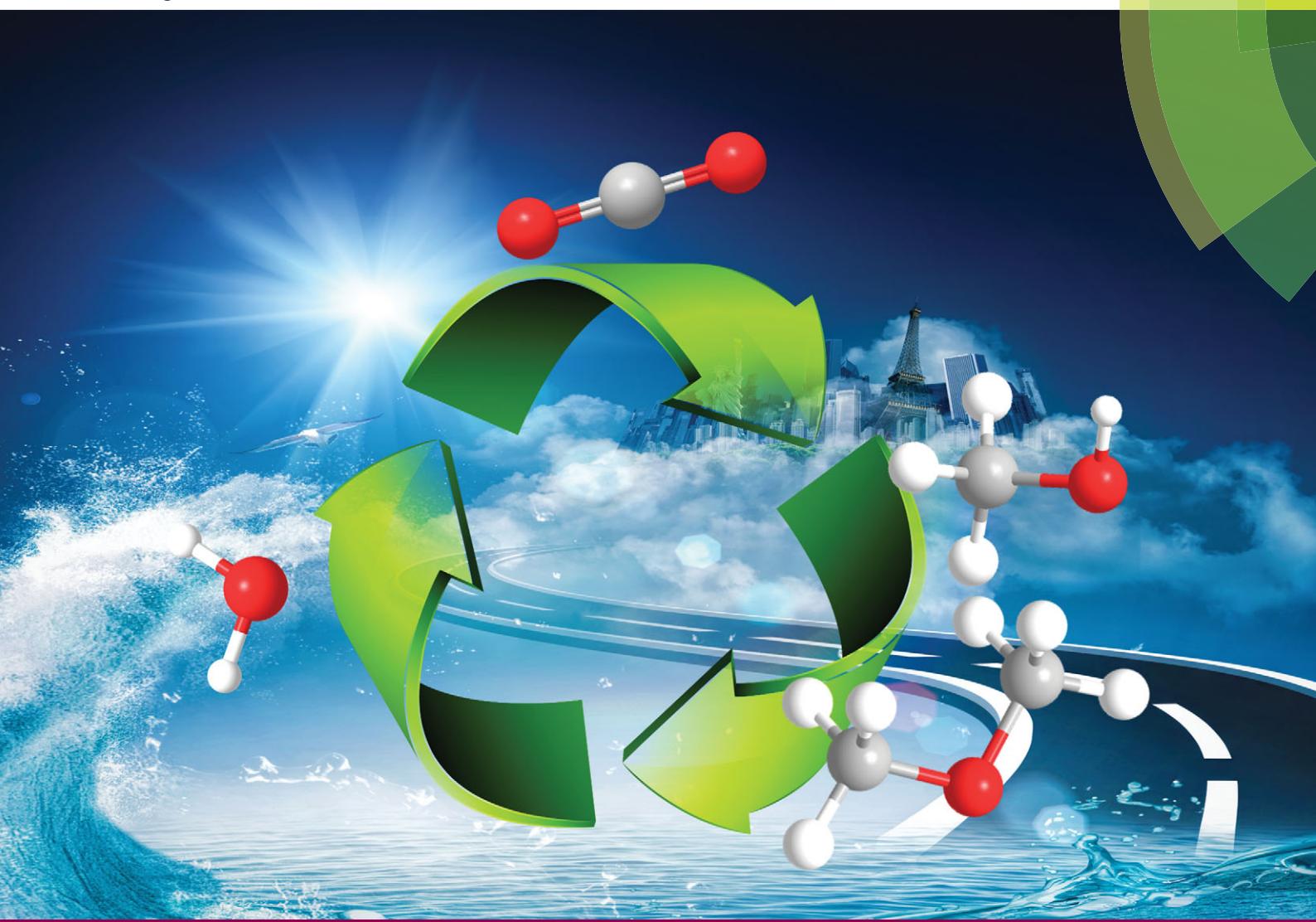


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REVIEW ARTICLE

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the loop

Recycling of carbon dioxide to methanol and derived products – closing the loop

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Starting with coal, followed by petroleum oil and natural gas, the utilization of fossil fuels has allowed the fast and unprecedented development of human society. However, the burning of these resources in ever increasing pace is accompanied by large amounts of anthropogenic CO₂ emissions, which are outpacing the natural carbon cycle, causing adverse global environmental changes, the full extent of which is still unclear. Even though fossil fuels are still abundant, they are nevertheless limited and will, in time, be depleted. Chemical recycling of CO₂ to renewable fuels and materials, primarily methanol, offers a powerful alternative to tackle both issues, that is, global climate change and fossil fuel depletion. The energy needed for the reduction of CO₂ can come from any renewable energy source such as solar and wind. Methanol, the simplest C₁ liquid product that can be easily obtained from any carbon source, including biomass and CO₂, has been proposed as a key component of such an anthropogenic carbon cycle in the framework of a "Methanol Economy". Methanol itself is an excellent fuel for internal combustion engines, fuel cells, stoves, etc. It's dehydration product, dimethyl ether, is a diesel fuel and liquefied petroleum gas (LPG) substitute. Furthermore, methanol can be transformed to ethylene, propylene and most of the petrochemical products currently obtained from fossil fuels. The conversion of CO₂ to methanol is discussed in detail in this review.

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as the development of regenerative sorbents for the separation and capture of CO₂ from various sources including the air. He is a co-author of the book "Beyond Oil and Gas: The Methanol Economy".

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1. Introduction

To satisfy the energy demand of an increasing world population, fossil fuels including coal, petroleum and natural gas are being burnt on an unprecedented scale. Presently, about 22 million



Miklos Czaun

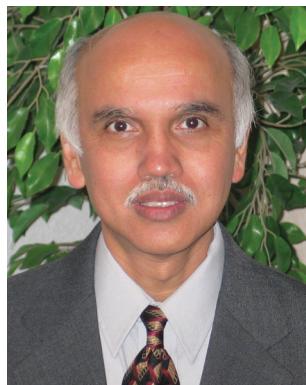
Miklos Czaun received his chemical engineering degree from the University of Veszprem (Hungary) in 1998 and completed his PhD (*Summa Cum Laude*, 2003) under the supervision of Prof. Gabor Speier. He joined the research group of Profs. George A. Olah and G. K. Surya Prakash at the Loker Hydrocarbon Research Institute at University of Southern California in 2009. Presently, he is a Senior Research Associate focused on the development of solid adsorbents for carbon dioxide capture and the conversion of carbon dioxide to synthesis gas (dry-reforming and bi-reforming reactions). He is also interested in carbon neutral energy- and hydrogen storage systems.

tonnes of coal, 85 million barrels of oil (around 12 million tonnes) and 10 billion m³ of natural gas are consumed each and every day to fulfill some 82% of the energy demand.¹ Together they contribute to the annual release of more than 30 billion tonnes of carbon dioxide into the environment.² While part of this CO₂ is utilized by plants and absorbed into the oceans, contributing to seawater acidification, about half of it remains in the atmosphere where it accumulates over time. From a pre-industrial level of about 270 ppm, the concentration of CO₂ in the atmosphere has now surpassed the 400 ppm mark. CO₂ being a so-called greenhouse gas has the effect of trapping the sun's heat and is believed to be one of the main contributors to the presently observed climate change phenomena. The natural carbon cycle has been exceeded and is presently unable to keep up with the input of large amounts of anthropogenic CO₂ emitted. Numerous solutions have been proposed to alleviate the problems associated with this inevitable by-product of fossil fuel combustion. Energy



John-Paul Jones

John-Paul Jones is a graduate student in the research group of Professors Prakash and Olah, where he is studying electrochemical CO₂ reduction, particularly under pressure. He obtained his Bachelor of Science degree in Chemistry from the University of California, Berkeley. After that, he worked for Amyris Biotechnologies in Emeryville, California, where he focused on the development of synthetic replacements for diesel, gasoline, and jet fuels.



G. K. Surya Prakash

are in fluorination and synthetic methods, mechanistic studies, superacid chemistry, electrochemistry and hydrocarbon chemistry. He is a co-proponent of the Methanol Economy concept, prolific and has received several American Chemical Society National Awards.

conservation can help but will not solve the problem by itself. The use of renewables as well as nuclear energy to fulfill an increasing part of our energy mix is also being pursued but they will be hard pressed to replace fossil fuels, at least in the short term. The gift that nature has given us in the form of fossilized sunshine, *i.e.* fossil fuels, has enabled an extraordinary development of human societies to a level that could only be dreamed of a few centuries ago. To put it in perspective, it has been determined that a single barrel of oil has an energy content equivalent to 12 humans working all year round or about 25 000 man-hours. Considering that each American on average consumes 25 barrels of oil annually, about 300 people working on a yearly basis would be required to power the industries, fuel the transportation sector and provide for many of their household needs to cover and maintain the current standard of living of each of them.

Despite their considerable size, our fossil fuel reserves are finite and limited, and will therefore be increasingly depleted. While the exploitation of unconventional fossil fuel resources such as shale oil and shale gas, and possibly methane hydrate in the future, could significantly increase the availability of affordable fossil fuels, the impact of their production on the environment is also raising numerous concerns. A number of countries including France and Germany banned or put a moratorium on the use of hydraulic fracturing, also called "fracking", technologies used to exploit shale resources as long as they are not proven safe for the environment. The utilization of these unconventional resources exacerbates the problems associated with greenhouse gas emissions. If humankind wants to continue using fossil fuels, a solution is clearly needed to control these problems. The most commonly proposed one is carbon capture and sequestration (CCS) where CO₂ would be captured from various point sources including power plants and industrial facilities, concentrated, pressurized and then pumped underground into geological formations. It could also



George A. Olah

George A. Olah is a Distinguished Professor of Chemistry and Founding Director of the Loker Hydrocarbon Institute at the University of Southern California. His pioneering research on hydrocarbon chemistry and fundamental aspects of carbocations in superacids fetched him the unshared 1994 Nobel Prize in Chemistry. He is prolific with 1400 publications, 20 books and 120 patents. His current research interests are in new energy areas covering chemical carbon dioxide recycling and the derived methanol economy concept. He has received many awards and recognitions including 12 honorary degrees from various universities and memberships in some 20 National Academies and Scientific Societies.

be used for enhanced oil recovery (EOR).³ Alternatively, the captured CO₂ could be mineralized either on the surface or underground. For the CO₂ capture, different technologies including absorption into liquids, adsorption on solids and membrane separation could be utilized depending on the CO₂ concentration, temperature, presence of impurities, *etc.* in the effluent to be treated. Eventually, even the CO₂ present in the air could be captured and technologies are presently being developed for this purpose.^{4,5} Direct air capture is important to address about half the CO₂ emissions that originate from small and dispersed fossil fuel burning units such as cars, airplanes, trains, stoves, domestic heating, *etc.* for which CO₂ capture at the source would be impractical and/or not economically feasible. However, CCS has not been proven yet on the immense scale needed, tens of billions of tonnes of CO₂ per year, and we have to make sure that all the CO₂ stored underground also remains there and does not leak overtime, rendering the overall process pointless. Monitoring of stored CO₂ over decades and probably centuries is therefore very important but might be difficult to enforce. The storage of large amounts of CO₂ underground has also seen pushback from local populations, which do not wish to have such facilities located close to them. While in general people agree that something has to be done about CO₂ emissions, on a local level, we are therefore facing the classical "not in my backyard (NIMBY)" syndrome.

In the recent past it was thought that demand for petroleum oil and natural gas would outpace the global production capacity in the relatively near term (the so-called global Hubbert's peak), after which the availability of these resources would decrease and their prices increase sharply. With the recently found shale gas and oil resources and the future possibility of economical exploitation of methane hydrate and still very large reserves of coal, it seems that we will not run out of fossil fuels for quite a while. However, if no acceptable and economical solution is found for the CO₂ problem, it could well be that our usage of fossil fuels will be strongly constrained by the levels of CO₂ emissions and the accompanying environmental effects that we are willing to accept and not by their actual availability. Sheik Zaki Yamani, a former oil minister from Saudi Arabia might therefore well be right when he said that "the stone age didn't end for lack of stone, and the oil age will end long before the world runs out of oil".⁶

At the same time, renewable energies, in particular wind and solar, which are realistically the main sources available on the scale needed (beside safe nuclear energy) to replace fossil fuels, are becoming more feasible and economical. They will increasingly compete favorably with fossil resources, especially if environmental benefits are also taken into account.

Whether humankind uses up most of the fossil fuel resources (combined with carbon capture) or uses increasingly alternative energies, the need for transportation fuels and materials that we currently obtain from petroleum oil and natural gas will remain. With increasing population, products based on carbon from plastics to medicines will also be required in increasing quantities. In order to fulfill the demand for carbon based products, CO₂ will have to be recycled in an

anthropogenic version of nature's own carbon cycle. Carbon capture and recycling (CCR) will capture CO₂ from any source, and eventually mainly from the atmosphere, and recycle it to new materials and fuels using any alternative energy source. In one way most of our energy comes from the sun: solar, wind, hydro, waves and even fossil fuels, which are the decomposition product of some plant and animal matter that lived on earth millions of years ago.⁷ Nuclear fission or possibly fusion, albeit made safer, will also have a significant role to play. One of the most versatile, simple and easy to obtain liquid product from CO₂ is methanol through hydrogenation, electrochemically and by other means. Biomass, which is already a form of recycled CO₂ can also be transformed efficiently to methanol. The produced renewable and sustainable methanol can then be further processed into dimethyl ether, ethylene, propylene, gasoline and all other products currently obtained from petroleum and natural gas. Once methanol and its derivatives are combusted they will release CO₂ which can then be recycled back, effectively closing the carbon loop (Fig. 1). The object of this review is to give an overview of the conversion of CO₂ to methanol substantially solving our carbon conundrum.

2. Advantages of using methanol

Renewable energy sources including wind, solar, hydro and geothermal as well nuclear energy that are bound to play an increasing role in the world's energy mix, produce primarily electricity. While electrical energy is a good way to transfer energy over relatively short distances, its storage on a large scale remains a challenge. Pumped hydro, compressed air storage, flywheels and batteries are all possible but have limited capacity. This is especially problematic for the two most promising renewable energies, solar and wind, which by their nature are intermittent and highly fluctuating. Solar produces much less power under cloudy conditions and none at night. Wind, on the other hand does not blow constantly or consistently at the same speed. For these renewable sources to fulfill more than a marginal portion of our energy needs, evening out these fluctuations in production will be essential for the stability of the electrical grid. Presently, the production of electrical power follows closely the demand by varying the production of power plants. While this is possible when using fossil fuels, especially natural gas, it does not seem to be an option for intermittent renewable energy sources. Storing excess capacity and use it when needed is therefore required. One way of achieving this is by storing electrical energy in the form of chemical energy (bonds) in compounds such as hydrogen, methanol, methane and higher hydrocarbons. These chemicals can then be stored and/or transported and used at a later time to produce electricity or in other applications such as transportation, heating, cooking, *etc.*

The simplest compound that can be produced from electrical energy is hydrogen, by splitting of water. The sole practical method to split water into hydrogen today is electrolysis, but others such as photochemical and thermal splitting as well as high temperature chemical cycles (*vide infra*) are also under

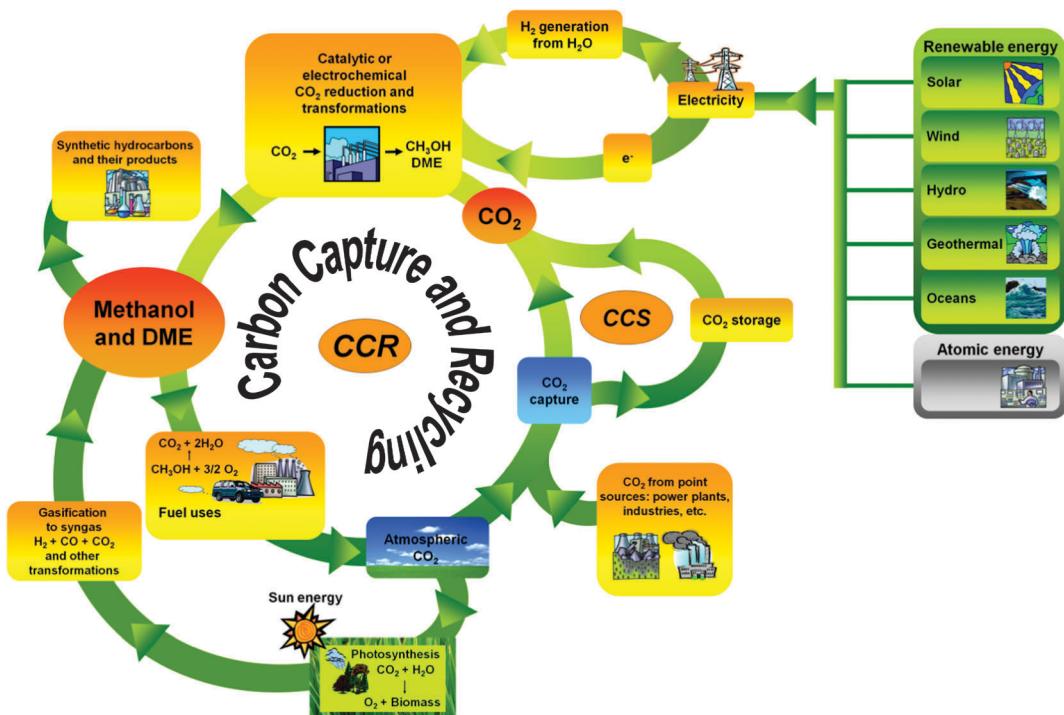


Fig. 1 Anthropogenic carbon cycle within the Methanol Economy.

investigation. Electrolysis of water has been practiced for more than 100 years and is efficient with overall system conversions higher than 75 to 80% with further improvements possible.

Hydrogen gas, has been proposed as an energy storage media and is an excellent and clean fuel which produces, besides energy, only water when combusted. In theory a "Hydrogen Economy" based on simple recycling of water to hydrogen would be very attractive.⁸ In practice, however, due to its physical and chemical properties, hydrogen has a number of serious drawbacks.⁹ Because of its low volumetric density it requires either compression to high pressures (350 to 700 bars) or liquefaction at very low temperature (-253°C), making its storage problematic and energy intensive. It is also highly flammable and explosive and can diffuse through many commonly used metals and materials. The infrastructure needed to transport, store and dispense hydrogen safely would therefore be very expensive.

Other, less cumbersome ways of storing electrons in chemical bonds are thus needed. Among the possible chemical storage media, a liquid would be preferable to a gaseous one in most applications. In the transportation sector in particular, a transition from liquid fossil fuel derived products (gasoline, diesel fuel, kerosene etc.) to a renewable and sustainable liquid fuel would be highly desirable. This would enable the use of the existing infrastructure with only minor modifications. Among the possible candidates fulfilling these requirements, methanol,¹⁰ the simplest liquid compound containing only one carbon can be produced easily through hydrogenation of CO₂ whereas direct electrochemical reduction methods are also being developed.^{11–13} Methanol has many advantages and its use as an energy carrier has been promoted in the past.^{14–22} Due to its high octane rating,

it is an excellent additive or substitute for gasoline in internal combustion engines (ICE). Methanol can also be used efficiently in modified diesel engines^{23,24} as well as in direct methanol fuel cells (DMFC) converting the chemical energy in methanol to electrical power directly at ambient temperature.²⁵ Dimethyl ether (DME), produced from methanol by simple dehydration, is a gas that can be easily liquefied at moderate pressure, much like liquefied petroleum gas (LPG). DME, which is an excellent diesel fuel substitute with high cetane rating producing almost no soot emissions has attracted much interest.^{26,27} It can also replace LPG in most applications such as heating and cooking. Furthermore, methanol and DME are superior fuels for electric power generation in gas turbines.^{28–30} If needed methanol can even be transformed to gasoline through the methanol-to-gasoline (MTG) process developed by Mobil in the 1970–1980s.³¹ Besides its fuel application, methanol is also a feedstock for numerous chemicals such as formaldehyde, acetic acid and methyl *tert*-butyl ether (MTBE). Through the methanol-to-olefins process (MTO), it can produce light olefins including ethylene and propylene used in polymers (chiefly polyethylene and polypropylene), as well as any hydrocarbon and product currently obtained from petroleum oil.

Methanol is already one of the most important organic feedstock in the chemical industry with a current worldwide annual production of about 65 million tonnes.³² Although, for economic reasons, methanol is presently almost exclusively produced from fossil fuels (natural gas and coal), it could be made from any carbon containing feedstock including biomass and any CO₂ source in the future. Such a "Methanol Economy" concept includes an anthropogenic carbon cycle to produce

methanol, which can then be used as a renewable fuel or for the synthesis of nearly all products presently derived from fossil fuels. Many aspects of a “Methanol Economy” have been described in detail in our recent papers and a monograph.^{11–13,33}

3. Methanol from CO₂ and fossil fuels

Methanol synthesis from syngas

Almost all methanol produced worldwide is synthesized from synthesis gas (syngas)³⁴ with a composition of CO:2H₂, called metgas according the reactions shown in eqn (1) and (2). While the conversion of H₂-CO mixture to methanol and the hydrogenation of CO₂ to methanol are exothermic, the reverse water gas shift reaction (RWGS, eqn (3)) is endothermic.



All three reactions are reversible and the optimal reaction conditions were developed to shift these equilibria to the formation of methanol, which require higher pressures and lower temperature according to the Le Chatelier's principle. Although the original methanol synthesis technologies introduced by BASF in the 1920's were operated at high pressures of 250–300 atm and temperatures of 300–400 °C over zinc oxide/chromium oxide catalysts, present technologies require milder reaction conditions (200–300 °C, 50–100 atm) using copper-based catalysts. Methane from any source such as natural gas and shale gas is the preferred feedstock for syngas production due to the relatively low level of impurities (H₂S, COS and mercaptans) and ease of handling compared to coal-based gasification technologies. Using methane as a feed thus allows the application of more active and selective catalysts at lower pressures and temperatures resulting in fewer side products (higher alcohols, DME and hydrocarbons) and lower capital cost. Almost all present processes are carried out *via* the gas phase reaction of H₂ and CO. However, the catalyst arrangement (*e.g.* tube, fixed bed or suspension) and the reactor design may differ.

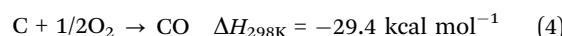
Syngas production

Despite some differences in the process parameters, the conversion of syngas to methanol is a well established technology, while the syngas production shows more diversity. The next several paragraphs will give a brief summary of processes and methods resulting in mixtures of H₂ and CO using a variety of starting materials, giving particular attention to those that utilize recycled carbon dioxide.

Syngas from fossil fuels. Traditionally syngas was produced by coal gasification³⁵ processes that combine partial oxidation and steam treatment of coal as described by the eqn (4) and (5) below. Although most of the syngas worldwide is presently produced from natural gas, coal-based technologies are still practiced in countries such as China and South Africa, where

huge coal reserves are still available but natural gas resources are scarce.

Partial oxidation of coal



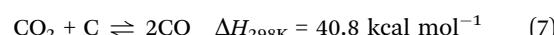
Steam treatment of coal



Water gas shift reaction



Reverse Boudouard reaction



The water gas shift (WGS, eqn (6)) reaction is applied to adjust to the proper H₂ to CO ratio and the symproportionation of CO₂ and carbon to CO (eqn (7), also called the reverse Boudouard reaction, *vide infra*) also takes place under the reaction conditions.

Endothermic catalytic conversions of hydrocarbons to synthesis gas using steam or CO₂ are called reforming reactions. Steam reforming of methane (SMR, eqn (8))³⁶ or other hydrocarbons is a widely used method to produce the mixture of hydrogen and carbon monoxide (syngas) mainly for methanol or ammonia synthesis (utilizing H₂).



This highly energy demanding process ($\Delta H_{298\text{K}} = 49.1 \text{ kcal mol}^{-1}$) is generally carried out on nickel containing catalysts at temperatures of 800–1000 °C and pressures of 20–40 atm.

In order to maximize or adjust the proper H₂/CO ratio required by the subsequent utilization of the syngas (*e.g.* ammonia synthesis, commercial H₂ production) the water gas shift reaction (WGS, eqn (6)) is often carried out after steam reforming.

One of the advantages of SMR is the lower possibility of coking due to the high partial pressure of water. However the resulting H₂/CO ratio ($S = 3$) is not practical for methanol synthesis (eqn (1)) which require a lower ratio ($S \approx 2\text{--}2.2$) and therefore appropriate adjustments.

Partial oxidation of methane (eqn (9)) is the reaction between methane and less than 2 equivalents of oxygen (that would lead to complete combustion) giving the mixture of hydrogen and CO in the ratio of 2 to 1 either in the presence or absence of a catalyst.³⁷ Practically, the gas mixture contains CO₂ and H₂O due to side reactions such as H₂ or CO oxidation (eqn (10) and (11)) reactions and complete oxidation of methane to CO₂ (eqn (12)), which cause losses in product gases and also lead to safety concerns.

Partial oxidation of methane



Oxidation of hydrogen



Oxidation of carbon monoxide



Complete combustion of methane



If we want to render the syngas production energy neutral in order to simplify the process heat management, the endothermic reforming reactions should be combined with exothermic (partial) oxidation as it is conducted in autothermal reforming and tri-reforming.³⁸

Autothermal reforming of methane *viz.* the combination of partial oxidation and steam reforming or CO₂ reforming of methane (depending on the addition of H₂O or CO₂) can be carried out either in two separate reactors or in one reactor, lowering capital cost. Even though the two reactor arrangement increases the complexity of the system, this solution allows optimization of the reaction temperature for each reaction and the unreacted methane from the steam reformer can be oxidized in the second reactor leaving low amount of residual methane in the product gas.³⁹

Tri-reforming is a process that combines the exothermic methane oxidation reactions such as complete combustion and partial oxidation of methane and the endothermic reforming reactions such as methane CO₂ reforming and steam reforming.^{38,40–43} In this process gas mixtures that contain CO₂, steam and oxygen can be combined with methane and converted to syngas with the desired H₂/CO ratio. By adjusting the relative amount of oxidants (O₂, CO₂ and H₂O) to CH₄ and the H₂/CO ratio can be shifted and the coke formation reduced.

Korean gas (KOGAS) developed a natural gas-based tri-reforming process to produce syngas providing a H₂/CO ratio in the range of 1.2–1.5 (Fig. 2).⁴³

The process includes a pre-reformer where C₂ and C₃ components are converted into C₁ species and hydrogen at 30 bar and 350 °C, and a tri-reformer unit. In the tri-reformer, the combustion of methane takes place in the catalyst-free homogeneous region, while the reforming reaction occurs in the heterogeneous region where a NiO–Mg/Ce–ZrO₂/Al₂O₃

catalyst is placed. The exothermic methane combustion provides the necessary heat for the endothermic syngas formation. The obtained syngas exits the tri-reformer at a temperature of 1000 °C and a pressure of 20 bar. It was found that the coke formation on the reactor wall could be significantly suppressed using tri-reforming.

CO₂ conversion to methanol using fossil fuels: syngas and subsequent methanol production from CO₂ using fossil fuels

Dry reforming of methane (MDR). Carbon dioxide reforming of methane (eqn (13), also called “dry” reforming indicating the absence of steam) is the reaction between equimolar amount of CO₂ and CH₄ giving one to one ratio of CO and H₂ (*S* = 1).⁴⁴ In commercial processes, the reaction is conducted on Ni/MgO or Ni/MgAl₂O₄ catalyst at temperatures from 800–1000 °C.

Dry reforming



Methanation reaction



Boudouard reaction



Methane decomposition



Dry reforming of methane and other hydrocarbons was applied commercially (Calcor process) to produce high purity carbon monoxide.⁴⁵ The chemical composition of the obtained product (CO, H₂, H₂O, CH₄), in addition to the carbon deposits indicates the appearance of side reactions such as the reverse water gas shift reaction (RWGS, eqn (3)) and methanation of CO₂ (eqn (14), also called the Sabatier reaction).⁴⁶

The advantage of dry reforming is that it utilizes very cost effective raw materials and the fact that one molecule of CO₂ is used for each CH₄ molecule, making the process even more attractive as an alternative to mitigate global warming. This process can be environmentally beneficial if the reaction heat comes from renewable energy and the utilized CO₂ is obtained from a CO₂ rich stream or from the air. It should be also noted that natural gas deposits contain various amounts of CO₂ and its removal can be avoided if used in dry reforming, thus lowering the purification cost. The price of the raw materials will obviously increase and chemical technologies which utilize CO₂ may be subsidized in the future, making the envisioned anthropogenic carbon cycle more feasible. Regardless of all its advantages, dry reforming suffers from coking, severely shortening the lifetime of the applied catalysts. This undesired carbon formation can be due to the Boudouard reaction (eqn (15)) and the thermal decomposition of methane (eqn (16)). The Boudouard reaction (eqn (15)), named after the French chemist Octave L. Boudouard, who first investigated this equilibrium in detail, is the disproportionation of carbon monoxide into CO₂ and carbon. Although the Boudouard

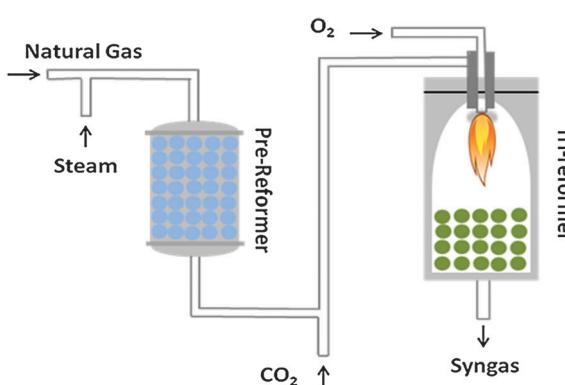


Fig. 2 Schematic representation of KOGAS tri-reforming process. Based on ref. 43.

reaction is used to produce a variety of graphites and carbon nanotubes and takes place in blast furnaces, this reaction is often undesirable since it is responsible for the deactivation of industrial catalysts due to coke formation.

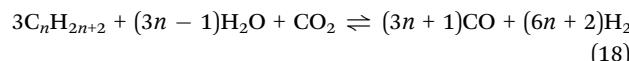
Another disadvantage of dry reforming in the context of methanol production is the low H₂/CO ($S = 1$) ratio in the product gas, which is not suitable for methanol synthesis. Enrichment of the obtained H₂-CO mixture by adding H₂ from other sources, would be a solution to adjust the needed H₂/CO ratio ($S \approx 2$) but it would also increase the complexity and cost.

Bi-reforming of methane for methanol production. Production of metgas ($S \approx 2$) can also be achieved by a selective process that has been termed “bi-reforming”,^{47,48} (Registered Trademark). Bi-reforming (eqn (17)) can be described as the combined steam reforming and dry⁴⁴ reforming of methane giving exclusively metgas, the needed feed for subsequent methanol synthesis (Fig. 3).⁴⁹

The bi-reforming of methane is also a practical procedure for natural (shale) gas that contains CO₂ because it does not require the removal and release of CO₂ into the atmosphere and it allows the adjustment of the feed ratio according to local conditions.

Bi-reforming compared to MDR, gives exclusively the 2H₂/CO ratio, and the fact that similar catalysts active for steam reforming or dry reforming (Ni/MgO at 800–1000 °C) can be used is also an advantage. The presence of steam in this process helps to suppress carbon formation (coking) that otherwise could lead to catalyst deactivation. Finally, higher aliphatic hydrocarbons can also be utilized as feedstocks for

bi-reforming (eqn (18))^{47,48,50} allowing the utilization of wet shale gas without separating the homologous alkanes.



Since most of previous works on the combination of dry- and steam reforming^{51–55} were carried out at atmospheric pressure, it seemed challenging to conduct bi-reforming at higher pressure in order to move closer to practical application. In the study of Olah *et al.*, a MgO supported NiO catalyst with a NiO content of 5–35% was used for the reforming of a gas feed of CH₄/CO₂/H₂O with a molar ratio of 3/1.2/2.4 in a temperature range of 800–950 °C at pressures of 5–30 atm under flow conditions.⁵⁶ The catalyst with 15% NiO showed good stability and high performance. For example, conversions up to 80–85% could be obtained in a single pass.

Oxidative bi-reforming of methane. A practical modification of methane bi-reforming (*vide supra*); so called “*oxidative bi-reforming*”⁵⁷ has been reported by Olah *et al.* (Fig. 4). Complete combustion of methane providing CO₂, steam and reaction heat was combined with bi-reforming,⁵⁶ resulting in a 2 : 1 mixture of H₂ and CO (metgas) for exclusive methanol synthesis.

Oxidative bi-reforming offers a solution for a long lasting challenge, namely how to incorporate one oxygen atom into the C–H bond of methane for synthesizing methanol. As is well known, direct oxygenation of methane to methanol could be carried out either with high selectivity but low conversion or *vice versa* but there is no report that both high selectivity and high conversion of methane have been achieved.⁵⁸

Carnol process. Although methanol synthesis from H₂-CO mixture is an exothermic reaction, the conventional metgas production *via* reforming reactions is very energy intensive. Since the required heat energy is derived from burning fossil fuels in conventional syngas production processes, it results in significant CO₂ emission. Consequently, environmentally more benign processes emitting less or no CO₂ have to be considered for hydrogen production.

The Carnol process, which was also used to produce carbon black as a filler material or pigment has been developed by the Brookhaven National Laboratory.⁵⁹ As indicated in Fig. 5, methane is thermally decomposed at temperatures above 800 °C in the absence of air to hydrogen and carbon (fossil fuel decarbonization).^{60,61} In the following step, catalytic hydrogenation of CO₂ (captured from any industrial or domestic sources or from the atmosphere) can be carried out to produce methanol.

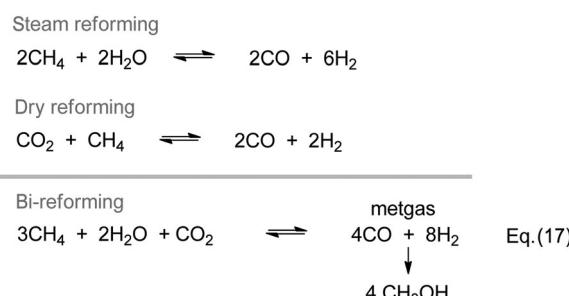


Fig. 3 Bi-reforming of methane.

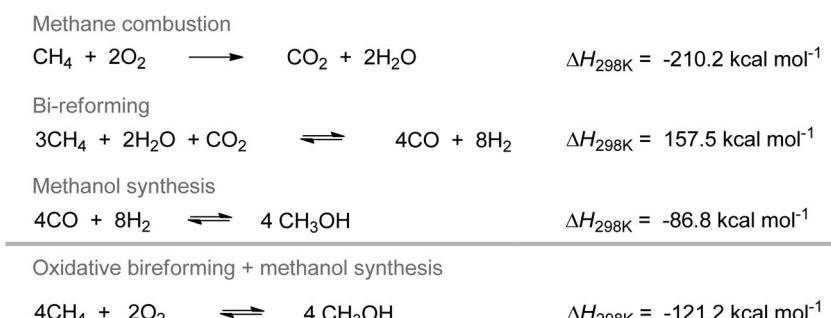


Fig. 4 Oxidative bi-reforming for producing metgas exclusively for methanol synthesis.

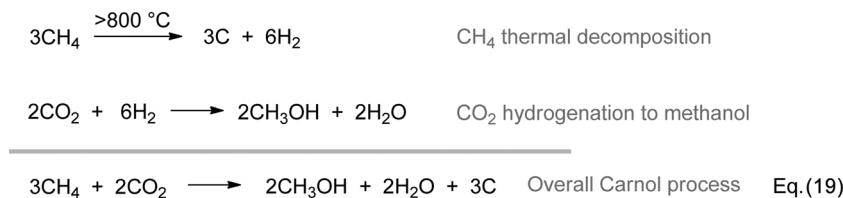


Fig. 5 Carnol process.

It is apparent, that all three carbon atoms from methane end up in elemental carbon (eqn (19)) while carbon atoms from the added CO_2 are incorporated into methanol.

Combination of methane decomposition with dry reforming.

Carbon dioxide can be converted into methanol by the combination of methane decomposition⁶² and dry reforming as described in Fig. 6.

Compared with the Carnol process, less carbon derived from methane is converted to elemental carbon, so this method results in more CO_2 emission after using the produced methanol as a fuel for example.

Fig. 7 gives a summary of processes for converting carbon dioxide to methanol using still abundant natural gas resources.

Addition of CO_2 to syngas from steam reforming. Not only by the combination of steam reforming and dry reforming can the proper H_2/CO ratio of 2 be achieved, but also by the addition of CO_2 to the syngas from steam reforming during the methanol synthesis

step leading to the same overall composition (Fig. 8). The advantage of this method is that the excess hydrogen produced by steam reforming can be also utilized in the same process.

H_2 from CH_4 without CO_2 formation (CH_4 decomposition)

Large scale cost effective production of hydrogen is essential for industry since hydrogen is a starting material for numerous important technologies such as ammonia synthesis, hydro-cracking, methanol synthesis, etc. Hydrogen is also considered a “clean fuel” for H_2/air fuel cells and for cars powered by liquefied hydrogen because its only combustion product is environmentally benign water. It must be noted however that due to the fact that these technologies utilize fossil fuels, the production of H_2 is accompanied by high CO_2 emissions. Direct methane decomposition⁶² to hydrogen and elemental carbon may give a promising alternative for hydrogen production because all carbon atoms from the fossil fuel end up in solid

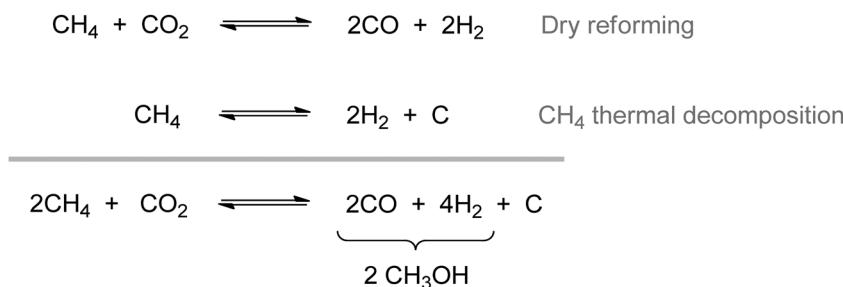
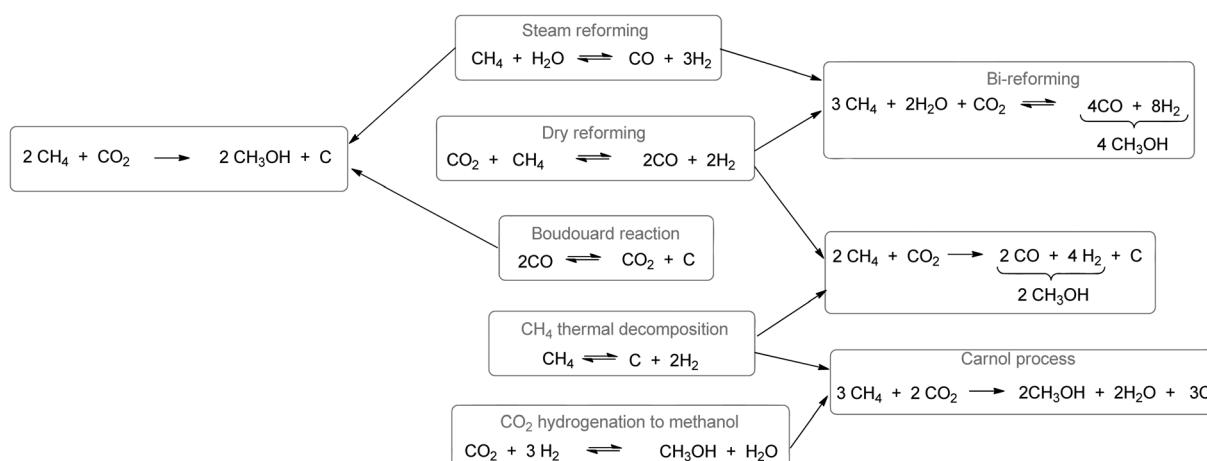
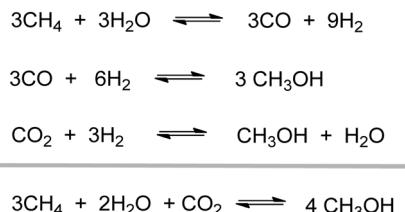


Fig. 6 Combination of methane decomposition with dry reforming.

Fig. 7 Processes to convert CO_2 to methanol using methane.

Fig. 8 Addition of CO₂ to syngas from steam reforming.

form (carbon), which can be easily disposed or utilized as a construction material or as a filler giving a lower net carbon dioxide emission.⁶³

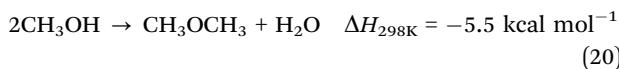
Generally, there are two groups of catalyst that are used for reducing the required temperature for the thermocatalytic decomposition of methane (TCD). Among the metal catalysts the activity decreases in the order of Co, Ru, Ni, Rh > Pt, Re, Ir > Pd, Cu, W, Fe, Mo. However further studies are necessary to establish a general agreement on this order due to some discrepancies in the literature.⁶⁴

Any of these catalysts will eventually become deactivated due to carbon deposition (coking) on the catalyst surface. Utilization of a carbon catalyst⁶⁵ helps to overcome this problem in addition to other advantages such as lower price and the fact that such catalysts cannot be poisoned by sulfur.

Dimethyl ether (DME)

As it was shown earlier in this article, methanol is an excellent fuel or fuel additive due to its high octane number and clean burning properties, but we can find promising fuel candidates among methanol derived products as well. Dimethyl ether (DME, also called wood ether or methyl oxide) is the simplest ether and has been used mainly as a pressurizing agent in consumer products, in paints and for insect control. Although at ambient pressure DME is a gas (bp = -25.1 °C) due to its low vapor pressure (VP^{25 °C} = 0.6 MPa), it is easy to liquefy, simplifying its handling and transportation. Not only because of its high cetane number but also due to its advantageous combustion properties such as no soot and SO_x emission and low NO_x emission, DME is an excellent diesel substitute. In addition, unlike other alkyl ethers its low propensity to form explosive peroxides makes this material a safe diesel car fuel, an electric power generation fuel and LPG substitute.⁶⁶

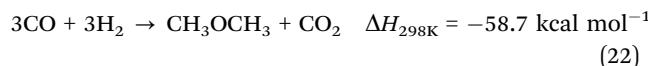
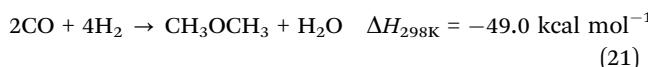
Traditionally, DME is synthesized from methanol by bimolecular dehydration over a variety of acidic catalysts (alumina or phosphoric acid modified γ-Al₂O₃) according to eqn (20).



The required methanol is mainly derived from natural gas or coal-based syngas but eventually methanol from any other source such as electrochemical or catalytic reduction of carbon dioxide or biomass conversion is suitable for DME synthesis.

In order to simplify the process, the synthesis of DME directly from syngas by combining the methanol synthesis with the dehydration of methanol has gained increasing attention.

The combination of methanol synthesis catalyst (Cu/ZnO/Al₂O₃) with that used for dehydration of methanol resulted in excellent equilibrium conversion.



Japan Steel Engineering (JSE) has used the reaction in eqn (22), a combination of reactions in eqn (1), (6) and (20), in its technology.⁶⁷ The source of syngas is autothermal reforming of methane *viz.* the combination of the exothermic partial oxidation of methane with the endothermic dry reforming (eqn (23)).



As it is indicated in eqn (23), two hydrogen atoms from methane form water, which is a significant H₂ loss.

Haldor Topsøe has applied the pathway in eqn (21), a combination of eqn (1) and (20), in its DME plant, which uses metgas, with a H₂/CO ratio of 2. As it was discussed, this ratio can be achieved by bi-reforming of methane. The obtained water from eqn (21), if needed, can be recovered and used in bi-reforming and thus all hydrogen utilized in producing DME.^{47,50,68} This is of significance in arid areas, where water resources are scarce.

Current reserves of methane from natural gas are still very large. The exploitation of unconventional natural gas resources such as shale gas and methane hydrates could also significantly increase the amounts of methane available to humankind. Nevertheless, these resources are finite and will eventually run out. On the other hand, innovative processes are being explored for the transformation of methane into easy-to-handle liquid fuels, primarily methanol, but this will not solve the problem of increasing CO₂ concentrations in the atmosphere and its detrimental effects on the global climate. Even though methane does release less CO₂ upon combustion than coal or petroleum, its increased utilization to fill the world's growing energy needs will still produce vast quantities of CO₂. Thus, new ways are needed to fulfill humankind's ever increasing appetite for energy, without adversely affecting our environment. In the long term, methanol will, therefore, have to be produced from sources that release only minimal quantities of CO₂, if at all. In this respect, the use of biomass is one possibility that is being explored and described, *vide infra*.

4. Biomass and waste based methanol and DME – bio-methanol and bio-DME

Biomass, based on recycled CO₂, is generally referred to as any type of plant or animal matter, *i.e.* any materials produced by life forms. This includes wood and agricultural crops and their waste byproducts, municipal solid waste, animal waste as well as aquatic plants and algae. Methanol itself was originally

named wood alcohol because it was made exclusively through the thermal destructive distillation of wood. This relatively inefficient route was however quickly abandoned with the development of syngas based synthetic processes at the beginning of the 20th century. Current socio-economical factors such as energy security, availability, and cost but also climate change concerns have prompted a reconsideration of biomass, which should play a more significant role in our energy mix on a global scale. Because biomass itself is a very general term used to describe a variety of heterogeneous materials (in most cases bulky solids such as wood and agricultural crops and by-products) its conversion to a single, convenient and easy to transport liquid product such as methanol could be advantageous. The methods for producing bio-methanol from biomass are now much more efficient than a century ago.^{69,70} Depending on the nature of the feedstock, various technologies, namely pyrolysis, liquefaction, gasification and combinations thereof can be used (Fig. 9).^{71–75} For solid feedstocks such as wood and other cellulosic materials the technologies are similar to the ones used to convert coal to methanol, *i.e.* gasification to syngas followed by methanol synthesis. For some other biomass feedstocks such as animal manure, the conversion to biogas, a mixture rich in methane and CO₂, followed by reforming to syngas and finally methanol synthesis is a possibility. An overview of various options is shown in Fig. 10. In theory any organic carbon containing material can be utilized in the process, making it relatively flexible. The direct conversion of biomass to methanol following enzymatic routes is also an attractive alternative but is still in early research phase.

Gasification

The most straightforward method for the transformation of biomass to an intermediate product that can be used to make methanol is gasification. Gasification is a thermochemical process in which a carbon containing feedstock, in this case biomass, is converted at high temperature to a gas mixture containing carbon monoxide, hydrogen, CO₂ and steam, *i.e.* syngas. For the gasification process, the biomass feedstock (most commonly a solid) is usually first dried and pulverized

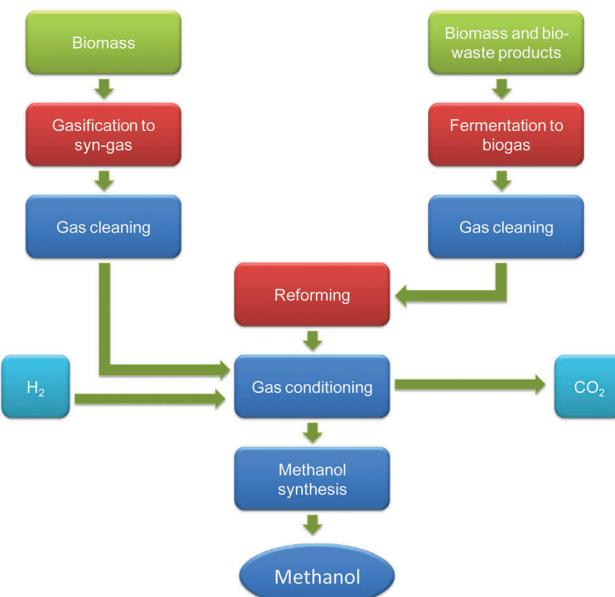


Fig. 10 Simplified schematic illustrating the methanol production from biomass based feedstocks. Based on ref. 77.

to obtain particles with a more uniform size and a moisture content no higher than 15–20% to yield optimal results. The pre-treated biomass is then sent to a gasifier where it is mixed with water and oxygen, generally under pressure. Oxygen is used to burn a part of the biomass, generating the heat necessary for the gasification. The generated combustion gases, CO₂ and steam, also react with the biomass to produce hydrogen and carbon monoxide. Biomass, being the heating fuel in the process, requires no external heat source. The production of syngas from biomass in a single partial oxidation step is very elegant, but this method has experienced significant technical problems. Therefore, gasification of biomass is generally conducted in a two-step process. In the first step, named “pyrolysis” or “destructive distillation”, the dried biomass is heated to 400–600 °C in an atmosphere deficient in oxygen to avoid complete combustion. The obtained pyrolysis gas is composed of carbon monoxide, hydrogen, carbon dioxide, steam, methane and volatile tars. The leftover residue, representing about 10–25% of the original biomass, is charcoal. In the second step of the process, called “char conversion”, this charcoal residue is reacted with oxygen at much higher temperature (1300–1500 °C) to produce carbon monoxide. The syngas obtained from the combination of the gases from the pyrolysis and char conversion has to be adjusted to right ratio of H₂/(CO + CO₂) and purified before being sent to the methanol production unit.

The advantage of biomass compared to most coals is its much lower sulfur content (0.05–0.20 wt%), while heavy metals impurities (mercury, arsenic, *etc.*) are present only in minute quantities. However, biomass gasification has its own issues. Tar formation in particular is problematic in the commercialization attempt of any biomass based gasification process. Composed mainly of oxygenated compounds due to the nature of the feedstock (basically sugar polymers, cellulose) and higher molecular

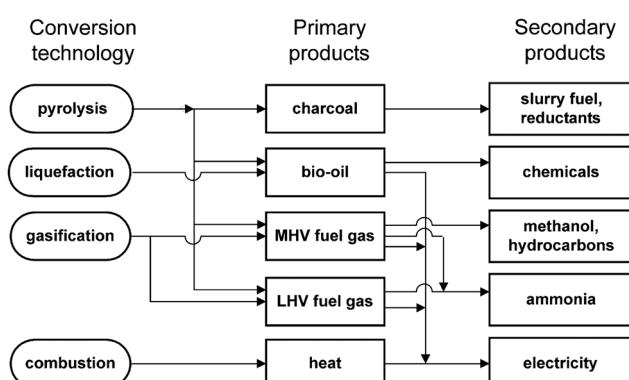


Fig. 9 Thermochemical conversion – products and uses. (LHV: lower heating value; MHV: medium heating value). Reproduced with permission from Elsevier from ref. 76.

weight hydrocarbons, these tars condense in pipes, boilers, transfer lines, particulate filters, *etc.* leading to flow restriction, clogging and other operational difficulties. The amount and nature of these tars is dependent on the biomass composition, gasification technology used and operating conditions. Selecting the proper gasification technology and operation conditions can significantly reduce their level.⁷⁸ Other gasification methods such as supercritical water reforming was proposed for glycerol gasification to H₂, CO, and CO₂ followed by methanol synthesis.⁷⁹ Using wood and forest residues, biomass to methanol conversion efficiencies as high as a 60% were achieved.^{10,80–82}

Sources of heat for the gasification

In conventional gasification systems, a part of the biomass feedstock is burned to provide the needed energy for the process. Significant amounts of heat are thus released, which can be used to dry the biomass before gasification. If no drying is needed, as in the case of the use of dry biomass, the excess heat could be directed to the generation of electricity and for district heating.⁸³ To improve the utilization of biomass and reduce the amount of CO₂ emitted, other sources of heat could also be used. However, due to the high temperatures required (>400 °C) only a few alternative energy sources could be potentially used for gasification, namely solar thermal^{84–88} and nuclear energy. Gasification of biomass at 800–1000 °C in a molten salt medium heated by concentrated solar energy has for example been proposed. Storage of energy in the form of heat in the molten salt could allow the production of syngas from solar energy without interruption.⁸⁹ Lower grade heat from solar, geothermal and nuclear could also be used to dry wet biomass prior to the gasification step, reducing somewhat the required energy input.

Bio-crude

Transporting bulky biomass products with relatively low energy density over long distances is in most cases not economical. In order to keep transportation cost at a reasonable level, one of the solutions is therefore to operate medium sized methanol plants in the center of a biomass collection area with a limited range (50–100 km from the plant). Such a model has for example been proposed for Germany and Austria.^{90,91}

Although the conversion of biomass to methanol is possible on a small scale, large scale methanol production facilities are generally preferable due to substantial economies of scale resulting in lower production costs and increased efficiency. The high volume of biomass needed to feed a world scale 2500 tonnes-per-day methanol plant (about 1 million tonnes per year) are however tremendous; on the scale of about 1.5 million tonnes per year. Biomass would therefore have to be collected over large areas.⁹² To avoid excessive transportation costs of biomass, their transformation *via* fast pyrolysis to an intermediate liquid product, which would be easier to handle and transport has therefore been proposed.⁹³ In this process, which can be more easily conducted in smaller units, biomass is heated rapidly to 400–600 °C at atmospheric pressure to produce oxygenated hydrocarbon gases. These gases are then



Fig. 11 "Biocrude".

immediately quenched to avoid further decomposition through cracking. The product of fast pyrolysis is a black liquid called "bio-crude" due to its resemblance to crude oil (Fig. 11).^{94,95} Bio-crude has potentially a wide range of applications. It can be processed into a substitute for fuel oil and used in furnaces for electricity and heat generation. After altering its chemical composition, bio-crude could also be processed alongside traditional petroleum crude in refineries able to handle this feedstock. Beside bio-crude obtained in 70–80% yield, fast pyrolysis also generates other combustible gases as well as char, a fraction of which is used to drive the overall process. Parts of the char could also be ground to a fine powder, added to bio-crude to form a slurry. This slurry, like bio-crude itself could be stored, pumped and transported *via* pipelines, freight cars, *etc.* in much the same way as crude oil today. The handling of biomass in this form would thus be made much easier. Although fast pyrolysis still requires further developments, it is a relatively simple process, operating at low pressure and moderate temperature, it could be used on both small and large scale. The production of bio-crude from delocalized plants, followed by its conversion to methanol *via* syngas using well established technologies in a centralized large scale methanol plant (2500 tonnes per day and larger) seems therefore to be a feasible and economical option depending on the right set of local conditions.

The production of bio-crude from algae through hydrothermal liquefaction under high pressure (100–300 bars) and temperature in the range of 300–400 °C has also been studied.^{72,96–98} The liquid bio-crude obtained in this case was composed of lipid derived alkanes and heterocyclic compounds. By catalytic hydro-treatment, the heteroatoms could be separated from the bio-crude and the obtained liquid blended in existing petroleum refineries. Catalytic hydrothermal gasification of the algal feedstock is also possible.^{72,98} The resulting gas is mostly composed of methane and CO₂ (similar to biogas) and has therefore to be further processed *via* reforming reactions to syngas followed by methanol synthesis.

Combination of biomass and coal

Because of the seasonality of biomass production especially in temperate and colder climates, the production of methanol in plants able to handle both coal and biomass has also been proposed.^{76,99–102} When not enough or no biomass is available, these plants could continue to operate at full capacity. The co-gasification of biomass and coal using solar thermal energy was also reported.⁸⁵ Polygeneration of power, methanol and FT hydrocarbons using biomass and coal have been modeled by Chen *et al.*¹⁰³ Depending on the conditions including product pricing, carbon tax policies, carbon capture and sequestration, etc. different optimal product portfolios were obtained.

The co-production of methanol and electricity from biomass¹⁰⁴ as well as the co-production of methanol and district heating have been considered.¹⁰⁵ Guang-jian *et al.* showed that the energy savings in such a system were mainly due to heat exchange processes.¹⁰⁶ The co-production of methanol, electricity and heat was also reviewed and studied by Holmgren *et al.*⁸³ They reported that addition of a MTO process unit to a stand alone biomass to methanol plant was found to have little impact on the overall energy balance of the system. Electricity and steam are needed for the MTO process but less is necessary for the methanol production step since distillation can be omitted.

Excess CO₂ in the gas mixture derived from biomass

Production of methanol from biomass suffers from some of the same problems as its production from coal. Due to their chemical composition, both of these feedstocks produce a syngas mixture with a low hydrogen/carbon ratio and a high CO₂/CO ratio. For methanol synthesis the optimal ratio $S = (H_2 - CO_2)/(CO + CO_2)$ has to be close to 2. To adjust the ratio, part of the CO₂ is generally separated after gasification. A pressure swing adsorption (PSA) process has, for example, been discussed by Ribeiro *et al.* to obtain a CO₂ stream with a purity higher than 95% besides methanol.¹⁰⁷ Preferably, the captured CO₂ should be sequestered or used for some other process but it could also simply be vented. Because the production of methanol from biomass generates a lot of CO₂, the apparent conversion of biomass into methanol is reduced.⁷⁷

Another possibility is to react the excess CO₂ with hydrogen from some other source.¹⁰⁸ Syngas with a H₂/CO ratio close to 3 obtained from steam reforming of natural gas could be used to compensate for the lack of hydrogen in the syngas produced from biomass.^{109,110} Biomass–natural gas hybrid plants would avoid the need for a H₂/CO ratio adjustment and CO₂ addition usually practiced in natural gas based plants. At the same it would avoid the need for CO₂ removal encountered in the biomass based plant.

The Hynol process, originally developed at the Brookhaven National Laboratory, was successful in converting materials such as woodchips into methanol on a pilot scale.^{111–113} In this case, the biomass was directly treated with hydrogen and steam in a hydrogasification step followed by steam reforming of the process gas with natural gas and finally ending with methanol synthesis. One of the advantages is that the hydrogasification avoids the need for oxygen generally used in the gasification step. For this, part of the hydrogen-rich gas after the methanol synthesis was recycled to the hydrogasification unit. The combination of biomass gasification products with steel-work off-gases such as coke oven gas containing typically about 66% hydrogen was also studied.¹¹⁴ While natural gas and other industrial gases can be used, renewable sources of hydrogen would be preferable to lower the carbon footprint of overall methanol production.

The use of nuclear based energy is also a possibility due to its low carbon footprint. Such a hybrid system based on biomass and alternative energy sources has been proposed for the production of methanol^{22,93,108,115–118} as well as Fischer-Tropsch hydrocarbon liquids.¹¹⁹ Ouellette *et al.* for example discussed the production of bio-methanol from biomass and hydrogen produced *via* electrolysis of water using hydroelectricity.¹¹⁵ In Denmark, the combination of hydrogen produced from water in a solid oxide electrolyzer cell (SOEC) and biomass was studied for the production of methanol and DME (Fig. 12).¹²⁰ This study reported that in comparison to a traditional methanol synthesis plant operating on biomass gasification without electrolysis, the output of methanol from the plant is doubled and the methanol production efficiency is boosted from 59% to 71%. The total plant efficiency was 81.6%.

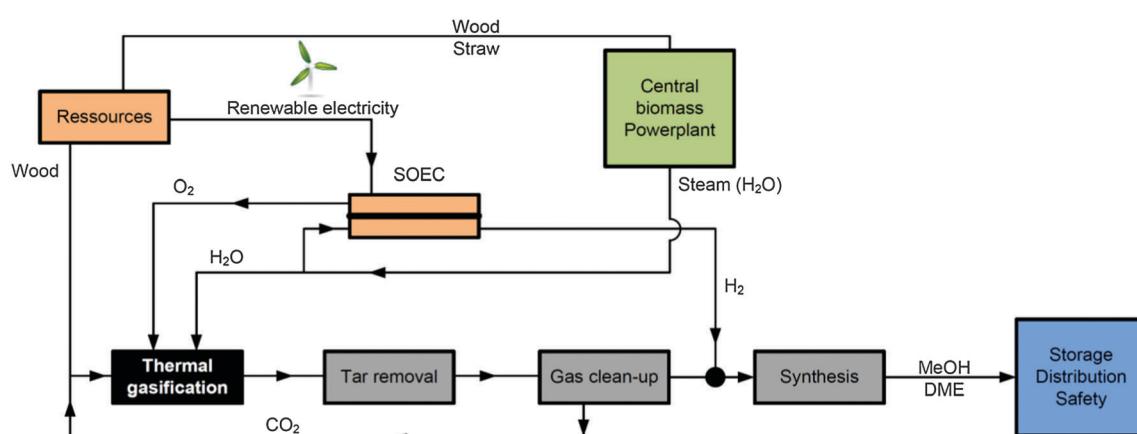


Fig. 12 Methanol/DME synthesis based on electrolysis assisted gasification of wood. From ref. 120.

With this process, it should be possible to synthesize 1053 t of methanol per day with 1000 t of wood per day and 141 MW of installed SOEC. Oxygen produced as a by-product of water electrolysis could also be used to gasify the biomass, eliminating the need for a stand-alone air separation unit. The cost of the methanol produced was estimated at between \$120–140 per barrel of oil equivalent (energy contained in one barrel of petroleum oil) using SOEC.

Methanol from biogas

Most mammals, as well as termites and other bio-organisms, produce a flammable gas called “biogas” when they digest their food. Biogas is also generated in wetlands, swamps and bogs where large amounts of rotting vegetation may accumulate. It is formed when anaerobic methanogenic bacteria break down organic material in the absence of oxygen in a process called “methanogenesis”. Biogas is in fact a waste product of such microorganisms, composed mainly of methane and CO₂ in variable proportions, and trace levels of other gases such as hydrogen sulfide. This biological process has been adapted commercially in anaerobic digestion reactor to treat various feedstocks such as animal dung, municipal organic waste, sewage sludge and wastewater from food, paper and pulp, fiber, meat, milk, brewing and pharmaceutical plants.¹²¹ All types of biomass can be used as substrates for biogas production as long as they contain carbohydrates, proteins, fats, cellulose, and hemicelluloses as main components. However, strong lignified organic substances such as wood are generally not suitable due to their slow anaerobic decomposition. The gas produced in anaerobic digesters, depending on the feedstock and effectiveness of the process, consists of 50–70% methane with the remainder being mostly CO₂. At present, the gas is mainly used to produce electricity or heat. Biogas is however also used as a transportation fuel in the form of compressed methane, notably in Sweden in buses. After purification and the removal of impurities (especially hydrogen sulfide), biogas could also be used for the production of methanol in much the same way as natural gas. However, as in the case of biomass gasification, biogas contains an excess of CO₂, which would have to be

removed, and possibly stored, or reacted with hydrogen from another source.¹¹⁷ Utilization of wind energy to produce H₂ by electrolysis of water in a SOEC and combination with biogas has for example been studied in Denmark for the production of methanol and DME (Fig. 13).^{120,122} Bi-reforming of biogas is also a possibility.^{57,123}

Whereas the syngas route to methanol is the only viable one presently for the conversion of biogas to methanol, alternative routes for the conversion of methane have also been proposed, but remain in the developmental stage. These include direct oxidation of methane to methanol and conversion through monhalogenated^{124–127} or sulfonated^{128,129} intermediates. Biological routes as well as photochemical pathways for the synthesis of methanol from methane have also been studied but practical application remains elusive.

Industrial activity in the biomass to methanol and DME conversions

Over the past two decades, a number of commercial entities have been involved in the development and production of methanol from various biomass sources ranging from wood products to municipal waste. BioMCN in The Netherlands has been producing methanol from the gasification of glycerin left over from processing vegetable oil (a by-product from bio-diesel production) and animal fat.¹³⁰ Rising glycerin prices have however forced the company to diversify its feedstock to biogas and residues from the forestry and wood processing industry.

Chemrec, in Sweden has built and is operating a bioDME plant, where methanol is produced as an intermediate. The process relies on gasification of black liquor (mostly lignin), a by-product of pulp and paper mills. At the pilot scale, the plant has an annual capacity of about 1400 t of renewable methanol (4 t per day), equivalent to about 1.8 million liters per year.^{131,132} The DME produced at this plant is being field-tested in Volvo trucks, which have driven more than 1 million miles on this fuel as of the end of 2013. Worldwide, the pulp and paper industry produces about 170 million tonnes of black liquor each year. The United States alone could potentially produce 28 million tonnes of methanol per year from black liquor.¹³³

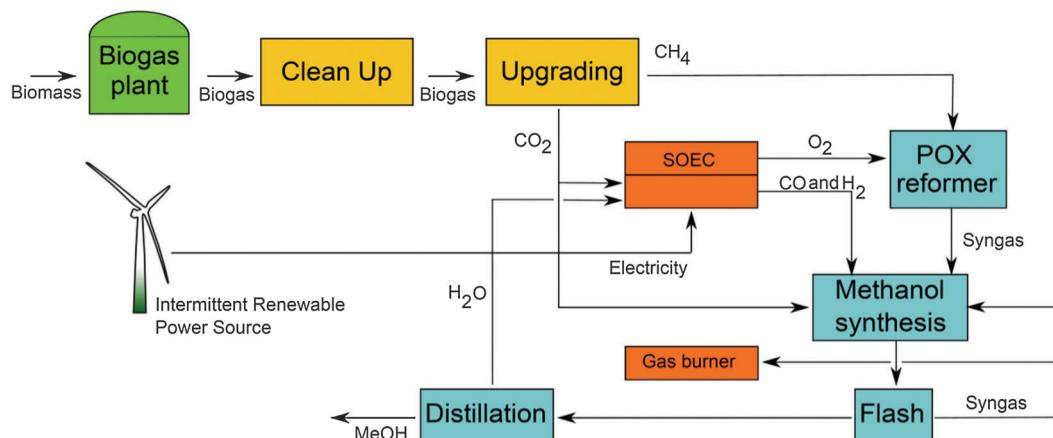


Fig. 13 Methanol production concept from biogas and H₂ via SOEC using wind energy. Reproduced with permission from ref. 122.

Also in Sweden, VärmlandsMetanol is planning the construction of a full scale plant for the production of 100 000 t of fuel grade methanol per year based on forest residues. It will be strategically placed in the forest rich province of Värmlands. The plant will gasify about 1000 t of wood per day while also providing district heating.^{134,135}

Enerkem, based in Canada, is producing methanol from municipal solid waste (MSW) by first gasifying it to syngas.¹³⁶ The methanol is currently being used as an intermediate product for the production of renewable ethanol and chemicals. After successful operation of a pilot and commercial plant, a full scale commercial plant with a capacity of 38 million liters of methanol/ethanol per year (\sim 30 000 t per year) is under construction and should begin production in 2014. Oberon Fuels in California is commercializing small scale plants (\sim 40 000 L per day) for the production of DME and methanol from biogas. Other companies are also working on various aspects of the production of methanol and DME from biomass sources.

The Bioliq process developed by the Karlsruhe Institute of Technology (KIT) is based on decentralized production of biocrude by fast pyrolysis of biomass followed by gasification under pressure at a temperature of 1200 °C in a larger facility. The produced syngas is then transformed to methanol, DME or gasoline through the MTG process.^{137–139}

Limitations of biomass

Although waste products from wood processing, agricultural residues and by-products, as well as solid municipal waste, represent suitable feedstocks for methanol production, the quantities that can be generated from these resources are limited. In the long term, growing demand for bio-methanol will necessitate larger and reliable sources of raw biomass. There is growing concern that the use of food crops for the production of fuels, such as ethanol from corn (1st generation biofuels), contributes to increasing food prices by competing for the same agricultural resources.¹⁴⁰ For the production of bio-methanol, non-food crops selected specifically for energy purposes would therefore have to be cultivated on a large scale if a significant amount of methanol were to be produced from biomass resources. Suitable “energy crops” are being identified, and the most promising – essentially fast-growing grasses and trees – are being field tested. In large countries with a relatively low population density such as the United States, Australia or Brazil, a significant portion of idle food-crop lands, pasture range and forest land could be used for energy crops. Marginal land would be preferable to the production of energy crops if adapted species and cultivation methods are identified. However, in more densely populated areas such as Western Europe, Japan and China, most of the arable land is already in use for food production. Unless surplus land is available, energy crops will directly and adversely compete with food and fiber production. In developing countries already struggling to produce the necessary food for their growing population, the production capacity for energy crops is clearly limited. Furthermore, crop production requires sufficient water, a suitable temperature range, fertilizers (mostly derived from fossil fuel resources) as well as agricultural

land. Energy crops should also not compete with food crops for these essential resources. Increased pollution due to fertilizer run-off leading to such problems as “dead zones” in the ocean is also a concern¹⁴¹ as is the carbon footprint of biomass production.^{142,143} Taking these and other factors into account, it has been estimated that biomass produced in a renewable and sustainable manner can cover at most about 20% of our energy needs of the future.^{144–147}

5. Methanol production from CO₂ and H₂

The most straightforward ways to produce methanol and DME from CO₂ is by catalytic hydrogenation with H₂, eqn (2). Chemists have known since the early 20th century how to convert CO₂ and H₂ to methanol.¹⁴⁸ Some of the earliest methanol plants operating in the 1920s and 1930s in the U.S. were in fact commonly using CO₂ and H₂, obtained as by-products of fermentation processes, for methanol production.^{149,150} Both homogeneous and heterogeneous catalysts have been studied for the hydrogenation of CO₂. The latter is however preferable in terms of cost, stability, separation, handling and reuse of the catalyst as well as reactor design and is also the one currently practiced for the industrial production of methanol from syngas. We will therefore first focus on these heterogeneous catalysts.

Heterogeneous catalysts for the production of methanol from CO₂ and H₂

Efficient heterogeneous catalysts based on metals and their oxides, notably copper and zinc, have been developed for the conversion of CO₂ to methanol.^{151,152} These catalysts are very similar to those used presently in the industry for methanol production *via* fossil fuel based syngas based on Cu/ZnO/Al₂O₃. In view of the mechanism of methanol synthesis from syngas, this is not unexpected. It is now generally accepted that methanol is most probably formed by hydrogenation of CO₂ contained in syngas on the catalyst's surface. To be converted to methanol, the CO in the syngas first undergoes a water gas shift reaction to form CO₂ and H₂. The formed CO₂ then reacts with hydrogen to yield methanol.^{148,153–156} CO would therefore serve essentially as a CO₂ source as well as a scavenger for the oxygen atoms in water, which acts as an inhibitor for the active metal sites.^{157,158} It has been shown that reacting on a commercial methanol catalyst (copper, zinc oxide and alumina (60%, 30% and 10%, respectively, by weight), a CO-H₂ mixture, carefully purified from CO₂ and water, produces no or very little methanol. Isotopic labeling also showed that CO₂ is the main source of carbon in methanol formed from syngas.¹⁵⁷

A number of reviews have been dealing with the various aspects of the production of methanol from syngas including catalyst design, catalyst preparation, reaction kinetics, catalyst deactivation, reactor design, *etc.*^{149,158–163} We will therefore focus here on the synthesis of methanol from CO₂ and H₂.

A good catalyst should remain active for several years, so as to sustain high plant output. Deactivation through sintering

(clustering of copper sites), carbon deposition and other phenomena should therefore be minimal to avoid premature catalyst replacement and associated costs. Improvement to the catalyst system's activity and stability over time is therefore of prime importance for the economics of any methanol plant.¹⁶⁴

Lurgi AG, a leader in methanol synthesis process technology in collaboration with Süd-Chemie, developed and thoroughly tested a high activity catalyst (C79-05-GL, based on Cu/ZnO) for methanol production from CO₂ and H₂.^{151,164,165} Operating at a temperature around 260 °C, slightly higher than that used for conventional methanol synthesis catalysts, the selectivity in methanol was excellent. The activity of this catalyst decreased at about the same rate as the activity of commercial catalysts currently used in methanol synthesis plants. Other companies commercializing methanol synthesis catalysts such as Sinetix, Haldor Topsøe and Mitsubishi Gas Chemical have also developed more stable catalysts over the years.

On a commercially standard catalyst (Süd Chemie), CO₂ hydrogenation was found to be slower than CO hydrogenation.¹⁶⁶ The selectivity was, however, higher, with less by-product formation, when CO₂ was used as a carbon source. More problematic was that conventional Cu/ZnO based methanol synthesis catalysts exhibit a tendency to deactivate prematurely at higher CO₂ partial pressures.¹⁶⁴ It appears, however, that the effect of high CO₂ levels have on the methanol catalysts is substantially due to the presence of water formed during the synthesis reaction and not the CO₂ itself. In the presence of CO, this water can react *via* the WGS reaction to form more CO₂ and H₂ as described by Clarke *et al.*¹⁶⁷ In the presence of a larger excess of CO₂ or even absence of CO₂, the presence of water can inhibit the metal active sites of the catalyst and lead to poorer performance and deactivation in conventional catalysts.^{156,168–170} Water accelerates the crystallization of Cu and ZnO resulting in faster sintering and associated deactivation of the catalyst.¹⁷¹

Cu and ZnO based catalysts. Due to the lack of long term stability of conventional syngas to methanol catalysts in the presence of high levels of CO₂, more stable catalysts have been studied and developed. A majority of them still rely on Cu and Zn as their main active components^{169,172} while modified with various metals including Zr,¹⁷³ Ga,^{169,174–177} Si, B,¹⁷⁸ Cr,¹⁷⁹ Ce,¹⁷³ V, Cr,¹⁷⁷ Ti and combinations of those.^{152,180} On Cu/ZnO, it was suggested that the high activity and selectivity resulted from the high dispersion of Cu and the preferential emergence of flat surface Cu species.¹⁸¹ One of the goals is to at least keep and preferably improve the high dispersion of Cu/ZnO crystallites responsible for the high activity.^{182,183} Modification of conventional Cu/ZnO/Al₂O₃ catalysts with Pd, Pt, Rh, Co, Mn, Ti, Zr, La, Ce, Y, etc. has been explored.^{180,182,184–189} Modifying the preparation method of Cu/ZnO/Al₂O₃ catalysts and ratio of the components¹⁹⁰ were also investigated. Hong *et al.*, for example, used a gel-network co-precipitation method to prepare an ultrafine Cu/ZnO/Al₂O₃ catalyst with high activity and selectivity.¹⁹¹ In a recent paper, de Jong *et al.* showed that the uniformity of Cu nanoparticle distribution in Cu/Zn/SiO₂ played an essential role in the catalyst activity and stability over time.¹⁹² Compared to a catalyst with a non-uniform nanoparticle

distribution or a reference Cu/ZnO/Al₂O₃ catalyst, the deactivation of the catalyst with uniform nanoparticle distribution slowed down by an order of magnitude. Cu/ZnO based catalysts modified with metal oxides Ga₂O₃, ZrO₂ and Cr₂O₃ were found to be more stable than commercial catalysts for the CO₂ hydrogenation to methanol over 3400 h experimental runs at 250 °C and 50 bars.^{168,193} In skeletal Cu/ZnO/Cr₂O₃ catalyst, it was described that Cr₂O₃ improved the structural development of high surface Cu.¹⁷⁹ It was also reaffirmed that the promoting effect of ZnO on the hydrogenation of CO₂ to methanol was due to its role as an inhibitor for the RWGS reaction. In another study, Cu/ZnO/Ga₂O₃ showed high activity and selectivity towards methanol as well as superior stability due in part to the highly dispersed Cu⁺ species on the surface.¹⁷⁶ Multi-component catalysts based on Cu/ZnO/Ga₂O₃ supported on hydrophobic silica were shown to be effective and stable with selectivity to methanol higher than 99% at temperatures of 250–270 °C.¹⁷⁵ The combination of Ga₂O₃ and Pd was also found to be beneficial for CO₂ hydrogenation.¹⁶⁹ Pd promoted Cu/ZnO/Al₂O₃ catalyst had a higher activity for CO₂ hydrogenation to methanol.¹⁹⁴ This was explained by the promotion of hydrogen spillover from Pd to Cu.

Cu/ZrO₂ based catalysts. For CO₂ hydrogenation, high activity of the catalysts containing Cu and zirconia has been well documented.^{170,195–200} Wambach *et al.* in particular gave a good overview of this field up to 1999.¹⁹⁶ Cu and Ag on ZrO₂ catalyze mainly the formation of methanol, while methanation is preferred over, *e.g.*, Ni and Ru on ZrO₂. The simultaneous formation of methanol, carbon monoxide (by RWGS reaction) and methane is catalyzed by less reactive metal constituents Pd, Rh, Pt and Au.¹⁹⁶ A similar trend was observed for Cu, Ag and Au on ZrO₂ by Baiker *et al.*^{201,202} Whereas the selectivity to methanol was similar for Cu and Ag, the activity of Cu/ZrO₂ was markedly higher.²⁰³ Au, on the other hand, favored the RWGS reaction, exhibiting the lowest methanol selectivity.

The addition of chromium oxides to Cu/ZrO₂ and to a lesser extent the addition of manganese oxides, had a positive effect by retarding the sintering of the copper particles and shifting the crystallization of ZrO₂ to higher temperature, thus resulting in an increased thermal stability of the catalyst.²⁰⁴ The addition of La to Cu/ZrO₂ in the right amounts (~5% of the total amount of Cu and Zr) was found to increase the Cu surface area.²⁰⁵ A linear relationship was described between this Cu surface area and conversion of CO₂. The selectivity to methanol in this system is related to the distribution of basic sites on the surface.

The phase of ZrO₂, tetragonal (t-) or monoclinic (m-) was also found to be of importance for Cu/ZrO₂ catalysts.²⁰⁶ Whereas the surface area and Cu dispersion was essentially identical on both phases, Cu/ZrO₂ prepared with m-ZrO₂ was 4.5 times more active for CO₂ hydrogenation to methanol than the one prepared with t-ZrO₂. Similarly, a 10 times higher activity was observed by Bell *et al.* for Cu/m-ZrO₂ compared to Cu/t-ZrO₂.²⁰⁷ The use of nanocrystalline ZrO₂ improved both the CO₂ conversion and selectivity to methanol compared to catalysts prepared in a conventional co-precipitation method.²⁰⁸

The addition of B_2O_3 or Ga_2O_3 to the Cu/nanocrystalline ZrO_2 also improved the activity.

Cu/ZnO/ZrO₂ based catalysts. Cu/ZnO systems modified with ZrO_2 have been particularly well studied. The presence of ZrO_2 induces a high copper dispersion, leading to a higher activity for CO_2 hydrogenation to methanol.²⁰⁹ The lower water affinity of catalysts based on ZrO_2 compared to commercial Al_2O_3 based ones also plays a role.^{156,163,170} Employing a series of Cu/ZnO/ZrO₂ catalysts of varying contents of ZrO_2 and ZnO, it has been suggested that in this ternary system ZrO_2 , rather than ZnO, plays a more effective role in the formation of methanol from CO_2 .²¹⁰ The addition of ZnO in the proper amounts to Cu/ZrO₂ increased the catalytic activity of the system, however. Arena *et al.* indicated that on a Cu/ZnO/ZrO₂ catalyst, ZnO promotes the dispersion and reactivity of metal Cu, while both ZnO/ZrO₂ supports enhance the surface CO_2 adsorption in the proximity of Cu⁰ hydrogenation sites.²¹¹ ZrO₂ compared to two other metal oxides, CeO₂ and Al₂O₃, was found to be a superior support for Cu/ZnO due to better synergy with zirconia.²¹² The catalytic activity seems to depend on this synergy of metal and basic oxide sites, pointing to a dual-site reaction path. The oxide carrier controls the texture and adsorption properties of the Cu-ZnO system.

The Cu-ZnO-ZrO₂ system itself has been modified with small amounts of B, Ga, In, Gd, Y, Mn and Mg oxides.²¹³ The addition of these oxides influenced the catalytic activity, dispersion of Cu and stability of the catalyst. Here again, the addition of Ga_2O_3 resulted in the highest yield of methanol. In₂O₃ on the other hand, reduced drastically the activity of the catalyst. Mn and Mg helped the Cu dispersion in the reduced catalysts and led to an increase in activity for methanol synthesis.²¹⁴ A similar increase in activity with the addition of Mn was also observed by Lachowska *et al.*²¹⁵ The promotional effect of Ga on Cu/ZnO/ZrO₂ was also observed by Ladera *et al.*, who ascribed it to a selective segregation of Cu towards the surface, increasing the number of active sites.²¹⁶ A methanol selectivity of 89% was obtained at 210 °C, decreasing to 69% at 250 °C.

Multi-component catalysts Cu/ZnO/ZrO₂/Al₂O₃ and Cu/ZnO/ZrO₂/Al₂O₃/Ga₂O₃ were also found to have high activity for CO_2 hydrogenation to methanol.^{188,217} The addition of small amounts of colloidal SiO₂ to these catalysts improved greatly the stability of the catalyst and crude methanol with a purity of 99.9% was obtained in a bench-scale synthesis unit.

Besides Cu, Ag and Au were also tested on this same system (ZnO/ZrO₂).^{213,218} The catalyst containing Cu exhibited, by far the highest catalytic activity due to synergy between Cu and ZnO or ZrO₂.

Other Cu based catalysts. Silica, SiO₂, is commonly used as a catalyst support due to favorable properties such as thermal stability, porosity, texture and acidic nature. Cu supported on high purity silica was, however, found to be almost inactive for the methanol synthesis.²¹⁹ The addition of Ca, La or Zn oxide had a strong promoting effect on Cu/SiO₂. In the case of Cu/Zn/SiO₂ the activity for methanol synthesis increased with increasing CO₂ content in a CO-CO₂-H₂ mixture suggesting that CO₂ was the source for the methanol. However, the main product remained

CO, probably formed by the RWGS reaction. Fujitani *et al.*, on the other hand, found that Cu/SiO₂ had some activity for the CO₂ to methanol reaction, whereas the addition of ZnO was also found to increase considerably the activity of Cu/SiO₂.^{177,220} Similarly, the addition of ZrO₂ to Cu/SiO₂ greatly enhanced (25 times) the activity for methanol synthesis.²²¹⁻²²³ Multicomponent catalysts Cu/Zn/Ga supported on hydrophobic SiO₂ were found to be efficient and very stable over time.¹⁷⁵ On Cu/SiO₂, Bell *et al.* found that the rate of methanol synthesis was an order of magnitude faster with H₂/CO₂ compared to H₂/CO.¹⁶⁷ The selectivity to methanol remained, however, low due to the strong preference of CO₂ to undergo RWGS reaction. At 0.72 MPa, a selectivity of only 12% was obtained for methanol. With increasing pressure, selectivity increased dramatically and a selectivity higher than 90% at 573 K and 2.16 MPa using a Cu/SiO₂ catalyst.²²⁴ The addition of K to Cu/SiO₂ accelerated the RWGS reaction but hindered the methanol synthesis.

Interestingly, Fujitani *et al.* found that the activity for methanol synthesis was correlated with the oxygen coverage of the Cu surface and was dependant on the support/additive used.¹⁷⁷ A maximum activity was obtained for a coverage of about 0.16 oxygen atom per Cu atom. At lower and higher coverage, the activity diminished.

Other Cu systems studied for the hydrogenation of CO₂ to methanol include Cu/ γ -Al₂O₃,²²⁵⁻²²⁸ Cu/ γ -Al₂O₃/TiO₂,²²⁷ YBa₂Ca₃O₇,²²⁹ LaCr_{0.5}Cu_{0.5}O₃ perovskite,²³⁰ La-M-Cu-Zn-O perovskites where M = Y, Ce, Mg or Zr,²³¹ CuB and CuB doped with Zr, Th and Cr,²³² Cu/V/ γ -Al₂O₃,²²⁶ Cu/Zr/ γ -Al₂O₃,²²⁵ Cu/CeO₂/ γ -Al₂O₃ and Cu over yttria doped CeO₂,²²⁸ Cu/Zr/V,²³³ and Cu on various metal carbides including Mo₂C, Fe₃C and WC.²³⁴

Catalysts based on metals other than Cu. In the noble metal series, Pd-based catalysts are the most commonly used because they exhibit considerable activity and selectivity for hydrogenation of CO₂ to methanol. Pd supported on Al₂O₃, SiO₂, TiO₂ and MgO showed only modest selectivity for methanol.²³⁵ Pd/CeO₂ had a methanol selectivity of up to 92%; however at very modest CO₂ conversion of about 3%.²³⁶ The method of preparation and the calcinations and reduction temperature had a major effect on Pd/ZnO catalysts with maximum selectivity to methanol remaining modest (~50%), however.²³⁷ Pd/ZnO supported on carbon nanotubes (CNT) showed a relatively high selectivity for methanol (up to 99.6% at 30 bars and 250 °C). Similarly, Pd/ZnO supported on activated carbon and γ -Al₂O₃ had a lower activity and selectivity. Fujitani *et al.* studied catalysts based on Pd on various supports including Al₂O₃, Cr₂O₃, TiO₂, ZnO and ZrO₂.²³⁸ Pd/Ga₂O₃ was the most active the series with a CO₂ conversion close to 20% at 50 bars. The turnover frequency was actually 20 times higher on a Cu/ZnO catalyst they also tested. At the other end of the reactivity spectrum, Pd/SiO₂ showed essentially no activity. The products obtained on Pd/Ga₂O₃ were methanol and CO in almost equal amounts. Ga₂O₃-Pd/SiO₂ was also studied.^{239,240}

Pt-W/SiO₂ was also reported to reach methanol selectivity of up to 92.2% at a relatively modest CO₂ conversion of 2.6%.²⁴¹ Pt-Cr/SiO₂ in the same study had a much lower selectivity of 51.1%.

Some researchers attempted to use transition metal carbides for CO₂ hydrogenation to methanol. The results indicated that Mo₂C and Fe₃C had high CO₂ conversion but modest methanol selectivity, while TaC and SiC were almost inactive.²³⁴ On WC, significant amounts of DME were produced. In all cases the main products were CO and CH₄.

Recently, Sturd *et al.* reported the discovery of a Ni–Ga based catalyst for CO₂ reduction to methanol.²⁴² Ni₅Ga₃ was found to be particularly active and selective. In comparison to conventional Cu/ZnO/Al₂O₃ catalysts, a similar methanol synthesis activity was observed with, however, a much lower CO generation. This is of interest for the production of methanol at lower pressures and possibly even ambient pressure.

Influence of catalyst preparation conditions. For all catalysts, the preparation methods and conditions including co-precipitation,^{170,181,191,200,213,214,218,243} impregnation,^{175,183} leaching, sol–gel,^{203,244,245} deposition–precipitation and combustion synthesis^{246,247} as well as calcination temperature²⁴⁸ also played a major role in the behavior of the catalysts.^{163,208,243,247–252} Practical catalyst preparation is based substantially on used “art” and not only science. This topic is, however, outside the scope of our review. What is in fact needed is a more rational design of catalysts based on controlling closely the nature and stability of the active sites as well as detailed mechanistic studies to improve the state of the art.

Reaction mechanism of CO₂ hydrogenation to methanol. To understand the high selectivity of Cu based catalysts, especially when combined with ZrO₂ and ZnO, for the synthesis of methanol from CO₂ hydrogenation a number of studies on the reaction mechanism were carried out. Bianchi *et al.* reported the spillover of adsorbed hydrogen from zirconia to copper.²⁵³ On Cu/ZrO₂, Bell *et al.* studied the reaction of CO₂

and CO to methanol and proposed a dual-site, bifunctional, mechanism.^{207,221–223,254} Studying the reaction of CO₂ and H₂ on Cu/ZnO/ZrO₂, Arena *et al.* proposed a similar mechanism.²¹¹ Two active centers are thus involved in this catalytic process. According to the currently accepted dual-site or bifunctional mechanism, the adsorption and dissociation of hydrogen occur on the Cu site, while the adsorption of CO₂ as a bicarbonate takes place on the ZrO₂ site. *Via* spillover, the atomic hydrogen then transfers from the surface of Cu onto the surface of ZrO₂ and hydrogenates stepwise the adsorbed carbon containing species to methanol, which is desorbed from the surface (Fig. 14). Formate was proposed as a common intermediate for the synthesis of methanol and the reverse water–gas shift (RWGS) reaction by Fisher *et al.*²²¹ A similar conclusion was reached by Hong *et al.* using first-principle kinetic Monte Carlo simulations.²⁵⁵ In light of the proposed mechanism, higher surface area of Cu, appropriate adsorption, both in strength and amount of CO₂ and effective interaction between the active parts of the catalyst are of prime importance for the hydrogenation reaction, providing a guideline for the preparation of highly effective catalysts. Modifications by various additives to improve one or several aspects of the catalytic steps is one of the possible pathways to influence these parameters, and has been studied extensively (*vide supra*) to increase the catalytic activity. The addition of La₂O₃ onto Cu/ZrO₂, for example, was reported to affect the dispersion of Cu as well as increase the surface basicity, which in turn had an effect on the adsorption of H₂ and CO₂, respectively.²⁰⁵ Used in the right proportions, La₂O₃ increased the activity of the catalyst for methanol production from CO₂.

To describe the reaction mechanism of methanol synthesis from CO and CO₂, a micro-kinetic model based on 13 individual

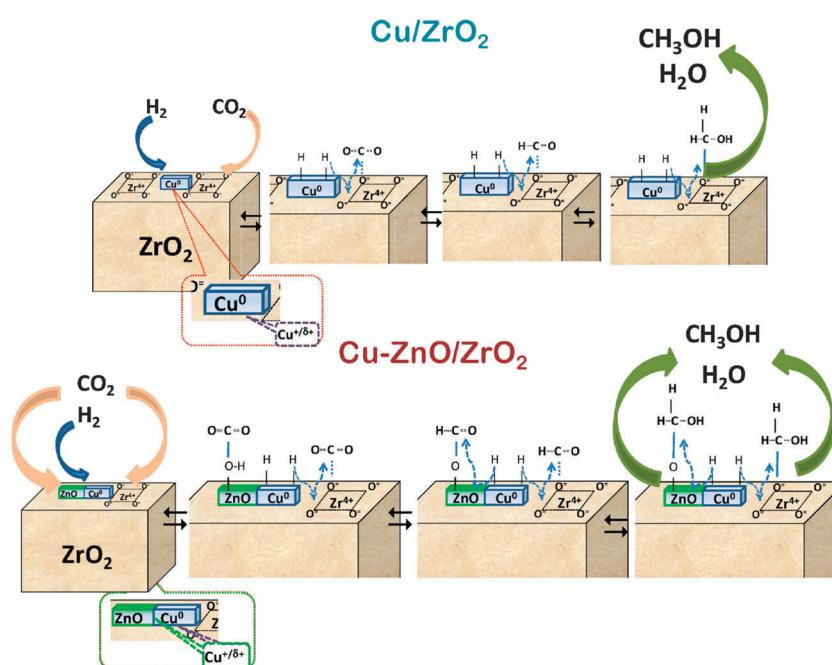
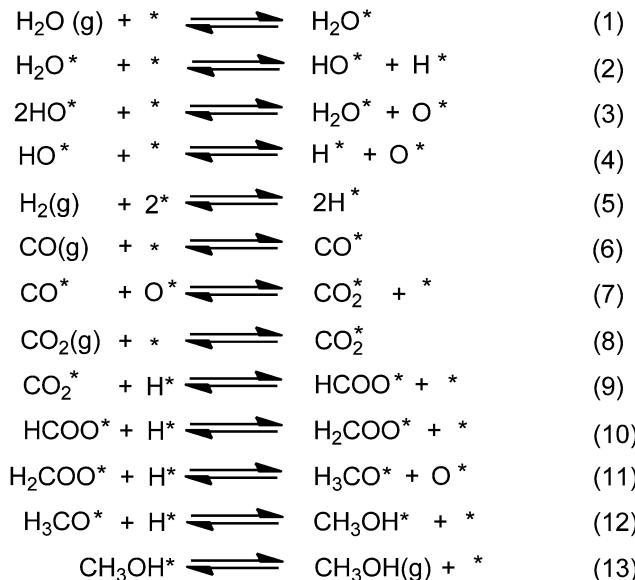
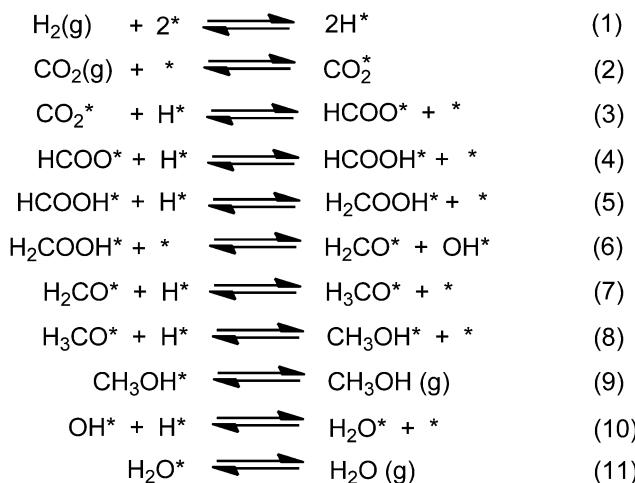


Fig. 14 Catalyst surface and functionality of the various surface sites on Cu/ZrO₂ and Cu-ZnO/ZrO₂ under CO₂ hydrogenation conditions. Reproduced with permission from ref. 211.



Scheme 1 Micro-kinetic model of the methanol synthesis. * represents a free surface site and X* symbolizes the adsorbed atom or molecule X. Reproduced from ref. 256 with permission from Springer.

steps was suggested by Rasmussen *et al.* (see Scheme 1).²⁵⁶ The hydrogenation of dioxomethylene (eqn (11)) was described as the most probable rate limiting step.¹⁴⁸ Interestingly, the syngas based methanol synthesis and carbon dioxide chemical recycling to methanol seem to essentially share the same type of chemical intermediates. However, some studies have found that methanol can be obtained with higher rates and carbon utilization factors by CO₂ hydrogenation than by CO hydrogenation.^{156,158,257} More recently, Grabow *et al.* considered many different reaction paths and determined by DFT calculations that the steps represented in Scheme 2 and Fig. 15 were the most likely one for the synthesis of methanol from CO₂ and H₂.²⁵⁸ In this model,



Scheme 2 Micro-kinetic model of the methanol synthesis from CO₂ and H₂ on Cu proposed by Grabow *et al.* based on DFT calculations. * represents a free surface site and X* symbolizes the adsorbed atom or molecule X. Based on ref. 258.

HCOO* preferentially led to the formation of HCOOH* and not H₂COO* as suggested in Scheme 1. HCOOH* is then further hydrogenated to H₂COOH*, which itself forms H₂CO* by splitting off a OH group. H₃CO* is the final intermediate for the formation of CH₃OH* and subsequently CH₃OH(g). A similar mechanism was proposed by Behrens *et al.* on Cu/Zn(211) surfaces.²⁵⁹ Using a combination of experimental data and DFT calculations, they determined that the active sites consist of steps of Cu decorated with Zn atoms, stabilized by well defined bulk defects. The presence of both steps of Cu and ZnO_x in close proximity, serving as adsorption sites for oxygen-bound intermediates, creates the ensemble needed for highly active catalysts for the conversion of CO₂ (and CO) to methanol.

As can be seen, a large number of studies have been devoted to the development of efficient and stable heterogeneous catalysts for the production of methanol from CO₂ hydrogenation. Most of the studied catalysts are based on Cu on a support such as ZrO₂ and diverse additives to improve the activity, stability and other parameters (Fig. 16). Some of these catalysts are already used in pilot and demonstration plants.

Production of DME from CO₂ hydrogenation over heterogeneous catalysts

DME can be produced by conventional bimolecular dehydration of methanol, which is readily carried out catalytically over varied solid acids such as alumina or phosphoric acid-modified γ-Al₂O₃, eqn (20).^{166,260} Like methanol, dimethyl ether (DME) can also be produced by direct catalytic hydrogenation of CO₂. Similar to the route from syngas to DME, CO₂ hydrogenation to DME can use a hybrid catalyst system consisting of a combination of methanol synthesis and dehydration catalysts.^{261,262} These “bi-functional” catalyst systems thus contain two different catalysts, one for the methanol synthesis, and another for the dehydration. Combinations of Cu/ZnO/Al₂O₃/Ga₂O₃/MgO for the methanol synthesis and γ-Al₂O₃ or ZrO₂/Al₂O₃ for the dehydration step have been studied and it was shown that the catalyst bed was the most effective when the methanol synthesis catalyst was placed in a layer upstream of the dehydration catalyst layer.^{261,263} A number of other systems were also tested. They include: (Cu/ZnO/Al₂O₃/ZrO₂)/HZSM-5,^{264,265} (Cu/ZnO/Al₂O₃/La₂O₃)/HZSM-5,²⁶⁶ (Cu/ZnO/Al₂O₃)/γ-Al₂O₃,^{267,268} (Cu/ZnO/Al₂O₃)/HZSM-5,²⁶⁷ (Cu/ZnO/ZrO₂)/HZSM-5,²⁶⁹ and (Cu/TiO₂/ZrO₂)/HZSM-5.²⁷⁰

A core-shell type catalyst with a CuO/ZnO/Al₂O₃ core and an outer shell composed of a membrane of metal doped silica-alumina was also recently proposed for DME synthesis by CO₂ reduction.²⁷¹

Homogeneous reduction of CO₂ to methanol

Hydrogenation of CO₂ to methanol using homogeneous catalysts. While numerous heterogeneous systems were described for the direct hydrogenation of carbon dioxide to methanol, just a limited number of homogeneous catalysts have been reported in the literature. A recent work by He *et al.*²⁷² reviewed the literature of homogeneous hydrogenation of carbon dioxide to methanol and its repetition here is therefore not necessary. However, an outline of

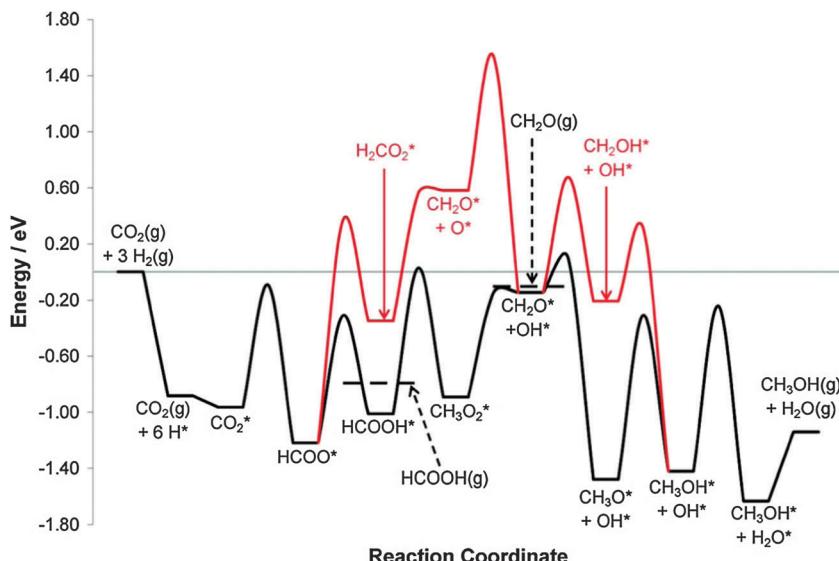


Fig. 15 Potential energy surface of methanol synthesis via CO_2 hydrogenation. To improve legibility, H^* was omitted from the labels after the adsorption of six H atoms in the first step. The black line indicates the lowest-energy pathway through the HCOO^* , HCOOH^* , CH_3O_2^* , CH_2O^* , and CH_3O^* intermediates. The main intermediates along the red path are HCOO^* , H_2CO_2^* , CH_2O^* , and CH_2OH^* . The two dashed horizontal lines indicate the desorption barriers of HCOOH and CH_2O . Reprinted with permission from ref. 258 Copyright 2011 American Chemical Society.

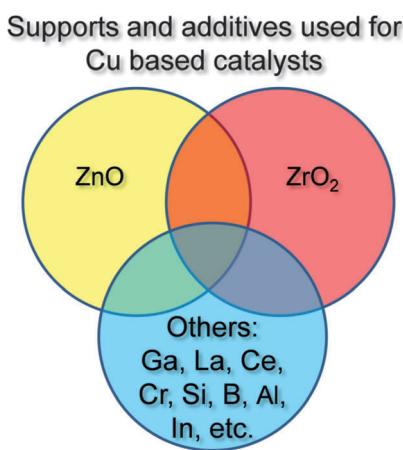


Fig. 16 Most common combinations of supports and additives used for Cu based heterogeneous catalysts for the hydrogenation of CO_2 to methanol.

the applied approaches and catalysts is given in the next few paragraphs.

The first example of direct hydrogenation of CO_2 to methanol under homogeneous conditions was reported by Tominaga *et al.*²⁷³ using $\text{Ru}_3(\text{CO})_{12}$ catalyst precursor in the presence of KI additive. In addition to methanol, the formation of CO , CH_4 and C_2H_6 was also observed. It was also shown by the same authors that the catalytic performance of $\text{Ru}_3(\text{CO})_{12}$ -KI system exceeds the ones of other transition metal carbonyls such as $\text{Ir}_4(\text{CO})_{12}$, $\text{Rh}_4(\text{CO})_{12}$, $\text{W}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, $\text{Fe}_2(\text{CO})_9$ and $\text{Co}_2(\text{CO})_8$.²⁷⁴

Instead of the six electron reduction of CO_2 to methanol, the so called cascade process²⁷⁵ divides it into three steps (1) reduction of CO_2 to formic acid (FA), (2) esterification of FA to formate esters and (3) hydrogenation of formate ester to methanol (Fig. 17).

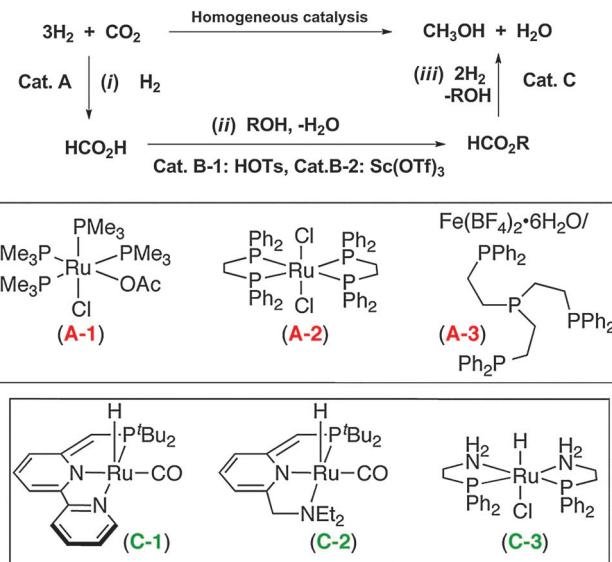
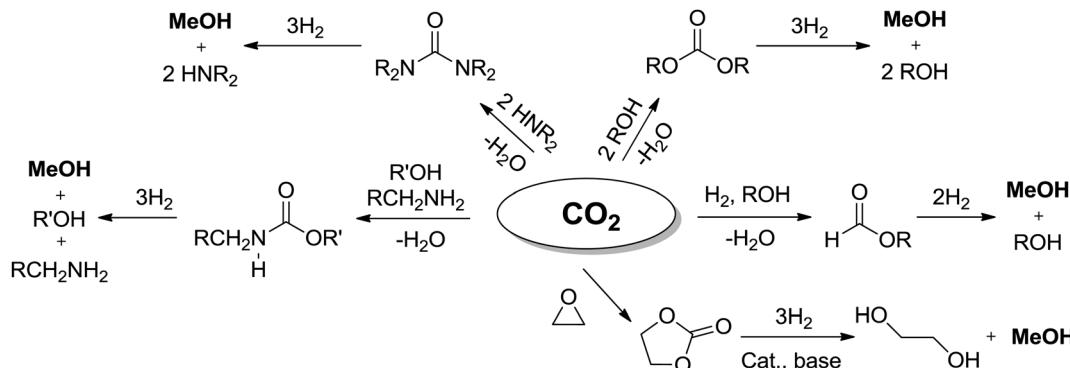


Fig. 17 Hydrogenation of CO_2 to methanol in a cascade system.²⁷⁵

This approach requires a different catalyst for each step which can coexist and must each be tolerant to the reaction conditions and relatively high temperature (135°C) and pressure (40 bar).

Leitner and Klankermayer²⁷⁶ reported the hydrogenation of CO_2 (60 bar H_2 , 20 bar CO_2 , 140°C) in the presence $[(\text{triphos})\text{Ru}-(\text{TMM})]$ (TMM = trimethylenemethane, Triphos = 1,1,1-tris(diphenyl-phosphinomethyl)ethane) giving a maximum TON of 221. The authors also showed that the same catalyst is active for the hydrogenation of formate esters (Et- or Me-formate) to methanol.

In addition to the direct hydrogenation of CO_2 itself to methanol, the hydrogenation of CO_2 derivatives such as carbonates,

Fig. 18 Methanol production by indirect hydrogenation of CO₂.

polycarbonates, carbamates, urea derivatives and formates²⁷⁷ has gained a lot of attention²⁷⁸ because the activation barriers of these reactions are smaller and the above molecules can be readily synthesized from CO₂ (Fig. 18).²⁷⁸

Homogeneous chemical reduction of CO₂ to methanol. A variety of reducing agents such as silanes and hydrides can be used in the presence of organocatalysts, e.g. N-heterocyclic carbenes (NHC) or with sterically encumbered Lewis acid–Lewis base ion pairs (so called “frustrated” pairs, FLP).

Although silanes are not cost effective reducing agents it was shown in the study by Zhang *et al.*²⁷⁹ that the NHC-catalyzed reduction of CO₂ to methoxides takes place under ambient conditions. The subsequent hydrolysis of methoxysilanes results in methanol and silanol derivatives (Fig. 19). Computational studies²⁸⁰ confirmed the formation of intermediates such as formoxysilane, bis(silyl)acetal, silylmethoxide, and disiloxane, which were experimentally observed earlier.²⁷⁹ This metal-free system²⁷⁹ showed better performance than that applied the [Ir(CN)(CO)dpp] catalyst in C₆D₆ at ambient temperatures and CO₂ pressures using Me₃SiH, Me₂SiH₂ and Et₂SiH₂ hydride sources.²⁸¹

Another interesting example of the metal-free catalysis is the application of frustrated Lewis pairs for CO₂ reduction to methanol.²⁸² In the first step, sterically encumbered TMP/B(C₆F₅)₃ promotes the heterolytic cleavage of molecular hydrogen (TMP = 2,2,6,6-tetramethylpiperidine, Fig. 20) giving [TMPh]⁺[HB(C₆F₅)₃]⁻. The reaction between CO₂ and [TMPh]⁺[HB(C₆F₅)₃]⁻, results in a formato borate derivative. The coordinatively unsaturated B(C₆F₅)₃ attacks the nucleophile and a formato bridged intermediate forms.

The latter reacts with [TMPh]⁺[HB(C₆F₅)₃]⁻ giving a formaldehyde acetal derivative, which subsequently undergoes a stepwise cleavage

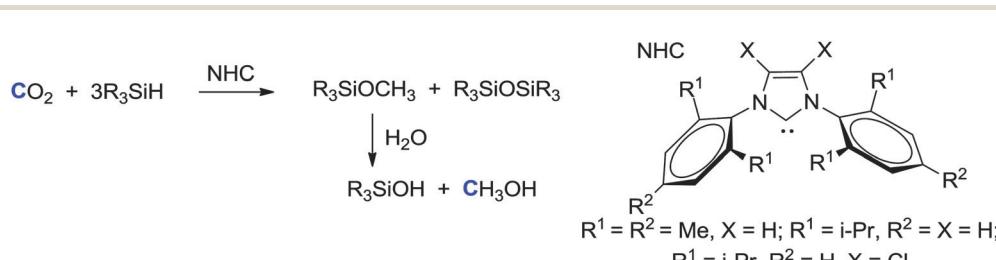
and reduction leading to a methanol precursor, a methyl borate derivative.

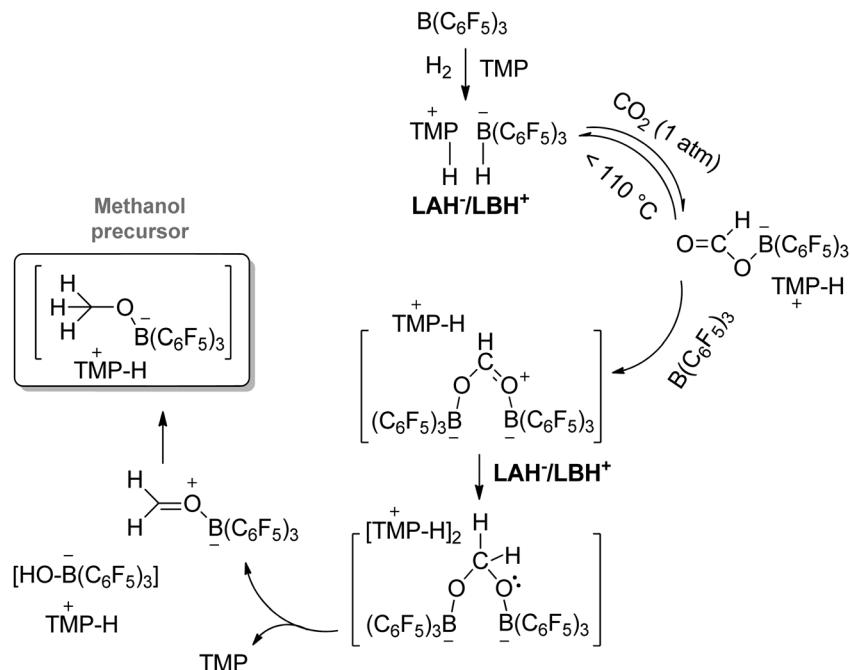
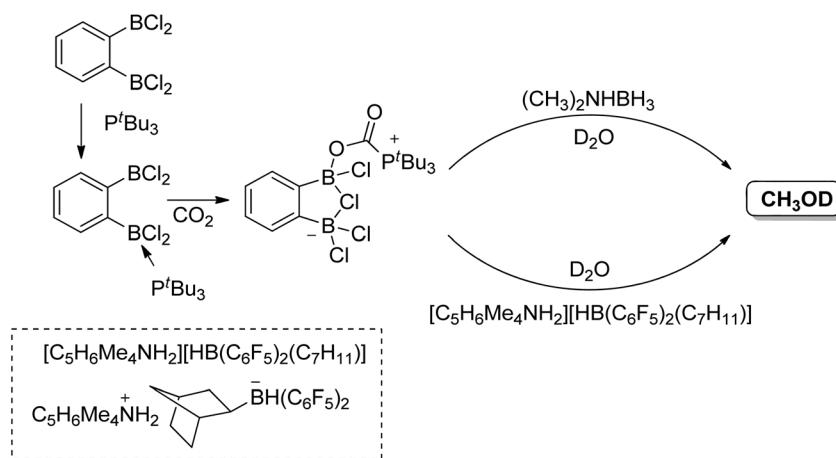
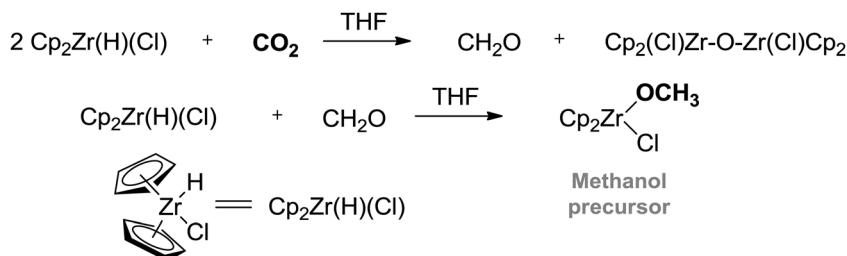
Bis-borane 1,2-C₆H₄(BCl₂)₂ in combination with P^tBu₃ was shown to react as a FLP and activate CO₂ (Fig. 21).²⁸³ The obtained stable formate species was reduced by ammonia borane derivatives and subsequently hydrolyzed with D₂O giving deuterio methanol (CH₃OD).

Schwartz's reagent, [(Cp)₂Zr(H)(Cl)], (Cp = η⁵-C₅H₅) was applied as a hydride source for the stepwise stoichiometric reduction of carbon dioxide to formaldehyde and methanol, respectively (Fig. 22).^{284,285} While the conversion of CO₂ to formaldehyde accompanied by the formation of the μ-oxo complex was observed in the first step, the deeper reduction of CH₂O by addition of more Schwartz's reagent occurred resulting in a zirconium methoxide in the second step.

Reduction of CO₂ to methanol with various boranes. The reactivity of Ni-PCP catalyst was studied towards boranes as well as catecholborane (HBcat), BH₃·THF and 9-BBN (9-borabicyclo[3.3.1]nonane).^{286,287} The impact of the substituent's bulkiness on the P donor atoms of the ligands on the efficiency of Ni-hydrides for the catalytic reduction of CO₂ with boranes was investigated. Two advantages of bulky substituents were found, minimizing catalyst degradation by protecting the P–O bonds of the pincer ligand from borane attack and acceleration of catalytic reduction when bulky substituents are present on the phosphorus atom (Fig. 23).

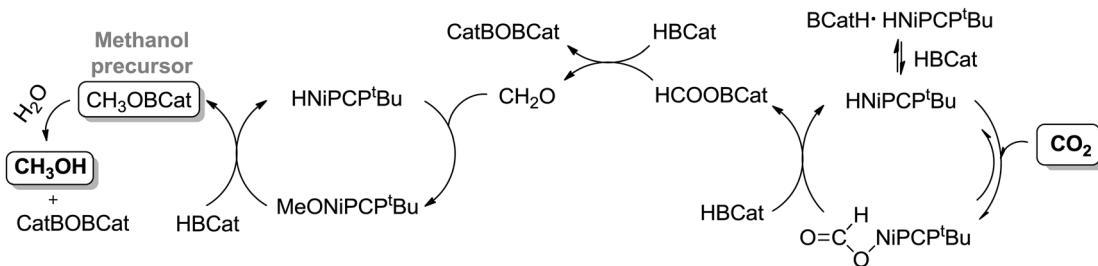
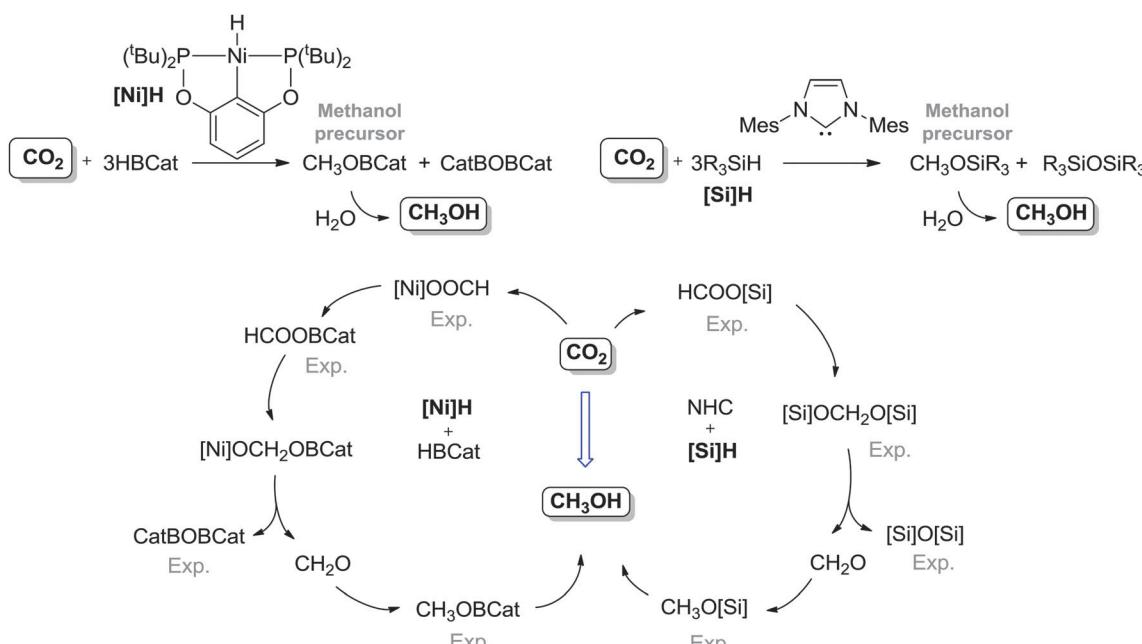
A comparative study was reported by Guan *et al.*²⁸⁹ on the Ni-pincer hydride-catalyzed reduction of CO₂ with catecholborane and the NHC-catalyzed reduction of CO₂ using silanes (R₃SiH) as reducing agents (Fig. 24).

Fig. 19 NHC-catalyzed reduction of CO₂ and the subsequent hydrolytic liberation of methanol.

Fig. 20 Lewis acid/Lewis base-catalyzed hydrogenation of CO_2 .Fig. 21 FLP-catalyzed reduction of CO_2 to methanol using borane derivatives.Fig. 22 Two step reduction of CO_2 to methanol with Schwarz's reagent.

In addition to the obvious similarities between the Ni and the Si containing systems *e.g.* the necessity of three equivalents of reducing agent for one equivalent of CO_2 , it was found that

among the experimentally detected complexes there are some one-to-one correlations such as $\text{CH}_3\text{OBcat} \leftrightarrow \text{CH}_3\text{O}[\text{Si}]$, $\text{catBOBcat} \leftrightarrow [\text{Si}]\text{O}[\text{Si}]$ and $\text{HCOOBcat} \leftrightarrow \text{HCOO}[\text{Si}]$. The formation

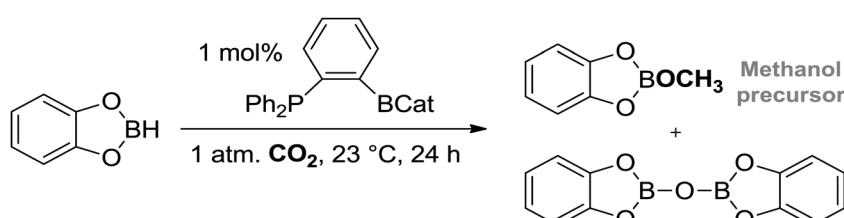
Fig. 23 Catalytic reduction of CO_2 with catecholborane over Ni-PCP catalyst.²⁸⁸Fig. 24 Comparison of Ni-catalyzed CO_2 reduction with catecholborane and NHC-catalyzed CO_2 reduction with silanes.²⁸⁹ Note: "Exp." stands for experimentally observed species.

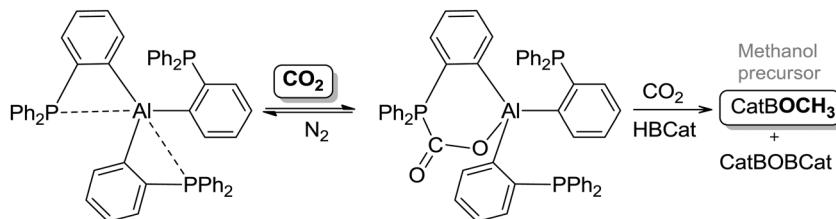
of the formaldehyde intermediate was also suggested in both catalytic systems. The major difference between the two systems was that while the presence of $[\text{Si}]O\text{CH}_2\text{O}[\text{Si}]$ has been confirmed experimentally, no evidence was found to support the formation of $\text{CatBOCH}_2\text{OBCat}$.

Activation and reduction of CO_2 was demonstrated in the presence of an ambiphilic metal-free catalyst 1-Bpin-2-PPh₂-C₆H₄ using catecholborane.²⁹⁰ The carbon dioxide molecule itself has ambiphilic character involving an electrophilic carbon atom and two nucleophilic oxygen atoms and consequently it does not

require a strong bonding interaction with an ambiphilic catalyst to undergo reduction using hydroboranes as the hydrogen source. CO_2 was treated with a variety of borane derivatives such as HBCat (catecholborane), HBPin (pinacolborane), 9-BBN, $\text{BH}_3\cdot\text{SMe}_2$ and $\text{BH}_3\cdot\text{THF}$ resulting in methanol precursors, CH_3OBCat or $(\text{CH}_3\text{OBO})_3$, respectively which molecules could then be hydrolyzed to methanol (Fig. 25). TON and TOF were measured up to 2950 and 853 h⁻¹, respectively.

The same research group reported reduction of CO_2 to boronic acid methylesters with catecholborane catalyzed by

Fig. 25 Reduction of CO_2 to methanol with catecholborane in the presence of a phosphine–borane organocatalyst.²⁹⁰

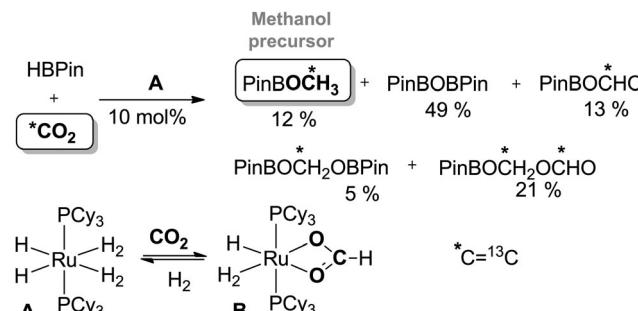
Fig. 26 $\text{Al}(\text{C}_6\text{H}_4(\text{o}-\text{PPPh}_2))_3$ -catalyzed reduction of CO_2 with catecholborane.²⁹¹

the ambiphilic $\text{Al}(\text{C}_6\text{H}_4(\text{o}-\text{PPPh}_2))_3$ wherein the aluminum center is surrounded by a trisarylphosphine scaffold.²⁹¹ The organo-aluminium compound depicted in Fig. 26 was shown as a precatalyst for the reduction of CO_2 with catecholborane (HBCat) to form CH_3OBCat , a direct precursor of methanol.

Other aluminum and phosphorus based FLPs system developed by Stephan *et al.*^{292,293} ($\text{Mes}_3\text{P}\text{-AlX}_3$, where $\text{X} = \text{Cl}$ or Br and $\text{Mes} =$ mesitylene) were also shown to be able to reduce CO_2 to methoxide derivative in the presence of ammoniaborane (NH_3BH_3).

The pinacolborane–Ru-tris(aminophosphine) system was also shown to reduce CO_2 to methyl borate which can be eventually hydrolyzed to methanol (Fig. 27).²⁹⁴ The Ru-hydride complex²⁹⁵ was reacted with CO_2 resulting in its insertion to the Ru–P bond. The obtained complex was then subjected to reduction by adding five equivalents of pinacolborane in CD_2Cl_2 solution. The stoichiometric reduction of the obtained complex was confirmed by NMR spectroscopy by detecting CH_3OBpin and $\text{O}(\text{Bpin})_2$. Neither the application of higher excess of pinacolborane nor the increase of CO_2 pressure from 1 to 5 atm affected the product distribution. Similarly, the addition of different reducing agents such as catecholborane or 9-borabicyclo[3.3.1]nonane did not help to increase the reaction rate.

Another example of CO_2 reduction with pinacolborane over an organoruthenium catalysts [$\text{RuH}_2(\text{H}_2)_2(\text{PCy}_3)_2$] ($\text{Cy} =$ cyclohexyl) was presented by Sabo-Etienne *et al.*^{296,297} Formation of $[\text{RuH}(\kappa^2\text{-CO}_2\text{H})(\eta^2\text{-H}_2)(\text{PCy}_3)_2]$ took place *via* the insertion of CO_2 into Ru–H bond (Fig. 28). NMR tube experiments proved that the reaction between CO_2 and pinacolborane in the presence of

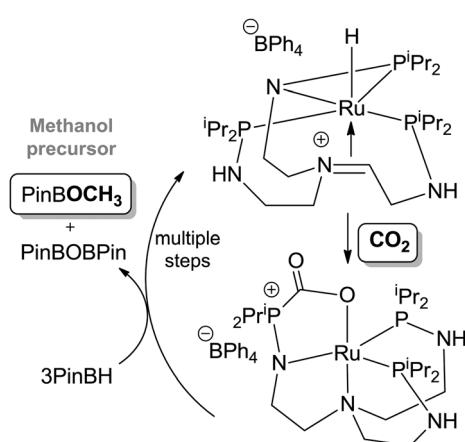
Fig. 28 CO_2 reduction to a borate ester with pinacolborane in the presence of $[\text{RuH}_2(\text{H}_2)_2(\text{PCy}_3)_2]$ ($\text{Cy} =$ cyclohexyl).²⁹⁶

$[\text{RuH}_2(\text{H}_2)_2(\text{PCy}_3)_2]$ affords a series of reduction products such as $\text{PinBOCH}_2\text{OCHO}$ (derives from the reductive coupling of two CO_2 molecules) $(\text{PinB})_2\text{O}$, PinBOCHO , $\text{PinBOCH}_2\text{OBPin}$, and PinBOCH_3 . The latter can be hydrolyzed to methanol.

We have reviewed numerous elegant approaches to reduce CO_2 to methanol/methanol precursors in homogeneous systems based on chemistry, which make a significant contribution to fundamental science and pave the way for further development. It must be noted here that in general the main driving force of CO_2 reduction using boranes or silanes is the formation of high stability B–O or Si–O bonds. However, the obtained organoboranes and siloxanes have to be recycled and converted back to reducing agents by renewable energy sources directly or using hydrogen generated with renewables. In cases where the exhausted reducing agents are not reusable, the application of these processes raises serious feasibility concerns.

Other reducing agents. Na *et al.*²⁹⁸ have demonstrated a visible light-driven multicomponent system, that is capable of selectively reducing CO_2 to MeOH. The RuQ complex (Fig. 29) collects two electrons upon the reaction with ascorbate in a light driven step and then RuQ^{2+} reduces CO_2 to MeOH in the presence of $[\text{Co}(\text{NDS})_2]^{2-}$ in aqueous solution (NDS = 1-nitroso-2-naphthol-3,6-disulfonate). Even though the performance of the system is low (four turnovers on $[\text{Co}(\text{NDS})_2]^{2-}$ and 73 turnovers based on RuQ), it was found that the reduction of CO_2 is not stoichiometric on the cobalt catalyst and RuQ.

MacDonnell *et al.*²⁹⁹ reported another elegant photoinduced reduction of CO_2 to formic acid and in lower yield to methanol under homogeneous conditions using pyridine as a catalyst for CO_2 reduction applying visible light irradiation at $470 \pm 20 \text{ nm}$. $[\text{Ru}(\text{phen})_3]^{2+}$ was applied as a chromophore and ascorbic acid

Fig. 27 Ruthenium tris(aminophosphine)-catalyzed reduction of CO_2 to methanol with pinacolborane (PinBH).²⁹⁴

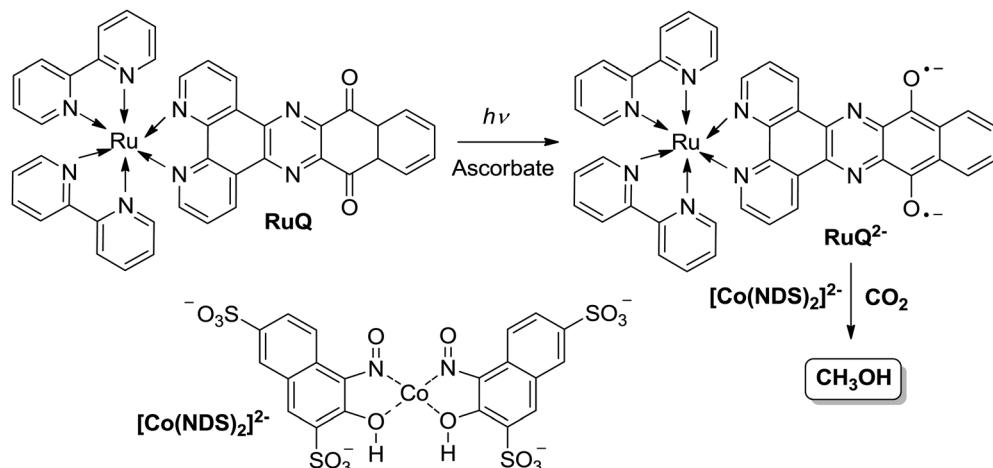


Fig. 29 Light-driven multicomponent system for CO₂ reduction to MeOH.²⁹⁸

was added as a sacrificial reducing agent, using visible light irradiation at 470 ± 20 nm. This system showed 76 and 0.15 turnovers per Ru for formate and methanol, respectively, but it became inactive due to the degradation of the chromophore over 6 hours of irradiation.

Practical applications of direct CO₂ hydrogenation to methanol

Practically, only heterogeneous catalysts have been used for the synthesis of methanol from CO₂ and H₂. Beside the experience of Lurgi AG described *vide supra*, the synthesis of methanol from CO₂ and H₂ has also been demonstrated on a 50 kg CH₃OH per day laboratory pilot scale in Japan where a methanol selectivity of 99.8% was achieved over a Cu/ZnO based catalyst.^{152,300} A liquid-phase methanol synthesis process was also developed, which allows a CO₂ and H₂ conversion to methanol of about 95% with very high selectivity in a single pass.³⁰¹

The first contemporary commercial CO₂ to methanol recycling plant using locally available, cheap geothermal energy is presently being operated in Iceland by the Carbon Recycling International (CRI) company. The demonstration plant, with an initial annual capacity of 4500 m³ of methanol (10 ton per day), is based on the conversion of CO₂ accompanying the readily available local geothermal energy (hot water and steam) sources (Fig. 30). The needed H₂ is produced by water electrolysis using cheap geothermally produced electricity.^{130,302} Iceland embarked on this development as a means to exploit and possibly export its cheap and clean electrical energy. The produced methanol, called Vulcanol, is currently mixed with gasoline. In Japan, Mitsui chemicals has also announced the planned construction of a 100 tonne-per-year demonstration plant to produce methanol from CO₂, obtained as an industrial by-product, and hydrogen generated by photochemical splitting of water using solar energy.³⁰³ Blue Fuel Energy in Canada is planning to use hydroelectricity and concentrated CO₂ emissions from natural gas processing to produce methanol preferably.³⁰⁴ There is also significant industrial interest in CO₂ to methanol conversion in China, Australia, the European Union and other countries, in conjunction with widespread research interest. Graves *et al.*



Fig. 30 The "George Olah Renewable Methanol Plant" of Carbon Recycling International (CRI) in Iceland. Based on local geothermal energy and CO₂. Courtesy: K. C. Tran (CRI).

claimed an electricity-to-fuel efficiency of about 70% in a state of the art methanol plant operating on CO₂ and H₂ feedstocks.³⁰⁵ The capital investment for a methanol synthesis unit using CO₂ and H₂ is estimated to be about the same as that for a conventional syngas based plant.¹⁵¹ The limiting factor for large scale-up of such processes is the availability and price of CO₂ and H₂ and primarily the necessary electrical energy.

Alternative two step route for CO₂ hydrogenation to methanol

Methanol can also be produced in two steps from CO₂. In a first step, CO₂ and H₂ are fed to a reactor where part of the CO₂ is converted to CO through the RWGS reaction. After elimination of the water produced, the resulting gas composed of CO/CO₂/H₂ is fed to a methanol synthesis reactor. This process called CAMERE (carbon dioxide hydrogenation to methanol *via* RWGS reaction) was developed by the Korean Institute of Science and Technology (KIST).³⁰⁶ It was claimed that the two step process allows a sizable reduction in size of the methanol synthesis reactor with respect to the direct route. The process is also described as having higher efficiency, with twice the methanol

production yield, and lower operating costs. The RWGS reaction has to be operated at temperatures higher than 600 °C to obtain a reasonable CO₂ conversion to CO (>60%). The catalyst employed is based on zinc aluminate.³⁰⁷ The catalyst for the second step, methanol synthesis, is composed of Cu/ZnO/ZrO₂/Ga₂O₃.³⁰⁶ A pilot plant using the CAMERE process with a production capacity of 100 kg methanol per day has been built in Korea to test this concept.³⁰⁷

6. Electrochemical conversion of CO₂ to methanol

Electrochemical reduction of CO₂ has been used for many decades on a lab scale, but has not yet successfully made the transition to an industrial process. Part of this reluctance by industry to adopt electrochemical CO₂ processing techniques has been the lack of a driving force to utilize CO₂. Part of it has been due to the lack of practical technology to electrochemically convert CO₂ into useful products. Both of these areas are rapidly changing, and this section describes some of the recent progress made in developing new solutions to the problems encountered in CO₂ electrolysis. A much more in-depth review of CO₂ reduction on metal electrodes was published by Hori.³⁰⁸ Depending on the conditions and electrocatalyst, a variety of reduced products can be generated electrochemically from CO₂, some of which are presented in Table 1.

None of these reactions are well-separated by potential, so the control between various products must come from choice of catalyst and conditions rather than potential. Although all of these standard potentials are close to the standard potential for hydrogen evolution, generation of the first intermediate (carbon dioxide radical anion, CO₂^{•-}) has been estimated to occur only at -1.89 V vs. SHE.³⁰⁹ Although it can be stabilized, this high energy intermediate must be produced for CO₂ reduction to occur on a traditional metal electrode, and the result is that CO₂ reduction generally requires significant overpotentials to occur at a reasonable rate. Water is typically present as a proton source (and electrolyte) and thus the competing hydrogen evolution reaction (HER) must be taken into account while considering CO₂ reduction. For this reason, many metals that are reported for CO₂ reduction also have relatively high HER overpotentials. A balancing act must be conducted to find the optimal CO₂ reduction electrode that will reduce CO₂ selectively at high rates and low overpotentials without reducing water simultaneously.

Overcoming the large overpotential to CO₂ reduction also results in low energy efficiency values. Table 2 gives the

Table 1 Standard potentials for CO₂ reduction from ref. 309

Half-cell reaction	E° vs. SHE
CO ₂ + 2H ⁺ + 2e ⁻ → HCOOH	-0.11
CO ₂ + 2H ⁺ + 2e ⁻ → CO + H ₂ O	-0.10
CO ₂ + 4H ⁺ + 4e ⁻ → CH ₂ O + H ₂ O	-0.028
CO ₂ + 6H ⁺ + 6e ⁻ → CH ₃ OH + H ₂ O	+0.031
CO ₂ + 8H ⁺ + 8e ⁻ → CH ₄ + 2H ₂ O	+0.17

Table 2 Full cell electrochemical reactions derived from thermodynamic heat of formation³¹⁰

Reduction product	Full cell reaction	E° _c (V)
Formic acid	CO _{2(aq)} + H ₂ O _(l) → HCOOH _(aq) + 1/2O _{2(g)}	1.496
Formate	CO _{2(aq)} + OH ⁻ _(aq) → HCOO ⁻ _(aq) + 1/2O _{2(g)}	1.207
Carbon monoxide	CO _{2(aq)} → CO _(g) + 1/2O _{2(g)}	1.567

standard full cell reaction potentials instead of the half-cell reactions for CO₂ reduction to formic acid, formate and carbon monoxide converted from thermodynamic heats of formation. The full cell potential must then be compared to these values to determine the efficiency of the overall process. Very few, if any, high rate processes described in the literature would achieve even 50% energy efficiency based on these values. Improvements in this area are critical if electrochemical CO₂ reduction is ever to become a viable choice for energy storage since a loss of energy efficiency must be made up with additional renewable energy.

Electrochemical CO₂ reduction mechanism

The mechanism for electrochemical reduction of CO₂ has been studied with the aim of being able to provide an explanation for the selectivity of various products on various metal surfaces. Since the electrocatalyst is generally regarded as the most important factor determining selectivity, it is often helpful to group electrodes together based on product for the purposes of determining the mechanism, as has been depicted in Fig. 31. This general mechanism has been compiled from several sources,^{311–321} with the aim of providing an overarching guideline for metal electrodes. Although much of the recent literature has focused on non-metallic electrodes or molecular co-catalysts, understanding these mechanisms can still be helpful, especially since many of the reports in the literature of high-rate electrochemical reduction of CO₂ still rely on metal electrodes.

We can generally divide metal electrodes into three groups for CO₂ reduction based on their ability to bind CO₂^{•-} and reduce CO. These groups are not exclusive, however; for example, tin can be made to produce CO instead of formate by changing the electrolyte and operating pressure.^{311,314,322,323} This indicates that metals have the ability to reduce CO₂ by multiple mechanisms, probably determined by surface oxidation^{324–327} and crystal faces^{328–336} as well as the reaction conditions. Group 1 (Hg, Pb, Sn, etc.) metals do not bind either CO₂^{•-} or reduce CO to any appreciable degree, and therefore the mechanism for electron transfer from the electrode to CO₂ must take place through the electrical double layer. As a result of this inability to bind CO₂^{•-}, it is generally surrounded by solvent (typically water), with which it reacts immediately due to its unstable nature. In the absence of water, these radicals can dimerize to form oxalate instead of formate.³³⁷ Group 2 (Au, Ag, Zn, etc.) metals bind CO₂ or stabilize the CO₂^{•-} intermediate to varying degrees, but cannot reduce CO, and therefore release it as a product in CO₂ reduction. As a result of the coordination of CO₂^{•-}, water cannot coordinate with the carbon atom to generate the C–H bond in formate. The group 3 metals (copper) reduce CO to further products such as methanol, methane, and even higher alcohols and hydrocarbons with C–C

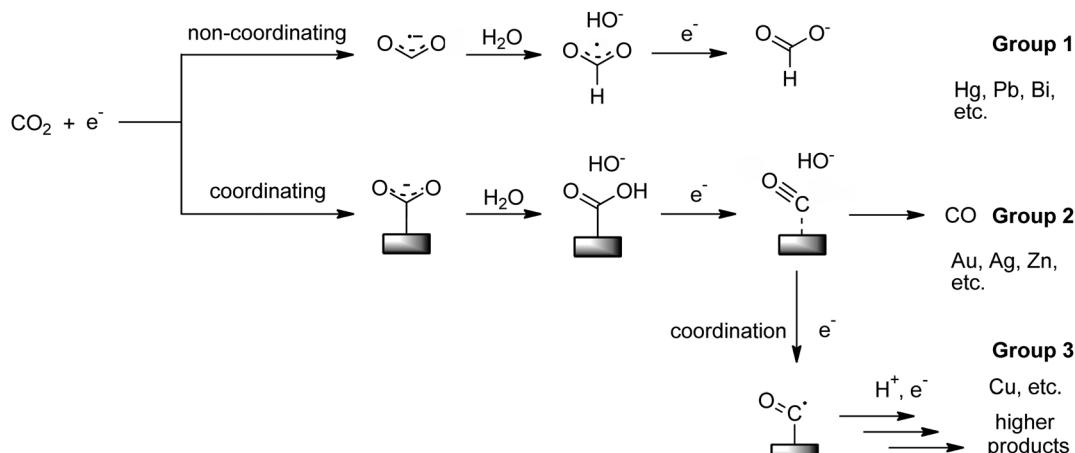


Fig. 31 Mechanism for electrochemical CO_2 reduction on metal surfaces in water.

bonds such as ethanol and ethane. Unfortunately, this last group of metals generally ends up producing a wide variety of products rather than a specific one,^{338–340} making them problematic to consider for industrial scale-up. Selective processes for higher products using copper must thus rely on control of conditions to achieve selectivity.³⁴¹ Other potential solutions to this problem include developing novel non-metallic electrodes including GaAs, InP³³⁴ and various oxides³⁴² or adding molecular co-catalysts.³⁴³

Energy efficiency is potentially the biggest issue facing commercialization of electrochemical CO_2 reduction because the cost of electricity would likely be the main factor influencing the cost of the product. In alkaline water electrolysis, probably the closest commercial process, the cost of electricity is estimated to contribute to 80% of the total cost of the product. If we take the work from Li and Oloman from 2007³⁴⁴ as an example, we can see that, using a tin electrode in a flow cell, they were able to reduce CO_2 to potassium formate at -2.7 V and 60 mA cm^{-2} . Since the heat of formation for the full cell reaction (taken from Table 2) is 1.207 V , the electrical energy efficiency of the process was therefore 45%. Although this is a good value for electrochemical CO_2 reduction, it pales in comparison to electrochemical hydrogen evolution, where energy efficiency is generally reported to be from 60 to over 80%.³⁴⁵ Many recent efforts to increase the energy efficiency of CO_2 reduction have showed promise, but there is still much work to be done to achieve energy efficient systems capable of high current. The potential at which CO_2 reduction takes place is directly related to the energy efficiency of the process, but most CO_2 reduction experiments are conducted relative to a reference electrode, so care must be taken by the reader to avoid misinterpretation. The full cell potential is rarely reported, and this is the potential which is required to determine the efficiency of the system (see Table 2). Some electrolysis cells, however, do not have reference electrodes due to their design, therefore authors reporting results from these cells often give the full cell potential. This can make their results look inferior at first glance since the voltage will be higher because oxygen evolution (which typically occurs at $>1.4\text{ V}$ on platinum depending on the current density) is included in the potential. Some authors also correct for

resistance^{346–348} in their papers, while others do not,^{349,350} making comparisons challenging.

Yield based on CO_2 , which is always used in large excess, is rarely calculated because it would be much more challenging to recover the unreacted CO_2 . In an industrial setting, however, the yield based on CO_2 would be just as important as faradaic efficiency because the CO_2 that is not converted must be re-circulated. It is unclear if the low conversion of CO_2 reported in most processes is the significant hurdle to overcome before industrial electrochemical reduction of CO_2 can be practiced.

Direct electrochemical CO_2 reduction to methanol

Converting CO_2 to methanol directly has the distinct advantage of producing a useful product that can be directly utilized by many energy-consuming devices. This would allow for very simple anthropogenic carbon recycling where methanol could be used by energy consuming devices, giving off CO_2 that could then be recycled directly in an electrolysis cell back to methanol in one step. There is considerable interest in this field, given its allure from a practical standpoint. Table 3 presents a collection of conditions reported in the literature to achieve methanol directly from CO_2 .

One of the most striking features of Table 3 is that very few metals have been used for the generation of methanol directly. The only example is entry 4, with the remainder being semiconductors (entries 1–3 and 8), oxides (entries 5 and 9), alloys (entry 6), or electrolytes containing a homogeneous catalyst (entries 7 and 8). Canfield and Frese first determined that semiconductors have some ability to form methanol from CO_2 in 1983,³³⁴ albeit at extremely low faradaic efficiencies (FEs) and current densities. Subsequent efforts by a variety of research groups increased both the FE of the process as well as the current density. Bocarsly *et al.*³⁵⁴ introduced the concept of adding a homogeneous co-catalyst (pyridine) and then improved their method by switching to a semiconductor irradiated with light.³⁴³ The latter example has the highest FE, coupled with the lowest applied potential (entry 8) in Table 3. Using pyridine (which is protonated to form the active pyridinium species *in situ*)

Table 3 Direct electrochemical reduction of CO₂ to methanol

Entry	Electrode	E vs. NHE (V)	Major product	FE (%)	Current density (mA cm ⁻²)	Ref.	Electrolyte
1	n-GaAs	-1.06	MeOH	1.0	0.16	334	Sat. Na ₂ SO ₄
2	p-GaAs	-1.06	MeOH	0.52	0.08	334	Sat. Na ₂ SO ₄
3	p-InP	-1.06	MeOH	0.8	0.06	334	Sat. Na ₂ SO ₄
4	Mo	-0.56	MeOH	84	0.12	351	0.2 M Na ₂ SO ₄
5	CuO	-1.3	MeOH	28	6.9	352	0.5 M KHCO ₃
6	Pt-Ru/C	-0.06	MeOH	7.5	0.4	353	Flow cell
7	Pd	-0.51	MeOH	30	0.04	354	0.5 M NaClO ₄ + pyridine
8 ^a	n-GaP	-0.06	MeOH	90	0.27	343	10 mM pyridine pH 5.2
9	RuO ₂ /TiO ₂ nanotubes	-0.6	MeOH	60	1	355	0.5 M NaHCO ₃

^a Solar irradiation of the working electrode.

as a co-catalyst has been explored extensively recently, particularly with the aim of determining the mechanism of activation precisely.^{356–361} Entry 8 also involves an irradiated semiconductor, so some of the energy for CO₂ reduction is coming from the light irradiation.

These examples of direct CO₂ to methanol reduction all exhibit relatively low current density when compared to two electron reduction products such as CO and formate, likely due to the increased complexity of reducing CO₂ with 6 electrons. Direct electrochemical reduction of CO₂ to methanol certainly holds much promise. However, at these current densities, it is not practical on a large scale since it has been shown that investment cost is almost proportional to the surface area of the electrode.³⁶² To minimize these costs, therefore, current density must be in the range of at least hundreds of mA cm⁻², which is several orders of magnitude higher than anything reported in Table 3. For this reason, we will consider the electrochemical reduction of CO₂ by 2 electrons (since these processes have been demonstrated at relatively high current densities) followed by its subsequent conversion to methanol using more traditional chemical processes (see Section 5).

Methods for high rate electrochemical CO₂ reduction

Electrochemical reduction of CO₂ directly to methanol would be ideal, but is currently outside the scope of industrially viable processes. Therefore we will consider the application of two electron reduction products (CO or formate/formic acid) to the production of methanol. As Fig. 32 shows, CO₂ and H₂O can be electrochemically reduced either simultaneously or separately

to yield any given ratio of H₂:CO. In the case of methanol synthesis, the most desirable H₂:CO ratio is 2:1, which can be directly converted into methanol using known processes, as described in more detail in Section 3 of this review. Alternatively, CO₂ can be reduced to formic acid (another two electron reduction product) to be converted into syngas for methanol synthesis as described *vide infra* of this review, or esterified to methyl formate and then hydrogenated (with hydrogen from water electrolysis) to yield methanol, as shown in Fig. 33. Although hydrogenation of methyl formate is not commonly practiced industrially due to the higher value of formic acid and methyl formate compared to methanol, it can be accomplished using heterogeneous catalysts.^{363,364}

Most electrochemical CO₂ reductions reported have been conducted in aqueous systems with metal working electrodes and CO₂ introduced into the solution.³⁶⁵ When increased CO₂ reduction rate was desired, one of the first approaches was to increase the pressure of CO₂, thus increasing its concentration locally.^{366,367} Increased pressure has two positive effects on CO₂ reduction; increased faradaic efficiency and the prospect for increased rate, an example of which can be found in Fig. 34. By increasing the pressure, one can even use metals for CO₂ reduction that would typically evolve far too much H₂, such as platinum.³⁴⁸ Another strategy to increase the efficiency of CO₂ reduction has been to use a continuous flow reactors,^{368,369} like the one depicted in Fig. 35, instead of a static electrochemical cell. Flow reactors are widespread in industrial chemical processes, making these studies more conducive to scale up, however, the membranes typically used to separate the anode and cathode can lead to changes in CO₂ reduction selectivity and efficiency.³⁷⁰

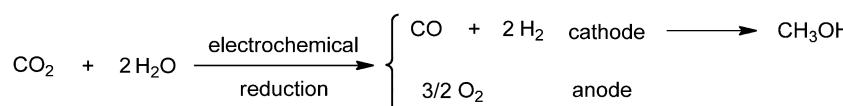


Fig. 32 Two electron reduction of CO₂ to CO with concomitant H₂ evolution for subsequent production of methanol.

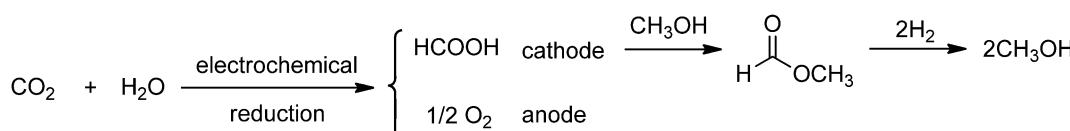


Fig. 33 Two electron reduction of CO₂ to formic acid with subsequent esterification to methyl formate and further hydrogenation to methanol.

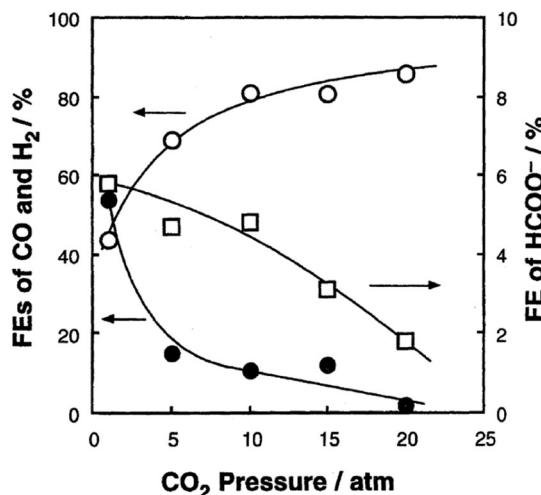


Fig. 34 The dependence of the faradaic efficiencies of reduction products on the CO₂ pressure in the electrochemical reduction of CO₂ on a Ag-GDE at 300 mA cm⁻² in 0.5 mol dm⁻³ KHCO₃: (○) CO, (□) HCOO⁻, (●) H₂. Reproduced with permission from ref. 371.

Instead of increasing pressure to increase performance for CO₂ reduction, one can instead focus on developing chemical solutions to the problems of throughput and selectivity. Molecular catalysts offer the possibility to use an additional chemical to chaperone the electrons from the working electrode to CO₂ in a way that hopefully gives better selectivity, higher energy efficiency or both. Fig. 36 depicts the interaction between a pyridinium radical and CO₂ that allows for a lower energy barrier to generate the CO₂^{•-} intermediate. This concept is actually quite old, with the first report dating back to 1980,³⁷³ but this is the one that has seen significant attention as of late.^{374,375} The concept is certainly a sound one. However, most of the reports in the literature focus on reducing the energy barrier of CO₂ reduction without much concern for current density. While the energy barrier to electrochemical CO₂ reduction is definitely one of the biggest hurdles to

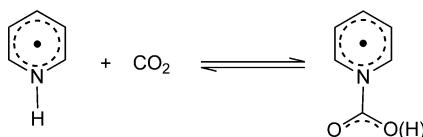


Fig. 36 Pyridinium radical complex interacting with CO₂, from ref. 356.

commercialization, one must also be able to build a cost effective reactor to process vast quantities of CO₂, and that cannot be realized without large current densities. The concept of physically or chemically attaching a catalyst (e.g. metal-porphyrines) to an electrode^{376,377} appears to be quite promising for large scale application.

Using non-aqueous solvents for CO₂ reduction is another way to chemically alter the mechanism of CO₂ reduction rather than engineer a solution. Several solvents dissolve CO₂ more readily than water, methanol being a prime example of such a solvent.³⁷⁸ Kaneko and co workers have extensively studied CO₂ reduction in methanol using a wide variety of conditions, including low temperatures, different cathodes, and the effect of the electrolyte cation.^{326,379-388} Protons are required for CO₂ reduction to formate, and generally necessary for CO production as well, so some water is often utilized³⁸⁹ to provide the necessary protons for the reaction to take place. Ionic liquids have also been used recently as solvents or co-solvents for CO₂ reduction,³⁹⁰⁻³⁹² where the anion (BF₄⁻, for example) can potentially interact with CO₂ directly to lower the barrier for electrochemical CO₂ reduction, as depicted in Fig. 37.

A collection of some of the highest reported current densities for efficient electrochemical CO₂ reduction is presented in Table 4.

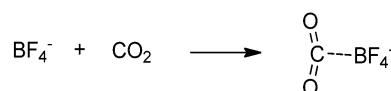


Fig. 37 Possible interaction between ionic liquid and CO₂.

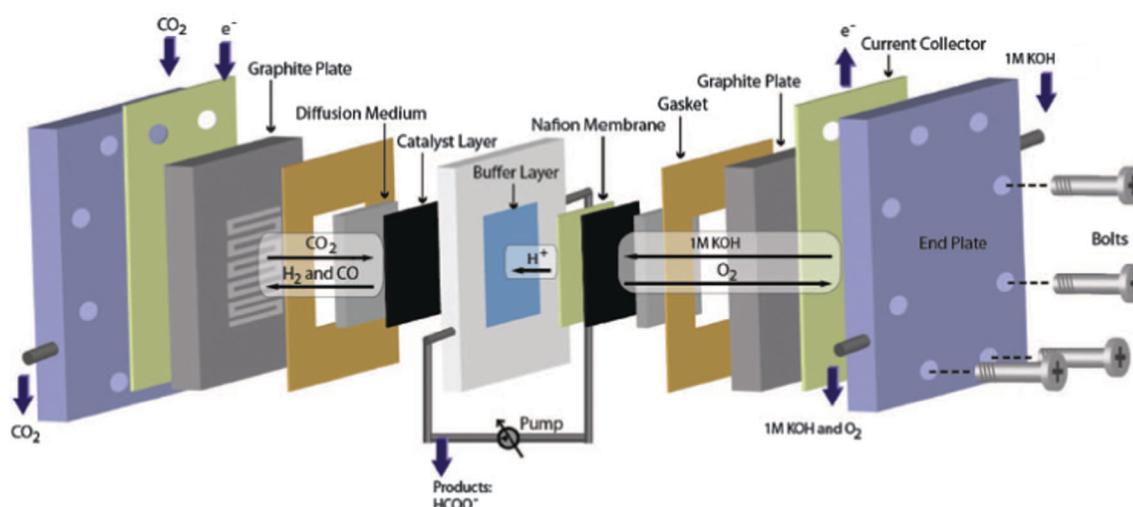


Fig. 35 Example of a flow electrolyzer. Reprinted with permission from ref. 372.

Table 4 Efficient, high rate two-electron CO₂ reduction

Entry	Electrocatalyst	E vs. SHE (V)	Current density (mA cm ⁻²)	Major product	FE (%)	Ref.	Electrolyte	Notes
1	Ag	-1.02	300	CO	86	371	0.5 M KHCO ₃	20 atm CO ₂
2	Au/C	-2.22	200	CO	64	315	0.5 M KHCO ₃	Flow PEM Cell
3	Sn	-1.19	163	HCOO ⁻	92	367	0.1 M KHCO ₃	30 atm CO ₂
4	Pb	-1.37	163	HCOO ⁻	96	367	0.1 M KHCO ₃	30 atm CO ₂
5	Co-TPP	-0.88	100	CO	97	376	0.5 M KHCO ₃	Metal porphyrin catalyst, 20 atm CO ₂
6	p-InP	-2.7	100	CO	93	393	MeOH	Photoelectrochemical, 40 atm CO ₂
7	Ag	-2.96	100	CO	53	394	0.5 M K ₂ SO ₄	Static PEM cell
8	Ag	-3.5 ^a	80	CO	33	395	0.5 M KHCO ₃	Flow PEM cell
9	Sn	-2.7 ^a	60	HCOO ⁻	91	344	0.45 M KHCO ₃ + 2 M KCl	Flow PEM cell
10	40 wt% Ag/TiO ₂	-1.6	100	CO	90	396	1 M KOH	Flow cell

^a Cell voltage, not referenced.

While certainly not all-encompassing, this table is intended to give an idea of the range of conditions that researchers have used to generate systems capable of high rate CO₂ reduction. It would not be feasible to scale up many of the processes in these reports (only two of them are flow cells), but the potential for high rate electrochemical CO₂ reduction is clearly there. With the exception of entry 6, which also includes light irradiation, all of the examples utilize electricity as the only source of energy for the transformation.

Solid oxide electrolysis cells for CO₂ reduction

Recently, solid oxide electrolysis cells (SOECs) have been used for CO₂ reduction^{397,398} coupled with steam electrolysis, which presents a different strategy compared to the methods described earlier. Instead of relying on electricity for all of the energy required to reduce CO₂, SOECs operate at very high temperatures (typically ~800–900 °C) where some of the energy required for CO₂ reduction can be supplied by heat. The reverse water gas shift reaction can come into play as well as direct electrochemical CO₂ reduction at these temperatures. SOECs have the advantage of being capable of producing extremely high current densities compared to other processes while simultaneously operating at relatively low cell potentials. Research is still very active in understanding the mechanisms at play in a SOEC used for CO₂ reduction.³⁹⁹

Hydrogen and occasionally CO are often fed into SOEC reactors along with CO₂ and water, making faradaic efficiency

calculations challenging. In an attempt to provide some information to the reader about the efficiency of the processes reported in the literature, “CO FE Equivalent” has been calculated for each SOEC report when it was possible. This was accomplished by subtracting out the amount of H₂ and/or CO being fed into the reactor to compare with the net CO produced with the applied current. Since CO may also be formed by way of the reverse water gas shift reaction, however, this value is not directly comparable to faradaic efficiency for a pure electrochemical process. That being said, the output of the reactors is directly comparable, and the FE equivalent value represents the number of electrons which eventually end up in CO₂ reduction products compared to the number that end up in either H₂ or side products. SOECs are capable of operating at very high current densities of up to 1500 mA cm⁻² at very reasonable cell potentials of 2.65 V or less (Table 5).⁴⁰⁰

One limitation of SOECs is that they are essentially limited to CO as the product, since other products decompose at such high temperatures. Hallinder *et al.* have been investigating this constraint by developing a system designed to function at intermediate temperatures (~300 °C) where hydrocarbon products would be stable.⁴⁰¹ This system would benefit from some of the thermodynamic advantages of SOECs, while still being capable of producing hydrocarbon products instead of CO exclusively. Another related technology inspired by SOEC for CO₂ reduction is the use of solid proton conductors, which have been reported to yield both CO and CH₄ electrochemically.⁴⁰⁰

Table 5 SOECs for CO₂ reduction

Entry	Cathode	T (°C)	Cell potential (V)	Feed (H ₂ :CO ₂ :H ₂ O:CO:inert)	CO FE equivalent	J (mA cm ⁻²)	Ref.	Notes
1	Ni/ScSZ	800	1.15	7:14:19:0:61	50	230	397	Button cell
2	Ni/Sc/SZ	800	1.4	12:12.7:11.4:0:63.3	62	188	397	Stack
3	Ni/YSZ	800	1.3	1:1:2:0:0	n/a	1000	402	
4	LSCM/YSZ	900	2.25 ^a	0:9:0:1:0	n/a	540	403	Three electrodes
5	LSCM/GDC	900	2.25 ^a	0:9:0:1:0	n/a	610	403	Three electrodes
6	Ni/YSZ	900	2.25 ^a	0:9:0:1:0	n/a	800	403	Three electrodes
7	Ni/YSZ	850	1.25	0:1:1:1:1	n/a	900	404	
8	BCYZ	614	2.65	0:1:0:0:0	29.5	1500	400	Proton conductor

^a E vs. LSM/scandium stabilized zirconia quasi-reference electrode.

	Acid	Base
Cathode	$4\text{H}^+ + 4\text{e}^- \longrightarrow 2\text{H}_2$	$4\text{H}_2\text{O} + 4\text{e}^- \longrightarrow 2\text{H}_2 + 4\text{OH}^-$
Anode	$2\text{H}_2\text{O} \longrightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^-$	$4\text{OH}^- \longrightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^-$
Overall	$2\text{H}_2\text{O} \longrightarrow 2\text{H}_2 + \text{O}_2$	$2\text{H}_2\text{O} \longrightarrow 2\text{H}_2 + \text{O}_2$

Fig. 38 Water electrolysis in acid and base.

Electrochemical water splitting

While not the focus of this review, electrochemical water splitting is a critical technology that impacts most of the anthropogenic carbon cycles in some way. Water electrolysis takes place according to the equations in Fig. 38 depending on whether the media is acidic or basic. The overall reaction is, however, the same regardless of the pH of the solution. Ursua *et al.* recently reviewed this field comprehensively,³⁶² therefore we will give only an overview here. There are three types of water electrolysis based on the type of electrolyte: alkaline, PEM, and SOEC. Alkaline electrolyzers (Fig. 39) are by far the most mature of the three, with the first demonstration in 1800,⁴⁰⁵ and virtually all of the large scale electrolysis facilities utilize this technology. The main advantages that alkaline electrolysis cells have over competing technologies are maturity, low installation cost, large scale, and long lifetime. Since alkaline electrolysis is the oldest technology, improvements must be demonstrated relative to it.

The alkaline electrolyzers on the market today are mostly considered “advanced alkaline electrolyzers”,⁴⁰⁶ which feature several design improvements including minimized distance between the electrodes,⁴⁰⁷ new separator materials,^{408,409} higher temperature of operation, and new electrocatalysts. These advancements have led to electrolyzers capable of achieving >80% energy efficiency. Very high hydrogen production rates can be achieved using alkaline electrolyzers, with power demands reaching into the megawatt range. A concern with alkaline electrolyzers is that they cannot be quickly switched on and switched off, which is

problematic if they are to be coupled with fluctuating energy generation from wind, solar, or even in an environment when they must only be used during low energy demand.

PEM electrolyzers are available commercially,³⁶² often from the same companies that produce alkaline electrolyzers. However, they struggle with high initial cost and short lifetime compared to alkaline electrolyzers. Their main advantages include the production of higher purity gases (limiting the need for purification), high current density, high voltage efficiency, and rapid response to changes in load.³⁴⁵ Their consistent performance across a relatively wide load range is their main advantage compared to alkaline electrolyzers. Given that many renewable energy sources are intermittent, this could prove to be a valuable advantage. These advantages are offset by their high cost, shorter lifetime, and smaller size compared to alkaline electrolyzers. The cost of a PEM stack is broken down in Fig. 40, with the largest single portion going to the flow fields and separators and the next largest one to the MEA itself. These values are high due to the specialized materials required for operation within the acidic environment of the PEM electrolyzer. Conversely, most of the advantages of PEM electrolyzers (high current density, high voltage efficiency, and rapid response) are related to their acidic nature.

SOECs operate by utilizing materials capable of transporting oxygen atoms through solid ceramic materials at very high temperatures. These designs offer very high efficiencies and current densities and are potentially much cheaper than PEM cells due to the use of non-noble metal catalysts, but they are still in the process of being commercialized. The very high temperatures they require constitutes both a strength and a weakness, as it increases the electrical efficiency to values much higher than those achievable with either alkaline electrolyzers or PEM cells, but induces many problems in the form of

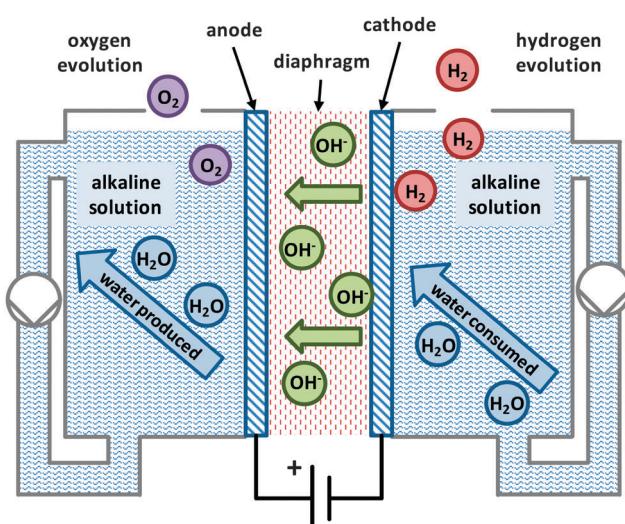


Fig. 39 Alkaline electrolysis cell.

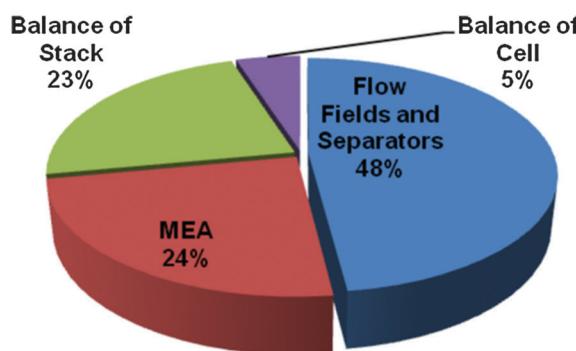


Fig. 40 Capital Cost Breakdown of PEM Electrolyzer (MEA: membrane electrode assembly). Reprinted with permission from ref. 410.

material durability and compatibility at such high temperatures. Another disadvantage of SOECs is their inability to tolerate many start-stop cycles due to the strain to internal components caused by varying degrees of thermal expansion at high temperature.⁴¹¹ Also, their high temperature of operation indicates that they likely would only operate efficiently within a narrow load range, much like alkaline electrolyzers. The ability to use waste heat makes this technology very attractive to nuclear power, however, where the excess heat generated by the reactor could be used to heat the SOEC and thereby significantly increase the overall efficiency of a nuclear power plant.

Syngas (metgas) production from formic acid synthesized by electrochemical reduction of CO₂

Direct electrochemical reduction of CO₂ can result in the formation of formate in a basic aqueous medium.³⁵⁰ The unique feature of formic acid (FA) is that it can be decomposed in two different pathways and should be considered to produce syngas (metgas) from recycled carbon dioxide using renewable energies (Fig. 41). The decomposition of FA to the mixture of CO and H₂O (decarbonylation, also referred to as dehydration) was first reported by Paul Sabatier⁴¹² in 1911 and it is usually conducted over heterogeneous catalysts.⁴¹³ On the other hand, the dehydrogenation of FA⁴¹⁴ (also called decarboxylation) to form CO₂ and H₂ is mainly carried out in the presence of homogeneous catalysts for example Ru,^{415–419} and Ir,⁴²⁰ etc.

After the separation of water (in the decarbonylation pathway) and carbon dioxide (in the decarboxylation pathway) the combined metgas streams with a H₂/CO ratio of 2 can be subjected to methanol synthesis.

The catalytic activity of RuCl₃ for FA dehydrogenation has been investigated extensively and it was found that RuCl₃ is converted to [Ru₄(CO)₁₂H₄]⁴¹⁹ upon heating with FA and Na-formate in aqueous solution. The latter complex was shown to be an active catalyst for the decarboxylation of FA. The reaction between RuCl₃ and FA/Na-formate in the presence of PPh₃ or O = PPh₃ results in the mixture of [Ru(HCO₂)₂(CO)(PPh₃)₂], [Ru(CO)₃(PPh₃)₂], [Ru₂(HCO₂)₂(CO)₄(PPh₃)₂] and [Ru₁₂C₃₀H₁₄Na₂O₅₀·6(C₁₈H₁₅OP)₂(C₇H₈)·4(H₂O)]⁴²¹ respectively. These findings also highlight the importance of FA as a carbonyl source and a reducing agent

that allows the synthesis of metal carbonyls without using toxic and explosive gases like CO and H₂, respectively.

7. Thermochemical and photochemical routes to methanol

Thermochemical production of CO and H₂ for methanol synthesis

Solar driven conversion of CO₂ to CO. Roughly 174 PW (1 PW = 10¹⁵ W) energy arrives from the Sun to the upper atmosphere of the Earth continuously.⁴²² This energy is several orders of magnitudes higher than the potential of other renewable energies such as wind, hydro, tidal, etc. Both silicon- and organic photovoltaics-based solar cells are of particular interest and their global contribution to the renewable energy production will become even more significant. In addition to solar photons, the thermal effect of sunshine accounts for an enormous amount of energy which humankind should also take increasingly advantage of. The thermal energy of (concentrated) sunshine can be utilized for example in households to heat/preheat water or air but this energy can be converted to fuels as well.⁴²³ The concept of “sunshine to fuels” or “solar fuels” developed among others at the Sandia National Laboratories may sound unusual at first glance, but in fact it simply stands for the conversion of stable carbon and/or hydrogen sources (where the elements are in their most stable oxidation state) to fuels utilizing the energy of sunshine; much like nature uses solar energy to recycle CO₂ and H₂O.

The solar-driven conversion of carbon dioxide and water to carbohydrates and other plant based materials, as well as the subsequent formation of fossil fuels, readily take place in Nature, but humankind consumes these natural sources much faster than they can form. As an ultimate solution, the artificial conversion of CO₂ to fuels (anthropogenic carbon cycle) has to be developed in order to provide forthcoming generations with fuels and commodity materials in a sustainable way.

Due to the high stability of CO₂, its direct splitting (thermolysis) is not favorable and even at 2000 °C only approximately 2% of CO₂ is decomposed to CO and O₂.⁴²⁴ In addition to choosing the proper materials that can resist such high temperatures other issues such as separation of explosive product gases or

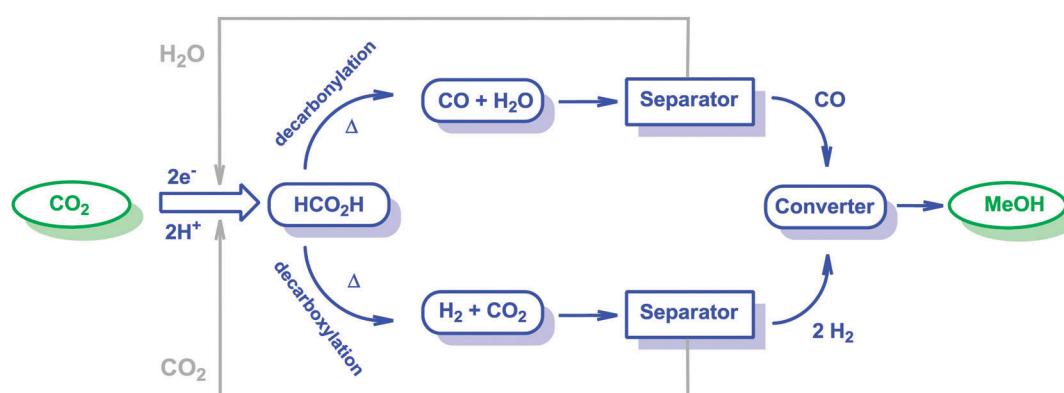


Fig. 41 Methanol production from CO₂ by sequential electrochemical reduction to FA, FA decomposition and metgas conversion to methanol.

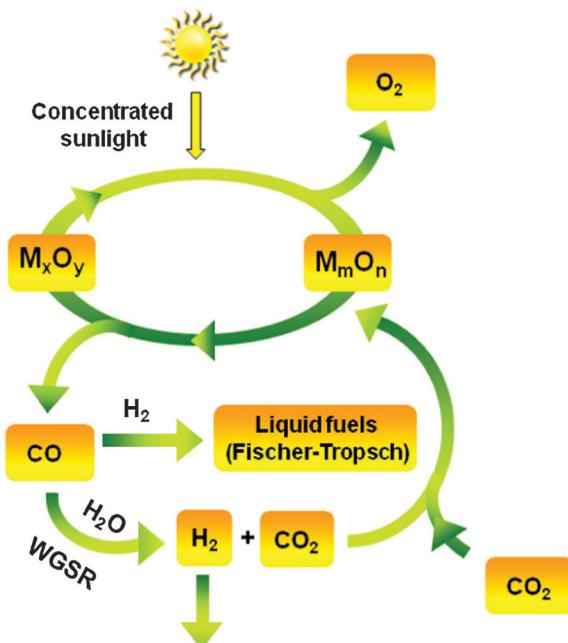


Fig. 42 Solar thermochemical cycle for metal oxide-assisted reduction of CO_2 to CO . M_xO_y : metal oxide with the metal in its higher oxidation state, M_mO_n : metal oxide with the metal in its lower oxidation state.

fast quenching in order to avoid recombination upon cooling makes the direct thermal splitting challenging.

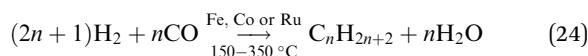
Two step thermochemical cycles operated at lower temperatures can overcome the above issues associated with the direct thermal splitting of carbon dioxide (Fig. 42).

In the first, solar driven, endothermic step a metal oxide is dissociated to oxygen and elemental metal or to a metal oxide in which the metal is in its lower oxidation state. This step is followed by a non-solar exothermic reaction between CO_2 and the reduced metal/metal oxide giving CO and recovering the initial metal oxide. It should be added here that elemental carbon may form in the course of the second step as well which can be safely stored but this approach is not discussed in the present review. The only gas which has to be separated in the first step is oxygen.

Numerous redox systems have been developed for the thermochemical splitting of CO_2 such as $\text{Fe}_3\text{O}_4/\text{FeO}$,^{424,425} ZnO/Zn ,⁴²⁶ SnO_2/SnO ,⁴²⁴ nonstoichiometric ceria⁴²⁷ or Ni-, Fe-, Mg- and Mn-doped ceria/zirconia solid solutions⁴²⁸ which differ in the decomposition temperature of the oxide material.

Carbon monoxide derived from CO_2 is then mixed with hydrogen and can be used for methanol synthesis (eqn (1)) or Fischer-Tropsch synthesis (eqn (24)) to produce synthetic hydrocarbons. The required hydrogen can be generated from any source, including reforming reactions, water electrolysis, and water gas shift reaction of the obtained CO from CO_2 splitting.

Fischer-Tropsch synthesis



Thermochemical cleavage of H_2O to H_2 with solar or nuclear energy. Similar to CO_2 , water can be split thermally into H_2 and O_2 at very high temperatures ($2000-2500^\circ\text{C}$ and higher). This reaction suffers, however, from the same problems. The thermolysis products, H_2 and O_2 , have to be rapidly separated or quenched to avoid their recombination. To obtain the high temperatures needed, solar furnaces have to be used and materials able to withstand such high temperatures over prolonged periods of time have to be developed. This makes the direct, high temperature, thermal decomposition of water impractical for the time being.

Thermochemical water splitting, based on chemical cycles, can, on the other hand, be achieved at a more reasonable temperature. One of the most extensively studied thermochemical cycle, among many, is the so called iodine–sulfur cycle.⁴²⁹ In that cycle, SO_2 and iodine are added to water to form sulfuric acid and hydrogen iodide. When heated above 350°C , HI decomposes to hydrogen and iodine, 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 iodine and SO_2 and iodine continuously recycled, the only feeds to the process are water and high temperature heat and the products are hydrogen, oxygen and low grade heat. The overall reaction is basically the splitting of water to hydrogen and oxygen. Thermochemical cycles have often been proposed in conjunction with nuclear energy. New, generation IV nuclear power plants currently in development would be especially well suited for this application as they are planned to operate at temperatures of 700 to 1000°C ; compared to only 300 and 400°C for presently used reactors. Heat provided by concentrated solar sources could also be used.⁴³⁰ Problems remain however, such as the corrosive nature of chemicals employed.

Interestingly, similar thermochemical cycles to the ones proposed for the reduction of CO_2 to CO , employing less corrosive intermediates, have also been tested for the production of H_2 from water. For example $\text{Fe}_3\text{O}_4/\text{FeO}$,⁴³¹ multivalent ferrites ($\text{M}_x\text{Fe}_{3-x}\text{O}_4$, with $\text{M} = \text{Mn, Co, Ni, and Zn}$),⁴³² or ZnO/Zn ,⁴³³ and SnO_2/SnO ⁴³⁴ were developed for water-splitting to produce and store hydrogen as a “solar fuel”.⁴³⁵

The thermochemical splitting of both CO_2 and H_2O are promising in the long range, but remain, for now, far from practical large scale deployment.

Direct photochemical reduction of CO_2 to methanol

Direct photochemical reduction of CO_2 to methanol shares some similarities with electrochemical CO_2 reduction, particularly when it comes to molecular catalysts used in both cases. One recent report in particular cites the pyridinium approach to photoelectrochemical CO_2 reduction, but instead uses ruthenium(II) trisphenanthroline as a chromophore to generate the electrons necessary for CO_2 reduction instead of a semiconductor.²⁹⁹ Although the selectivity for methanol is quite low, the conversion of CO_2 directly to methanol using photochemistry has been demonstrated. Typically, photochemical (or photocatalytic) CO_2 reduction gives either formate or CO as a major product, an area which was reviewed in 2010.⁴³⁶

One of the major limitations to photochemical CO₂ reduction as it is generally practiced is that a sacrificial hydride source (generally an amine, ascorbic acid, or 1-benzyl-1,4-dihydronicotinamide) must be added to the solution to substitute for the anode, which would generally be used in electrochemical CO₂ reduction. While several groups are actively working on photochemical regeneration of hydride donor,⁴³⁷ it remains a major challenge. Turnover frequency and turnover number for photochemical catalysts for CO₂ reduction are still limited (TOFs are generally around 20 h⁻¹), and will require significant improvement if these processes are to be considered for industrial application. In addition to the molecular catalyst approach, several research groups have experimented with semiconductors and metal oxides such as silicon carbide,⁴³⁸ WO₃,⁴³⁹ InVO₄,⁴⁴⁰ TiO₂,⁴⁴¹⁻⁴⁴⁴ InTaO₄,⁴⁴⁵ NiO,⁴⁴⁴ and ZnO⁴⁴⁴ either by themselves or in combination with various other heterogeneous catalysts to achieve the same goal. Contamination of semiconductors can cause spurious results,⁴⁴⁶ however, so meticulous cleaning of the surface is essential to obtain reproducible results. A challenge to producing methanol on semiconductors irradiated with light is that the reaction can be reversible,^{438,444} so strategies to mitigate methanol oxidation are essential to realizing a practical industrial process.

Instead of directly reducing CO₂ photochemically, one could produce hydrogen using a photochemical cell^{447,448} and use this renewable hydrogen to hydrogenate CO₂ in a separate process. While this approach would not be as straightforward as direct photochemical CO₂ reduction, it could still reduce the number of steps required for CO₂ reduction by combining light harvesting with hydrogen evolution. A perspective was recently written on this subject describing the current state of the art and the challenges to its commercialization.⁴⁴⁹ Typically, a photovoltaic material (*e.g.* a silicon semiconductor), an oxygen evolution catalyst (*e.g.* cobalt oxide), and a hydrogen evolution catalyst (*e.g.* NiMoZn) are combined to form a device which can capture energy from sunlight using the photovoltaic, oxidize water to oxygen on one catalyst, and reduce water to hydrogen

gas on the other catalyst.⁴⁵⁰ Compared to photochemical CO₂ reduction, water splitting can occur at higher efficiencies (>12%) and current densities (120 mA cm⁻²) using a system comprised of *p*-GaInP₂ in tandem with GaAs.⁴⁵¹ A significant amount of research is currently ongoing in this area, with centers like the Joint Center for Artificial Photosynthesis (JCAP) focused entirely on photochemical reactions and their potential commercialization.

8. Sources of CO₂

CO₂ capture from relatively concentrated sources

To produce fuels from CO₂, the first step is to capture it from natural and anthropogenic sources the most efficiently and economically possible. Because of their relatively high CO₂ concentration, typically between 5 and 15% CO₂ by volume, flue gases from fossil fuel burning power plants are presently the most readily available large scale source of CO₂. Technologies for the capture of CO₂ from such sources have been described extensively in the literature (Fig. 43).⁴⁵² They include retrofitting existing power plants for post combustion CO₂ capture and purification using well known as well as emerging separation technologies.^{453,454} In new, advanced power plants it would be advantageous to apply pre-combustion CO₂ capture and oxy-fuel combustion.⁴⁵⁵ In pre-combustion capture the fossil fuel is first gasified to a mixture of H₂, CO and CO₂ that is further subjected to the WGS reaction in order to obtain a gas mixture containing mostly H₂ and CO₂. The resulting high concentration CO₂ under high pressure is separated from the H₂ that is sent to a gas turbine for electricity production. In the case of oxy-fuel combustion, the fossil fuel is burned in a mixture of O₂ and CO₂. The absence of nitrogen in the flue gas makes the separation of CO₂ much easier. So called “clean coal” power plants based on these technologies are under development or being built. Besides fossil fuel burning power plants, carbon dioxide emissions from

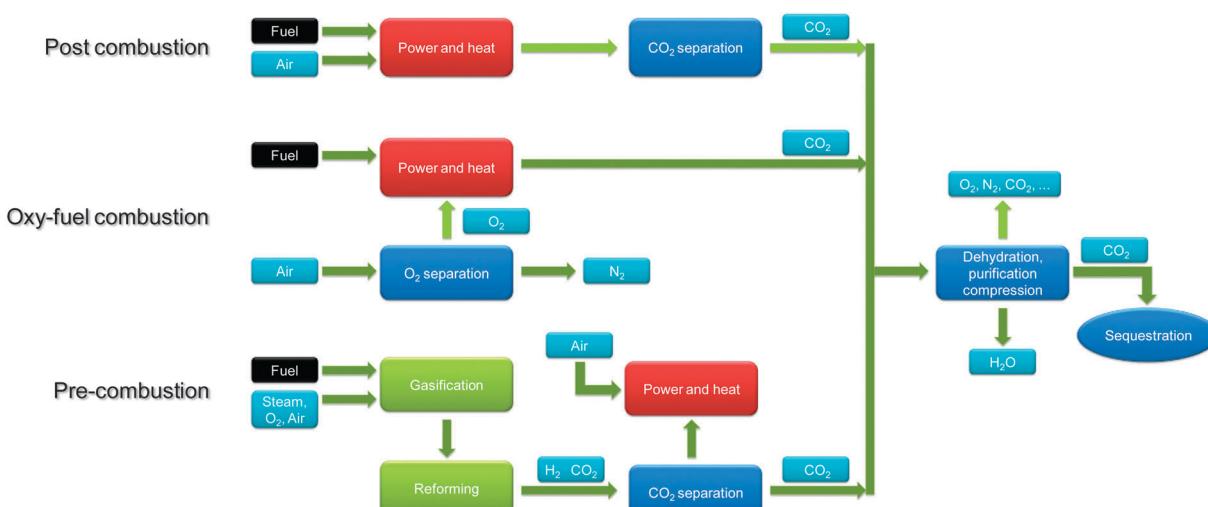


Fig. 43 Currently favored carbon capture and sequestration (CCS) processes from fossil fuel burning power plants. Adapted from ref. 452.

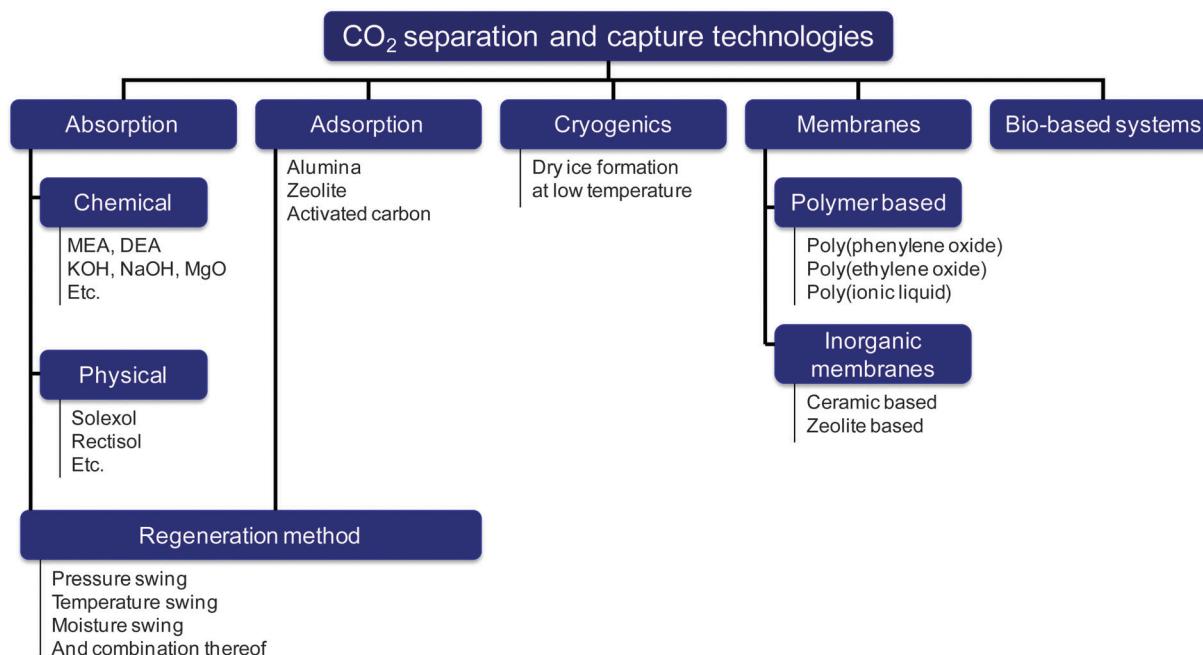


Fig. 44 CO₂ separation and capture technologies.

numerous industrial facilities such as cement, aluminum, iron, steel factories as well as fermentation plants, which also contain high CO₂ concentrations, could also be utilized. Natural gas, in some cases, also contains substantial amounts of CO₂ (in excess of 50% for some gas fields).

The removal and capture of CO₂ from gas streams can be achieved by a range of separation techniques depending on CO₂ concentration, pressure, temperature, *etc.* They are based on different physical and chemical processes including absorption into a liquid solution system, adsorption onto a solid, cryogenic separation and permeation through membranes (Fig. 44). The use of these techniques for the separation of CO₂ from relatively concentrated sources have been reviewed in the recent past and will therefore be only briefly summarized here.^{452,453,455–461}

Cryogenic distillation, although widely used for the separation of gases such as nitrogen and oxygen, is very energy intensive and generally considered impractical for large scale CO₂ separation. Membranes are more suited for relatively high concentrations of CO₂ such as those encountered in some natural gas deposits or for pre-combustion separation in fossil fuel burning power plants. They might therefore not be the best choice for post-combustion CO₂ capture or from other more dilute sources.

Alcohols, polyethyleneglycols (PEG) and other oxygenated compounds have been used as physical solvents for acid gas removal, mainly CO₂ and H₂S for at least four decades. Commercial processes include for example SELEXOL® from Union Carbide (now a UOP process, using polyethylene glycol dimethyl ethers), Rectisol (methanol chilled at -40 °C) and Sepasolv MPE® from BASF (mixture of polyethylene glycol dialkyl ethers).⁴⁶¹ These physical solvents are generally used

for the separation of CO₂ at high pressure such as in the purification of syngas or natural gas sweetening. The regeneration by heating or reduced pressure is less energy intensive than in the case of chemical sorbents. Another advantage is that these sorbents are non-corrosive. However, due to their relatively low selectivity for CO₂, they are not well suited for the separation of CO₂ from dilute and low pressure sources.

The use of solid physical sorbents for the separation of CO₂ is based on the ability of porous solids to reversibly adsorb certain components in gas mixtures. These solids can have a large distribution of pore size such as silica gel, alumina and activated carbon or a pore size controlled by the crystal structure like zeolites. At lower temperature (*e.g.* room temperature), zeolite based adsorbents have shown high absorption capacities for CO₂ (zeolite 13X: 160 mg CO₂ per g and zeolite 4A 135 mg CO₂ per g at 25 °C in pure CO₂).⁴⁶² One of the drawbacks of these adsorbents is their fast decline in adsorption capacities with increasing temperature. Moreover, as the gases are only physically adsorbed, the separation factors between different gases (such as CO₂-N₂ mixtures) are low, which makes capture from sources containing lower CO₂ concentrations impractical. Moreover, the usefulness of most of these adsorbents decreases dramatically in the presence of water.

Among the various CO₂ separation technologies, one of the most suitable and widely employed for high volume flue gas streams treatment is based on amine solutions, which have been used industrially for more than half a century. The commonly used absorbents are typically 25–30 wt% aqueous solutions of alkanolamines such as monoethanolamine (MEA) and diethanolamine (DEA), which form carbamates and bicarbonates with CO₂.⁴⁶¹ However, the energy required to use this well developed amine solution for CO₂ capture is intense.

The energy penalty for CO₂ capture from a coal-based power station using a MEA solution has for example been estimated to be 25 to 40%. High energy requirements for the regeneration step, limited concentration of amines due to corrosion problems and amine degradation are major drawbacks warranting the development of more efficient, regenerable and robust CO₂ sorbents.

To circumvent some of the problems associated with the use of liquid amines and still achieve a high selectivity for CO₂ the use of solid amines or hybrid materials (amine/support) is a promising pathway.⁴⁵⁶ For this, different approaches can be envisioned including: (i) use of solid amines or polyamine directly as absorbents,⁴⁶³ (ii) amines or polyamines deposited (physical adsorption) on a solid support such as silica or alumina,^{5,456,464–470} (iii) amines or polyamines chemically bonded to the surface of a solid.^{456,471–476}

Other materials for the separation of CO₂ such as ionic liquids and metal-organic frameworks (MOFs) have also gained attention in recent years. Readers interested in the synthesis and CO₂ capture performance of these materials are directed to recent reports and references therein.^{477,478}

CO₂ capture from the air

As long as industrial and natural sources with relatively high CO₂ concentrations are available, it would be more economical and less energy demanding to separate CO₂ from these sources. However, while about half of the anthropogenic CO₂ emissions are the result of large industrial sources such as power plants and cement factories, the other half originates from small distributed sources such as home and office heating and cooling, and the transportation sector.⁴⁷⁹ The collection of CO₂ from these countless small fossil fuel burning units at the source would be difficult if possible at all, and probably economically prohibitive. Capture of CO₂ onboard an airplane, for example, would be impossible because of the added weight involved. Moreover, CO₂, once captured would have to be transported to a sequestration or conversion site, requiring the construction of a vast and costly infrastructure. To avoid the need for such an enormous CO₂ collection infrastructure, CO₂ could be captured directly from the atmosphere. The atmosphere would thus essentially serve as a “CO₂ conveyor belt” to transport CO₂ at no cost from the source point to the site of capture. Direct air capture (DAC), which has already been proposed in the past, would make the CO₂ collection independent from the CO₂ source.^{15,22,480–493} This means that CO₂ from any source, large or small, static or mobile, could be captured. The CO₂ concentration being similar all around the globe, CO₂ extraction plants could be placed anywhere, ideally, close to sequestration site or hydrogen production sites for recycling. The fact that DAC is independent from CO₂ sources could also open the possibility to actually extract more CO₂ than is emitted from human activity and not only control but eventually even reduce the concentration of CO₂ in the atmosphere. In the long term, when our fossil fuel reserves will be depleted, CO₂ from the air will also continue to provide humankind with an almost limitless carbon source.

Despite the very low concentration of CO₂ in the atmosphere, presently around 400 ppm, the theoretical minimum

energy requirement for DAC to go from a concentration of 400 ppm to a relatively pure gas (>90% CO₂) is only about 5 kcal mol⁻¹ (equivalent to ~0.4 GJ per tCO₂).^{485,494,495} Theoretically, DAC would therefore require only between 1.8 and 3.4 times as much energy as capture of CO₂ from a fossil fuel power plant.^{485,496} Of course, the actual energy needed for air capture will be significantly higher than the theoretically determined minimum energy and depend on a number of factors including the technology employed for the capture. Nevertheless, DAC is clearly possible and this subject has been reviewed recently.⁴ We will therefore only give a brief overview of the type of sorbents that can be used for DAC.

Due to the low CO₂ concentration in air (~400 ppm), the presence of moisture, the necessity to operate close to room temperature and ambient pressure, many of the technologies described *vide supra* for gases containing higher CO₂ concentration can be ruled out. At atmospheric pressure, physical adsorbents such as zeolites, activated carbon and alumina can be excluded due to their low selectivity for CO₂ in the presence of moisture and very low heat of adsorption, which result in low adsorption capacities. Physical adsorption in liquids for the capture of CO₂ at rather high pressure is also not applicable. In practice, only sorbents having a chemical interaction can be used effectively for the capture of CO₂ from the air. Widely used MEA based sorbents suffer from stability problems when contacted with air as well as evaporation issues due to the large volume of gas to be handled. While strong bases such as calcium hydroxide, potassium hydroxide, sodium hydroxide and their aqueous solutions can be used, they bind CO₂ too strongly, thus requiring high temperature for their regeneration. Amine and polyamine based solid sorbents either physically adsorbed or chemically bound on a support such as silica, mesoporous solids (MCM-41, MCM-48, SBA-15, etc.), polymers as well as carbon fibers have been recognized as potential candidates for DAC.^{467,473,497–508} Hyperbranched aminosilicas (HAS) prepared by *in situ* polymerizing of aziridine on porous solids have also been reported for DAC.^{509,510} Adsorbents based on modified metal-organic frameworks (MOF)^{511,512} and porous polymer networks⁵¹³ as well as quaternary ammonium functionalized anionic exchange resin that can be regenerated by moisture swing protocols are another possibility.^{482,514–516}

Whereas practical applications have been developed for the essential removal of CO₂ from submarines and spacecrafts,^{467,517} the separation and recovery of CO₂ from ambient air on a larger scale is still in its infancy.⁵¹⁸ While there is no question that the capture of CO₂ from the air is possible, more research and development is clearly needed to optimize this technology and determine its economic viability. Using current technologies, the cost of removing a ton of CO₂ from point sources such as a coal burning power plant that contain 10–15% CO₂ has been estimated at between \$30–100. The estimated cost of DAC, on the other hand, still varies greatly from about \$20 to more than \$1000 per ton of CO₂.^{482,483,485,495,496,519–526}

The cost of a commercial plant will depend on many factors including the process used, labor cost, materials and energy use.

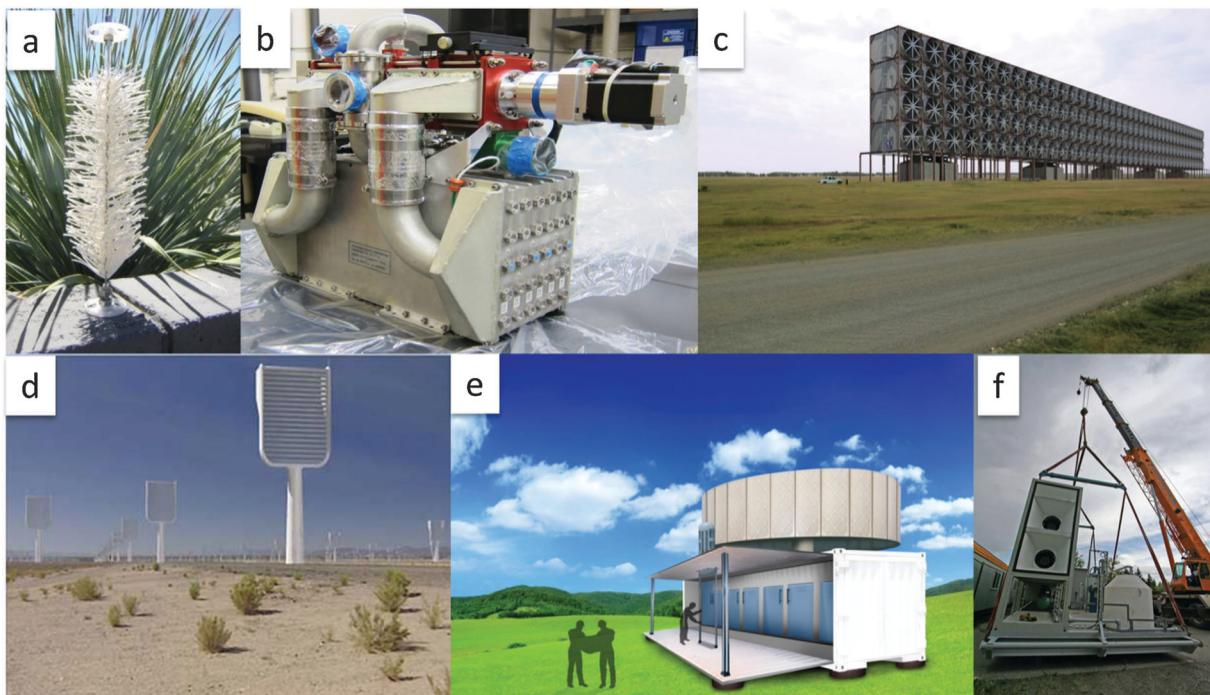


Fig. 45 Examples of prototypes and proposed designs for the separation of CO_2 from the air. (a) Prototype for CO_2 capture from the air. Reproduced by permission of Kilimanjaro Energy. (b) Solid amine based swing bed for CO_2 removal in human spaceflights. Currently undergoing tests in the International Space Station (ISS). Reproduced by permission of NASA. Courtesy J. C. Graf. (c) Artist rendering of an atmospheric CO_2 capture contactor. Reproduced by permission of Carbon Engineering. (d) Artist rendering of an array of atmospheric CO_2 capture units also known as Synthetic Trees. Reproduced by permission of Stonehaven Production. (e) Artist rendering of a prototype for CO_2 capture from the air using an anionic exchange resin and regeneration by moisture swing. Reproduced by permission of Kilimanjaro Energy. (f) Construction of a prototype for CO_2 capture from the air in Alberta, Canada. Reproduced by permission of Carbon Engineering.⁴ Reproduced from ref. 4 with permission from The Royal Society of Chemistry.

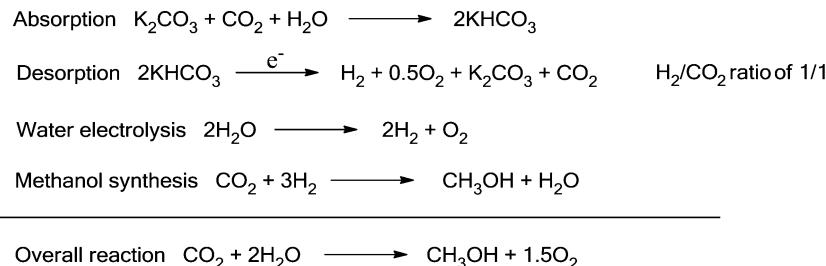
Only with the construction of demonstration and pilot plants will we have a better understanding of the total cost associated with DAC. A few start-up companies including Carbon Engineering,^{527–529} Kilimanjaro Energy,^{530–533} Global Thermostat⁵³⁴ and Climeworks^{535,536} have started such efforts. Examples of proposed devices and prototypes for DAC are represented in Fig. 45. It should also be pointed out that the costs associated with DAC units are not “stand alone”. Once captured, the CO_2 can be used for applications such as enhanced oil recovery (EOR) or recycling into chemicals and fuels including methanol, DME and hydrocarbons (CCR). This will give an economic value to the captured CO_2 , lowering the *de facto* cost of DAC and provide a more favorable overall picture of the process. Depending on the process, water (moisture) could also be separated from the air at the same time as CO_2 , which could provide clean water as an added value.

Atmospheric CO_2 to methanol

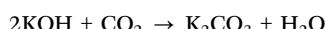
The collection of CO_2 from the atmosphere and its transformation to methanol and other fuels and materials has been proposed in the past.^{15,22,537–539} As early as the 1970s, Steinberg *et al.* described the use of nuclear energy for electrolysis of water to H_2 and subsequent methanol synthesis from atmospheric CO_2 .^{489,491,540,541} Eight different methods for DAC were proposed. Among them, the absorption/stripping of air with

dilute potassium carbonate solutions was found to require the least energy. After CO_2 adsorption at room temperature and atmospheric pressure, the formed KHCO_3 solution was treated in a stripper with steam to get K_2CO_3 back and obtain a concentrated CO_2 flow for methanol synthesis. The needed heat for the absorbent regeneration was provided by nuclear heat as also proposed by Sherman.⁵⁴² A similar approach using a K_2CO_3 solution for DAC and subsequent methanol production was presented in the frame of the Green Freedom project at the Los Alamos National Laboratory.⁵⁴³ However, instead of the traditional thermal stripping process for the regeneration of the adsorbent and separation of CO_2 , a selective electrolytic stripping was developed. Furthermore, this process also produces hydrogen as a by-product, reducing the needed supplemental hydrogen production by 33%. Overall the process produces methanol and oxygen (Scheme 3). Capture of 95% of the CO_2 present in the air in a single pass as well as 96% less energy consumption compared with conventional thermal stripping was claimed using this process.

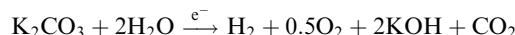
Stucki *et al.* have captured atmospheric CO_2 with potassium hydroxide (KOH) on microporous hollow fiber membranes.⁵⁴⁴ CO_2 was desorbed by electrolysis of the resulting K_2CO_3 and KOH recycled back to the absorption unit. As in the case of the Green Freedom process, beside CO_2 , the electrolysis cell also produced an equivalent of H_2 for methanol synthesis.

Scheme 3 Methanol from atmospheric CO₂ and water in the Green Freedom™ process.

Absorption



Desorption



H₂/CO₂ ratio 1/1

Specht *et al.* at the Center for Solar Energy and Hydrogen Research (ZSW) have also proposed the production of methanol from atmospheric CO₂ and H₂ obtained from renewable sources and have been testing this reaction on a bench scale.²² DAC with a solution of NaOH and desorption with solar heat was described.^{165,545} A similar approach was followed by the Air Fuel Synthesis company in Canada, capturing CO₂ from the atmosphere using a solution of NaOH and combining it with H₂ obtained by electrolysis of water to produce hydrocarbon fuels and methanol in a demonstration plant with a capacity of 5–10 L per day.¹³⁰

Graves *et al.* have also reviewed the possibilities to recycle CO₂ from the atmosphere and other sources to methanol and hydrocarbons with renewable or nuclear energy.³⁰⁵ The use of exchange resin based sorbents, which can be regenerated by moisture swing has been first suggested by Lackner *et al.*^{483,514,515} Because the evaporative drying of water on this solid sorbent provides the energy needed to drive the adsorption–desorption cycle, the energy consumption is relatively low. Such resins placed in passive collectors standing in the wind have therefore been proposed for DAC. Combined with H₂ obtained from wind energy, such systems have been proposed for the production of Fischer–Tropsch liquids in a remote location, *i.e.* the Kerguelen Islands.⁵⁴⁶ Methanol could, however, also be produced. Such a remote location was chosen to illustrate the possibility of capturing CO₂ from the atmosphere and sequestering it far from an inhabited area while at the same time using part of the captured CO₂ for the production of renewable fuels from wind energy.

Regardless of the method used to separate CO₂ from various sources, once CO₂ has been purified and compressed to the right pressure it can be converted to methanol using the catalysts described earlier.

9. Economics of CO₂ and biomass conversion to methanol

The cost of producing methanol and DME from renewable sources will depend on a variety of factors including feedstock,

technology choice, energy demand, production capacity, operating conditions, desired purity of the product, *etc.*

Presently, the most mature technology for the production of methanol from biomass is gasification to syngas followed by methanol synthesis with or without the addition of supplemental H₂ to make the best use of carbon contained in biomass. In the case of CO₂ from industrial sources or the atmosphere, the most mature and scalable method to prepare methanol sustainably without the use of fossil fuels remains the combination of water electrolysis and subsequent catalytic methanol synthesis with CO₂. 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.

A number of studies have been conducted on the cost of producing methanol using these routes. In 2007, Cifre and Badr,¹¹⁶ reviewing the results of previous studies, evaluated the cost of methanol production from biomass to lie in a range of €300–400 per tonne of methanol and the production cost of CO₂-based methanol between €500 and 600 per tonne. They observed that despite the higher production costs compared with methanol produced by conventional natural gas reforming (*i.e.* €100 to 200 per tonne, aided by the low current price of natural gas), these new processes incorporate environmentally beneficial aspects that have to be taken into account.

The cost of methanol obtained by gasification of biomass in conjunction with H₂ from the electrolysis of water was summarized in 2010 in the framework of the GreenSynFuels project.¹²⁰ Prices of methanol ranged from \$129 per tonne all the way to \$933 per tonne, depending mainly on the operational expenditures (OPEX) assumptions of the different studies. Besides being significantly influenced by the price of electricity and biomass, the possibility to generate revenue by supplying excess heat from the process for district heating also had a considerable effect, resulting in a reduction of 40% or more of the price of methanol. The report itself determined a cost of \$470–560 per tonne methanol on a production basis of 1053 t methanol per day using a combination of wood gasification and H₂ from SOECs in Denmark.

In a more recent review, from 2013, on bio-methanol production published by the International Renewable Energy Agency (IRENA),⁵⁴⁷ the production costs of methanol from coal, natural gas, wood, waste and CO₂ were compared. These costs were found to be highly sensitive to local conditions, which will influence the technology used and have a significant impact on the economics. This translates into a wide range of production costs estimates as shown in Fig. 46.

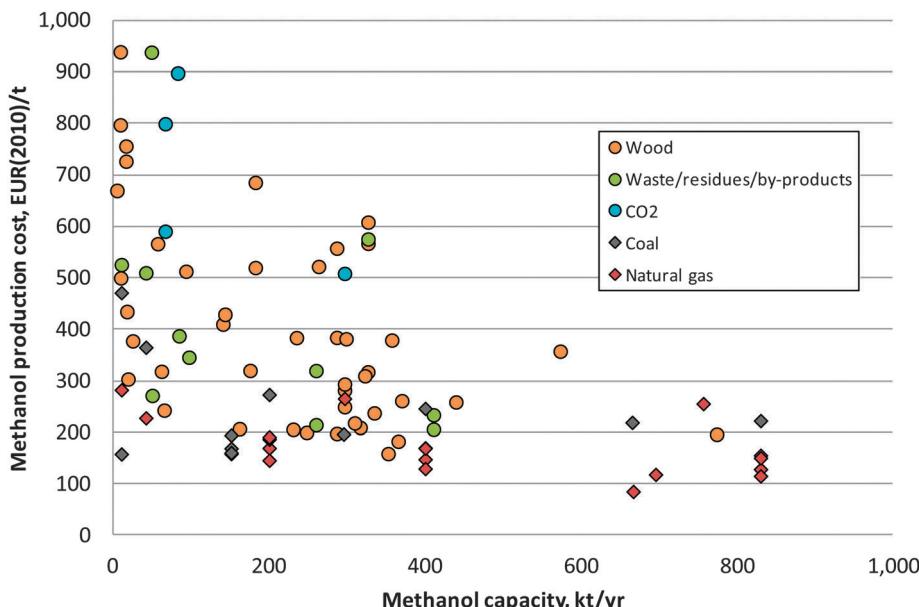


Fig. 46 Production costs and production capacity of (Bio-)methanol for various feedstocks from the literature. Source: IRENA analysis.⁵⁴⁷ Excludes co-feed set-ups; all costs converted to 2010 Euro values using national GDP deflators (World Bank); assumed Organisation for Economic Co-operation and Development (OECD) average inflation if no specific region is mentioned; assumed 8000 operational hours per year (if necessary); for costs beyond 2010, 2.5% annual inflation was assumed (OECD average for 1995–2010). Based on ref. 22, 80, 91, 105, 108, 117, 118, 165, 548–557 and 560–567. Reproduced with permission of IRENA from ref. 547.

Bio-methanol was found to be about 1.5 to 4 times more expensive to produce compared to natural gas based methanol at €100–200 per tonne. Estimated production costs of wood based bio-methanol went from €160 per tonne all the way to €940 per tonne.^{70,80,90–92,105,108,117,118,548–552} When using waste streams, the estimated costs were between €200–940 per tonne).^{114,133,551,553–556} Production costs from either CO₂ captured from flue gases or the atmosphere were estimated at between €510–900 per tonne.^{116,117,165,557} Not taking into account some outlier data points, Fig. 46 suggests that, as in the case of natural gas plants, a considerable economy of scale can be achieved with lower costs for larger plants. On a purely cost basis, it seems that renewable methanol can presently only compete with methanol produced from coal and natural gas in the most optimistic scenarios. In some cases, the co-production of methanol and DME, heat, electricity or hydrogen was found to be advantageous to reduce the price of bio-methanol. The cost could also be lowered if a market for the oxygen co-produced during the electrolysis step was available.⁵⁵⁸

Considering production costs, most of the current bio-methanol and bio-DME projects are focused on the use of waste streams from other industrial processes, such as black liquor (lignin) in Sweden,^{131,132} municipal waste in Canada¹³⁶ or glycerin in the Netherlands.¹³⁰ The cost of bio-DME from black liquor has been estimated at \$65 per barrel of oil equivalent.⁵⁵⁹

In the short term, the production of methanol from biomass and waste products seems to be the most economical in most locations. However, although the available amounts of biomass and derived materials are enormous, they are also limited and will not be able to cover all our energy needs by themselves, as

discussed, *vide supra*. The largest potential for the production of renewable methanol remains with the hydrogenation of CO₂ to methanol. Production from CO₂ does not suffer of the same limitations as biomass or waste products in terms of feedstock availability. CO₂ can be collected from many point sources such as fossil fuel burning power plants, cement and iron factories or eventually the atmosphere. The production cost of methanol from CO₂ will mainly depend on the cost of the starting materials, CO₂ and H₂. The price of carbon dioxide will depend on many factors such as its source, local policies (carbon tax or trading scheme) but is expected to remain the “cheap” component compared to the other feedstock, H₂. Whereas hydrogen can certainly be produced from fossil fuels, through syngas, at a relatively low cost (\$0.5–1.00 per kg), the production costs for H₂ from electrolysis of water are generally higher.⁵⁶⁸ The cost of hydrogen itself is closely linked to the cost of electricity needed to produce it. It was determined by Clausen *et al.* that 65% of the cost of methanol from CO₂ and H₂ obtained by electrolysis of water was electricity.¹¹⁷ This is not surprising considering that electrolysis of water is an energy intensive process. To produce 1 kg of hydrogen with a 100% theoretical efficiency requires 39.4 kW h of electricity. In practice, however, it is closer to 50 kW h kg⁻¹.⁵⁶⁹ In electrolyzer units with a capacity of 1000 kg H₂ per day, it was determined that the cost of electricity represents about 80% of the cost of hydrogen produced. Capital investment represents only 11%.⁵⁷⁰ In larger electrolysis units the contribution of the cost of electricity is expected to be even higher. The cost of electricity is therefore the major driving force to minimize the cost of producing hydrogen from electricity.

Comparing the cost of electricity generation from renewable energy sources, it can be seen in Fig. 47 that small hydro,

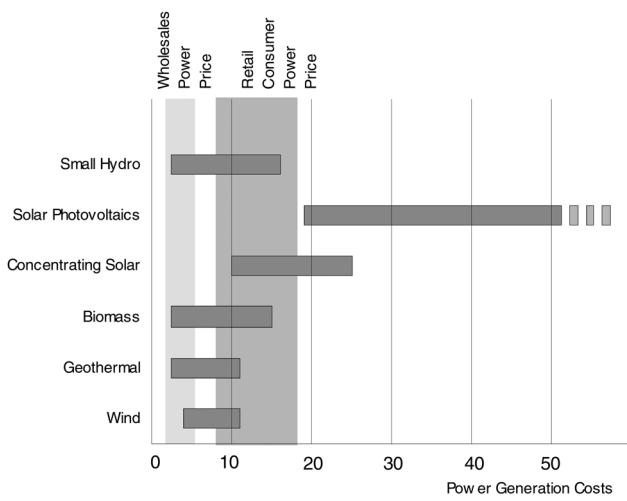


Fig. 47 Cost-competitiveness of selected renewable power technologies, before credit for carbon savings (Source: IEA).⁵⁷⁹

biomass, geothermal and wind can be competitive with the wholesale power price produced with conventional fossil fuels or nuclear energy. Hydroelectricity, which is very cost competitive and covered 15.8% of the world consumption of electricity in 2011 is still the largest renewable electricity source.⁵⁷¹ The addition of new large hydro capacity is, however, limited due to a number of factors including capital costs and environmental concerns. Solar thermal, in some cases can be competitive at the retail power price. Although photovoltaic electricity prices are dropping, they remain too expensive at present. Among the renewable energy sources competitive with wholesale power price, geothermal, small hydro and biomass have only relatively limited growth capacity. Wind, on the other hand, does not have these limitations, and possible sites with good wind speeds, for installation of wind turbines either onshore or offshore, are plentiful all around the world.⁵⁷² Considering these factors, wind has been the renewable energy source with the second highest growth rate in the last 20 years at 23.1% per year, after photovoltaics (Fig. 48).⁵⁷¹ This explains the exponential

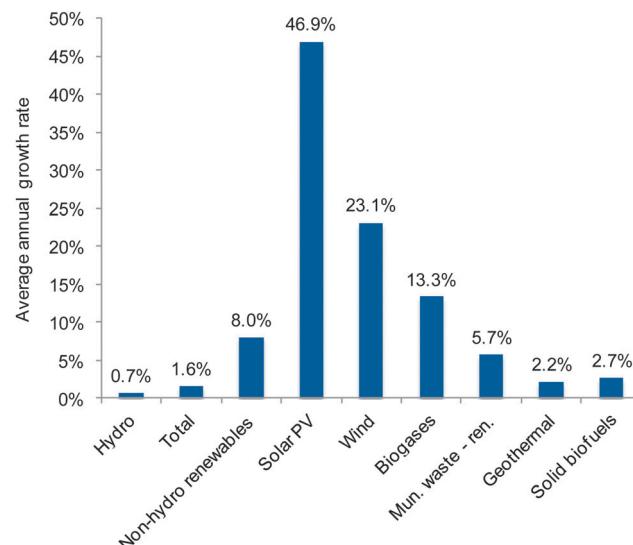


Fig. 49 Annual growth rates of electricity production between 1990 and 2012 in OECD countries (Source: IEA).⁵⁷¹

growth in wind mill installations around the world (Fig. 49). Over 280 GW of wind generating capacity is now installed worldwide (as a comparison, a typical nuclear power plant has a generating capacity of about 1 GW).⁵⁷³ According to the IEA, by 2050, wind energy could generate 18% of global electricity demand from 2.6% today.⁵⁷⁴

The price of electricity generated from wind is expected to decrease to an average of about 4 ¢ kW⁻¹ h⁻¹ (including transmission) in the future.⁵⁷⁵ Among renewable sources (except hydro), wind power is economically the most competitive, with electricity prices at 4 to 5 ¢ kW⁻¹ h⁻¹ at the best wind sites (without subsidies) General Electric estimates that it would cost about \$3.4 per kg to produce hydrogen from electricity derived from wind with a large wind farm of 500 MW installed capacity and 40% efficiency. This wind farm would allow the production of 108 000 kg of H₂ per day (4500 kg h⁻¹).⁵⁷⁶ In "The Hydrogen Economy, Opportunities, Costs, Barrier and R&D Needs" published by the National Research Council and National Academy of Engineering, it is estimated that with improvements in technologies, hydrogen from wind could be produced at a cost of \$2.86 per kg.⁵⁷⁵

Locally, some other sources of electricity could be used. In Iceland for example, the company Carbon Recycling International (CRI) is using cheap and plentiful geothermal energy to produce H₂ for CO₂ hydrogenation to methanol. Countries like Canada could probably also utilize some of their large hydro resources to produce methanol. Besides renewables, nuclear energy, either fission or fusion if realized, is also a possible option. Despite the current backlash on this form of energy in many countries, it is a relatively economical method to produce H₂ by electrolysis of water at an estimated cost of about \$2 per kg.⁵⁶⁸ Countries, such as France, which produce a large portion 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 same is true for wind

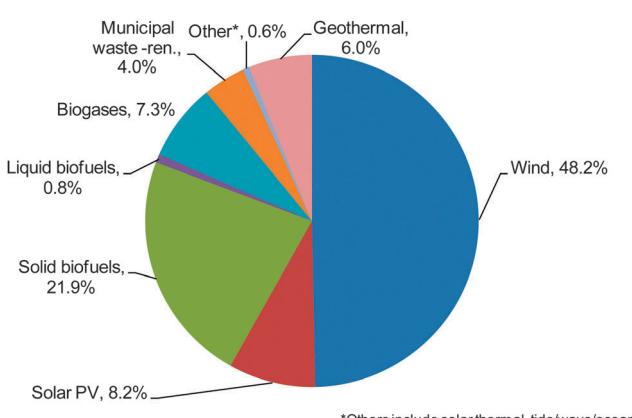


Fig. 48 Share in OECD non-hydro renewable electricity in 2012 (Source: IEA).⁵⁷¹

energy for which excess capacity might exist, especially at night when demand is low. In Denmark, a champion of wind energy, for example, according to Energinet, the Danish grid operator, the production capacity of wind now often exceeds the consumption of electricity. On December 1st, 2013, between 4:00 and 5:00, wind power produced 135.8% of the electricity needs of the country.⁵⁷⁷ As the percentage of power generated by wind increases in a grid, so does the period of time when the average power spot price for wind energy is close to zero.⁵⁷⁸ Instead of being stranded, wasted or having to export it, this low-cost electricity could be used to produce hydrogen and methanol. In the U.S., using this electricity would also allow the producer to claim the currently available federal renewable production tax credit (PTC) of 2.3 ¢ kW⁻¹ h⁻¹.

Even considering relatively low renewable electricity prices of 4 ¢ kW⁻¹ h⁻¹, the production of hydrogen through electrolysis (\$2.5–3 per kg) remains, however, high, compared with more traditional ways to produce H₂ from fossil fuels. The cost of producing methanol from CO₂ and H₂ at about \$3 per kg can be estimated at around \$600 per tonne in a large plant with a methanol production capacity of 5000 t per day.⁵⁸⁰ This price is well above the historic methanol prices around \$100–200 per tonne, but close to recent prices in North America; about \$630 per t in January 2014 (Methanex non-discounted reference price).⁵⁸¹ This translates into ~\$0.5 for 1 liter of methanol or \$1.8 per gallon. Taking into account that methanol contains only about half the energy density of gasoline, about 2 liters of methanol would be needed to replace 1 liter of gasoline in existing ICEs, which means about \$1 to replace a liter of gasoline (\$3.6 per gallon). 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 with prices as high as \$2.5 per liter (\$10 per gallon) in Norway. In Europe it could, already today, make sense to make and sell methanol produced from electrolytically generated H₂ and CO₂. Indeed, the methanol produced by CRI from geothermal energy and CO₂ is already being used for blending with gasoline not only in Iceland but also in Holland where it is being exported and sold under the name "Vulcanol".¹³⁰

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. Any reduction in the cost of electricity would therefore greatly decrease the price of methanol.

Advantages of producing methanol from CO₂ and H₂

In a conventional natural gas to methanol plant, the natural gas has to be reformed first (with steam, CO₂ and/or oxygen) to syngas in an endothermic process. Part of the energy contained in the natural gas raw material is used for this step. Subsequently, syngas is reacted in an exothermic reaction to produce methanol.

In the case of CO₂ hydrogenation with H₂, the energy consuming endothermic step of syngas generation is eliminated; hydrogen and CO₂ being generated from other sources. Only the methanol synthesis step is left unchanged. This is important because the syngas generation unit generally accounts for more than half of the total capital investment in

a natural gas based methanol plant.¹⁶⁶ For plants using coal, the capital cost of the syngas step represents even more, usually between 70–80%. The elimination of the syngas generation step simplifies and lowers the cost of the methanol plant considerably. In addition, the lower by-product content of methanol produced from CO₂ may simplify the methanol distillation step.¹⁶⁶ The capital cost to build a methanol plant based on electrically generated H₂ and CO₂ should therefore be considerably reduced compared to a conventional fossil fuel based methanol plant. Of course the methanol plant would still require the energy intensive H₂ generation from water electrolysis.

10. Reduction of greenhouse gas emission

One of the main advantages of biomass and CO₂ based methanol and DME production is the reduction of overall CO₂ greenhouse gas (GHG) emissions. For a complete life-cycle analysis, or cradle-to-grave analysis, all steps of the methanol production, distribution and use as well as the environmental impact of each of these steps including GHG emissions, other pollutant emissions (NO_x, CO, particulates, SO_x, etc.) and water use have to be taken into account. These depend on a number of parameters including the nature of the feedstocks, by-product generation, process used, type of utilization, and so on, which are beyond the scope of this article. More specific well-to-wheel (WTW) analysis for the use of methanol, DME and other fuels in the transportation sector have been performed and focus generally on GHG emissions and overall energy efficiency of the fuel pathways. The WTW analysis itself can be divided in two individual steps: Well-to-tank (WTT) and tank-to-wheel (TTW) analysis. The WTT focuses on the extraction of the raw materials, production of the fuel and its distribution to the vehicle. The TTW accounts for the utilization of the fuel in the vehicle, *i.e.* the conversion of the chemical energy contained in the fuel to kinetic energy in the power train.

Relative to conventional fuels on a well-to-tank (WTT) basis, producers estimate that renewable methanol offers carbon reduction benefits ranging from 65% to 95%.⁵⁸² These GHG benefits were among the highest for alternative fuels that can displace gasoline and diesel.

For the tank-to-wheels (TTW) portion of the full fuel cycle, methanol as a transportation fuel can also offer advantages. Methanol has a higher octane number than gasoline (RON + MON average of 100), allowing higher compression ratios, resulting in more efficient use of energy in the appropriate engine, translating into lower tailpipe emission of CO₂.¹⁶ RON and MON stand for research octane number and motor octane number, respectively. Methanol-gasoline blends also have considerably higher octane numbers than gasoline alone and were also found to reduce CO₂ emissions.^{11,583,584} Furthermore, methanol is cleaner burning than regular gasoline, reducing the emission of other pollutants. Methanol could also be used in advanced vehicles propelled by fuel cells, reducing further the tailpipe emissions. Direct methanol fuel cell vehicles are expected to be virtually zero emission vehicles (ZEV; in regard

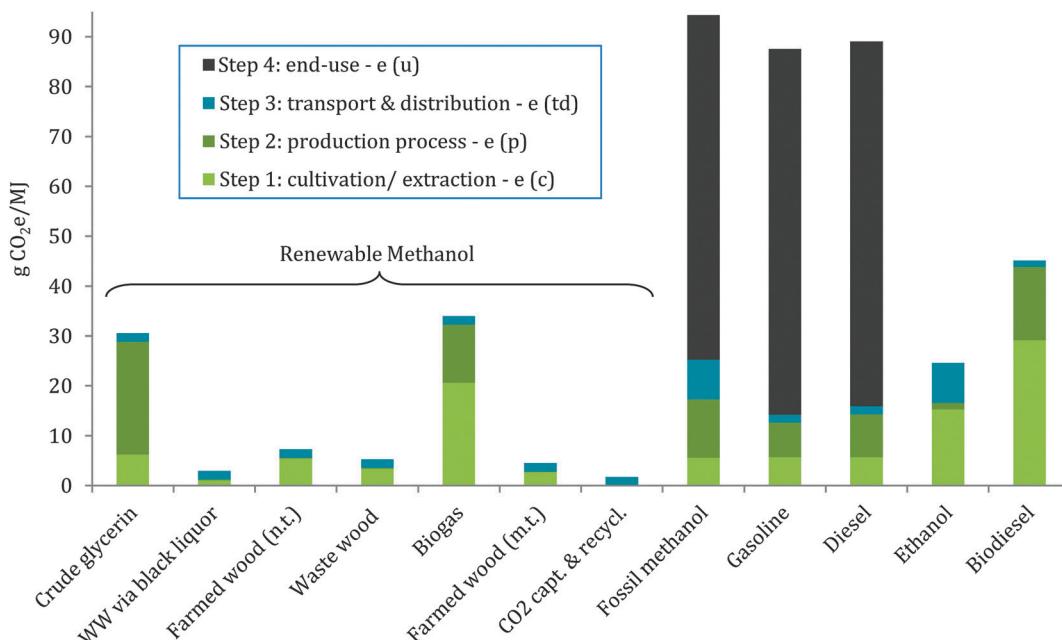


Fig. 50 WTW GHG emissions of renewable methanol and comparative fossil and biofuel pathways (gCO₂e per MJ). Reproduced with permission from ref. 589.

to pollutants other than CO₂).⁵⁸⁵ Tests conducted with Georgetown University's reformed methanol fuel cell bus have shown that it is almost a ZEV, releasing only negligible amounts of carbon monoxide and hydrocarbons, and no NO_x or particulate matter (PM).⁵⁸⁶ DME trucks developed and tested in Japan and Sweden are satisfying the most stringent PM, CO and hydrocarbon emission regulations of Japan, the EU and the U.S.^{11,587,588} Due to the intrinsic clean burning characteristics of DME, the exhaust treatment system is simpler than in existing diesel vehicles.

Comparing various biomass sources for the production of methanol, Chaplin determined that black liquor, wood waste and farmed wood had WTW CO₂ emissions of 3.3, 5.32 and 7.32 gCO₂e per MJ, respectively.⁵⁸⁹ Methanol from crude glycerin and biogas had somewhat higher emissions, with 30.6 and 34.4 gCO₂e per MJ (Fig. 50). With improvement in the farmed wood WTW CO₂ emission is expected to be lowered to 4.57 gCO₂e per MJ. The WTW CO₂ emissions of methanol from CO₂ recycling and H₂ from renewable sources was estimated at 1.74 gCO₂e per MJ. Compared to a reference fossil fuel emission of 83.8 gCO₂e per MJ,⁵⁹⁰ this is a substantial decrease. Methanol from black liquor and farmed wood, reduced WTW CO₂ emissions by about 96% and 95%, respectively. WTW CO₂ emissions reduction of methanol from CO₂ capture and recycling were estimated at 98% compared to gasoline and diesel. As such, these routes to methanol already fulfill the emission saving requirements for biofuels in the European Union, which require that all biofuels to have GHG emission reduction of at least 35% compared to emissions of 83.8 gCO₂e per MJ from a fossil fuel reference. These emission reduction requirements will be gradually increased to 50% in 2017 and 60% in 2018.

Volvo⁵⁹¹ also found that the WTW GHG emissions were reduced by about 90% for methanol and 95% for DME when

these fuels were produced from black liquor. Similar results were reported by the European Commission Joint Research Center, Institute of Energy-EUCAR-CONCAWE collaboration (JEC), which showed that for example for a diesel motor (DICI 2010 no DPF), the WTW emissions were reduced from 145 gCO₂eq per km for regular diesel to 5 gCO₂eq per km for DME from black liquor; a reduction of 97%.⁵⁹² For DME from waste wood and farmed wood the reduction was 94% and 92%, respectively.

This is well below the 95 gCO₂eq per km needed to comply with the recently proposed EU regulation on GHG emissions from new passenger cars for 2020.⁵⁹³

For heavy duty buses, WTW reductions of 94% and 96% in GHG emissions were calculated for when using DME in compression engines and methanol combined with fuel cells, respectively. In this case methanol and DME were obtained from poplar.⁵⁹⁴

As we move forward, the increased use of biomass and CO₂ recycled with H₂ from renewable energies will make carbon fuels increasingly carbon neutral and renewable on the human time scale. Eventually, CO₂ contained in the atmosphere either recycled directly or through biomass will be our predominant source of carbon, solving at the same time the problem of excess emissions of this GHG.

11. Conclusions and outlook

The energy harvested by burning of fossil fuels has allowed the rapid and unprecedented development of human society. However, the utilization of this fossilized sunshine has come at the price of adverse global environmental changes, the full extent of which we are only starting to grasp. On the other hand, even

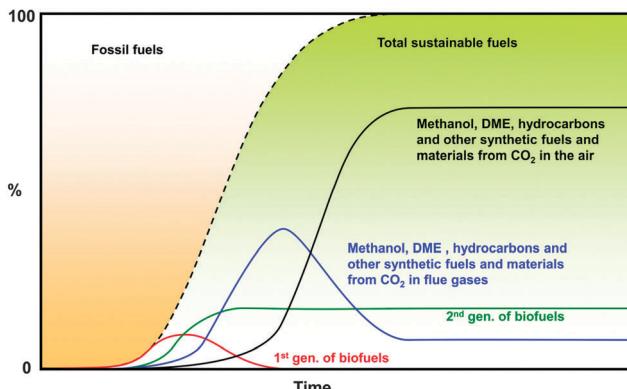


Fig. 51 Possible transition to a sustainable fuel future based on methanol and derived products. Based on ref. 595.

if reserves of fossil fuels, either conventional or unconventional are still considerable, they will eventually be depleted. As these are complex issues, there will not be a single solution. The discussed approach of chemical recycling of carbon dioxide to produce carbon neutral renewable methanol fuels and derived materials offers, however, a feasible and powerful new alternative to tackle both problems; global climate change and the inevitable depletion of fossil fuels.

The production of methanol, DME, hydrocarbons and other synthetic materials from natural and anthropogenic sources including biomass and recycling of CO₂ in flue gases of various industries could be the first steps towards an anthropogenic carbon cycle. As fossil fuels become less abundant and their use regulated by stricter emission standards, related CO₂ emissions will eventually diminish. At the same time, the amounts of biomass that can be generated in a sustainable way are large but nevertheless limited and will not be able to cover all our needs by themselves. These limitations imply that methanol and derived products would be increasingly produced from CO₂ captured from the air, which offers a nearly inexhaustible carbon source for humankind. The required energy could be provided by renewable energy sources or atomic energy, albeit made safer. Depending on varied factors, including policies, state of development, locally available resources and competing technologies, the timeline and layout for the transition to sustainable fuels and products could vary from country to country, and location to location. A tentative outline for the transition to a sustainable future for carbon fuels and hydrocarbon products is shown in Fig. 51.

Processes and catalysts for the efficient conversion of CO₂ are in various stages of development. The most mature technology for CO₂ to methanol relies on hydrogenation with H₂ on heterogeneous catalysts based on copper. However, significant bottlenecks remain, such as the cost of electricity from renewable sources needed to produce hydrogen. The amount of energy required to replace petroleum oil and other fossil fuels is also staggering. With half the volumetric energy density compared to gasoline, about 62 billion barrels of methanol (7.8 billion tonnes) would be required to replace the 31 billion barrels of petroleum presently used globally each year. This represents more than hundred times the current

methanol production of 65 million tonnes per year.³² Nevertheless, these problems are not unique to methanol and all alternative fuels face similar economic and scale hurdles.

Methanol from non-renewable sources such as natural gas and coal is already competitive with gasoline and diesel fuel, and could therefore constitute a bridge towards renewable methanol. Hybrid systems using both renewable and fossil fuels with less or no CO₂ emissions to produce methanol could also be used during the transition period. Once the infrastructure for the distribution of methanol is in place, it could be seamlessly shifted to sustainable renewable methanol in the future.

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