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PERSPECTIVE

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Anthropogenic Chemical Carbon Cycle for a Sustainable Future

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ABSTRACT: 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, millions of years, can new fossil fuels be formed naturally. The burning of our diminishing fossil fuel reserves is accompanied by large anthropogenic CO_2 release, which is outpacing nature's CO_2 recycling capability, causing significant environmental harm. To supplement the natural carbon cycle, we have proposed and developed a feasible anthropogenic chemical recycling of carbon dioxide. Carbon dioxide is captured by absorption technologies from any natural or industrial source, from human activities, or even from the air itself. It can then be converted by feasible chemical transformations into fuels such as methanol, dimethyl ether, and varied products including synthetic hydrocarbons and even proteins for animal feed, thus supplementing our food chain. This concept of broad scope and framework is the basis of what we call the Methanol Economy. The needed renewable starting materials, water and CO_2, are available anywhere on Earth. The required energy for the synthetic carbon cycle can come from any alternative energy source such as solar, wind, geothermal, and even hopefully safe nuclear energy. The anthropogenic carbon dioxide cycle offers a way of assuring a sustainable future for humankind when fossil fuels become scarce. While biosources can play a limited role in supplementing future energy needs, they increasingly interfere with the essentials of the food chain. We have previously reviewed aspects of the chemical recycling of carbon dioxide to methanol and dimethyl ether. In the present Perspective, we extend the discussion of the innovative and feasible anthropogenic carbon cycle, which can be the basis of progressively liberating humankind from its dependence on diminishing fossil fuel reserves while also controlling harmful CO_2 emissions to the atmosphere. We also discuss in more detail the essential stages and the significant aspects of carbon capture and subsequent recycling. Our ability to develop a feasible anthropogenic chemical carbon cycle supplementing nature's photosynthesis also offers a new solution to one of the major challenges facing humankind.

NATURE'S CARBON CYCLE

Despite the much emphasized and discussed energy shortage of the future, most of our energy, including fossil fuels (coal, oil, natural gas), comes in some way or other from the energy of the sun.[1] As the sun is estimated to last for at least another 4.5 billion years, the challenge is to find more efficient and feasible ways to capture and utilize its energy. Beside fossil fuels, which are formed over long geological times by anaerobic conversion of plant and animal life, we are increasingly using renewable alternative energy sources, such as hydro, geothermal, solar, wind, etc., including atomic energy, to satisfy our ever increasing energy needs.

In the natural carbon cycle, nature uses the sun's energy to recycle carbon dioxide from natural sources through photosynthesis. It captures CO_2 from the atmosphere with vegetation, plankton, algae, etc., and using water as the hydrogen source, the energy from the sun, and green chlorophyll acting as the catalyst, new plant life is created, which eventually, over million of years, can be converted to fossil fuels. Primo Levi, in his book, *The Periodic Table*, gives a captivating tale of a CO_2 molecule being liberated through human activity from limestone, followed by its capture by leaves of a tree from the atmosphere and conversion to new plant life by photosynthesis, i.e., the natural carbon cycle.[2] Carbon is an essential building block for all life forms on Earth, and its natural recycling from the atmosphere is a perpetual process (Figure 1). Photosynthesis is however relatively inefficient at converting the sun's energy into chemical energy in the form of sugars, cellulose, lignin, etc. Although some plants, such as sugar cane, can convert up to 8% of the sun's energy into biomass, most crops' photosynthetic efficiency is generally limited to 0.5−2%. This is understandable since the main priority for plants is to ensure their own survival and be able to reproduce under variable climatic conditions such as drought, heavy rainfall, variation in temperature, etc. Under most conditions, the availability of water and nutrients, especially phosphorus, nitrogen, and potassium (soil conditions), might be more of a limiting factor than the amount of sunlight the plant can process. Products of photosynthesis can eventually become fossil fuels, which are produced from anaerobic plant and animal decay. Fossil fuels can therefore also be considered stored, fossilized sun energy. The natural cycle to reproduce fossil fuels occurs however only under specific conditions and is very slow, taking many millions of years, for which humankind cannot wait.[3]

CARBON IN THE INDUSTRIAL AGE

For its existence, humanity has been relying on biomass such as wood and other vegetation for cooking, heating, building shelters, and making clothes and varied products. Mechanized agriculture, irrigation, and land management have helped to increase the output of biomass. Humankind's survival and development is however limited by the availability of natural resources, including any suitable energy source, and their ability to be replenished by nature's cycles. Only with the dawn of the industrial revolution, in which coal became a main energy source,

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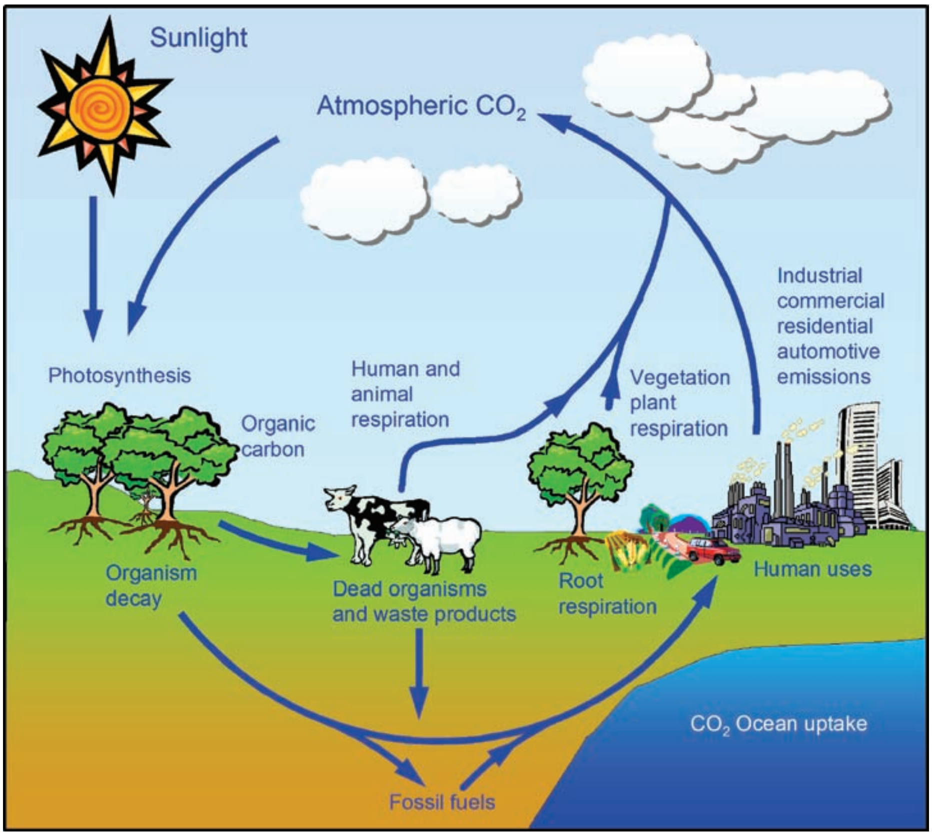


Figure 1. Natural carbon cycle.

did humans manage to expand this natural cycle. The concomitant invention of the steam engine triggered a golden age for industrial development and increased productivity. It also allowed for new modes of transportation such as trains and steam engine-powered ships, revolutionizing how people and merchandise were moved. In the late 19th century petroleum oil, followed by natural gas in the 20th century, began to supplement coal, allowing an unprecedented era of prosperity and development as well as a population boom from less than 1 billion people in 1800 to 7 billion people today. As the population as well as standards of living increased, so has our consumption of fossil fuels. Presently, about 85 million barrels of oil (around 12 million tonnes), 8 billion m^3 of natural gas, and 16 million tonnes of coal are consumed each and every day.[4] Nature has given us a remarkable gift in the form of fossil fuels, but it is nevertheless limited and is being irreversibly used up. It has been shown that a single barrel of oil has the energy content of 12 people working all year, or 25 000 man-hours. With each American consuming on the average about 25 barrels of oil per year, this would amount to the equivalent of 300 people working all year long to power industries, fuel cars, and other transport and provide for the many needs of their households to maintain the current standards of living of each of them.

Our existing fossil fuel reserves are limited and are increasingly depleted. Affordable and easily accessible oil and gas will essentially last only for this century.[3,5] When the demand for petroleum oil and natural gas outpaces the global production capacity (the so-called Hubbert's peak), availability will decrease and their prices will increase sharply.[5] The estimated time for the Hubbert's peak for global oil production ranges anywhere from 2005 to 2025, depending on the information source, meaning that we may have already reached it or are nearing it.[3,6,7] A similar Hubbert's peak for natural gas is predicted for sometime in the latter part of this century. Exploitation of shale gas and methane hydrate could significantly increase the amounts of natural gas available. The impact of their production on the environment is however raising increasing concerns.[8] Coal could last for another two centuries,[1] although recent studies have shown that readily accessible reserves of coal might have been overestimated.[9]

■ EXCESS CARBON DIOXIDE: A HARMFUL GREENHOUSE GAS

Another major problem with the extensive use of fossil fuels and their products is that upon combustion or other oxidative processes they eventually transform their carbon content into carbon dioxide, which as a major greenhouse gas contributes to global warming. The relationship between the carbon dioxide content of the air and the temperature, the so-called greenhouse effect, was first suggested by the French mathematician, Joseph Fourier, two centuries ago and later proven by the Swedish chemist, Svante Arrhenius, at the end of the 19th century.[10] It is consequently generally accepted that increasing CO$_2$ content of the air substantially contributes to global warming.[11] It is however possible as well that warming cycles of our climate by natural causes can also contribute to an increase in natural CO$_2$ release. Variation in the sun's activity, such as sun spots, as well as the cycles of changes in the Earth's rotational axis can also contribute to natural climate change, as indicated by numerous prehistoric glacial periods alternating with warmer interglacial periods long before humans appeared on Earth.[11,12]

ESSENTIAL ASPECTS OF BIOLOGICALLY BASED ANTHROPOGENIC CARBON CYCLES AND THEIR LIMITATIONS

As mentioned, carbon is an essential element without which terrestrial life could not exist or be maintained. It thus cannot be "banned" or legislatively outlawed unlike the success achieved with the ban of man-made chlorofluorocarbons (CFCs) or other harmful environmental pollutants. Weaning us off fossil fuels as long as they are relatively easily accessible seems also difficult, as we are so dependent on them to fill our daily energy and material needs. In the near future, alternative sources of energy would be hard-pressed to replace a significant portion of still existing fossil fuels sources. Fossil fuels greatly contribute to the annual global emission of more than 30 billion tonnes of CO_2. Only about half of it is recycled or sequestered by nature's own cycles. Anthropogenic activities thus significantly contribute to the present trend of global warming, and we should do whatever possible to minimize their effect.

We face both a short- and long-range carbon conundrum: the environmentally harmful effect caused by excessive formation of atmospheric CO_2 and our diminishing relatively easily available fossil fuel resources. Besides changing to alternate low-carbon sources, savings, carbon taxes, and new technological approaches making carbon resources renewable and environmentally adaptable are clearly essential for the future.

It is frequently proposed to rely more heavily on biomass and derived products to fulfill our energy needs. The production of biofuels such as ethanol, obtained by fermentation of corn, wheat (first suggested in Russia after the Bolshevik revolution but later abandoned by Lenin himself), and sugar cane has increased rapidly in recent years. Whereas ethanol can be used mixed with gasoline or as an alternative fuel as well as a chemical raw material for synthetic hydrocarbons such as olefins, the enormous amounts of transportation fuel needed clearly limits the applicability of biofuels to specific countries and situations. In 2009, the U.S. produced about 40 million m^3 of ethanol from corn, which represented less than 5% of the fuels used in its road transportation. Replacing 100% of the transportation fuels would require all the arable land in the U.S. Other crops-based oils are also being developed primarily to produce biodiesel, equivalent to petroleum-based diesel fuel. Their economic production, however, remains limited. There is also growing concern that the use of food crops for the production of fuels contributes to increasing food prices by competing for the same agricultural resources. Furthermore, crop production requires sufficient water, a suitable temperature range, and fertilizers (mostly derived from fossil fuel resources) as well as agricultural land. Energy crops as potential fuel sources should not compete with food crops for these essential resources. It has been estimated that biomass produced in a renewable and sustainable manner can cover at most 10−15% of our energy needs of the future.[13a]

Former U.S. Vice President and Nobel Peace Prize laureate Al Gore, a major proponent of biofuels, recently publicly admitted that bioethanol as an alternative fuel was promoted mainly for political reasons and recommended discontinuing the subsidies for its production, distribution, and use as a fuel.[13b] We clearly must develop feasible technologically renewable fuel sources as well as new and efficient ways to store, transport, and use them to supplement and eventually replace the diminishing fossil fuels.

FEASIBILITY OF ALTERNATIVE ENERGY SOURCES

Alternative energy sources such as solar, wind, geothermal, wave, and safe nuclear energy are increasingly used to produce primarily electricity. Their overall share of the world energy production is however still limited. Whereas electricity is an excellent medium to transport energy over relatively short distances, it is difficult to store on a large scale. Batteries, flywheels, and pumped hydro and compressed air storage have limited capacities. Presently, electricity production closely follows the demand and has to adapt to daily and seasonal fluctuations. Renewable energies such as solar and wind are intermittent and do not follow closely the demand. Solar does not produce any power during the night or under cloudy conditions, and wind does not blow constantly. Storage of electricity to even out fluctuations in demand and production cycles is essential for the use of renewable energies on a large scale. A way of achieving this goal is by storing electric energy in the form of chemical compounds such as hydrogen, hydrocarbons, and methanol.

Hydrogen has been proposed as an energy storage medium in the context of the "Hydrogen Economy". Hydrogen is an excellent fuel, producing only energy and water when burned. Using hydrogen as an energy carrier has however a number of serious drawbacks mainly linked to its physical and chemical properties. It is a very volatile gas which has to be compressed at high pressure (350−700 bar) or liquefied at a cryogenic temperature of −253 °C to have a reasonable volumetric energy density. Hydrogen is also highly flammable and explosive, diffuses easily through numerous metals and materials, and requires an expensive and currently nonexistent infrastructure. Nobelist Steven Chu, the current U.S. energy secretary, in 2009 publicly summarized these difficulties and suggested ending federal funding for the development of hydrogen as a transportation fuel, although Congress later overruled him and restored the funding.

LIQUID ALTERNATIVE FUELS

A liquid energy carrier that is easy to handle, transport, and store is most desirable and preferable to hydrogen for most applications. Especially in the transportation sector, the transition from petroleum-based liquid fuels to a renewable and safe liquid fuel would require only minor modifications to the existing infrastructure. Methanol is one of the most promising candidates fulfilling these requirements, and the present Perspective focuses on this energy carrier. The numerous advantages of using methanol as a fuel and feedstock have been described in detail elsewhere.[14−21] Methanol, due to its high octane number, is an excellent gasoline substitute for internal combustion engines (ICEs). It can also be used in direct methanol fuel cells (DMFCs) that we developed jointly in collaboration with the Jet Propulsion Laboratory. DMFCs are able to transform the chemical energy contained in methanol directly into electrical power. Methanol can also be used as a fuel for gas turbines. Dimethyl ether (DME), obtained by simple dehydration of methanol, is by itself a superior diesel fuel substitute and a household gas. It can also replace liquefied petroleum gas (LPG) and liquefied natural gas (LNG) in most applications. Besides its fuel applications, methanol is also a convenient starting material to produce light olefins (ethylene, propylene) and practically any synthetic hydrocarbon and product currently obtained from petroleum.

Methanol can be efficiently produced from a wide variety of carbon-containing sources, including any still-available fossil fuel (natural gas, coal, oil shale, tar sands, etc.), but also from agricultural and natural sources including municipal waste, wood,

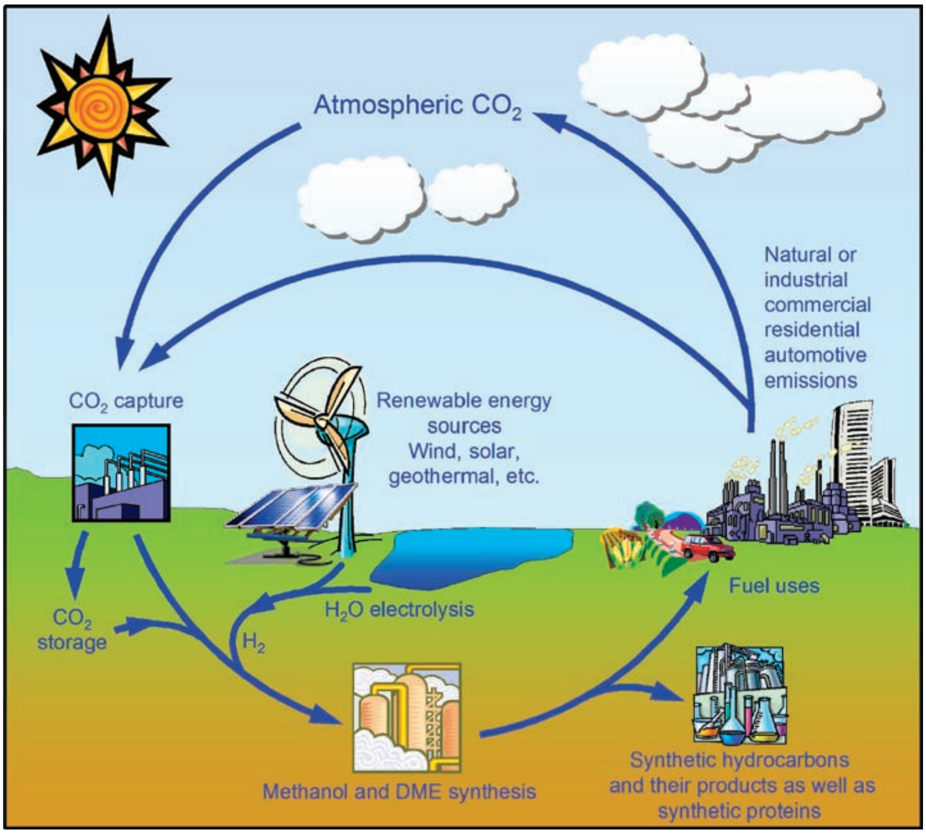


Figure 2. Anthropogenic chemical carbon cycle.

and varied biomass. The challenge is to obtain methanol in a sustainable and renewable way using any available source of alternative energy.

ANTHROPOGENIC CHEMICAL CARBON CYCLE

We have developed and discuss the concept that the natural photosynthesis-based carbon cycle can be supplemented by a feasible *anthropogenic chemical carbon cycle* (Figure 2). It is based on carbon dioxide capture and recycling to fuels and materials. When needed, capture and temporary *storage* is followed by *recycling* by chemical conversion with hydrogen derived from water into methanol and subsequently to synthetic hydrocarbons and derived fuels and products.[22−25] In contrast with the *natural* carbon cycle based on photosynthesis and subsequent slow anaerobic conversion under suitable conditions to fossil fuels, the *chemical* carbon cycle can be carried out on an industrial scale to provide a sustainable, renewable, and safe carbon source for the future to produce hydrocarbons, derived fuels, and synthetic products on which we depend so much. At the same time, the chemical recycling of carbon dioxide can mitigate or even eliminate the harmful environmental effect of excessive carbon dioxide buildup in the atmosphere contributing to global climate change.

Presently, the only feasible practical way to mitigate atmospheric increase of carbon dioxide is by decreasing our dependence on fossil fuel and using alternate low carbon energy sources while increasing where possible nature's own photosynthetic recycling or using carbon capture and storage (CCS).[26,27] CO_2 can be, and is presently starting to be captured and stored underground to a limited degree. It is captured mainly from extensive carbon dioxide emission sources such as coal-burning power plants and varied industrial plants. These include cement and aluminum factories, fermentation plants, etc. CO_2 is also a byproduct of natural gas or geothermal energy production facilities, where it accompanies these natural sources in significant amounts (10−70%). Most of the CO_2, however, is presently still vented into the atmosphere, contributing to an increase of global warming. As mentioned, to avoid environmental harm, it is proposed to be captured and sequestered (stored, CCS) underground in depleted oil and gas fields, coalbeds, suitable geological formations, saline aquifers, or subterranean cavities or at the bottom of the seas, as presently done in the Norwegian sector of the North Sea and in some parts of Algeria, Northern Germany, etc.[26,28] Industrial CO_2 separation and capture is affected mostly by liquid-phase absorbents, such as alkanolamine solutions,[29] or even by freezing out CO_2 as dry ice. Use of these processes is costly and energy intensive, however. Instead of liquid absorbents, effective solid absorbents would be preferable for the capture of CO_2 on a large scale. Research is ongoing in this direction.[30,31] We have developed effective new nanostructured silica-supported solid absorbents using polyethyleneimine or other polyamines that absorb CO_2 even from the air.[32] Sequestration (CCS) however is not only costly and provides no value but is also only temporary and potentially dangerous. Stored, volatile CO_2 tends to slowly leak or can even be released at once in case of geological events (earthquakes, slides, etc.), causing substantial instant danger for living beings. A sudden catastrophic natural release of CO_2 was the reason for a tragedy that took place around a lake in Cameroon in 1986, killing by asphyxiation almost 2000 people and thousands of animals.[33] Natural

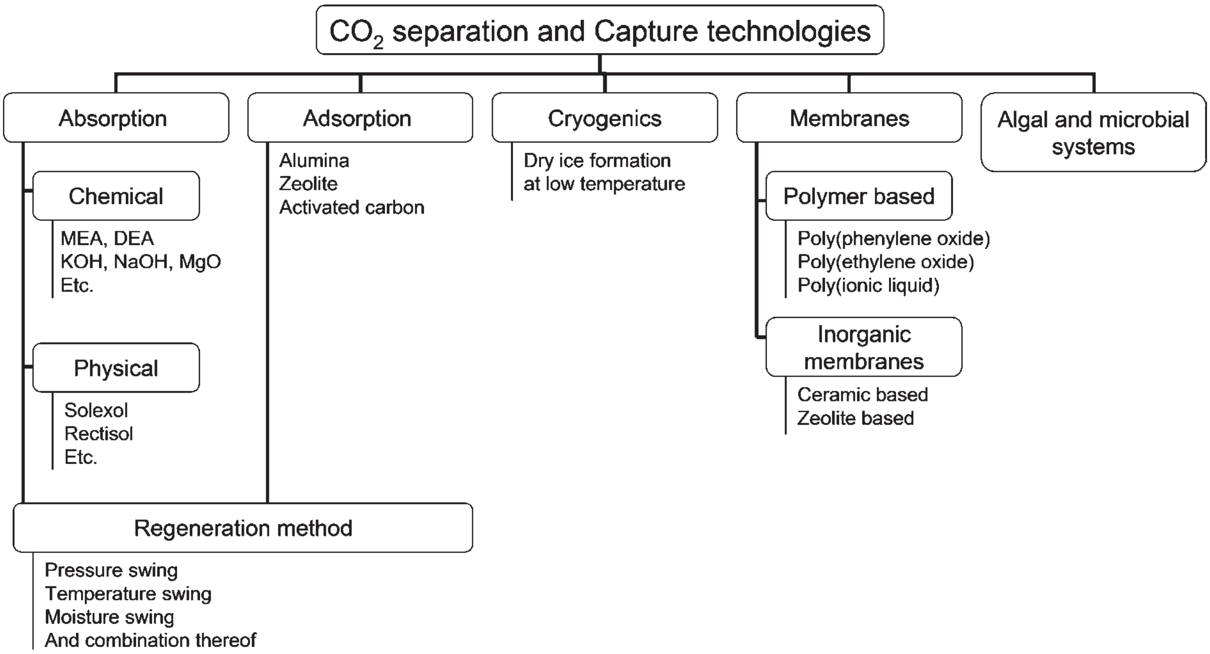


Figure 3. CO_2 absorption technologies.

carbonation of stored carbon dioxide in suitable geologic formations or when injected into the depth of the seas is feasible but is a process that takes a long period of time. CCS in our view can therefore not be considered as a solution for excess carbon dioxide disposal. There is also widespread public opposition to storing possibly billions of tonnes of CO_2 close to inhabited areas.

In contrast to CCS, retrieving and recycling of stored carbon dioxide for chemical conversion to methanol (carbon capture and recycling, CCR) and its derived products is based on developed, feasible, and sustainable chemistry that does not ignore economic considerations. Thus, the anthropogenic technological carbon cycle can liberate humankind from diminishing and limited fossil fuels and biological natural carbon sources including crops and biomass. The use of chemistry to supplement nature is indeed not new. The Haber−Bosch process provides ammonia by chemical synthesis using atmospheric nitrogen and hydrogen generated from any source, presently mostly natural gas but eventually by water electrolysis or splitting. The anthropogenic carbon cycle, which we have proposed and discuss here, eventually will vastly exceed the scope and significance of the synthetic ammonia cycle.

■ CO_2 CAPTURE FROM NATURAL AND ANTHROPOGENIC SOURCES

In order to produce fuels from CO_2, first CO_2 has to be efficiently captured from natural and anthropogenic sources. Some of the largest practical sources for CO_2 are presently fossil fuel-burning power plants as well as cement and aluminum factories. Flue gases from conventional fossil fuel-burning power plants contain concentrations of CO_2 around 10−15%. Existing power plants could be retrofitted for postcombustion CO_2 capture and purification using known and developing technologies. The energy required using, for example, well-developed monoethanolamine (MEA) solutions for the capture of CO_2 is high, however. The energy penalty for CO_2 capture from a coal-based power station has been estimated to be 25−40%. The volume of flue gases that has to be handled is also high because of ambient pressure of 1 atm at their relatively low CO_2 concentration. Therefore, for new power plants it would be advantageous to use different technologies such as precombustion CO_2 capture or oxy-fuel combustion. Using the precombustion process, the fossil fuel is first gasified to yield a mixture of H_2, CO, and CO_2 which is then subjected to water−gas shift reaction (WGSR) to obtain a gas mixture containing mostly H_2 and CO_2. The obtained CO_2 at high pressure and high concentration is easily separated, and the hydrogen is sent to a gas turbine to produce electricity. In oxy-fuel combustion, the fuel is burned in a mixture of pure O_2 and CO_2.[34] The flue gases do not contain nitrogen and have a high CO_2 concentration, making separation easier. The energy penalty in the oxy-fuel process comes from the need for oxygen separation from air, requiring large oxygen separation units based mainly on cryogenic or membrane technologies.

The vast majority of the power plants in use and even the ones currently under construction still use conventional technologies, which would require postcombustion capture. Exploitation of natural gas sources containing up to 70% CO_2 as well as geothermal vents, which are often accompanied by CO_2, also constitute considerable sources from which CO_2 could be separated and recycled to fuels (CCR) instead of being vented into the atmosphere or sequestered underground (CCS).

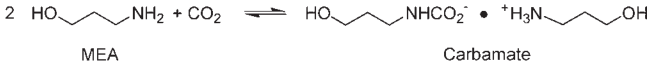
The removal and capture of CO_2 from gas streams can be achieved by a range of separation techniques depending on CO_2 concentration, pressure, temperature, etc. They are based on different physical and chemical processes, including absorption into liquid solution systems, adsorption onto a solid, cryogenic separation, and permeation through membranes (Figure 3, Table 1).[35]

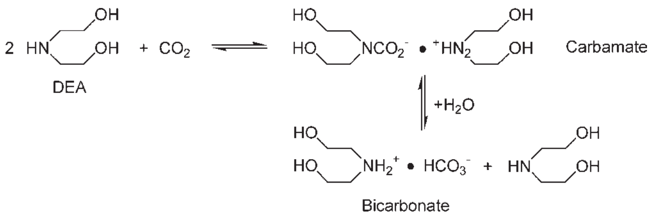
Cryogenic distillation is very energy intensive and generally considered impractical for large-scale CO_2 separation. Membranes are more suited for relatively high concentrations of CO_2 such as those encountered in some natural gas deposits or for precombustion separation.

Table 1. Estimated Energy Required To Remove and Recover CO_2 from Coal-Fired Power Plants Using Various Technologies[36]

process	CO_2 removal efficiency (%)	kWh(e)/lb CO_2 recovered
Improved amine absorption/stripping integrated plant	90	0.11
Oxygen/coal-fired power plant	100	0.15
Amine (MEA) absorption/stripping nonintegrated plant	90	0.27
Potassium carbonate absorption/stripping	90	0.32
Molecular sieves adsorption/stripping	90	0.40
Refrigeration	90	0.40
Seawater absorption	90	0.80
Membrane separation	90	0.36

Among the different CO_2 separation technologies, amine-based solution absorption/desorption systems are presently some of the most suitable technologies for high-volume flue gas streams. The commonly used absorbents are aqueous solutions of alkanolamines such as MEA and diethanolamine (DEA), which form carbamates and bicarbonates with CO_2.[29]





CO_2 absorption using liquid amines is a well-known and widely used technology that is highly selective for the separation of CO_2 from gas mixtures. However, it is far from being an optimal system. High energy requirements for the CO_2 regeneration step, limited loadings in amines due to corrosion problems, and amine decomposition and degradation are major drawbacks calling for the development of more efficient, regenerable CO_2 sorbents.

A possible way to get around the difficulties encountered by liquid systems is to use solid CO_2 absorption systems, which are either chemical or physical adsorbents. Solid chemical adsorbents include CaO, MgO, and hydrotalcites. They are attractive because of their low cost and wide availability from precursors such as limestone and dolomite. However, an acceptable adsorption rate can only be achieved at relatively high temperatures (200−500 °C). The desorption step requires an even higher temperature. Stability over repeated absorption/desorption cycles is also an issue.[30]

Physical CO_2 absorption on solids is based on the ability of porous solids to reversibly adsorb certain components in mixtures. Solids such as silica gel, alumina, and activated carbon can have a large pore size distribution. Others, like zeolites, have a defined pore size controlled by their crystal structure. At room temperature, zeolite-based adsorbents have shown high absorption capacities for CO_2 (zeolite 13X, 160 mg of CO_2/g, and zeolite 4A, 135 mg of CO_2/g at 25 °C in pure CO_2).[37] The problem with these adsorbents is the fast decline in adsorption capacities with increasing temperature. Moreover, as the gases are only physically adsorbed on these adsorbents, the separation factors between different gases (such as CO_2/N_2 mixtures) are low, which makes capture from sources containing low CO_2 concentrations impractical.

For practical applications, sorbents with high selectivity for CO_2, high capacity, and easy regeneration are desired. Recently, metal−organic frameworks (MOFs) with high CO_2 storage capacity have been discovered. 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 of CO_2 per gram of MOF at a pressure of 30 atm.[38,39] However, at lower pressure and with gas mixtures, MOFs had much more limited absorption capacity.

To achieve a higher selectivity to CO_2 in solid absorbents, chemical absorption is one of the possible pathways. For this, different approaches can be envisioned: (a) use of solid amines or polyamines directly as absorbents,[40] (b) amines or polyamines chemically bonded to the surface of a solid,[41−45] or (c) amines or polyamines deposited (physical adsorption) on a solid support such as silica or alumina.

As long as relatively high concentration CO_2 sources are available, it would be easier, more cost-effective, and less energy demanding to separate it from these sources. As our fossil fuel reserves are however finite, we would have to rely increasingly on alternate sources to provide the needed CO_2. Ultimately CO_2 recycling from the air would provide an almost limitless source of carbon, but such processes, although feasible, are presently still very expensive.

■ CAPTURE AND RECYCLING OF CO_2 FROM THE AIR: AN INEXHAUSTIBLE INDUSTRIAL CARBON SOURCE FOR THE FUTURE

More than half of CO_2 emissions are the result of small dispersed sources such as home and office heating and cooling, agricultural operations, and most importantly the transportation sector. The collection at the source of CO_2 from millions, even billions, of small fossil fuel-burning units would be difficult and costly if at all possible. For example, while capturing CO_2 from vehicles onboard may be technically feasible, it would be economically prohibitive. Moreover, CO_2, once captured, would have to be transported to a sequestration and conversion site, requiring the construction of a massive and expensive infrastructure. Capturing CO_2 onboard airplanes is even less feasible because of the added weight involved. In homes and offices, producing highly dispersed and limited amounts of CO_2, the capture and transportation of CO_2 would also require an extensive and costly infrastructure. While collection of these dispersed CO_2 emissions is not feasible at present, they represent a significant part of the global CO_2 emissions, and their future importance cannot be ignored.

To deal with small and dispersed CO_2 emitters and to avoid the need to develop and construct an enormous CO_2-collecting infrastructure, CO_2 should be eventually captured from the atmosphere itself—an approach that has already been proposed by some in the past.[19,46−49] The atmosphere could thus serve as a means of transporting CO_2 emissions to the site of its capture, acting as a cost-free "natural CO_2 conveyor belt". This would make CO_2 collection independent of CO_2 sources, and CO_2 could be captured from any source—small or large, static or mobile. With the concentration of CO_2 in air being at equilibrium all around the world, CO_2 extraction facilities could be located anywhere, allowing for any subsequent chemical recycling to fuels and products. They should ideally be placed close to hydrogen production sites and major population centers. As equilibration of CO_2 in the air is relatively rapid, local depletion of CO_2 is not likely to pose any problem. If this were not the case, emissions from power plants would cause much higher local concentration of CO_2 near the plants, which is not the case.

Due to the low CO_2 concentration in the air of only 0.0390% presently, its efficient and economic capture from this source remains a challenge. Carbon dioxide can be captured from the atmosphere, although at a substantial expense, using basic absorbents such as calcium hydroxide ($Ca(OH)_2$), potassium hydroxide (KOH), or sodium hydroxide (NaOH) which react with CO_2 to form calcium carbonate ($CaCO_3$), potassium carbonate (K_2CO_3), and sodium carbonate (Na_2CO_3), respectively.[50,51] Due to its low CO_2 content, very large volumes of air must be contacted with the sorbent material, and this should be achieved with minimum energy input, preferably using natural air convection. After capture, CO_2 would be recovered from the sorbent by desorption, through heating, vacuum, electrochemical means, or any other method. Calcium carbonate, for example, as is well known in the cement industry, can be thermally calcinated to release carbon dioxide. Calcium hydroxide and sodium hydroxide require high energy input for recovery and therefore are probably not the most suitable and practical candidates for CO_2 capture from air. Less energy intensive alternatives should be found. One of the possibilities is to use carbonates instead of hydroxides. Calcium carbonate and sodium carbonate bind CO_2 more weakly to form bicarbonates, making their regeneration easier. Using an electrochemical recovery process, potassium carbonate, which reacts with CO_2 in water to form potassium bicarbonate ($KHCO_3$), has been proposed as an absorbent for CO_2.[52] The CO_2 absorption rates on carbonates are however slow and require long contact times and/or larger amounts of absorbent.

In submarines and space flights, removal of CO_2, which is essential to keep the air breathable, is already carried out using regenerable polymeric or liquid amine scrubbers. To capture CO_2 on a larger scale, anionic resins that absorb CO_2 from the air when dry and release it when exposed to moisture have also been developed using a so-called moisture swing absorption process.[53] In our own work, a nanostructured silica-supported polyethylenimine absorbent was found to absorb CO_2 from air quite efficiently, although further work is needed to increase the efficiency of CO_2 capture at these low concentrations.[54]

It should be pointed out that our air also contains other essentials for mankind's sustainable future in considerably higher concentration than the low (0.0390%) CO_2 content: (a) Pure water vapor in concentrations from 1 to 6%, depending on the moisture content of the air in varied locations, which is essential to life and an inexhaustible and renewable source of hydrogen. In arid areas and as an alternative to seawater desalination, it could provide water and decrease the cost of CCS and CCR. (b) Some 79% nitrogen, for the synthesis of ammonia and derived synthetic nitrogen-containing compounds, especially fertilizers, as well as together with CO_2 and water for producing synthetic proteins, urea, etc. (c) 20% oxygen, also essential to life and for combustion processes. Utilizing all these atmospheric resources can ensure a sustainable future for most of humankind's needs.

The cost of capturing CO_2 from the atmosphere has been estimated at between \$100 and \$200/t of CO_2, but further improvements are expected to drive these costs lower.[55−57] Among the various advantages of CO_2 extraction from air is the fact that it is independent of CO_2 sources and allows more CO_2 to be captured than is actually emitted from human activities. This technology could allow humankind not only to stabilize CO_2 levels (making us carbon neutral) but also eventually to lower them, making our carbon emissions negative. By capturing more carbon emissions, it is even possible to reduce the atmospheric level of carbon dioxide. Such capture would actually permit Earth to return to a lower concentration of CO_2 in the air without having to rely on natural processes to absorb excess anthropogenic CO_2 emissions.

CHEMICAL CARBON DIOXIDE RECYCLING TO FUELS

Recycling of CO_2 with Water-Based Hydrogen. In order to produce hydrocarbon fuels and products from CO_2, the captured CO_2 has to be combined with hydrogen. To reduce our dependence on depleting fossil fuels and the limitations associated with the natural photosynthetic cycle, we will have to rely increasingly on sources other than fossil fuels-derived hydrogen to reduce CO_2, primarily abundant water resources.

Methanol from CO_2 and H_2. It has long been known that CO_2 can be converted to methanol by catalytic hydrogenation.[58] In fact, some of the earliest methanol plants operating in the 1920s and 1930s in the U.S. commonly used CO_2 and H_2 obtained as byproducts of fermentation processes.[18,59]

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

$$\Delta H_{298K} = -11.9\ \mathrm{kcal \cdot mol^{-1}}$$

Efficient catalysts, notably based on copper and zinc, have been developed for the reaction.[60,61] They are similar to the ones currently used for the production of methanol from syn-gas. In view of our present understanding of the mechanism of methanol synthesis from syn-gas, this is not unexpected. It is now established that methanol is most probably almost exclusively formed by hydrogenation of CO_2 contained in syn-gas on the catalytic surface. In order to be converted to methanol, the CO in the syn-gas first undergoes a WGSR to form CO_2 and H_2. The formed CO_2 then reacts with hydrogen to yield methanol.[58,62−64]

$$\underset{\text{water−gas shift reaction (WGSR)}}{CO + H_2O \rightarrow CO_2 + H_2}$$

$$\Delta H_{298K} = -9.8\ \mathrm{kcal \cdot mol^{-1}}$$

On a commercial methanol catalyst composed of copper, zinc oxide, and alumina (60%, 30%, and 10%, respectively, by weight), it has been shown that reacting a CO/H_2 mixture, carefully purified from CO_2 and water, produces no or very little methanol. Isotopic labeling also showed that CO_2 is the main source of carbon in methanol formed from syn-gas.[65] A microkinetic model of the reaction based on 13 individual steps was suggested to describe the mechanism (see Scheme 1). The rate-limiting step is most likely the hydrogenation of dioxomethylene (eq 11 in Scheme 1).[58] It is interesting that the syn-gas-based methanol synthesis and carbon dioxide chemical recycling to methanol seem essentially to share the same type of chemical intermediates.

Scheme 1. Microkinetic Model of the Methanol Synthesis[a]

$$
\begin{aligned}
&H_2O(g) + * \rightleftharpoons H_2O^* && (1)\\
&H_2O^* + * \rightleftharpoons HO^* + H^* && (2)\\
&2HO^* + * \rightleftharpoons H_2O^* + O^* && (3)\\
&HO^* + * \rightleftharpoons H^* + O^* && (4)\\
&H_2(g) + 2* \rightleftharpoons 2H^* && (5)\\
&CO(g) + * \rightleftharpoons CO^* && (6)\\
&CO^* + O^* \rightleftharpoons CO_2^* + * && (7)\\
&CO_2(g) + * \rightleftharpoons CO_2^* && (8)\\
&CO_2^* + H^* \rightleftharpoons HCOO^* + * && (9)\\
&HCOO^* + H^* \rightleftharpoons H_2COO^* + * && (10)\\
&H_2COO^* + H^* \rightleftharpoons H_3CO^* + O^* && (11)\\
&H_3CO^* + H^* \rightleftharpoons CH_3OH^* + * && (12)\\
&CH_3OH^* \rightleftharpoons CH_3OH(g) + * && (13)
\end{aligned}
$$

[a] Reproduced from ref 66, with permission from Springer. Here * represents a free surface site and X* symbolizes the adsorbed atom or molecule X.

Lurgi AG, a leader in methanol synthesis process technology, in collaboration with Süd-Chemie developed and thoroughly tested a high-activity catalyst for methanol production from CO_2 and H_2.[60] Operating at a temperature around 260 °C, slightly higher than that used for conventional methanol synthesis, the selectivity in methanol is excellent. The activity of this catalyst (C79-05-GL, based on Cu/ZnO)[67,68] decreased at about the same rate as the activity of commercial catalysts currently used in methanol synthesis plants. Conventional Cu/ZnO-based methanol synthesis catalysts exhibit a tendency to deactivate prematurely at higher CO_2 partial pressures.[68] The synthesis of methanol from CO_2 and H_2 using a Cu/ZnO-based multicomponent catalyst has also been demonstrated on a laboratory pilot scale in Japan, where a 50 kg CH_3OH/day production with a selectivity of methanol of 99.8% was achieved.[61,69] 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.[70] Others (Süd Chemie, Haldor Topsøe, etc.) developed their own effective catalysts and processes for methanol synthesis.

The first contemporary commercial CO_2-to-methanol recycling plant using locally available, cheap geothermal energy is being constructed and put into operation after a successful pilot plant scale operation in Iceland by the Carbon Recycling International (CRI) company. The plant, with an initial annual capacity of 4500 m^3 of methanol, is based on the conversion of CO_2 accompanying the abundant locally available geothermal energy (hot water and steam) sources. The needed H_2 is produced by water electrolysis using cheap geothermal- or hydropower-based electricity.[71] Iceland embarked on this development as a means to exploit and potentially export its cheap and clean renewable electrical energy. In Japan, Mitsui Chemicals has also announced the construction of a 100 tonne-per-year demonstration plant producing methanol from CO_2, obtained as an industrial byproduct.[72] There is also significant research and industrial interest in CO_2-to-methanol conversion in China, Australia,[73] the European Union, and other countries.

The capital investment for a methanol plant using CO_2 and H_2 is estimated to be about the same as that for a conventional syn-gas-based plant.[60] The limiting factor for large scale-up of such processes is the availability of CO_2, and the price of H_2, which is dependent on the cost of energy for its production.

Like methanol, DME can also be produced by direct catalytic hydrogenation of CO_2. Similar to the route from syn-gas to DME, CO_2 hydrogenation to DME can use a hybrid catalyst system consisting of a combination of methanol synthesis and dehydration catalysts.[74] Water formed can be recycled into the electrolysis step.

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

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O$$

$$2CO_2 + 6H_2 \rightarrow CH_3OCH_3 + 3H_2O \qquad \text{(overall reaction)}$$

PRODUCTION OF HYDROGEN FOR CO_2 REDUCTION

Presently, technologies for the production of hydrogen from water include electrolysis, thermolysis, thermochemical splitting, photoelectrolysis, and photobiological cleavage.

Electrolysis of Water. While hydrogen can be produced by water electrolysis, this approach in our time of still abundant hydrocarbons is not widely used. Only about 4% of the global hydrogen production of about 50−60 million tonnes comes from water electrolysis, mostly for the production of high-purity hydrogen. In most locations, hydrogen production through electrolysis of water is still about 3−4 times more expensive than that from natural gas reforming. With depletion of our easily accessible fossil fuels however, water-based hydrogen will provide our hydrogen needs of the future. Electrolysis is a mature technology that has been used for more than a century, unlike other possible ways such as thermolysis, thermochemical cycles, and photoelectrolysis.

Electrolysis is the decomposition of water into hydrogen and oxygen, according to

$$H_2O \xrightarrow[\text{reduction}]{\text{electrochemical}} \left\{ \begin{array}{l} H_2 \text{ at the cathode} \\ 1/2\ O_2 \text{ at the anode} \end{array} \right. \qquad \Delta H_{298K} = 68.3\ \text{kcal} \cdot \text{mol}^{-1}$$

Electrolysis is an energy-intensive process. 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.[75] To produce 1 kg of hydrogen, 9 L of water is required. The needed electric energy can be obtained from any suitable source.

The conversion efficiency of water to hydrogen, depending on the system, is between 80 and 95%. Considering the power needed for the overall electrolyzer system, the best energy efficiency is today around 73% (higher heating value of H_2).[76] This means that about 53 kWh of electricity is needed to produce 1 kg of hydrogen at 1 atm and 25 °C. Current research and development efforts are aimed at improving net system efficiencies of commercial electrolysis toward 85%.[77] Better efficiencies can for example be obtained at higher water temperatures or with steam electrolysis under pressure.

Alkaline electrolyzers and polymeric electrolyte membrane-based electrolyzers are the most common types of commercially available electrolyzers. Alkaline electrolyzer is a well established technology and is composed of electrodes separated by a microporous diaphragm and an alkaline electrolyte enabling the conduction of ions between electrodes, typically a 25−30 wt % aqueous solution of KOH or NaOH. They generally operate at temperatures between 60 and 90 °C at atmospheric pressure and current densities of 100−300 $mA \cdot cm^{-2}$ of electrode. The reactions at the cathode and anode are as follow:

$$\text{Cathode}: \quad 2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

$$\text{Anode}: \quad 2OH^- \rightarrow 2e^- + 1/2\ O_2 + H_2O$$

Proton exchange membrane electrolyzers are historically related with the development of proton exchange membrane-based fuel cells (PEMFCs) starting in the 1950s. In fact, they are basically fuel cells running in reverse. They are based on a membrane coated on both sides with a selective electrode usually composed of noble metals such as Pt, Ru, or Pd or a mixture thereof. The membrane not only separates the electrodes but serves also as an ion conductor and a gas separator. The membrane has to be proton conducting but not electrically conducting. The water is introduced at the anode side where it dissociates into protons, electrons, and oxygen. The protons are pulled through the membrane under the action of an applied electric field and recombined with the electrons to form hydrogen. The separation of oxygen and hydrogen is an integral part of the process. The reactions on the electrodes are as follow:

$$\text{Cathode}: \quad 2H^+ + 2e^- \rightarrow H_2$$

$$\text{Anode}: \quad H_2O \rightarrow 2H^+ + 2e^- + 1/2\ O_2$$

PEMFCs operate at much higher current densities (up to 2000 $mA \cdot cm^{-2}$)[78,79] than alkaline fuel cells, which offsets to some extent the higher capital expenditure due to the use of noble metals and expensive membranes. Use of much lower catalyst loading or development of cheaper catalysts, based for example on Ni and Co, is necessary. Currently proton exchange membrane electrolyzers generally operate between 80 and 150 °C at pressures up to 30 bar, although higher pressure would be preferable. Proton Energy Systems[80] and Giner[81] are among the companies developing electrolyzers able to produce hydrogen at pressures up to 200 bar with very limited additional electric power input. This would avoid the expensive and very energy consuming postgeneration compression of hydrogen by multistage compressors for storage or use as a feed stock in high-pressure reactions such as methanol synthesis.

Solid oxide electrolysis cells have been proposed for the high-temperature generation of hydrogen. Operating generally at temperatures between 600 and 1000 °C has several advantages. Inexpensive catalysts based on nickel can be used instead of noble metals. The electrolyte is solid, which avoids problems such as corrosion encountered in alkaline fuel cells. The total energy demand for water splitting (ΔH) is also lowered by simply passing from the liquid phase (68.3 $kcal \cdot mol^{-1}$) to the vapor phase (57.8 $kcal \cdot mol^{-1}$) (Figure 4).[82] With steam, the overall total energy demand for electrolysis increases slightly with increasing temperature. The demand for electrical energy however decreases due to a lowering of the anode and cathode overpotentials, which causes power loss. The additional energy needed to drive the reaction is supplied by heat, which is cheaper and more easily accessible than electricity. This heat can for example be supplied by high-temperature solar or nuclear energy sources. Challenges remain such as the long start-up time and long-term stability of the solid oxide electrolytes and catalysts at high temperature and high current densities.[83,84]

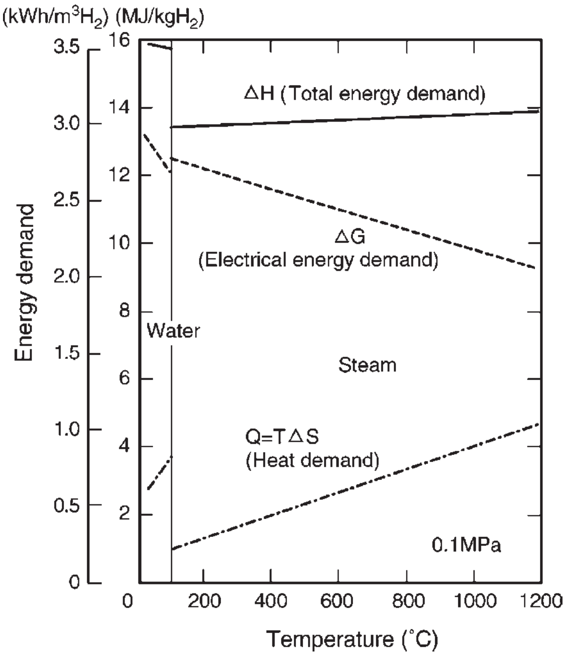


Figure 4. Energy demand for water and steam electrolysis. Reprinted from ref 82, with permission from Elsevier.

Thermolysis. Water can be thermally split at temperatures in the range of 2000−2500 °C or higher. The products of this thermolysis have to be rapidly separated or quenched to avoid their recombination. To obtain such high temperature, the use of solar furnaces has been proposed and explored with some success. Thermolysis, besides being very energy intensive, would also require the development of materials able to withstand such high temperatures for extended periods of time and under varying conditions. For the time being, the direct high-temperature thermolysis of water is yet impractical.

Thermochemical Water Splitting. Thermochemical water splitting, on the other hand, can be achieved at a more reasonable temperature and is based on chemical cycles. Among the many cycles that have been proposed, the so-called iodine−sulfur cycle has been one of the most extensively studied.[85] In that cycle, SO_2 and iodine are added to water to form sulfuric acid and hydrogen iodide. Above 350 °C, HI decomposes to hydrogen and iodide, the latter being recycled. Sulfuric acid decomposes at temperatures above 850 °C into SO_2 and water, which are recycled, as well as oxygen. With SO_2 and iodine being continuously recycled, the only feeds to the process are water and high-temperature heat, giving hydrogen, oxygen, and low-grade heat. The overall reaction is basically a splitting of water to hydrogen and oxygen. Thermochemical cycles have most often been proposed in conjunction with nuclear energy. The new generation IV nuclear power plants would be especially suited for this application as they are planned to operate at temperatures of 700−1000 °C, much higher than present reactors operating between 300 and 400 °C. Heat provided by concentrated solar sources could also be used.[86] Problems remain however, such as the corrosive nature of the chemicals employed. This technology is consequently also far from being ready for practical large-scale deployment.

Photoelectrolysis. Combining the photovoltaic generation of electricity with the production of hydrogen in a single photoelectrochemical cell has been proposed.[78,87] Instead of having a photovoltaic cell producing electricity and a separate water electrolyzer, both operations could be combined in a single unit, decomposing water directly into hydrogen and oxygen using sunlight.[79,88,89] Efficiency around 12% for water splitting into hydrogen has been reported for a system consisting of two semiconductors, p-$GaInP_2$ and GaAs, combined into a single monolithic device.[90] The Joint Center for Artificial Photosynthesis (JCAP), led by N. S. Lewis, is aiming at making this technology practical and economical to produce hydrogen, methanol, and other fuels directly from sunlight, water, and CO_2 using abundant and robust materials. The group of D. G. Nocera at MIT, on the other hand, has developed water-splitting catalysts based on cobalt−phosphate or nickel−borate catalysts operating at ambient conditions in neutral water.[91−94] Durability, stability in aqueous media, complexity, and cost of this system as well as other factors remain however a challenge, and much further development is needed.

Photobiological Water Cleavage. Using the sun's energy and microorganisms such as green algae and cyanobacteria to directly split water into hydrogen could potentially be several-fold more efficient than obtaining hydrogen through biomass gasification.[95] The microbes used at present, however, cleave water at a rate much too slow for efficient hydrogen production, and significant research and development would be needed for this technology to become practical.

Despite the potential long-term prospects of thermochemical, photochemical, and photobiological water splitting, hydrogen generation through electrolysis is presently the only possible pathway to produce hydrogen from renewable and nuclear energy sources practically on a large scale.

■ CO_2 REDUCTION TO CO FOLLOWED BY HYDROGENATION

In order to utilize hydrogen more efficiently for CO_2 conversion to methanol and DME, the initial chemical or electrochemical reduction of CO_2 to CO to minimize hydrogen use in water formation is feasible. Carbon dioxide reduction to CO can be achieved by the reverse Boudouard reaction, i.e., the thermal reaction of carbon dioxide with carbon (including coal).

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

This endothermic reaction of coal gasification with CO_2 can be used at temperatures above 800 °C. The advantage over the steam reforming of coal, which is somewhat less endothermic (31.3 $\text{kcal}\cdot\text{mol}^{-1}$), 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).[96] Two-step thermochemical coal gasification combined with metal oxide reduction has also been proposed and tested.[97,98] Coal gasification via 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.

Whereas biomass can also be used as a carbon source, other technologies are probably more efficient at transforming it into fuels. The natural CO_2 cycle further depends on land availability, water, and suitable growth conditions.

The direct conversion of CO_2 to CO using a thermochemical cycle and solar energy is also being intensively studied. Researchers at the Sandia National Laboratories working on the sunshine-to-petrol (S2P) project recently developed a solar furnace which heats a device containing 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, producing CO and ferrite, which can be recycled.[99] This technology shows promise, but its viability on an industrial scale is still unproven.

$$Fe_3O_4 \xrightarrow{1400-1500^\circ C} 3FeO + 1/2\ O_2$$

$$3FeO + H_2O \rightarrow Fe_3O_4 + H_2$$

$$H_2O \rightarrow H_2 + 1/2\ O_2 \qquad \text{(overall reaction)}$$

■ ELECTROCHEMICAL REDUCTION OF CO_2

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

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

This approach has been studied using various metal electrodes in aqueous media.[100,101] 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, has been extensively studied as a medium for the electrochemical reduction of CO_2.[102−104]

During the electrochemical reduction of CO_2 in water or methanol, hydrogen formation competes with CO_2 reduction, thereby reducing the Faradaic efficiency of the CO_2 reduction. Progress is being made to suppress hydrogen formation.

However, instead of considering H_2 formation as a problem in the CO_2 electrochemical reduction, it could be advantageous to generate CO and H_2 concomitantly at the cathode in a H_2:CO ratio close to 2, producing a syn-gas mixture (called "metgas"), which is then further transformed into methanol.[105,106] An additional advantage is the valuable pure oxygen produced at the anode. This pure oxygen could be used in coal-burning power plants in the oxy-combustion process, which is more efficient than regular coal combustion and produces a very high CO_2 concentration effluent. The electrochemical reduction reaction of CO_2, however, still has overpotential and efficiency problems, which must be overcome.

$$CO_2 + 2H_2O \xrightarrow[\text{reduction}]{\text{electrochemical}} \begin{cases} [CO + 2H_2]\ \text{at the cathode} \rightarrow CH_3OH \\ 3/2\ O_2\ \text{at the anode} \end{cases}$$

Regardless, methanol and DME can be produced selectively from CO_2 via electrochemically generated 1:2 CO:H_2 syn-gas (metgas) in the same way as from natural gas or coal. The advantage is that no separation step is required, and no impurities such as sulfur dioxide are present which could deactivate the methanol synthesis catalyst. The electrochemical reduction of CO_2 and water is preferably run under pressure to feed the metgas directly into the methanol synthesis reactor operating at pressures of 50−60 bar.

The direct electrochemical reduction of CO_2 to methanol has also been explored.[107−114] High methanol selectivity could be achieved in aqueous solution on Ag, W, and C electrodes.[115] The current densities are however low, ranging from about 10 to 30 $\mu\text{A}\cdot\text{cm}^{-2}$. At higher current densities the main products, depending on the electrode, are formic acid, CO, and

Chart 1. Standard Electrochemical Reduction Potentials of CO_2 vs NHE, pH = 7, NTP Conditions

$$\begin{array}{lcll}
CO_2 + 2H^+ + 2e^- & \rightarrow & HCOOH & E^\circ = -0.61\ V \\
CO_2 + 2H^+ + 2e^- & \rightarrow & CO + H_2O & E^\circ = -0.52\ V \\
CO_2 + 4H^+ + 4e^- & \rightarrow & HCHO + H_2O & E^\circ = -0.48\ V \\
CO_2 + 6H^+ + 6e^- & \rightarrow & CH_3OH + H_2O & E^\circ = -0.38\ V \\
CO_2 + 8H^+ + 8e^- & \rightarrow & CH_4 + 2H_2O & E^\circ = -0.24\ V
\end{array}$$

also traces of methane. On copper electrodes, methane selectivity up to 66% was obtained. Selectivity is one of the major problems with electrochemical reduction of CO_2. Besides methanol, depending on the electrodes and conditions, varying amounts of formic acid, carbon monoxide, formaldehyde, and methane are produced in two-, two-, four-, and eight-electron processes, respectively (Chart 1).[36]

Even if mixtures of products are obtained, they can be further reacted to increase production of methanol. Formic acid and formaldehyde for example in a subsequent chemical treatment step can be converted to methanol in different ways.[108,116,117] One possibility is dimerizing formaldehyde over TiO_2 or ZrO_2[118] to give methyl formate. Formaldehyde can also undergo conversion over solid-base catalysts such as CaO and MgO, a variation of the Cannizaro–Tischenko reaction, giving methanol and formic acid, which again readily react with each other to form methyl formate.

$$2HCHO \xrightarrow{TiO_2 \text{ or } ZrO_2 \text{ catalyst}} HCOOCH_3$$

$$2HCHO \xrightarrow{H_2O} CH_3OH + HCO_2H$$

$$CH_3OH + HCO_2H \xrightarrow{-H_2O} HCOOCH_3$$

If methyl formate is obtained, it can then be catalytically hydrogenated or electrochemically reduced in water using suitable electrodes (made from copper, tin, lead, etc.), giving two molecules of methanol for each methyl formate with no other byproduct.

$$HCOOCH_3 + 2H_2 \rightarrow 2CH_3OH$$

Formic acid formed during the reduction can serve as a hydrogen source to be reacted with formaldehyde in aqueous solutions at 250 °C or over suitable catalysts to produce methanol and CO_2 (*vide infra*).

$$HCHO + HCO_2H \rightarrow CH_3OH + CO_2$$

Formic acid itself can be obtained from electrochemical reduction of CO_2 in high Faradaic efficiency. It has also been proposed as an efficient fuel in direct oxidation fuel cells as well as a hydrogen storage medium.[119]

METHANOL AND DME FROM BIOMASS

As mentioned, another possibility to produce methanol sustainably is to use biomass, including wood, wood waste, agricultural crops and their byproducts, municipal waste, animal waste, etc. Present technologies to convert biomass to methanol are similar to the ones used to produce methanol from coal. They involve the thermochemical gasification of biomass into syn-gas, followed by purification and synthesis of methanol using the same processes employed with fossil fuels. Gasification can be achieved using a number of existing and fairly mature technologies, which nevertheless need further improvements to make them more efficient and economical. Tar formation, which accompanies biomass gasification and can clog pipes, boilers, transfer lines, and other elements, is particularly problematic. Typically about 650 L of methanol can be obtained from a tonne of dry wood, leading to overall wood-to-methanol efficiencies of 50–60%. Any biomass material can basically be gasified for methanol production. The overall energetic efficiency to produce methanol or DME from biomass has been estimated to be significantly higher than that for the production of Fischer–Tropsch liquids or ethanol from biomass.[20] The efficiency of the process will however depend on the nature and quality of the feedstock. In practice, “energy crops” such as switchgrass and sugar cane would have to be planted on vast lands and would need enormous amounts of fertilizers, water, and other resources, which would partially offset the expected environmental benefits of using biomass as an energy source. Limited and dwindling sources of easily accessible phosphorus, an essential element for plant growth, are of particular concern for the highly intensive agricultural production methods increasingly employed.[120]

Biogas resulting from the anaerobic digestion of vegetation and animal waste is generally composed of 50–70% methane, with the remainder being mostly CO_2. Biogas is therefore a good feedstock to be used for bireforming. In Sweden, bio-DME is being produced in a biorefinery through gasification of black liquor, a byproduct of paper manufacturing containing mostly lignin and hemicellulose.[121–124] A plant with a capacity of 100 000 tonnes of DME per year is currently being constructed by Chemrec in Örnsköldsvik to fuel about 2000 heavy trucks.[125]

Despite considerable resources, the exploitation of biomass in a responsible and sustainable way is expected to provide at most 10–15% of the total energy demand of the world in the future.[13] Due to discussed limitations, humankind needs to find alternative ways to cover the increasing energy needs of a growing population.

CO_2 RECYCLING USING FOSSIL FUELS

Hydrogen is not present in its free form on our planet due to its high affinity for oxygen, a major component of the atmosphere. Presently, hydrogen is produced mainly from fossil fuels, mostly natural gas through reforming, as well as to a lesser extent through electrolysis of water. As discussed, to be sustainable, it will eventually be generated exclusively from water using varied processes and future development. However, as long as fossil fuels are available they will be used. Nevertheless, it is necessary to find ways to use them while avoiding or a least mitigating their concurrent CO_2 emissions. In a process called “Carnol”, natural gas is thermally decomposed at temperatures above 800 °C to produce hydrogen and carbon. The generated hydrogen can be combined with CO_2 to form methanol and hydrocarbons. Overall the net emission of CO_2 from this process is close to zero, because the CO_2 produced when methanol is combusted as a fuel is recycled from existing emissions. All the carbon present in methane (in natural gas) ends up as a solid carbon which can be handled more easily than CO_2 and disposed of or used as a commodity material.

Methane thermal decomposition:

$$CH_4 \xrightarrow{>800°C} C + 2H_2 \qquad \Delta H_{298K} = 17.9 \text{kcal} \cdot \text{mol}^{-1}$$

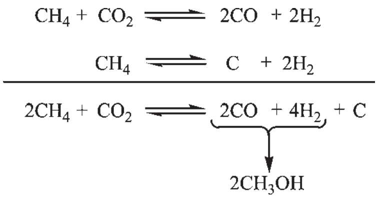
Methanol synthesis:

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

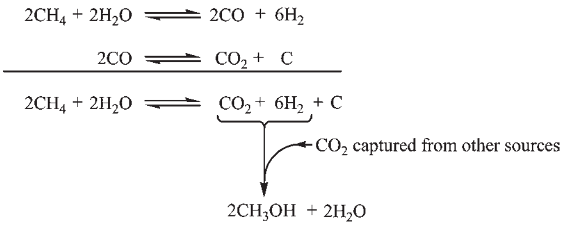
Overall Carnol process:

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

To produce methanol or hydrocarbons from CO_2 by sequestering some of the carbon in the form of solid carbon, methane decomposition could also be combined with dry reforming of methane with CO_2 to form a syn-gas with an H_2:CO ratio of 2:1. For 2 moles of methane, 2 moles of methanol and 1 mole of carbon are produced. The environmental benefit is not as high as with the Carnol process, but the economic costs might be lower.



A similar overall reaction can be obtained by combining steam reforming of methane with the Boudouard reaction followed by CO_2 conversion to methanol, as depicted in the following scheme:



The overall reaction is

$$2CH_4 + CO_2 \rightleftharpoons 2CH_3OH + C$$

Like in the Carnol process, the solid carbon formed can be handled and stored more easily than gaseous CO_2.

To obtain a syn-gas mixture with a suitable H_2:CO ratio for methanol synthesis, dry reforming can be combined with steam reforming. We call this process *bireforming* (of methane, natural gas, or when preferred coal). In bireforming, a proper ratio of steam and dry (CO_2) reforming produces a gas mixture with essentially a 2:1 ratio of hydrogen to carbon monoxide, which we have suggested be called "metgas" to underline its difference from the widely used syn-gas mixture of varying H_2:CO ratio, which is the basis of the Fischer–Tropsch chemistry.[25,126] This specific 2:1 H_2:CO gas mixture is for the sole purpose of preparing methanol with complete economic utilization of the hydrogen. The conversion of methane with CO_2 and water proceeds as follows.

Steam reforming:

$$2CH_4 + 2H_2O \rightarrow 2CO + 6H_2$$

Dry reforming:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2$$

Bireforming:

$$3CH_4 + 2H_2O + CO_2 \rightarrow 4CO + 8H_2 \rightarrow 4CH_3OH$$

Bireforming to metgas is also adaptable for reforming varied natural gas sources containing hydrocarbon homologues, which frequently are accompanied by substantial amounts of CO_2, in some cases in concentrations higher than 50%.[127]

$$3C_{3n}H_{(2n+2)} + (3n-1)H_2O + CO_2 \rightarrow$$
$$(3n+1)CO + (6n+2)H_2 \rightarrow 4nCH_3OH$$

Metgas can also be generated from other carbon sources including coalbed methane and methane hydrates as well as biomass. Combining steam reforming of coal and coalbed methane is also a possible pathway.

Recent findings of significant shale-trapped natural gas (methane) deposits in the U.S. considerably increased the overall reserves of natural gas. Shale gas production is made possible by horizontal drilling and rock fracking (hydraulic fracturing) using high-pressure water and chemical additives. These extraction technologies could potentially lead to serious environmental problems. To what degree this shale gas is accompanied by CO_2 is also not clear at this time, but the above-discussed ways to handle the problem should be equally applicable.

The same overall composition as the one obtained in bireforming with the combination of steam and dry reforming (4 moles of CH_3OH synthesized from 3 moles of CH_4 and 1 mole of CO_2) can be achieved by adding CO_2 into the syn-gas flow during the methanol synthesis. The syn-gas is prepared by steam reforming. This is already practiced in commercial modern methanol plants to use the excess hydrogen produced during steam reforming.

$$3CH_4 + 3H_2O \rightleftharpoons 3CO + 9H_2$$

$$3CO + 6H_2 \rightleftharpoons 3CH_3OH$$

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

$$3CH_4 + 2H_2O + CO_2 \rightleftharpoons 4CH_3OH \qquad \text{(overall reaction)}$$

The combination of steam and dry reforming provides the same end-result as the addition of CO_2 during the methanol synthesis step. The advantages and inconveniences of such methods should be weighed to determine which is preferable from an energetic and process point of view (Chart 2).

From the involved equations, it can be seen that there are basically only three reaction paths which describe the reaction of CH_4 with CO_2 to give methanol, accompanied in some cases by various amounts of carbon formed as a byproduct.

Coal also could be used for syn-gas production by gasification combining partial oxidation and steam treatment. Due to the low H/C ratio in coal, the obtained syn-gas is rich in carbon oxides (CO and CO_2) and deficient in hydrogen. Therefore it has to be subjected to the WGSR to enhance its hydrogen content. Ultimately all the carbon in coal can be converted with steam to H_2 and CO_2. To avoid emissions, the CO_2 generated would have to be captured and stored for later use. CO_2 from renewable sources such as biomass or the air could then be converted with the coal-generated hydrogen to methanol, as shown in the scheme below where coal is represented by C_n. Overall, this process would be CO_2 neutral as all the carbon in coal would be captured and stored as CO_2, allowing the use of still extensive coal reserves. This is especially significant for the U.S., which has very large reserves of coal equivalent to more than 200 years of production at current rates. China, which has also sizable coal reserves, embarked on building some 100 large (>1 million tonnes per year) new coal-based methanol and DME plants and derived products with plans to sequester at least part of the CO_2 produced.[128] The use of bireforming and CCR technologies instead of CCS would alleviate some of the CO_2 emissions while producing methanol and DME.

A similar approach has been proposed in the past for advanced coal-fired power plants, such as in the original FutureGen project and other "clean coal" technologies from the U.S. Department of Energy,[129−131] to produce not methanol but electricity and/or hydrogen. The cost to produce hydrogen from coal (C_n) using these advanced technologies is expected to be less than \$1/kg[85] but would require the sequestration (CCS) of large amounts of CO_2.

$$C_n + n/2\ O_2 \rightleftharpoons nCO$$

$$\Delta H_{298K} = -29.4\ \text{kcal}\cdot\text{mol}^{-1}\ \text{per C}$$

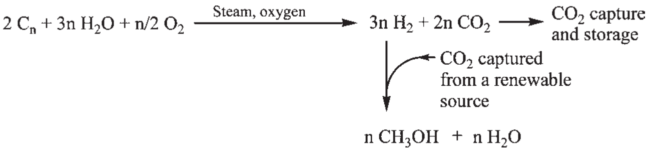
$$C_n + nH_2O \rightleftharpoons nCO + nH_2$$

$$\Delta H_{298K} = -31.3\ \text{kcal}\cdot\text{mol}^{-1}\ \text{per C}$$

$$nCO + nH_2O \rightleftharpoons nCO_2 + nH_2$$

$$\Delta H_{298K} = -9.8\ \text{kcal}\cdot\text{mol}^{-1}\ \text{per C}$$

Overall reaction:



The method of choice to produce methanol will depend on the amount of carbon dioxide to be used, recycled, or sequestered.

PRODUCTION OF DIMETHYL ETHER FROM CH_4 AND CO_2

A major product of subsequent methanol conversion already practiced on a large industrial scale is *dimethyl ether (DME)*, which is usually made by bimolecular dehydration of methanol.

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O$$

Methanol for this reaction can be produced by any of the methods described *vide supra*. Using bireforming, the water produced can be recycled, allowing an efficient way to produce DME without hydrogen loss to produce water as a byproduct.[126]

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

Chart 2. Summary of Different Pathways to Methanol Using CH_4 (Natural Gas) and CO_2

1. Steam and dry reforming combined in bireforming

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

2. Steam reforming and external CO_2 addition

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

3. Steam reforming, Boudouard reaction, and CO_2 addition

$$2CH_4 + CO_2 \rightarrow 2CH_3OH + C$$

4. Dry reforming and CH_4 decomposition

$$2CH_4 + CO_2 \rightarrow 2CH_3OH + C$$

5. CH_4 decomposition and CO_2 addition

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

DME is an excellent diesel fuel and household gas substitute. Industrial DME plants are already in operation or development in China, Japan, South Korea, Belgium, etc.[132−134]

COST OF PRODUCING METHANOL FROM CO_2 AND WATER

Presently, the most mature and scalable method to prepare methanol sustainably from CO_2 and water without use of fossil fuels remains the combination of water electrolysis and subsequent catalytic methanol synthesis with CO_2. The cost of methanol produced by this route is highly dependent on the cost of hydrogen. The cost of hydrogen itself is closely linked with the cost of electricity needed to produce it.

It was determined that in units of 1000 kg of H_2 per day, the cost of electricity represents about 80% of the cost of hydrogen produced. Capital investment represents only 11%.[135] In larger electrolysis units the proportion of the cost of electricity is expected to be even higher. The cost of electricity is therefore the major driving factor to minimize the cost of producing hydrogen from electricity. In Table 2, the electricity generation costs for different energy sources are presented. It can be seen that nuclear is very competitive with fossil fuels. Wind for the most part is in the same range as natural gas but generally more expensive than coal. The cost of solar energy, on the other hand, is presently much higher than that of fosssil fuels as well as nuclear and wind energy.

The price of electricity generated from wind is expected to decrease to an average of about 4¢/kWh (including transmission) in the future.[137] Among renewable sources (except hydro), wind power is economically the most competitive, with electricity prices at 4−5¢/kWh at the best wind sites (without subsidies)

However, even at a relatively low electricity price of 4¢/kWh, the production of hydrogen through electrolysis (\$2.5−3/kg) stays high compared with traditional ways to produce H_2 from fossil fuels. Hydrogen produced from natural gas or coal using

Table 2. Construction Costs and Electricity Generation Costs of Different Energy Sources[a]

	construction cost (U.S.$/kWe)	electricity generation costs (U.S.¢/kWh)
coal	1000−1500	2.5−5
natural gas	400−800	3.7−6
nuclear	1000−2000	2.1−3.1
wind	1000−2000	3.5−9.5 (mostly under 6.0)
solar	3000−10000	15−40

[a] Source: ref 136.

reforming has a cost of \$0.5−1/kg depending on the process used. The cost of producing H_2 from nuclear electricity with current technology is estimated to be around \$2/kg. The cost of producing methanol from CO_2 and H_2 at about \$3/kg can be estimated at around \$600 per tonne in a 5000 t/year methanol plant.[138] This corresponds to about \$0.5 for 1 L of methanol or \$1.8 per gallon of methanol. Taking into account that methanol contains about half the energy density of gasoline, about 2 gallons of methanol would be needed to replace 1 gallon of gasoline in existing ICEs, which means about \$3.6 to replace a gallon of gasoline. This is not too far from the retail prices paid today by U.S. car owners and much less than the retail price paid by Europeans. Presently, prices in Europe are around €1.3/liter or €4.9/gallon. This means that in Europe, already today, it could make sense to produce methanol from electrolytically generated H_2 and CO_2. Countries such as France which produce a large part of their electricity from nuclear power could already today make use of off-peak capacity to generate hydrogen for methanol synthesis at a reasonable price. The cost of the raw material, in this case hydrogen based on the cost of electric power, is the main factor setting the price of methanol. As in the rest of the world, U.S. prices for gasoline and diesel fuel are on the rise, making methanol production more attractive.

Producing methanol directly from CO_2 and H_2 in a conventional natural gas-to-methanol plant, the natural gas has first to be transformed in an endothermic process (steam reforming) to syn-gas. This step uses part of the energy contained in the natural gas raw material. In the second step, the syn-gas is reacted in an exothermic reaction to produce methanol.

In our approach, the energy-consuming endothermic step of syn-gas generation is eliminated, hydrogen and CO_2 being generated from other sources. Only the methanol synthesis step is left unchanged. This is important because the syn-gas generation unit generally accounts for more than half of the total capital investment in a natural gas-based methanol plant. For plants using coal, the capital cost of the syn-gas step represents even more, usually between 70 and 80%. The elimination of the syn-gas generation step simplifies and lowers considerably the cost of the methanol plant. The capital cost to build a methanol plant based on electrically generated H_2 and CO_2 should therefore be considerably reduced compared that of to a conventional fossil fuel-based methanol plant.

Nevertheless the cost of production of methanol from fossil fuels, due to the relatively low cost of still widely available natural gas and coal, is expected to remain cheaper than its production from renewable energy in the foreseeable future. The market price of a gallon of methanol produced from fossil fuels is today around \$1 (without any subsidy). This means that already today methanol is less expensive than gasoline (even after taking into account methanol's lower volumetric energy density compared to gasoline). The shift to methanol produced from biomass and ultimately CO_2 and H_2 will be accelerated if some value is given to the recycling of CO_2 and the energy security gained from domestic fuel production.

METHANOL-BASED FUELS, CHEMICALS SYNTHETIC MATERIALS, AND PROTEINS

Methanol is one of the most important raw materials for the petrochemical and chemical industries. More than 48 million tonnes of methanol that are produced yearly are mostly used for the production of a large variety of chemicals and materials, including basic chemicals such as formaldehyde, acetic acid, and MTBE as well as polymers, paints adhesives, construction materials, and others.

Methanol and DME are also increasingly used industrially, and other processes are under development to produce ethylene and propylene by dehydration over zeolites such as SAPO-34 and ZSM-5 or bifunctional catalysts.[139−141] This is the basis of the so-called methanol-to-olefin process (MTO).

$$2CH_3OH \rightarrow CH_2{=}CH_2 + 2H_2O$$

$$3CH_3OH \rightarrow CH_2{=}CH{-}CH_3 + 3H_2O$$

Ethylene and propylene are by far the two largest volume chemicals produced by the petrochemical industry. In 2007, about 115 million tonnes of ethylene and 73 million tonnes propylene were consumed worldwide. They are important starting materials in the production of plastics, fibers, and chemical intermediates such as ethylene oxide, ethylene dichloride, propylene oxide, acrylonitrile, and others, and most importantly polyethylene and polypropylene. These olefins are currently largely produced by cracking of petroleum fractions. The production of olefins from methanol could therefore supplement and eventually eliminate our dependence on petroleum for these essential products.

The methanol-to-gasoline (MTG) and related olefin-to-gasoline and distillate (MOGD) processes developed by Mobil in the 1970s and 1980s also allow the production of gasoline, diesel fuel, aviation fuels, and aromatics from methanol, if needed.[142]

$$2CH_3OH \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} CH_3OCH_3 \xrightarrow{-H_2O} \text{light olefins}$$

$$\longrightarrow \text{gasoline, diesel fuel, and aviation fuel aromatics}$$

As already pointed out, instead of producing gasoline and diesel fuel, methanol can be used directly as a fuel. Methanol is an excellent fuel for internal combustion engines, with a high octane number of 100 (average of research octane number and motor octane number) and clean burning properties. It could therefore be used already today to complement gasoline. In China, between 5 and 8 million m^3 of methanol per year is currently blended with gasoline.[20] At methanol concentrations below 10−15% blended in gasoline it can be used in existing cars. To be able to use higher methanol concentrations, the fuel delivery system and other car parts in contact with the fuel would however require minor modifications (similar delivery systems are already used in flex-fuel vehicles running on E-85). Methanol is also a fuel of choice for fuel cells and direct methanol fuel cells.[14,143,144]

Methanol is an excellent storage medium for energy from any source. LNG is presently widely used to transport natural gas over the seas or where a suitable electric grid is not available for the generation of electricity from natural gas. Regardless, the explosion of a loaded LNG tanker of 200 000 tonnes or more either by accident or sabotage would potentially cause significant damage equivalent to the explosion of a small atomic bomb.[145] Thus, instead of liquefaction to LNG, the conversion of natural gas to methanol for transportation could offer a safer and more convenient alternative.

Methanol is inherently much safer than gasoline in case of a fire; it has been used in race cars for many years. It is also an easy to transport and store liquid hydrogen carrier with close to twice the volumetric energy density of liquid hydrogen.[14,146] Methanol-derived DME with a high cetane value of 55−60 is a clean-burning diesel fuel as well as a natural gas substitute. It can replace LPG and LNG in most applications.[134]

Interestingly, methanol is also a plant growth promoter, substantially improving the photosynthetic productivity of numerous plants. Methanol penetrates most plant tissues and is rapidly metabolized to carbon dioxide, amino acids, sugars, and structural components.[18] In addition, methanol was found to be an excellent C_1 carbon source for single-cell protein (SCP) production by bacteria as food and feed substitute. ICI built and operated a plant based on this technology producing premium animal feed proteins.[18,147] The production of SCP could therefore also supplement in part the nutrition needs of an increasing world population.

METHANOL SAFETY

Caution concerning the Methanol Economy occasionally includes toxicity problems associated with the wide use of methanol. Methanol is only toxic at ingestion levels which are not generally encountered.[148] Gasoline and diesel fuel are widely used and are also toxic and not meant for human ingestion, but neither represents a significant health risk. Methanol spills if they occur can be easily managed due to the high solubility of methanol in water and ease of its biological metabolization. In fact, many water treatment facilities use methanol in their bacteria-based denitrification process.[14] Besides being produced industrially, methanol also occurs naturally on Earth in some fruits, such as grapes. Methanol is also detected in interstellar space. Recently, astronomers have observed an enormous methanol cloud around a nascent star in deep space that measures ∼460 billion km across![149] This is larger than the diameter of our solar system. Even if the concentration in the near vacuum of space is extremely low, the overall amount of methanol is mind-boggling. There must be an ongoing process for methanol formation, such as by reaction of hydrogen with carbon oxides on the surface of dispersed dust particles, to allow its presence to be observed despite its inevitable decomposition. Many aspects of the mode of formation and transformation of methanol as a C_1 species continue to present significant and ambiguous questions and are being investigated.

CONCLUSIONS AND OUTLOOK

In the past 15 years, we have developed the concept of the Methanol Economy and some of the underlying new chemistry for using methanol as an energy storage medium, transportation fuel, and raw material for producing synthetic hydrocarbons and their products. It is based on the chemical anthropogenic carbon cycle. Whereas methanol is currently produced from fossil fuels through syn-gas chemistry, these resources are finite and being rapidly depleted. The recycling of CO_2 using hydrogen generated eventually from water with any source of energy offers a sustainable long-term solution to our energy challenge. However, significant bottlenecks remain, such as the relatively high cost of electricity from renewable sources needed to produce methanol. Methanol can also be made sustainably from biomass, although the available amounts of biomass will be able to provide only a small portion of humankind's energy needs. The amount of methanol needed to replace petroleum is staggering. With half the volumetric energy density compared to gasoline, about 60 billion barrels of methanol (7.6 billion tonnes) would be required to replace the 30 billion barrels of petroleum used globally each year. This represents about 160 times the current methanol production of 48 million tonnes per year!

The anthropogenic chemical carbon cycle constitutes humankind's practical technological analogue of nature's slow photosynthetic CO_2 recycling, which eventually could give new fossil fuels. As CO_2 is available everywhere on Earth, it could liberate humankind from the reliance on diminishing and limited fossil fuels and associated dependence on obtaining them from increasingly expensive, frequently far away and geopolitically unreliable sources. Eventually, it also offers the possibility to produce all hydrocarbon-based products and materials including single-cell proteins from the CO_2 content in our atmosphere. The outlined anthropogenic carbon cycle combining carbon capture and storage with chemical recycling, we believe, is the basis of a technology which offers a most feasible and effective solution to our carbon conundrum. Not unlike the Haber−Bosch synthetic nitrogen cycle, it can help humankind solve one of its most significant problems for a sustainable future.

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