Carbon dioxide recycling to methanol, dimethyl ether and derived products for a sustainable future

Alain Goeppert, G.K. Surya Prakash and George A. Olah

Abstract To reduce our dependence on diminishing non-renewable and finite fossil fuels resources and at the same time mitigate the associated CO_2 emissions problem, it is time for humankind to switch from fossilized solar energy (*i.e.* fossil fuels) to current solar energy. We are not *per se* facing an energy crisis. Sunlight delivers to Earth each hour as much energy as consumed by humankind in an entire year. Rather than an energy problem we have an energy collection and storage problem. Nature's photosynthesis uses the Sun's energy with chlorophyll in plants as a catalyst to recycle carbon dioxide (CO_2) and water into new plant life. Mimicking Nature by capturing and recycling CO_2 to methanol, dimethyl ether and derived products using any alternative energy source will provide us with a sustainable carbon source for fuels and materials well beyond the fleeting fossil fuel era. The needed CO_2 can be at first collected from industrial sources but will eventually have to be captured from the atmosphere itself. Carbon dioxide thus can be chemically transformed from a detrimental greenhouse gas causing global warming into a valuable, renewable and inexhaustible carbon source.

Keywords **Carbon cycle, CO_2 recycling, methanol economy, renewable methanol, sustainable development.**

Résumé **Recyclage du dioxyde de carbone en méthanol, diméthyl éther et produits dérivés pour un développement durable**

Pour réduire notre dépendance vis-à-vis des ressources en combustibles fossiles et atténuer les problèmes associés aux émissions de CO_2, il est temps pour l'humanité de passer de l'énergie solaire fossilisée à l'énergie solaire en temps réel. Nous ne sommes pas à vrai dire en face d'une crise énergétique. Le Soleil délivre chaque heure sur la Terre l'équivalent de l'énergie consommée par l'humanité entière en une année. Plutôt qu'un problème énergétique, nous avons un problème de collecte et de stockage de l'énergie. La photosynthèse naturelle utilise l'énergie solaire avec la chlorophylle présente dans les plantes comme catalyseur pour recycler le dioxyde de carbone et l'eau. Imiter la Nature en capturant et en recyclant le CO_2 pour faire du méthanol, du diméthyl éther et des produits dérivés en utilisant n'importe quelle source d'énergie alternative nous offre une source durable de carbone pour nos besoins en carburants et matériaux, bien au-delà de la brève ère des combustibles fossiles. Le CO_2 nécessaire peut venir dans un premier temps de sources industrielles, mais devra éventuellement être capturé directement de l'atmosphère. Le CO_2 peut donc être transformé chimiquement d'un gaz à effet de serre causant le réchauffement climatique en une source de carbone renouvelable et inépuisable.

Mots-clés **Cycle du carbone, recyclage du CO_2, économie du méthanol, méthanol renouvelable, développement durable.**

Humankind, for its continued existence, needs not only such essentials as food, clean water, shelter and clothing material, but also large amounts of energy. Today, the world uses some 1.05 X 10^{18} calories per year (120 Petawatt-hours), equivalent to a continuous power consumption of about 13 terawatts (TW), comparable to the production of 13000 electric power plants, each of 1 GW output. Since the beginning of the industrial revolution in the 18th century, developed societies relied increasingly on coal, petroleum and natural gas to fulfill this need. Presently these fossil fuels cover more than 80% of the world's energy demand. Fossil fuels are also the raw materials for a great variety of derived hydrocarbon materials and products. These range from gasoline and diesel fuel to varied petrochemical and chemical products including synthetic fibers, plastics, fertilizers and pharmaceuticals. This "gift" from Nature allowed an unprecedented era of prosperity and advancement in human development in the past two centuries. The problem with fossil fuels is that they were formed naturally over millions of years and their amount is finite. They are not renewable on the human timescale and are used up rather rapidly by a growing population and increasing standards of leaving in developing countries such as China and India. Growing pressure on these resources is making them increasingly costlier. Whereas coal reserves may last for another two centuries, readily accessible oil and gas reserves – even considering new discoveries, improved technologies, savings and unconventional resources (such as heavy oil deposits, oil shale, tar sands, shale gas, methane hydrates, coalbed methane, etc.) – may not last much beyond the 21st century. To avoid a breakdown of society as we know it, it is therefore necessary to look for alternatives to petroleum and other fossil fuels.

In fact we are not *per se* facing an energy shortage. Almost all of our energy, including fossil fuels (coal, oil, natural gas), wind, hydro and of course solar comes in one-way or other from the energy of the Sun [1]. At any given time, sunshine delivers to Earth as light and heat about 10000 times more energy than the entire world is consuming. 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, store and utilize its energy in suitable energy storage devices and energy carriers.

Another problem associated with the use of fossil fuels is that upon their combustion they release carbon dioxide and water. CO_2 is a major greenhouse gas and the burning of large amounts of fossil fuels is significantly contributing to global climate change and the now widely accepted global warming of our atmosphere. Mitigating the harmful effects of CO_2 is a well recognized and major challenge for humankind. Econo-political approaches such as carbon quotas and trading were suggested and are increasingly put into effect in many countries including the state of California in the U.S. Carbon capture and storage (CCS) is also being developed. On the other hand, carbon capture and recycling (CCR) of CO_2 into fuels and materials offers a way to solve our carbon conundrum. In the short term CCR can mitigate the environmental harmful accumulation of CO_2 in the atmosphere. In the long term it can replace our diminishing fossil fuel resources as raw material.

One of the simplest and easiest molecule to produce from CO_2 is methanol. In fact methanol has been proposed as an alternative way to store, transport and use energy in the framework of the so-called "Methanol Economy" [2-7]. It is an excellent fuel for internal combustion engines (ICE) and new generation of direct oxidation methanol fuel cells (DMFC), as well as a convenient starting material for producing light olefins (ethylene and propylene) and subsequently practically any derived hydrocarbon product. Dimethyl ether (DME) produced by simple dehydration of methanol is itself a superior fuel for diesel engines (cetane number of 55-60) as well as a substitute for liquefied petroleum gas (LPG) and compressed natural gas (CNG). Practically, methanol could therefore replace petroleum in almost all of its current applications [4].

Sustainable production of methanol

Methanol can be efficiently produced from a wide variety of sources including still available fossil fuels (coal, oil shale, tar sands, etc.) by improved methods (see *insert 1*). However, in order to be renewable and sustainable in the long term, methanol has to be made increasingly from non-fossil fuel based sources including agricultural waste, municipal and industrial waste, wood and varied biomass as well as directly from CO_2.

Methanol from biomass

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, *i.e.* biomass. Converting biomass into methanol offers therefore a way to recycle CO_2 from the air. 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 synthesis gas (syngas), followed by purification and synthesis of methanol using the same processes employed with fossil fuels. In Sweden, bio-DME is being produced in a biorefinery through gasification of black liquor, a by-product of paper manufacturing containing mostly lignin and hemicellulose [8].

Insert 1

Production of methanol from fossil fuels

Synthesis gas (syngas), a variable composition mixture of hydrogen and carbon monoxide (and carbon dioxide) is produced by partial oxidation with steam and oxygen from virtually any carbon source (coal, oil shale, tar sands, gas shale, methane hydrate, biomass, etc.). Syngas is the intermediate for the large scale production of synthetic fuels and chemicals such as methanol, dimethyl ether and hydrocarbons. Although any carbon source can be used, natural gas (includes also shale gas) and methane are generally the preferred feedstock. The synthesis of methanol requires a syngas with a H_2/CO ratio of about 2. The most commonly used reforming technology for methane, steam reforming, produces a syngas with a H_2/CO ratio close to 3 (eq. 1). This means that additional steps are needed to adjust the H_2/CO ratio. Carbon dioxide reforming of methane, called dry reforming, produces a syngas with a H_2/CO ratio close to 1 (eq. 2), which is too low and has also to be adjusted. On the other hand, methane partial oxidation with oxygen can produce an ideal ratio of 2, but is difficult to control and can lead to local hot spots and associated dangers of explosions (eq. 3). The combination of steam reforming and partial oxidation (authothermal reforming) always produces a H_2/CO ratio higher than 2 necessitating further adjustment steps.

Steam reforming $CH_4 + H_2O \rightarrow CO + 3\ H_2$
$\Delta H°_{298K} = 49.1\ kcal.mol^{-1}$ (eq. 1)

Dry reforming $CH_4 + CO_2 \rightarrow 2\ CO + 2\ H_2$
$\Delta H°_{298K} = 59.1\ kcal.mol^{-1}$ (eq. 2)

Partial oxidation $CH_4 + ½\ O_2 \rightarrow CO + 2\ H_2$
$\Delta H°_{298K} = -\ 8.6\ kcal.mol^{-1}$ (eq. 3)

A syngas mixture with a 2/1 H_2/CO ratio suitable for methanol synthesis can be obtained by the combination of dry reforming and steam reforming in a single step in a process called *bi-reforming* (eq. 4). In bi-reforming, a ratio of methane, steam and CO_2 of 3/2/1 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 syngas mixtures of varying H_2/CO ratio [6, 20].

Steam reforming $2\ CH_4 + 2\ H_2O \rightarrow 2\ CO + 6\ H_2$ (eq. 1)
Dry reforming $CH_4 + CO_2 \rightarrow 2\ CO + 2\ H_2$ (eq. 2)

Bi-reforming $3\ CH_4 + 2\ H_2O + CO_2 \rightarrow 4\ CO + 8\ H_2 \rightarrow 4\ CH_3OH$ (eq. 4)

In the short term these new reforming approaches, such as bi-reforming, for producing syngas and methanol from fossil fuels can to some degree help mitigate CO_2 emission and associated problems. However, even with the increased exploitation of shale gas, it should be pointed out that none of the routes based on fossil fuels are sustainable in the long term as these resources will be increasingly depleted.

A plant with a capacity of 100000 tons of DME per year is currently being constructed by Chemrec in Örnsköldsvik to fuel about 2000 heavy trucks. Alternatively, biogas resulting from the anaerobic digestion of vegetation and animal waste generally composed of 50 to 70% methane with the remainder being mostly CO_2 can also be used.

However, 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. Competition of energy production with food production should also be avoided.

Methanol through CO_2 recycling

To overcome the limitations of the natural photosynthesis based carbon cycle, it can be supplemented by a feasible *anthropogenic chemical carbon cycle* (*figure 1*). This cycle is based on carbon dioxide capture and recycling to fuels and materials through methanol.

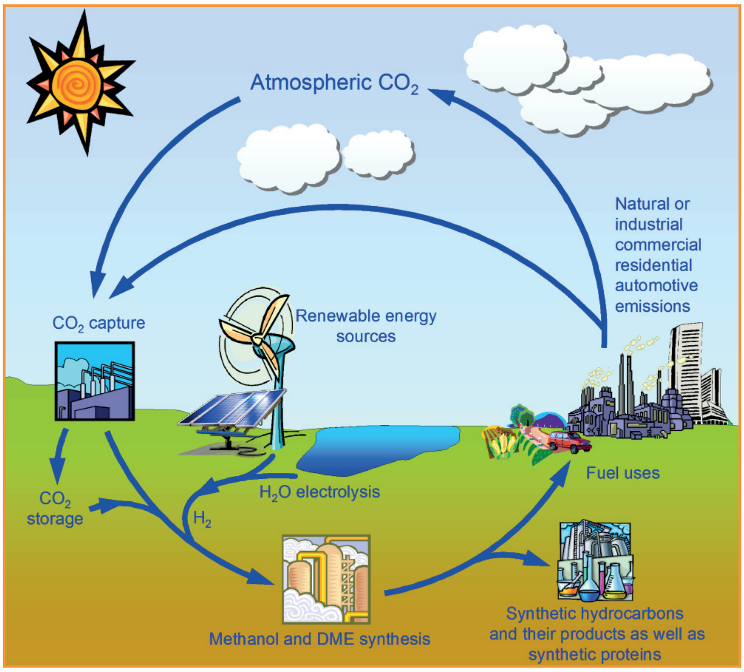

Figure 1 - **Anthropogenic chemical carbon cycle.**
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Methanol from CO_2 and H_2

It has long been known that CO_2 can be converted to methanol by catalytic hydrogenation [9]. 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 by-products of fermentation processes [10-11]:

$$CO_2 + 3\,H_2 \rightarrow CH_3OH + H_2O \qquad \Delta H°_{298K} = -\ 11.9\ kcal.mol^{-1}$$

$$CO + 2\,H_2 \rightarrow CH_3OH \qquad \Delta H°_{298K} = -\ 21.7\ kcal.mol^{-1}$$

Efficient catalysts, notably based on copper and zinc, have been developed for the reaction [12]. They are similar to the ones currently used for the production of methanol from syngas. In view of our present understanding of the mechanism of methanol synthesis from syngas, this is not unexpected. It is now established that methanol is most probably almost exclusively formed by hydrogenation of CO_2 contained in syngas on the catalytic surface. In order to be converted to methanol, the CO in the syngas first undergoes a water gas shift (WGS) reaction to form CO_2 and H_2. The formed CO_2 then reacts with hydrogen to yield methanol [6]:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H°_{298K} = -\ 9.8\ kcal.mol^{-1}$$

The hydrogen required for the chemical recycling of carbon dioxide can come from water (by electrolysis or other cleavage methods) or from still existing significant hydrocarbon sources. Presently, available methane, primarily natural gas, but also other natural sources such as coalbed methane, methane hydrate, methane from agricultural, domestic and industrial sources could be utilized to produce methanol using improved ways to minimize or even eliminate CO_2 emissions (see *insert 2*).

The CO_2 needed for the reaction will initially come from 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 390 ppm, could be captured and recycled to methanol, thus mimicking Nature's own photosynthetic CO_2 cycle. Efficient new absorbents to capture atmospheric CO_2 are also being developed [13].

Carbon Recycling International (CRI) in Iceland completed and operates the first commercial CO_2 to renewable methanol plant based on cheap geothermal electrical energy to produce the needed hydrogen by electrolysis of water. The needed CO_2 is separated from the geothermal steam. The present annual production of 3500 tons is planned to be increased to 35000 tons (*figure 2*).

Insert 2

Production of hydrogen from methane without CO_2 emission

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 at high temperature with carbon formed as a by-product. 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 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. The Carnol process offers therefore a possibility of using our still extensive methane resources without negatively impacting the climate.

Methanol thermal decomposition

$$CH_4 \rightarrow C + 2\,H_2 \qquad \Delta H°_{298K} = 17.9\ kcal.mol^{-1}$$

Methanol synthesis

$$CO_2 + 3\,H_2 \rightarrow CH_3OH + H_2O \qquad \Delta H°_{298K} = -11.9\ kcal.mol^{-1}$$

Overall Carnol process

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

CO_2 reduction to CO followed by hydrogenation

In the reaction of CO_2 with H_2, a mole of water is generated for every mole of methanol. When CO is used, only methanol and no water is formed. In order to utilize hydrogen more efficiently, the initial chemical or electrochemical reduction of CO_2 to CO is feasible. The direct conversion of CO_2 to CO using a thermochemical cycle and solar energy is for example being intensively studied. Researchers at the Sandia National Laboratories working on the sunshine to petrol project (S2P) 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 (*figure 3*). At a lower temperature, the reduced material FeO is then exposed

Figure 2 - The "George Olah carbon dioxide to renewable methanol plant" of Carbon Recycling International in Iceland based on local geothermal energy: the first commercial carbon dioxide recycling plant operating in the world. Courtesy: K.C. Tran, CEO, Carbon Recycling International, Iceland.

$$Fe_3O_4 \xrightarrow{1400\text{-}1500\,^\circ C} 3\,FeO + 1/2\,O_2$$
$$3\,FeO + CO_2 \xrightarrow{<1000\,^\circ C} Fe_3O_4 + CO$$
$$CO_2 \longrightarrow CO + 1/2\,O_2 \quad \text{Overall reaction}$$

Figure 3 - Thermochemical cycle for the production of CO from CO_2 at high temperature using solar heat.

to CO_2, from which it absorbs oxygen, producing CO and ferrite, which can be recycled [14]. This technology shows promise, but its viability on an industrial scale is still unproven.

Electrochemical reduction of CO_2 and co-electrolysis of CO_2 and water

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

$$CO_2 \rightarrow CO + ½\,O_2$$

This approach has been investigated using various metal electrodes in aqueous medias as well as in organic solvent media, in particular methanol.

During the electrochemical reduction of CO_2, 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 co-generate CO and H_2 at the cathode in a H_2/CO ratio close to 2, producing a syngas mixture (called "metgas"), which is then further transformed into methanol (*figure 4*) [15-16]. 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

$$CO_2 + 2\,H_2O \xrightarrow[\text{reduction}]{\text{electrochemical}} \left[\begin{array}{l} \left[CO + 2\,H_2\right] \text{ at the cathode} \longrightarrow CH_3OH \\ 3/2\,O_2 \quad \text{at the anode} \end{array}\right.$$

Figure 4 - Co-electrolysis of CO_2 and water to produce syngas for methanol synthesis.

process, which is more efficient than regular coal combustion and produces a very high CO_2 concentration effluent.

Methanol and dimethyl ether can be produced selectively from CO_2 *via* electrochemically generated 1/2 CO/H_2 syngas (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 to 60 bar and temperatures of 200-300 °C.

Direct electrochemical reduction of CO_2 to methanol

The direct electrochemical reduction of CO_2 to methanol has also been explored. High methanol selectivity could be achieved in aqueous solution on Ag, W and C electrodes. The current densities are however extremely low, ranging from about 10 to 30 µA.cm^{-2}. At higher current densities, lack of 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 2, 4, 6 or 8 electron processes, respectively (*figure 5*). Even if mixtures of products are obtained, they can potentially be further reacted to increase production of methanol. Each additional step adds, however, to the complexity of the system.

$$CO_2 + 2\,H^+ + 2\,e^- \rightarrow HCOOH \qquad E^0 = -\,0.61\ V$$
$$CO_2 + 2\,H^+ + 2\,e^- \rightarrow CO + H_2O \qquad E^0 = -\,0.52\ V$$
$$CO_2 + 4\,H^+ + 4\,e^- \rightarrow HCHO + H_2O \qquad E^0 = -\,0.48\ V$$
$$CO_2 + 6\,H^+ + 6\,e^- \rightarrow CH_3OH + H_2O \qquad E^0 = -\,0.38\ V$$
$$CO_2 + 8\,H^+ + 8\,e^- \rightarrow CH_4 + 2\,H_2O \qquad E^0 = -\,0.24\ V$$

Figure 5 - Standard electrochemical reduction potentials of CO_2 (vs NHE pH = 7, NPT conditions).

Methanol based fuels, chemicals synthetic materials and proteins

Methanol is one of the most important raw materials for the petrochemical and chemical industries. About 50 million tons of methanol are produced yearly worldwide and mostly used for the production of a large variety of chemicals and materials including basic chemicals such as formaldehyde, acetic acid and methyl *tert*-butyl ether (MTBE), as well as polymers, paints adhesives, construction materials (*figure 6*).

Methanol and DME are also used to produce ethylene and propylene by dehydration over zeolites such as SAPO-34 and ZSM-5 or bifunctional catalysts [17]. This is the basis of the so-called methanol to olefin process (MTO) (*figure 7*). Ethylene and propylene are by far the two largest volume chemicals produced by the petrochemical industry. In 2007, about 115 million tons of ethylene and 73 million tons of 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.

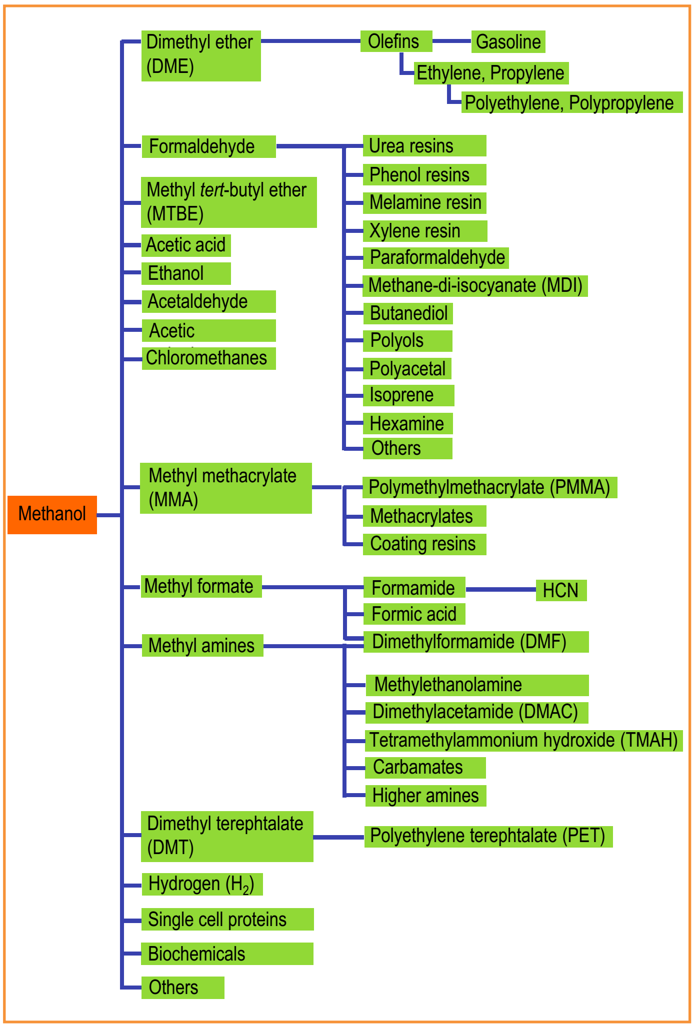


Figure 6 - Methanol-derived chemical products and materials.

The methanol to gasoline (MTG) and related olefin to gasoline and distillate (MOGD) processes developed by Mobil in the 1970s and 1980s also allows the production of gasoline, diesel fuel, aviation fuels and aromatics from methanol, if needed (*figure 7*).

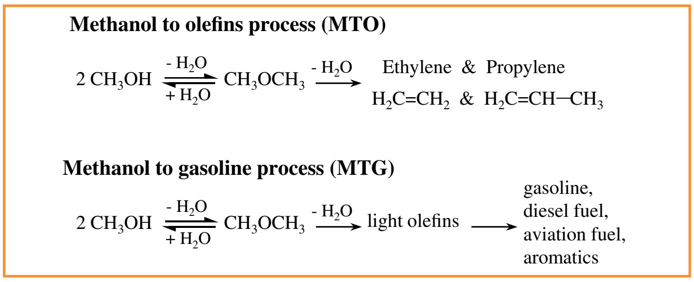


Figure 7 - Methanol to olefins (MTO) and methanol to gasoline (MTG) processes.

As pointed out, methanol itself is an excellent fuel for internal combustion engines (ICE) with a high octane number of 100 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 are currently blended with gasoline. At methanol concentrations below 10-15% blended in gasoline, it can be used in existing cars. Use of higher methanol concentrations requires minor modifications in the fuel delivery system and other car parts in contact with the fuel similar to the ones already in use in flex-fuel vehicles running on E-85. Methanol could also be used directly in modified diesel engines providing more torque with a smaller and lighter engine. Methanol is also a fuel of choice for fuel cells and direct methanol fuel cells (*figure 8*) [4, 18].

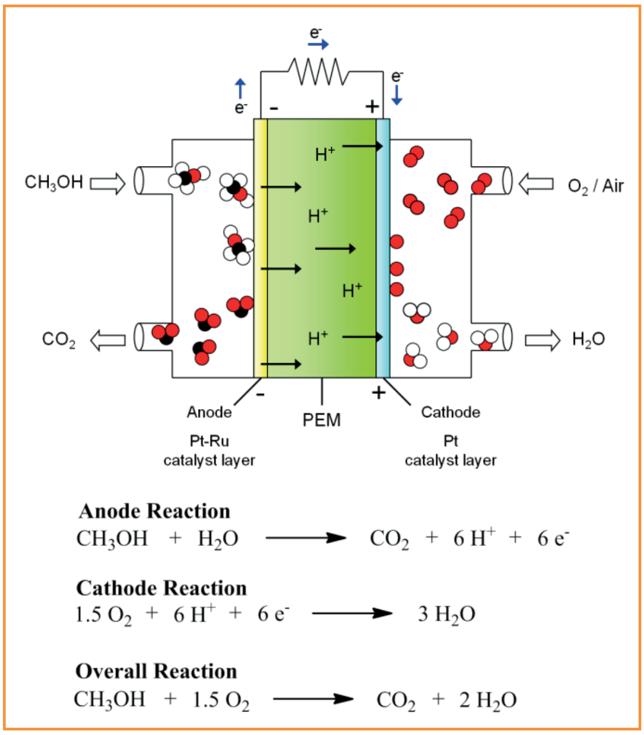


Figure 8 - Direct methanol fuel cell (DMFC).

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 [4]. 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 CNG in most applications.

Concerns about the toxicity of methanol are occasionally expressed and caution should be exercised in its use. Although toxic by ingestion the levels that are generally encountered in its dispensation in gas station has been found to be quite safe [4]. Gasoline and diesel fuel are also toxic and not meant for human ingestion but their wide usage does not represent a significant problem. 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 [4]. Interestingly, methanol is also a plant growth promoter, substantially improving the photosynthetic productivity of various plants. Methanol penetrates most plant tissues and is rapidly metabolized to carbon dioxide, amino acids, sugars and structural components [10]. 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 [11, 19]. The production of SCP could therefore also supplement in part the nutrition needs of an increasing world population.

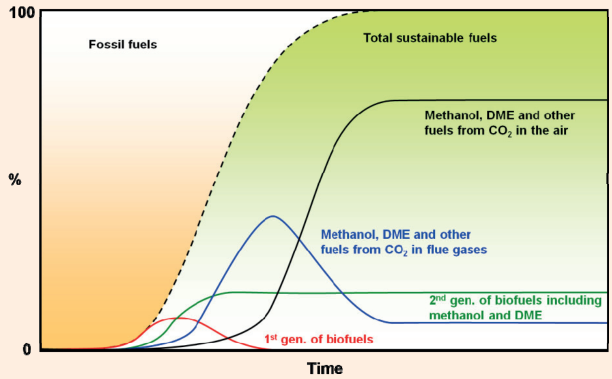
Conclusion

Chemical recycling of carbon dioxide produced through human activities, natural and industrial sources, or even from

Insert 3

Possible transition to a sustainable fuel future including methanol and DME as key components

The production of methanol and DME from biomass feedstocks and from recycling of CO_2 contained in flue gases of various industries could be the first steps toward the transition to a sustainable future for carbon fuels and hydrocarbon products. As fossil fuel become less abundant or their use regulated by stricter emission standards, related CO_2 emissions will eventually diminish. On the other hand, as discussed, the amount of biomass which can be generated in a sustainable way are large but nevertheless limited. These limitations all point to methanol, DME and derived products being increasingly produced from CO_2 captured from the air. Depending on various factors, including policies, geographical locations, state of development and available resources, the timeline and layout for the transition to sustainable fuels and products will clearly vary from country to country and location to location.



Insert 4

Methanol in space

Besides occurring naturally on Earth in some fruits, grapes, etc, 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! 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. Methanol is believed to be formed by reaction of hydrogen with carbon oxides on the surface of dispersed dust particles. This must be an ongoing process to allow methanol to be observed despite its inevitable short life.

the air to methanol and dimethyl ether and their varied products *via* capture followed by reductive conversion, offers a feasible way to render them renewable and environmentally carbon neutral, supplementing Nature's own photosynthetic cycle. In the context of the methanol economy, carbon dioxide can thus be turned from a detrimental greenhouse gas causing global warming into a renewable and inexhaustible carbon source of the future for humankind.

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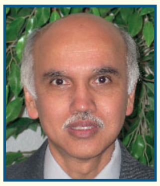

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