun, humankind will not experience a real energy shortage. We only need to find suitable new ways to capture, store, transport, and utilize energy.

Background

Methanol was first produced as a minor byproduct of producing charcoal by destructive distillation of wood and was therefore called wood alcohol. Methanol produced this way was used in the 19th century for lighting, cooking, and heating purposes but was later replaced by cheaper fuels, especially kerosene. Up to the 1920s, wood was the only source for methanol, which was also needed in increasing quantities in the developing chemical industry. Beginning in the 1920s, the production of methanol from syngas, a mixture of CO and H_2, on an industrial scale was introduced by BASF in Germany. Whereas coal was initially used as a feedstock for the syngas, natural gas became the preferred feedstock after World War II. It offered a higher hydrogen content and lower energy consumption and contained fewer harmful impurities such as sulfur, nitrogen, halogenated compounds, and heavy metals.[12−16]

Today, methanol is a primary raw material for the chemical industry. It is manufactured in large quantities (about 40 million tonnes in 2007) as an intermediate for the production of a variety of chemicals including formaldehyde, methyl *tert*-butyl ether, and acetic acid.[12,16] Most of these chemicals are subsequently used to manufacture many products of our daily life including paints, resins, adhesives, antifreezes, and plastics. Besides being produced industrially and occurring naturally on earth to a small extent in fruits, grapes, etc., methanol has also been found recently in outer space.[17] Astronomers have observed an enormous cloud of methanol around a nascent star in deep space that measures ∼460 billion km across !

The toxicity of methanol is frequently quoted as a hindrance for its use. Methanol is highly toxic only when ingested in larger amounts (30−100 mL),[18,19] causing blindness and eventually death. Of course, methanol, unlike ethanol, is not for internal consumption, but neither are gasoline and diesel fuel. However, according to the US FDA, daily intake of up to 500 mg/day of methanol is safe for adults. Methanol has long been used in consumer products as windshield washer fluids, deicing fluids, antifreezes, and fuels for camping and outdoor activities. Therefore, the use and dispensing of methanol as a general purpose fuel is not expected to cause any significant safety problems.

Methanol has excellent combustion characteristics making it a suitable and proven fuel for internal combustion engine (ICE) driven vehicles. It contains only about half the energy density of gasoline but has a higher octane rating of 100 (average of the research octane number (RON) of 107 and motor octane number (MON) of 92).[20] Due to its high octane rating and because it is also inherently safer than gasoline (fire safety), methanol has been used in race cars since the 1960s.[21] Gasoline-powered cars can be modified to run on methanol at a very modest cost. Flexible fuel vehicles (FFV) running on mixtures of methanol with gasoline, such as M15 or M85, containing 15% and 85% methanol, respectively, were used extensively commercially in the 1980s, for example, in California.[12] In Brazil, close to 80% of the cars produced are now FFVs able to run on any mixture of ethanol and gasoline; sugar cane based ethanol being available in Brazil at a low cost.[22] The wide commercial use of methanol in ICE vehicles would therefore not represent any difficulty.

Methanol, although it has been used in diesel engines, is not the best fuel to replace diesel fuel because of its low cetane number. The cetane number measures the propensity of a fuel to self-ignite under high heat and pressure conditions. A high cetane number is needed for efficient diesel engine operation. Dimethyl ether (DME) having a cetane number of 55−60, substantially higher than the 40−55 of conventional diesel fuel, is thus far superior to methanol as a substitute diesel engine fuel.[23] DME is presently produced by the bimolecular dehydration of methanol.

DME, the simplest of all ethers, is a colorless, nontoxic, noncorrosive, noncarcinogenic, and environmentally friendly chemical compound.[24] Unlike other homologous ethers, DME does not form explosive peroxides,[25] allowing its safe storage and handling. DME has a boiling point of −24.9 °C, being a gas under ambient conditions. However, DME is generally handled as a liquid and stored in pressurized tanks, much like liquefied petroleum gas.[26]

Consumption of DME is rapidly growing particularly in Asia as increasingly large quantities are used as a diesel fuel substitute. DME is also a convenient substitute fuel used for electric power generation as well as domestic heating and cooking applications.[26]

Methanol (or its flex-fuel mixtures with gasoline) and DME can also be used in new hybrid and plug-in hybrid vehicles, combining an ICE with electric motors. Besides its utilization in ICEs, methanol is an excellent fuel for efficient direct methanol fuel cells (DMFC), which we jointly developed with Caltech's Jet Propulsion Laboratory in the early 1990s.[27−29] Direct DME based fuel cells are also being studied.[30,31]

Methanol and DME, besides their use as transportation fuels, are proven and increasingly utilized starting materials for producing ethylene and propylene in the so-called methanol to olefin (MTO) process.[32,33]

$$2\,CH_3OH \underset{+\,H_2O}{\overset{-\,H_2O}{\rightleftharpoons}} CH_3OCH_3 \xrightarrow{-\,H_2O} \overset{\text{Ethylene \& Propylene}}{H_2C{=}CH_2 \;\&\; H_2C{=}CH{-}CH_3}$$

Acidic zeolitic solid catalysts such as SAPO-34 and ZSM-5 are most commonly used for this reaction. Olah et al. also reported in the 1980s the use of a nonzeolitic bifunctional WO_3/Al_2O_3 catalyst.[34,35] Ethylene and propylene can be subsequently transformed to polyethylene and polypropylene or to varied hydrocarbons and their products. Methanol is also the starting material in the methanol to gasoline (MTG) process for the direct production of gasoline, diesel fuel, and aromatics.[36] All products presently obtained from petroleum oil or natural gas can therefore be produced from methanol.

$$2\,CH_3OH \underset{+\,H_2O}{\overset{-\,H_2O}{\rightleftharpoons}} CH_3OCH_3 \xrightarrow{-\,H_2O} \text{light olefins} \longrightarrow \text{gasoline, diesel fuel and aromatics}$$

Current Manufacture of Methanol and DME from Fossil Fuel Based Syngas. Methanol and DME are presently exclusively produced from fossil fuel based syngas. The processes, which are well optimized, produce currently, as mentioned, about 40 million tonnes of methanol annually. Syngas is a mixture of hydrogen and carbon monoxide as well as carbon dioxide formed from partial combustion or reforming of coal or natural gas over a heterogeneous catalyst.

Syngas is produced from coal by gasification, a process combining partial oxidation and steam treatment:

$$C + 1/2\,O_2 \rightleftharpoons CO \qquad \text{partial oxidation} \qquad \Delta H_{298K} = -\,29.4\ \text{kcal.mol}^{-1}$$

$$C + H_2O \rightleftharpoons CO + H_2 \qquad \text{steam reforming} \qquad \Delta H_{298K} = 31.3\ \text{kcal.mol}^{-1}$$

Due to the low H/C ratio of coal, the obtained syngas is rich in carbon oxides (CO and CO_2) and deficient in hydrogen. Before being sent to the methanol production unit, the syngas must thus be subjected to the water gas shift reaction to enhance its hydrogen content. Alternatively, H_2 from other sources can be added.

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta H_{298K} = -\,9.8\ \text{kcal.mol}^{-1}$$

water gas shift reaction

In coal-rich countries,[37] particularly China and South Africa, coal-based syngas remains the major source for methanol. However, syngas production, especially from coal, always generates large amounts of carbon dioxide as a byproduct, which causes environmental problems.

Since World War II, the major source for syngas production became increasingly natural gas, which is more convenient, economic, and environmentally friendly to use.[15] The most widely employed technology to produce syngas from natural gas is presently steam reforming (eq 1). Its combination with partial oxidation (eq 2) is also increasingly used in a process called autothermal reforming. Dry reforming (eq 3) has also been used, although to a lesser extent.[38]

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad \Delta H_{298K} = 49.1\ \text{kcal.mol}^{-1} \qquad (1)$$

$$CH_4 + 1/2\ O_2 \rightleftharpoons CO + 2H_2 \qquad \Delta H_{298K} = -\ 8.6\ \text{kcal.mol}^{-1} \qquad (2)$$

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \qquad \Delta H_{298K} = 59\ \text{kcal.mol}^{-1} \qquad (3)$$

After adjusting the CO/H_2 ratio close to 1:2, the syngas is converted to methanol. Present processes to produce methanol from syngas use copper/zinc oxide based catalysts, which are extremely active and selective in heterogeneous gas-phase processes. Methanol synthesis is an exothermic reaction (−21.7 kcal mol^{-1}), and control of the process temperature is important to avoid rapid deactivation of the catalyst.[39]

$$CO + 2H_2 \rightleftharpoons CH_3OH \qquad \Delta H_{298K} = -\ 21.7\ \text{kcal.mol}^{-1}$$

The production of DME from methanol is readily carried out over varied mildly acidic catalysts such as alumina.[26]

Chemical Conversion of CO_2 to Methanol and/or Dimethyl Ether. The syngas-based production of methanol and subsequently DME inevitably generates large amounts of carbon dioxide. Of course, methanol and all carbon-containing fuels upon their combustion form carbon dioxide. Carbon dioxide, a significant greenhouse gas, is considered a harmful pollutant of our atmosphere and a major source for human-caused global warming. So far, however, besides the proposed collection and sequestration of excess CO_2, a costly and only temporary solution, which in seismically active areas could cause devastating releases of CO_2 in case of earthquakes or other earth movements, no new technology emerged for its disposal. In recent years, we suggested and carried out extensive work on the effective chemical conversion of carbon dioxide, thus allowing its recycling and reuse to essential fuels and materials.[40−43] This practical feasible approach, we believe, offers a solution to the environmental problem of carbon dioxide increase in our atmosphere and associated global warming, but also renders our fuels renewable and environmentally carbon neutral.

Catalytic Hydrogenative Conversion of Carbon Dioxide to Methanol. The most direct and studied route to methanol from CO_2 is the catalytic regenerative conversion of CO_2 with hydrogen according to

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O \qquad \Delta H_{298K} = -\ 11.9\ \text{kcal.mol}^{-1}$$

This reaction has been known to chemists for more than 80 years. In fact, some of the earliest methanol plants operating in the U.S. in the 1920−1930s commonly used carbon dioxide for methanol production, generally obtained as byproduct of other processes such as fermentation.[12] More recently, efficient catalysts based on metals and their oxides, in particular the combination of copper and zinc oxide, have been developed for this conversion. Lurgi AG, a leader in the methanol synthesis process, for example, developed and thoroughly tested a high activity catalyst for methanol production from CO_2 and H_2.[44] Operating at a temperature around 260 °C, slightly higher than conventional methanol synthesis catalyst, the selectivity to methanol is excellent. The activity of this catalyst decreased at about the same rate as the activity of commercial catalyst used in usual methanol synthesis plants. The synthesis of methanol from CO_2 and H_2 has also been demonstrated on a pilot scale in Japan, where a 50 kg CH_3OH /day production with a selectivity to methanol of 99.8% was achieved.[45] A liquid-phase methanol synthesis process was also developed, which allows a CO_2 and H_2 conversion to methanol of about 95% with very high selectivity in a single pass.[46] In our own work we have developed improved catalysts.

The first contemporary commercial CO_2 to methanol recycling plant using locally available cheap geothermal energy is presently being built after successful pilot plant scale operation in Iceland by the company Carbon Recycling International. The plant is based on the conversion of CO_2, a significant byproduct accompanying local geothermal energy sources or industrial sources (aluminum production). H_2 is produced by water electrolysis (vide infra).[47] In Japan, Mitsui chemicals is building a pilot plant producing methanol from CO_2 and H_2 with an annual capacity of 100 tonnes. Hydrogen will be generated by photochemical splitting of water using solar energy.[48] There is also significant interest in CO_2 to methanol processes in China, Australia, the European Union, and other countries for recycling CO_2 from industrial sources such as coal burning power plants, aluminum, and cement production, etc. So far, however, there is only limited interest in the US.

The general composition of the catalysts for CO_2 hydrogenation such as $Cu/ZnO/Al_2O_3$ is similar to the ones used presently for methanol production via syngas.[49−52] In view of our present understanding of the mechanism of the syngas based chemistry, this is not unexpected. Although still debated, it is now usually accepted that methanol is formed almost exclusively by hydrogenation of CO_2 contained in the syngas on the catalyst's surface. To be converted to methanol, some of the CO in syngas needs first to undergo a water gas shift reaction to give additional H_2 and form CO_2. The formed CO_2 then reacts with hydrogen to produce methanol.[39,53,54] In fact, it has been shown that reacting on a commercial methanol catalyst a CO/H_2 mixture carefully purified from CO_2 and water produces no or very little methanol.[39]

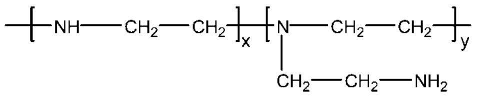
Varied process studies to produce methanol from CO_2 and H_2 were also reported.[44,49,50,55] The capital investment for a methanol plant using CO_2 and H_2 is estimated to be about the same as that of a conventional syngas based plant.[44] The key factor for the large scale use of such a process is the availability of the raw materials: CO_2 and H_2. Worldwide, presently more than 25 billion tonnes of CO_2 related to human activities are released into the atmosphere every year. Large amounts of CO_2 can thus be obtained relatively easily from various exhaust sources such as from fossil fuel burning power plants and varied industrial plants from cement factories to aluminum production to fermentation plants. Also, large natural CO_2 sources, such as CO_2 accompanying natural gas and geothermal energy producing wells, could be captured and stored or recycled to avoid atmospheric release. Even the small concentration of CO_2 contained in the air can be separated and chemically recycled to methanol and varied synthetic hydrocarbons and their products (vide infra). We will discuss the present status and challenges of capture and purification of CO_2 from industrial and natural sources, as well as production of hydrogen for chemical carbon recycling.

CO_2 Capture and Purification for Recycling. From Industrial and Natural Sources. Nature captures and recycles atmospheric CO_2 efficiently in its photosynthetic cycle. To chemically recycle CO_2 to methanol, it is necessary to be able to capture it from industrial or natural sources conveniently and economically in a pure form. This is currently best achieved by capturing and recycling CO_2 from sources where it is present in a sufficiently high concentration, through physical−chemical absorption and desorption cycles coupled when needed with chemical purification particularly from H_2S, SO_2, and other accompanying pollutants.

Globally, CO_2 emissions from electricity generation, cement and fermentation plants, industries, the transportation sector, heating (cooling), cooking, and other activities all contribute to the increase in CO_2 levels in the atmosphere, from 270 ppm at the beginning of the industrial era to about 380 ppm today. They are predicted to double by the end of the century. There is a well-established correlation, initially proposed by Arrhenius in the late 19th century, between atmospheric CO_2 content and global temperature.[56] Natural warming cycles by themselves may increase CO_2 concentrations. Thus, human activity caused CORegardless,$_2$ production is superimposed on that arising from natural processes.[57] it is obvious that humankind's excessive burning of fossil fuels since the dawn of the industrial revolution is producing large amounts of excess carbon dioxide contributing to the increase in global temperatures. The use of fossil fuels and other human activities are therefore considered environmentally harmful as they inevitably form excessive carbon dioxide, upsetting nature's recycling ability. Although our fossil fuel reserves are limited, they will for the foreseeable immediate future continue to provide the dominant share of humanity's energy needs. We should, however, do everything in our power to mitigate damage caused by human activities, even more so as we do not have control over nature's long-range cycles (change in the earth's axes to the sun, solar flairs, etc.). The Kyoto agreement, although not yet approved by all countries, is an effort to limit CO_2 emissions based primarily on quotas and carbon trading.[58] To reduce CO_2 emissions however, new technologies must be developed and enforced. More energy efficient technologies and conservation can help but will not be sufficient to stop the global increase of CO_2 emissions. To significantly reduce emissions, recovery of CO_2 from industrial and natural sources is clearly becoming necessary.

Capture of carbon dioxide, although not generally employed on a large scale, is a well studied process. The separation of CO_2 from gas streams can be achieved by diverse separation techniques. They are based on different physical and chemical processes including absorption into a liquid solution, adsorption onto suitable solids, cryogenic separation, and permeation through membranes.[59] Amine solution based CO_2 absorption/desorption systems using monoethanolamine (MEA) and diethanolamine (DEA) are some of the most widely employed for the separation of CO_2 from gas mixtures.[59] High energy requirements for the regeneration step and limited loadings in amines due to corrosion problems and amine degradation are, however, major drawbacks warranting the development of more efficient renewable CO_2 sorbents.

In our work, we have developed a new, highly effective CO_2 absorption−desorption system consisting of polyethylenimine (or related polymeric amino systems) supported on nanostructured silica.[60] Recently, metal−organic frameworks (MOF) with high CO_2 storage capacity have also been discovered. MOF are a class of highly porous materials with high surface area. MOF 177 composed of zinc clusters joined by 3,5-benzenetribenzoate units, for example, has a surface area of 4500 m^2/g and a CO_2 storage capacity of about 1.47 g CO_2 per g of MOF at a pressure of 30 bar.[61,62] Scale-up of these technologies as well as further improvements are necessary to reduce the cost of CO_2 capture, which presently is limited to more highly concentrated industrial or natural sources.



$$\left[NH-CH_2-CH_2 \right]_x \left[\underset{\displaystyle |\atop \displaystyle CH_2-CH_2-NH_2}{N}-CH_2-CH_2 \right]_y$$

Polyethyleneimine (branched)

Capturing of CO_2 from industrial and natural sources for recycling to methanol and its derived products also necessitates its purification from frequently present accompanying pollutants (especially H_2S and SO_x). This is particularly significant in developing "clean coal" technologies. These pollutants, besides their environmental effect, also frequently tend to poison the catalyst systems used in the chemical recycling processes discussed. Their removal is therefore also needed to allow technical carbon dioxide recycling. Methods for the removal of these contaminants are described in detail in the literature.[59] "Clean coal", however, should also mean CO_2 disposal by sequestration or more advantageously by our suggested chemical recycling, as burning coal or any other fossil fuel inevitably forms carbon dioxide.

It is also important to realize that more than half of human-caused CO_2 emissions are the result of small dispersed sources such as office and home heating, cooking, and most importantly the transportation sector. The collection at the source of CO_2 from millions, even billions, of small fossil fuel burning units will be difficult if at all possible. These dispersed CO_2 emissions represent a preponderant part of the global CO_2 emissions, and their importance cannot be ignored in the long run. However, recycling of CO_2 from high concentration industrial sources as well as natural CO_2 accompanying such large-scale operation as natural gas production, geothermal energy utilization, etc. is already feasible and should be vigorously pursued. It can significantly mitigate our overall CO_2 emissions before excess atmospheric CO_2 chemical recycling will be realized.

From the Atmosphere. To deal with small and dispersed CO_2 emitters and avoid the need of developing and constructing a huge CO_2 collecting infrastructure, CO_2 will have to be captured from the atmosphere to supplement nature's own photosynthetic recycling. Such an approach has already been proposed by some in the past.[63−67] The atmosphere could thus serve as a source of CO_2 for chemical recycling. The concentration of CO_2 in air being at equilibrium all around the world, CO_2 capturing facilities can be put in any place. To allow subsequent methanol synthesis they could be ideally placed close to hydrogen production sites.

Despite the low concentration of carbon dioxide of only 0.038% in air, nature recycles efficiently CO_2 by photosynthesis in plants, trees, algaes, etc. to produce carbohydrates, cellulose, lipids, etc. and eventually new plant life, while releasing oxygen, thus sustaining life on Earth. Following nature's example, humankind, we believe, will be able to capture excess CO_2 from air and recycle it to generate hydrocarbons and their products. CO_2 can be even presently captured from the atmosphere using basic absorbents such as calcium hydroxide ($Ca(OH)_2$) or potassium hydroxide (KOH), which react with CO_2 to form calcium carbonate ($CaCO_3$) and potassium carbonate (K_2CO_3), respectively.[68] After capture, CO_2 is recovered from the sorbent by desorption, through heating, applying vacuum, or electrochemically. Calcium carbonate, for example, as well-known in the cement industry can be thermally calcinated to release carbon dioxide. CO_2 absorption is an exothermic reaction, which liberates heat, and is readily achieved by simply contacting CO_2 with an adequate base. The energy-demanding step is the endothermic desorption, requiring energy to regenerate the base and recover CO_2. Calcium carbonate or sodium carbonate, requiring high energy input for recovery are therefore not well suited candidates for CO_2 capture from air. Research, which is still in its relatively early phase of development, is under way to find suitable absorbents and technologies to remove CO_2 from air for its recycling with the lowest possible energy input. For example, using KOH as an absorbent, it has been shown that the electrolysis of K_2CO_3 in water could efficiently produce not only CO_2 but also H_2 with relatively modest energy input.[69,70] With further developments and improvements, CO_2 capture from the atmosphere, which has already been described as technically feasible, will become economically more viable.[68] In submarines and space flights, the removal of CO_2, essential to keep the air breathable, is already carried out using regenerable polymeric or liquid amine scrubbers. In our own work, a nanostructured silica-supported polyethylenimine absorbent was found to be able to absorb CO_2 from the air, although further work is needed to increase the efficiency of CO_2 capture.[60]

Among the various advantages of CO_2 extraction from air is the fact that CO_2 capture, being independent from CO_2 sources, would allow more CO_2 capture than is actually emitted from human activities. This means that this technology could allow us to not only stabilize CO_2 levels, making us carbon neutral, but eventually even lower them, making our carbon emission balance negative.

It should be pointed out that our air also contains other building blocks essential for our sustainable future in considerably higher concentration than the low (0.038%) CO_2 content: (a) pure water in the form of moisture, essential to life and an inexhaustible source of hydrogen; (b) nitrogen, for the synthesis of ammonia and derived synthetic nitrogen containing compounds especially fertilizers; (c) oxygen, also essential to life as well as for combustion processes. Utilizing all these atmospheric resources can ensure a sustainable future for most of our needs using air as a most significant source material.

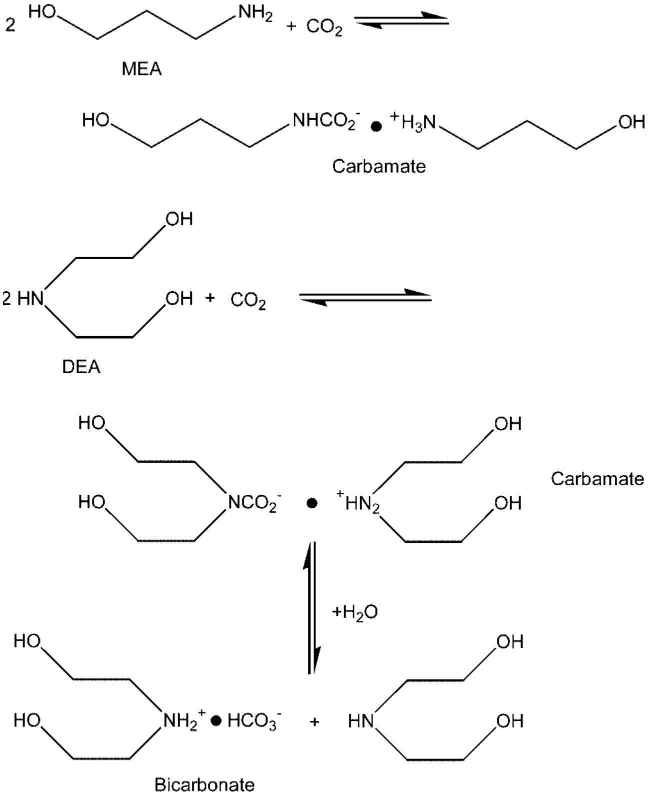
Hydrogen Production. The essential second component for the chemical recycling of carbon dioxide is hydrogen. The needed hydrogen for CO_2 conversion to methanol is not present on earth in its free form, because of its high affinity for oxygen of our atmosphere. However, it is abundant bound to oxygen in water or to carbon in fossil fuels and varied hydrocarbons sources. It is also an essential part of varied natural sources such as plant life, cellulosic materials (wood), carbohydrates, etc.

Hydrogen for the chemical conversion of CO_2 to methanol needs to be generated either by using still-existing significant sources of fossil fuels (mainly natural gas) or from splitting of water. The energy required for the latter (electrochemical, thermal, photolytic, etc) can come from any energy source, preferably renewable such as solar, from nuclear energy, or from enzymatic biological processes.

The *electrolysis of water* to produce H_2 and O_2 is a well-developed process.

$$H_2O \xrightarrow{e^-} H_2 + 1/2\ O_2 \qquad \Delta H_{298K} = 68.3\ \text{kcal.mol}^{-1}$$

CHART 1



Electrolysis is energy intensive. The power consumption at 100% theoretical efficiency is 39.4 kWh/kg of hydrogen; however, in practice it is closer to 50−65 kWh/kg.[71]

The conversion efficiency of water to hydrogen, depending on the system, can be between 80 and 95%. Considering the power needed for a complete electrolyzer system, the best energy efficiency is today around 73%.[72] This means that about 53 kWh of electricity is needed to produce 1 kg of hydrogen. Current R&D efforts are aimed at improving net system efficiencies of commercial electrolysis toward 85%.[73] In water electrolyzers of 1000 kg of H_2 per day, the cost of electricity has been estimated to represent about 80% of the cost of hydrogen produced, while capital investment represented only 11%.[72] In large electrolysis units, the cost of electricity would therefore dictate the overall economics and will be the major driving factor for producing hydrogen.

The electricity needed for the process can be provided by any form of energy. Presently, a large part of the electricity produced is still derived from fossil fuel burning power plants.[74] In the future, however, in order to be sustainable and environmentally adaptable, the electricity needed for electrolysis of water on a large scale will come from atomic energy (nuclear fission and eventually nuclear fusion) and any renewable energy source, preferentially solar but also hydro, geothermal, wind, wave, tides, etc. As mentioned, the pioneering commercial CO_2 to methanol recycling plant under development in Iceland uses available cheap geothermal electricity, making it commercially feasible without any subsidies or carbon credits.[47] Besides electrolysis, production of hydrogen through enzymatic, photo- and thermal water splitting cycles, as well as using chemical cycles such as the iodine−sulfur cycle operating at 800−1000 °C are also being developed and could be utilized in the future.[75]

Despite considerable advances in more efficient hydrogen generation from water by electrolysis, fossil fuels, especially natural gas and in some countries coal or even oil, still remain presently economical sources for the production of hydrogen via their reforming. However, their inevitable depletion and pressure from ever increasing prices and environmental concerns put a growing emphasis on the use of water to generate hydrogen, which eventually will be its sole inexhaustible renewable source utilizing any form of energy, preferably solar.

Improved Methanol Production from Natural Gas and Coal. To avoid excessive CO_2 emissions into the atmosphere, processes to produce methanol and its derivatives based on fossil fuels but generating less or even no CO_2 should be increasingly introduced. This progressive shift to a more "carbon neutral" economy will also ease the transition to alternative energy sources. Such approaches were pursued in our work over the past decade and are discussed subsequently.

As long as fossil fuels are still widely available, improved routes to produce hydrogen from them without releasing excess CO_2 are needed. For this purpose, the so-called "Carnol process" was developed at the Brookhaven National Laboratory. In this process, hydrogen is produced by thermal decomposition of methane with carbon formed as a byproduct.[76,77] The generated hydrogen is then reacted with CO_2 recovered from emission of fossil fuel burning power plants and other industrial flue gases to produce methanol. Overall, the net emission of CO_2 from this process is close to zero, because CO_2 released by the methanol used as a fuel is recycled from existing emission sources. The solid carbon formed as a byproduct can be handled and stored much more easily than the gaseous CO_2, and be disposed of or used as a commodity material in some applications.

$$\begin{array}{lll} \text{Methane thermal decomposition} & \mathrm{CH_4 \longrightarrow C + 2H_2} & \Delta H_{298K} = 17.9\ \mathrm{kcal.mol^{-1}} \\ \text{Methanol synthesis} & \mathrm{CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O} & \\ \text{Overall Carnol process} & \mathrm{3CH_4 + 2CO_2 \longrightarrow 2CH_3OH + 2H_2O + 3C} & \end{array}$$

The thermal decomposition of methane occurs when methane is heated to high temperatures in the absence of air. To obtain reasonable conversion rates under industrial conditions, temperatures above 800 °C are required.[76] This process has been long used not for the production of hydrogen but for carbon black in the tire industry and as a pigment for inks and paints. For the primary generation of hydrogen, different reactor designs have been proposed. Attention has recently been focused on reactors operating with a molten metal bath, such as molten tin heated to about 900 °C, into which methane gas is introduced.

The Carnol process is carbon neutral in the sense that all the carbon present in methane ends up as solid carbon. It should be clear, however, that, whereas methane steam reforming produces 3 mol of hydrogen for every mole of methane used, methane decomposition yields only 2 mol. On the other hand, methane's thermal decomposition byproduct, i.e., solid carbon, has no effect on the atmosphere and can be easily handled, stored, and used without much further treatment. The price to pay for this is a lower amount of H_2 generated from methane and therefore a higher cost.

Another way to produce methanol from CO_2 by sequestering some of the CO_2 in the form of carbon is the combination of CH_4 decomposition and dry reforming. The result is the production of methanol and carbon. For 2 mol of CH_4 used, 1 mol of solid carbon is formed. The formed carbon can be sequestered or used in reducing CO_2 to CO, which can be hydrogenated to methanol (vide infra).

$$\begin{array}{l} \mathrm{CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2} \\ \mathrm{CH_4 \rightleftharpoons C + 2H_2} \\ \hline \mathrm{2CH_4 + CO_2 \rightleftharpoons \underbrace{2CO + 4H_2}_{\textstyle \downarrow \atop \textstyle 2CH_3OH} + C} \end{array}$$

The environmental benefit is not as high as with the Carnol process, but the economic cost may be lower.

A further way to utilize more efficiently still available natural gas resources and at the same time convert CO_2 to methanol is to react CO_2 with natural gas or other hydrocarbon sources to produce syngas. In a process called "dry reforming", which does not involve steam, CO_2 is reacted with natural gas to produce syngas of H_2/CO (1:1) composition. With a reaction enthalpy of $\Delta H = 59$ kcal.mol^{-1}, this reaction is more endothermic than steam reforming.[78]

$$\mathrm{CO_2 + CH_4 \rightleftharpoons 2CO + 2H_2}$$

This reaction is carried out commercially at temperatures around 800−1000 °C using catalysts based on nickel (Ni/MgO, $Ni/MgAl_2O_4$, etc).[78−80] The syngas obtained has a H_2/CO ratio of about 1, much lower than the values around 3 obtained with steam reforming. The high CO and low hydrogen contents makes it a suitable feed gas for some processes, especially iron ore reduction and Fischer−Tropsch synthesis of long-chain alkanes. This syngas composition is, however, not suitable for the production of methanol using existing technology in which a H_2/CO ratio close to 2:1 is needed.

Hydrogen generated from other sources would thus have to be added to the 1:1 H_2/CO syngas produced by dry reforming to obtain a proper 2:1 H_2/CO ratio.

To overcome this disadvantage and to produce a H_2/CO mixture with a ratio close to 2 (what we call "metgas") suited for methanol synthesis, we developed a new advantageous way to use a specific combination of steam and dry reforming of methane or natural gas, in what we call "bireforming". It involves a 3:2:1 ratio of $CH_4/H_2O/CO_2$. The catalysts for bireforming can be those used for separate dry and steam reforming, combining thereafter the two streams. We have also developed a system combining dry and steam reforming in a single step. The useful temperature range of the reactions is between 800 and 1000 °C. The needed energy can come from any energy source, preferably renewable or nuclear.

$$\begin{array}{lll} \text{Steam reforming} & \mathrm{2CH_4 + 2H_2O \longrightarrow 2CO + 6H_2} & \\ \text{Dry reforming} & \mathrm{CH_4 + CO_2 \longrightarrow 2CO + 2H_2} & \\ \hline \text{Bireforming} & \mathrm{3CH_4 + 2H_2O + CO_2 \longrightarrow 4CO + 8H_2} & \mathrm{\longrightarrow 4CH_3OH} \end{array}$$

In practical use, natural gas is the major source of methane. Besides methane, natural gas also contains higher hydrocarbons in various concentrations, which can also undergo bireforming according to the overall conversion:

$$\mathrm{3C_nH_{(2n+2)} + (3n\text{-}1)\,H_2O + CO_2 \longrightarrow (3n{+}1)\,CO + (6n{+}2)\,H_2}$$

The combination of steam and dry reforming (in separate steps or in a single combined operation) can be used for the conversion of CO_2 emissions from coal and other fossil fuels burning power plants as well as industrial sources such as cement factories, aluminum plants, etc. to methanol. It is also advantageous for reforming natural gas and geothermal sources which frequently are accompanied by substantial amounts of CO_2. Otherwise, this CO_2 would have to be separated, vented into the atmosphere, or sequestered underground or at the bottom of the seas. Some natural gas sources contain CO_2 in concentrations up to 70%.[81] The natural gas produced at the Sleipner platform in Norway contains 9% CO_2. This CO_2 is currently already separated and sequestered beneath the North Sea in a deep saline aquifer.[82,83] Algerian natural gas contains CO_2 concentrations up to 30%. Iceland's rich geothermal hot water or steam have a CO_2 concentration around 10%.[84]

Coalbed methane, frequent in many coal mines, as well as *shale gas* and tight *gas sands* are also significant methane sources for carbon dioxide to methanol conversion.[85] When coal is the primary fossil fuel source used for electricity generation, CO_2 formed upon its combustion can be captured and then converted with coalbed methane available from coal mining operation to methanol via bireforming.

Methane hydrates present under the seas in coastal and continental shelf areas and in the permafrost of the arctic tundra are composed of methane trapped by water in cage like structures called clathrates. Their amount is estimated to be significantly higher than all our conventional methane (natural gas) resources.[86] Their recovery however is difficult and still a challenge.[87,88] Methane hydrates could also be processed, when CO_2 is available, through bireforming. Other sources such as methane formed by the hydrolysis of aluminum carbide could also be used.

It should be mentioned that building on the experience with autothermal reforming, the concept of "trireforming" was developed based on the synergetic combination of dry reforming, steam reforming, and partial oxidation of methane in a single step.[89] The exothermic oxidation of methane with oxygen produces the heat needed for the endothermic steam and dry reforming reactions, allowing a syngas mixture with a H_2/CO ratio close to 2 suitable for methanol production to be reached. As part of the natural gas is burned to produce the needed heat, it also generates excess carbon dioxide which can be recycled into the process. This would, however, require additional hydrogen from other sources and/or significantly reduce the amount of CO_2 to be recycled.

The viability of processes discussed depends on the availability of natural gas or other unconventional methane sources, which are finite and nonrenewable. They will increasingly get depleted and may become economically too prohibitive to exploit. In the long term, large-scale, cost-effective production of hydrogen by electrolysis of water or other water cleavage processes is therefore essential.

Combining Reduction and Hydrogenation of CO_2. Considering the chemical recycling of CO_2 to methanol the electrolysis of water is presently the only feasible alternative to fossil fuels for the production of hydrogen. However, as mentioned the catalytic hydrogenation of CO_2 to methanol produces water as a byproduct. A third of the hydrogen and the electricity used to produce it is thus diverted to produce water.

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

In order to utilize hydrogen more efficiently for CO_2 conversion to methanol, initial chemical or electrochemical reduction of CO_2 to CO to minimize water formation can be considered.

CO_2 reduction to CO can be achieved by the reverse Boudouard reaction via the thermal reaction of carbon dioxide with carbon, or coal itself.

$$CO_2 + C \xrightarrow{\Delta} 2\,CO \qquad \Delta H_{298K} = 40.8\ \text{kcal.mol}^{-1}$$

This endothermic reaction of coal gasification can be used at temperatures above 800 °C. The advantage over the steam reforming of coal, which is somewhat less endothermic (31.3 kcal mol^{-1}), is that it allows recycling of CO_2. Coal gasification with CO_2 can be conducted using packed bed or fluidized bed reactors and molten salt media (such as Na_2CO_3 and K_2CO_3 mixtures).[90] Two-step thermochemical coal gasification combined with metal oxide reduction have also been proposed and tested.[91,92] The coal gasification with CO_2 has especially been investigated for the conversion of solar thermal heat to chemical fuels, which would allow solar energy to be stored and transported in the form of a convenient fuel such as methanol. The direct conversion of CO_2 to CO using a thermochemical cycle and solar energy is also being studied.[93,94] Researchers at the Sandia National Laboratories recently developed a solar furnace that heats a device containing a cobalt-doped ferrite (Fe_3O_4) to temperatures around 1400−1500 °C, driving off oxygen gas. At a lower temperature, the reduced material FeO is then exposed to CO_2, from which it absorbs oxygen, leaving behind CO and ferrite, which can be recycled. This technology shows promise, but its viability on an industrial scale is still far away.

Another method to perform the reduction of CO_2 to CO, which does not require high temperatures, is electrochemical reduction in aqueous or organic media, i.e.

$$CO_2 \xrightarrow{e^-} CO + 1/2\,O_2$$

This approach has been studied using various metal electrodes in aqueous media.[95,96] Similar reductions in some organic solvent media were also studied. Methanol, in particular, used industrially as a physical absorber for CO_2 in the Rectisol process,[59] has been extensively studied as a medium for the electrochemical reduction of CO_2.[97−99]

Electrochemical Production of Methanol from CO_2 and H_2O. During the electrochemical reduction of CO_2 in water or methanol, hydrogen formation competes with the CO_2 reduction reaction, therefore reducing the Faradic efficiency of CO_2 reduction. Attempts are being made to suppress the hydrogen evolution.

In our studies of electrochemical CO_2 recycling, instead of considering H_2 evolution as a problem, we found it advantageous to generate CO and H_2 concomitantly at the cathode in a H_2/CO ratio close to 2, producing a syngas mixture (metgas), which is then further transformed into methanol, allowing the energy to be used efficiently for CO_2 reduction.[100] An additional advantage is the valuable pure oxygen produced at the anode, needed for example in new generation coal burning power plants. The electrochemical reduction reaction of CO_2, however, still has overpotential and efficiency problems, which must be overcome.

$$CO_2 + 2H_2O \xrightarrow{e^-} \begin{cases} \overset{\text{Syn-gas}}{\left[CO + 2H_2\right]} \text{ at the cathode} \longrightarrow CH_3OH \\ 3/2\,O_2 \quad \text{at the anode} \end{cases}$$

Regardless, methanol and dimethyl ether can be produced selectively from CO_2 via electrochemically generated syngas (metgas) in the same way as it is done from natural gas or coal. The advantage is that no purification step is required and no impurities such as sulfur, which could deactivate the catalyst, are present. The reaction is preferably run under pressure to feed directly the metgas into the methanol synthesis reactor.

Direct electrochemical reduction of CO_2 to methanol without syngas formation can also be achieved. This reaction is, however, kinetically rather complex and needs effective electrocatalysts. Generally, in the electrochemical reduction of CO_2 to methanol, formaldehyde and formic acid are also produced.[43,101−103] Photoelectrochemical conversion of CO_2 to methanol using light energy at a semiconductor electrode such as p-GaP has also been reported and direct conversion of CO_2 to methanol with solar energy shows promise.[104]

$$CO_2 + 2H^+ + 2e^- \longrightarrow HCOOH$$
$$CO_2 + 4H^+ + 4e^- \longrightarrow HCHO + H_2O$$
$$CO_2 + 6H^+ + 6e^- \longrightarrow CH_3OH + H_2O$$

To overcome difficulties associated with the formation of product mixtures in the electrochemical reduction of CO_2, Olah and Prakash developed a process in which formic acid and formaldehyde, without separation of the initial reaction mixture, can be converted to methanol in a subsequent secondary treatment step.[43] This involves initial formaldehyde dimerization (Tishchenko reaction) over catalysts such as TiO_2 and ZrO_2 to give methyl formate, followed by hydrogenation.

$$2CH_2O \longrightarrow HCOOCH_3$$
$$HCOOCH_3 + 2H_2 \longrightarrow 2CH_3OH$$

Formaldehyde can also undergo conversion over solid base catalysts such as CaO and MgO, in a variation of the Cannizaro reaction, giving methanol and formic acid. These can then further react to form methyl formate, which can be hydrogenated to methanol.

$$2\,HCHO \xrightarrow{TiO_2 \text{ or } ZrO_2 \text{ catalyst}} HCOOCH_3$$
$$2\,HCHO \xrightarrow{H_2O} CH_3OH + HCO_2H$$
$$CH_3OH + HCO_2H \xrightarrow{-\,H_2O} HCOOCH_3$$

Formic acid formed during the electrochemical CO_2 reduction and the Cannizaro reaction can itself serve as a hydrogen source in the reaction with formaldehyde to form methanol and carbon dioxide.

$$HCHO + HCO_2H \longrightarrow CH_3OH + CO_2$$

This, however, has the disadvantage of producing CO_2, which must be subsequently recycled.

The combination of these reactions in a secondary treatment step allows to significantly increase the overall efficiency of electrochemical reduction of CO_2 to methanol. It is, however, preferable to develop more effective catalysts that are able to increase the selective electrochemical reduction of CO_2 to methanol in order to minimize secondary treatments.

Dimethyl Ether (DME) Production from Carbon Dioxide. The conventional bimolecular dehydration of methanol to DME is readily carried out catalytically over varied solid acids such as alumina or phosphoric acid modified γ-Al_2O_3.

$$2\,CH_3OH \longrightarrow CH_3OCH_3 + H_2O$$

This is already a significant industrial process in countries such as Japan, Korea, and China with about 4 million tonnes of DME produced annually. The needed methanol, as discussed, is currently based on syngas obtained from either natural gas or coal. Methanol can, however, also come from any other discussed source. In recent years, direct synthesis of DME from syngas, combining methanol synthesis and dehydration in a single step, has been extensively studied. The process essentially combines methanol synthesis catalyst based on $Cu/ZnO/Al_2O_3$ with a methanol dehydration catalyst that is operating preferably between 240 and 280 °C at pressures between 30 and 70 bar. Interestingly, the equilibrium conversion in the DME synthesis is significantly higher than that in the methanol synthesis even at low pressure.[105] Using this technology, a demonstration plant producing 100t DME/day based on a slurry reactor has been built and tested by Japan Steel Engineering (JFE).

There are two main routes to produce DME directly from syngas, i.e., (1) and (2) producing water and carbon dioxide, respectively, as byproduct.[26]

Route (1) is a combination of methanol synthesis (3) and methanol dehydration (4) to DME. Reaction (2) combines reaction (3) and (4) with the water gas shift reaction (5). Both routes have been utilized. Route (1) is used by Haldor Topsoe and others, whereas JFE follows route (2). The byproduct of this route is CO_2, the separation of which from DME is much easier and less energy consuming than the separation of water from DME. Route (2) also allows a higher syngas conversion and has the advantage of using a syngas with a H_2/CO ratio of 1. This means that coal gasification or methane dry reforming could be used to produce the required syngas. The overall reaction combining methane dry reforming with DME synthesis through route (2) is basically the reaction of three moles of CH_4 with 1 mol of CO_2 with no hydrogen lost in byproduct water.

$$\begin{array}{c}
3CH_4 + 3CO_2 \longrightarrow 6CO + 6H_2 \\
6CO + 6H_2 \longrightarrow 2CH_3OCH_3 + 2CO_2 \\
\hline
3CH_4 + CO_2 \longrightarrow 2CH_3OCH_3
\end{array}$$

In its DME plant, JFE uses an autothermal reforming unit combining dry reforming and partial oxidation of methane to produce syngas with a H_2/CO ratio of 1. The exothermic oxidation reaction generates the heat needed for the process but produces water as a byproduct.

$$2CH_4 + O_2 + CO_2 \longrightarrow 3CO + 3H_2 + H_2O$$

Our discussed bireforming pathway can also effectively produce DME, either directly using the DME synthesis route (1) or through methanol. The water formed during the DME synthesis is recycled into the bireforming step, allowing all the hydrogen content of the used methane (or natural gas) to be utilized in DME production.[106]

$$3CH_4 + 2H_2O + CO_2 \longrightarrow 4CH_3OH \longrightarrow 2CH_3OCH_3 + 2H_2O$$

The overall reaction for DME synthesis is accordingly again

$$3CH_4 + CO_2 \longrightarrow 2CH_3OCH_3$$

If coal is the available fossil fuel instead of natural gas, CO_2 formed upon its combustion can be captured and converted to

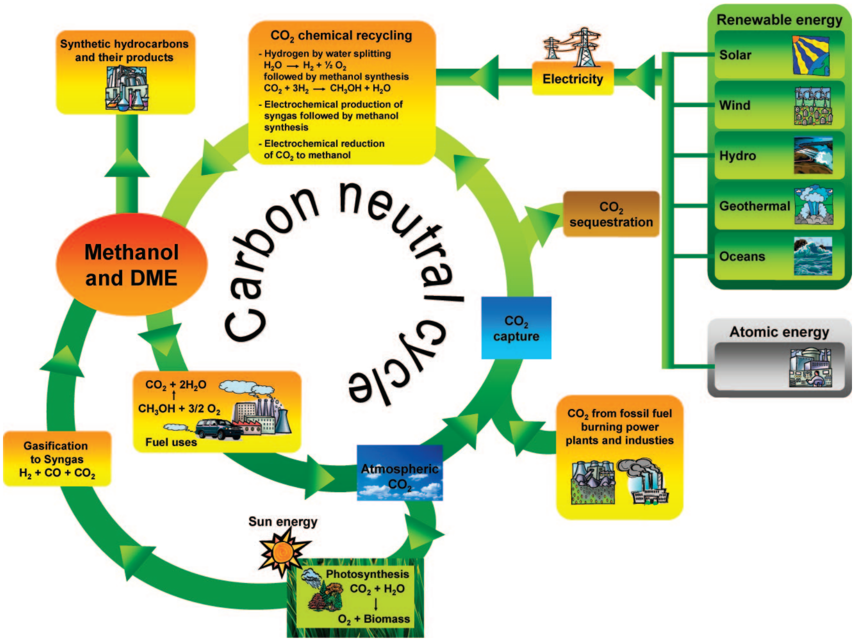


FIGURE 1. Carbon dioxide recycling in the Methanol Economy.

$$2CO + 4H_2 \longrightarrow CH_3OCH_3 + H_2O \qquad \Delta H_{298K} = -49.0\ \text{kcal.mol}^{-1} \qquad (1)$$

$$3CO + 3H_2 \longrightarrow CH_3OCH_3 + CO_2 \qquad \Delta H_{298K} = -58.7\ \text{kcal.mol}^{-1} \qquad (2)$$

$$2CO + 4H_2 \longrightarrow 2CH_3OH \qquad \Delta H_{298K} = -43.5\ \text{kcal.mol}^{-1} \qquad (3)$$

$$2CH_3OH \longrightarrow CH_3OCH_3 + H_2O \qquad \Delta H_{298K} = -5.5\ \text{kcal.mol}^{-1} \qquad (4)$$

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad \Delta H_{298K} = -9.8\ \text{kcal.mol}^{-1} \qquad (5)$$

methanol using frequently accompanying coalbed methane, readily available, for example, in the US, Australia, and China.

If natural gas or methane is not available, CO_2 can first be chemically (with the Boudouard reaction) or electrochemically reduced to CO and then reacted with H_2 generated from water.

$$CO_2 + C \longrightarrow 2CO \xrightarrow{4H_2} 2CH_3OH \longrightarrow CH_3OCH_3 + H_2O$$

$$4H_2O \xrightarrow{e^-} 4H_2 + 2O_2$$

Avoiding a separate CO-forming step, CO_2 can also be directly transformed into DME by catalytic hydrogenation. Like the direct route from syngas to DME, the CO_2 hydrogenation to DME route uses a hybrid catalyst consisting of a methanol synthesis and a methanol dehydration catalyst.[107] Water formed can, when needed, be recycled, particularly in arid areas or when the need for pure water would warrant it.

$$2CO_2 + 6H_2 \longrightarrow 2CH_3OH + 2H_2O$$

$$2CH_3OH \longrightarrow CH_3OCH_3 + H_2O$$

$$2CO_2 + 6H_2 \longrightarrow CH_3OCH_3 + 3H_2O$$

The Significance of Chemical CO_2 Recycling and the Methanol Economy. The recycling of CO_2 from industrial or natural emissions and capture of CO_2 from the atmosphere provides a renewable, inexhaustible carbon source and could also allow the continued use of derived carbon fuels in an environmentally carbon neutral way. As discussed presently, the captured CO_2 would be stored/sequestered in depleted gas- and oil- fields, deep aquifers, underground cavities, at the bottom of the seas, etc. This, however, does not provide a permanent safe solution, nor does it help our future needs for fuels, hydrocarbons, and their products. Recycling of the carbon dioxide via its chemical reduction with hydrogen to produce methanol and/or DME (i.e., the Methanol Economy) offers in contrast a viable new permanent alternative. As fossil fuels are becoming scarcer, capture and recycling of CO_2 and eventually atmospheric CO_2 would continue to support production and use of carbon-containing fuels such as methanol, DME, and all the synthetic hydrocarbons and their needed products. We do not believe that humankind is facing an energy crisis. We are, after all in the final analysis, obtaining most of our energy in one form or another from the sun. The problem is not the lack of energy, but its efficient capture, storage, transportation and use.

The proposed Methanol Economy can fulfill all these requirements if we can efficiently in a renewable and economic manner, recycle CO_2, and produce methanol, DME, and their derived products.[40−43] Upon their combustion and use, methanol, DME, and produced synthetic hydrocarbons will form CO_2 and water. Overall, the methanol cycle constitutes humankind's artificial version of nature's CO_2 recycling via photosynthesis (Figure 1). Using this approach, there will be no need to change drastically the nature of our energy use, storage, and transportation infrastructure or the continued use of synthetic hydrocarbons and products. As CO_2 is available to everybody on Earth, it would liberate us from the reliance on diminishing and nonrenewable fossil fuels frequently present only in geopolitically unstable areas.

Outlook. We do not believe that there will be a single solution to the discussed global problems. However, the approach of the chemical recycling of carbon dioxide to produce carbon neutral renewable fuels and materials offers a feasible and powerful new alternative and is entering the stage of gradual practical implementation.

In conclusion, it needs to be again emphasized that the chemical recycling of carbon dioxide to methanol and DME provides a renewable, carbon-neutral, inexhaustible source for efficient transportation fuels, for storing and transporting energy, as well as convenient starting materials for producing ethylene and propylene and from them synthetic hydrocarbons and their products. It thus essentially replaces petroleum oil and natural gas. While allowing the continued use of carbon-containing fuels and materials, it also curtains harmful excessive CO_2 emissions causing global warming. The concept of what we call the "Methanol Economy" and much of the underlying chemistry was developed in our work over the past 15 years and is discussed in our monograph.[2,108] The present discussion on the chemical recycling of carbon dioxide is an important part of our overall approach.

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