



**RESEARCH REPORT**

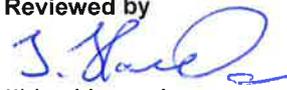
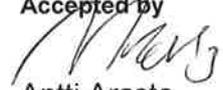
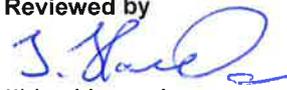
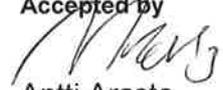
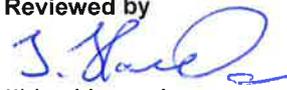
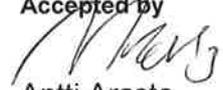
VTT-R-05484-15



# **CO<sub>2</sub> to chemicals and market study**

Authors: Vesa Arpiainen, Esa-Matti Turpeinen

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<p><b>Summary</b></p> <p>Carbon capture and utilisation (CCU) is an emerging option for controlling CO<sub>2</sub> emissions from industrial operations. Main challenges to chemical use of CO<sub>2</sub> relate to the fairly inert nature of carbon dioxide that lead to unfavourable kinetics and thermodynamics of CO<sub>2</sub> conversion. Supplies of co-reactants must be adequate and affordable and product must have demand in the markets. It has been suggested in a position paper from VCI and DECHEMA in Germany that chemical industry could convert at most around 1% of global CO<sub>2</sub> emissions in the fine and bulk chemicals sector and 10 % into synthetic fuels. Aresta estimates that chemical and fuel synthesis could utilize 7 % of the CO<sub>2</sub> emissions in the future. Therefore, CCU should not be regarded as an alternative to carbon capture and storage (CCS) but rather as a complementary technology.</p> <p>Liquid chemicals are the most interesting products from CO<sub>2</sub> due to their much higher volumetric energy content comparison to gases. Life-cycle assessments show that "CO<sub>2</sub> to chemical routes" can potentially produce more CO<sub>2</sub> than they use. So in practice all these processes need electricity from renewable energy sources in order to actually reduce CO<sub>2</sub> emissions to the atmosphere.</p> <p>The CO<sub>2</sub>-derived chemicals and fuels examined in this report were methanol, formic acid, dimethyl carbonate, ethylene carbonate and propylene carbonate. The selection of these chemicals and fuels was based on their market potential as well as their ability to consume carbon dioxide during the production step.</p> <p>It is also possible to use CO<sub>2</sub> as a feedstock for synthesis gas manufacture as well as further in C1-chemistry. Predicting the future market of such chemicals is however difficult as they are highly dependent on the development of manufacturing technology as well as possibly new emerging applications. There is a need for further investigations in terms of fundamental technology, catalyst optimization and reactor/process design in converting carbon dioxide into chemicals and fuels.</p> <p>The main part of the research (particularly catalyst development) work for various reaction routes converting CO<sub>2</sub> into chemicals is currently carried out with lab-scale equipment. At the moment methanol seems the most promising product from the CO<sub>2</sub> utilization point of view. Carbon Recycling International (CRI) is developing CO<sub>2</sub> to methanol technology with a demonstration plant producing 2 million litres per year methanol in Iceland with plans to construct a larger plant 50 million litres scale for export to other European countries. Audi has built a so called "e-gas" plant in Werlte, Germany. The plant produces about 1000 metric tons of e-gas (methane) per year, binding chemically some 2800 metric tons CO<sub>2</sub>.</p>				
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<p>Espoo 18.11.2015</p> <table border="0"> <tr> <td style="vertical-align: top;"> <p><b>Written by</b></p>             Vesa Arpiainen,            Senior Scientist         </td> <td style="vertical-align: top; padding-left: 20px;"> <p><b>Reviewed by</b></p>             Ilkka Hannula            Senior Scientist         </td> <td style="vertical-align: top; padding-left: 20px;"> <p><b>Accepted by</b></p>             Antti Arasto            Business Development Manager         </td> </tr> </table>		<p><b>Written by</b></p>  Vesa Arpiainen, Senior Scientist	<p><b>Reviewed by</b></p>  Ilkka Hannula Senior Scientist	<p><b>Accepted by</b></p>  Antti Arasto Business Development Manager
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<b>VTT's contact address</b> Teknologian tutkimuskeskus, VTT Oy, Vuorimiehentie 3, Espoo, PL1000 02044 VTT				
<b>Distribution (customer and VTT)</b> Risto Sormunen, Fortum; Mari Tuomaala, Gasum; Timo Haatainen and Steven Gust, Neste; Sebastian Teir, Ilkka Hannula and Antti Arasto, VTT; Riitta Keiski, University of Oulu				
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## Preface

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This work was carried out in the Carbon Capture and Storage Program (CCSP) research program coordinated by CLIC Innovation Oy with funding and support from Fortum Oyj, Neste Oyj, Gasum Oy and the Finnish Funding Agency for Technology and Innovation, Tekes. This work was part of the subtask 2.6.4 “Evaluation of CCUS concepts for biogenic CO<sub>2</sub> from biorefineries”. The selection of “CO<sub>2</sub> to chemicals” routes was based on survey carried out in University of Oulu during spring 2015. Market study, based on the results from the public literature, includes estimates on price and global demand of chemicals as well as a short survey in competing production routes of these chemicals. Market study was carried out at VTT during summer 2015. Steering group was comprised of Risto Sormunen, Fortum, Hannu Kaikkonen and Steven Gust, Neste and Mari Tuomaala, Gasum.

## Contents

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Preface .....	3
Contents .....	4
1. Introduction .....	5
2. Description of chemical and fuel market and production routes in use or developed for CO <sub>2</sub> utilization .....	7
2.1 Methanol.....	7
2.1.1 Methanol industry outlook .....	7
2.1.2 Carbon dioxide route for methanol .....	11
2.2 Synthesis gas .....	13
2.2.1 Industrial synthesis gas production and CO <sub>2</sub> routes for synthesis gas production.....	13
2.3 Synthetic natural gas (SNG).....	15
2.3.1 Synthetic natural gas from biomass or coal .....	15
2.3.2 CO <sub>2</sub> routes for synthetic natural gas.....	16
2.4 Formic acid .....	17
2.4.1 Formic acid industry outlook.....	17
2.4.2 CO <sub>2</sub> routes for formic acid .....	18
2.5 Cyclic carbonates .....	19
2.5.1 Industry outlook of cyclic carbonates .....	19
2.6 Dimethyl carbonate (DMC).....	20
2.6.1 Dimethyl carbonate industry outlook .....	20
2.6.2 CO <sub>2</sub> routes for dimethyl carbonate .....	23
3. Conclusions .....	25
References .....	26
Appendix 1 CO <sub>2</sub> to chemicals (Excel table from Teir et al. 2015).....	29

## 1. Introduction

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Carbon capture and utilisation (CCU) is an emerging option for controlling CO<sub>2</sub> emissions from industrial operations. According to Styring (2011), barriers to implementation include:

- The unfavourable thermodynamics of CO<sub>2</sub> conversion leading to high cost of energy associated with utilization;
- Limited availability of co-reactants and also in market demand for CO<sub>2</sub>-derived products;
- A position paper from VCI and DECHEMA in Germany (VCI and DECHEMA 2009) suggested that chemical industry could convert at most around 1% of global CO<sub>2</sub> emissions in the fine and bulk chemicals sector and 10 % into synthetic fuels. Aresta (Aresta 2010) estimates that chemical and fuel synthesis could account for 7 % of the CO<sub>2</sub> emissions in the future;
- Therefore, CCU should not be regarded as an alternative technology to CCS but as complementary technology;
- The low values predicted for utilisation are related to market demand for current products and cost of production. These problems should be addressed by identifying new C-1 chemistries and catalytic processes, and by reducing the cost of processing through intensification, and new capture agents with higher efficiencies and smaller volumes.

According Teir (Teir 2015) travel report from ICCDU-XIII International Conference CO<sub>2</sub> utilisation is gaining interest, with the possibility to use CO<sub>2</sub> as a raw material for energy storage being the latest option, particularly due to [Audi's e-gas project](#), that uses electricity and CO<sub>2</sub> to produce synthetic natural gas. Still, chemists at the conference were of the opinion that liquid chemicals are more interesting products due to their high volumetric energy density in comparison to gases and are therefore more especially suitable for energy storage solutions. At the conference, methanol was considered to be the most promising product from CO<sub>2</sub> utilisation.

During the ICDDU -XIII conference, Teir constructed a spreadsheet table giving an overview of various chemicals that can be produced from CO<sub>2</sub> (attached in appendix). The table is intended for use in the CCSP project task 2.6.4 as part of a deliverable. Table 1 shows a summary from the spreadsheet file of the current market and potential future market for chemicals that are produced from CO<sub>2</sub>. It should be noted that term "future market" is not the same in the various studies referred in Table 1. The "CO<sub>2</sub> chemicals or fuels" chosen for this report for further examination were methanol, formic acid, synthetic natural gas, cyclic carbonates (ethane carbonate and propene carbonate) and acyclic carbonates (dimethyl carbonate, DMC) shown also in Table 1. In addition to the above mentioned chemicals and fuels this report also discusses synthesis gas technologies as it is possible to use CO<sub>2</sub> in the manufacture of syngas and also in C1-chemistry. In dry reforming technology, which is in research and development (R&D) stage, carbon dioxide reacts with methane in the presence of catalyst. Other alternatives capable of utilising CO<sub>2</sub> in synthesis gas production, include bireforming and trireforming, which are also included in this report.

Large part of current R&D work is focused on catalyst development for various reaction routes converting CO<sub>2</sub> into chemicals. The main part of the current work is carried out in lab scale units with only a few exceptions. Life-cycle assessments show that in order to produce sustainable end-product, the energy input of the manufacturing process needs to come from renewable sources.

Table 1 Current and future market potential for chemicals and fuels that are produced from CO<sub>2</sub> (Teir 2015).

Product	Current market (Mtpa)	Current market (CO <sub>2</sub> Mtpa)	Future market (Mtpa)	Future market (CO <sub>2</sub> Mtpa)
Methanol (CH <sub>3</sub> OH)	60	10		>300
Urea (H <sub>2</sub> NCONH <sub>2</sub> )	180	132	210	154
Carbamates (RR'NCO <sub>2</sub> )	6	1	11	4
Salicylic acid (Carboxylic acids)	0.06	0.02	0.1	
Formic acid (HCOOH)	1	0.9		>300
<b>Organic carbonates ((RO)<sub>2</sub>CO, total market)</b>		0.2		100
Acyclic carbonates (Dimethyl carbonate, DMC)	< 2	0.5	10	5
Cyclic carbonates (ethene-, propene-, styrene carbonate)	2		45	
<b>Polymers, polycarbonates (total market)</b>	5	1	10	3
Polyethylene carbonate (assuming PEC could replace PE)	45	0	50	25
Polypropylene carbonate (assuming PPC could replace PP)	80	0	90	45
Polyurethane	10	<10		
<b>Inorganic carbonates (total market)</b>	200		400	100
Calcium carbonate (CaCO <sub>3</sub> )	114	50 (calculated)		
Sodium carbonates (Na <sub>2</sub> CO <sub>3</sub> )	50	15 (25% mined)		<1
Magnesium carbonates (MgCO <sub>3</sub> )	3.5	mainly mined		>300

Data references colour coded accordingly:

Mikkelsen 2010 and IPCC 2005
Styring 2011
GCCSI(2011)
Aresta (2014)
Aresta (2015)

In addition to the above-mentioned chemicals and fuels, there exist (at least in theory) numerous compounds that can be synthesized from CO<sub>2</sub>. Some of the most interesting ones are listed in Table 2. Detailed information on 123 different CO<sub>2</sub> utilization reactions is available in the review article by Otto (2015).

Table 2 Chemical compounds/groups from carbon dioxide depending on the co-reactants.

Co-Reactant(s)	Product
Hydrogen	Alcohols, ethers, hydrocarbons, aldehydes, carboxylic acids, carbon monoxide
Alcohols	Linear carbonates
Ammonia	Urea
Epoxides or Dioles	Cyclic carbonates
Alkenes	Unsaturated carboxylic acids
Alkynes	Lactones and pyrones
Amines	Linear urea derivatives
Diamines	Cyclic urea derivatives
Amines or ammonia + alcohols	Linear carbamates
Amino alcohols	Cyclic carbamates
Organic compounds	Carboxylic acids
Organometallic compounds	Carboxylic acids
Dienes	Lactones
Allenes	Pyrones

Due to the thermodynamically stable nature of CO<sub>2</sub> molecule, substantial energy input, active catalysts, and optimum reaction conditions are necessary for successful and viable CO<sub>2</sub> conversion. The main part of the CO<sub>2</sub> related R&D work has especially been focused on catalyst development for various reaction routes converting CO<sub>2</sub> into valuable chemicals and fuels.

The selection of CO<sub>2</sub> based chemicals and fuels (Table 2) for further study was based on their market potential as well as their ability to consume carbon dioxide in the production step (Table 1).

## 2. Description of chemical and fuel market and production routes in use or developed for CO<sub>2</sub> utilization

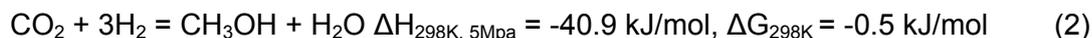
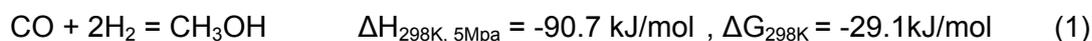
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### 2.1 Methanol

#### 2.1.1 Methanol industry outlook

Methanol is synthesised by hydrogenation of carbon oxides over catalysts composed of copper oxide and zinc oxide stabilised with alumina. These catalysts allow the production of methanol at over 99.9 % selectivity with higher alcohols as primary by-products. ICI process has been in use since 1960. Synthesis temperature and pressure is 250-280 °C and 6.0-8.0 MPa. H<sub>2</sub>S concentration in synthesis gas must be below 1 ppm (typical for synthesis gas from natural gas steam reformers). Largest plants produce methanol over 500 metric tons per day (MTPD) (Hannula 2013).

The main reactions in commercial synthesis are:



In addition to the equations (1) and (2) the reverse water-gas shift reaction (3) must be taken into account in the methanol synthesis.



Both reactions (1 and 2) are exothermic and result reduction of volume. Main reaction goes through carbon monoxide and hydrogen. The maximum content of carbon dioxide in methanol synthesis gas is about 5 volume%. In practice the content of carbon dioxide in synthesis gas is normally about 1 volume%.

As a chemical product, methanol is a key component of a variety products used daily. Methanol is produced in Asia, North and South America, Europe, Africa and the Middle East. Worldwide over 90 methanol plants have a combined production capacity of about 75 million metric tons, and each day more than 100 000 tons is used as a chemical feedstock or as a transportation fuel. Methanol is also a truly global commodity and each day there is more than 80 000 metric tons of methanol shipped from one continent to another. Methanol is used as a feedstock for the production of formaldehyde used to produce resins to bond woods used in building homes and furniture, or as component of urethanes and plastics used to make accessories for cars and in the production of acetic acid for making polyethylene terephthalate (PET). Acetic acid is also the basic component of terephthalic acid (PTA), which is used in making polyester fibre or clothing or carpets (Dibenedetto 2014). The demand of methanol for chemicals and fuels is visualized in Figure 1 (Chesko 2014).

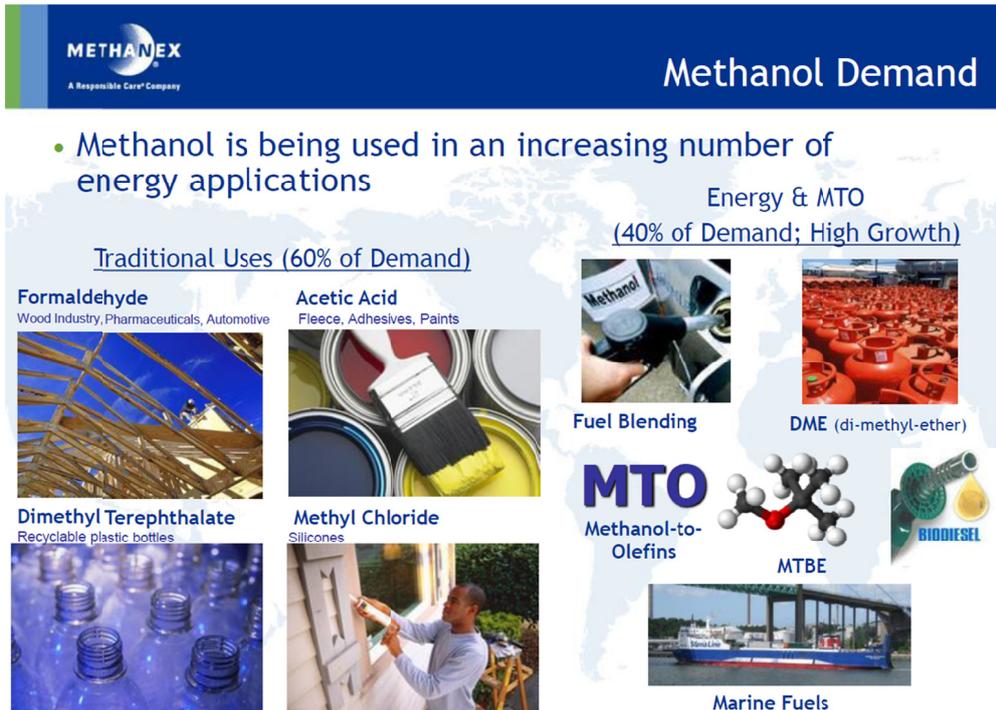


Figure 1 Methanol demand for chemicals and fuels (Chesko 2014).

Today methanol is mainly produced by reforming of natural gas or by gasification of coal (China). The simplified diagram of reforming process is shown in Figure 2. In the future the amount of methanol produced from lignocellulosic feedstocks via biomass gasification is predicted to increase (Chesko 2014). Linde Group has a contract with Saudi Basic Industries Corporation (SABIC) to build world largest CO<sub>2</sub> purification and liquefaction plant in Jubail City. Mechanical completion is set to be achieved in 2015. The plant will compress about 500 000 t/a CO<sub>2</sub> from ethylene glycol plants, which will then be piped for use in methanol (first and second reaction of commercial synthesis in this chapter) and urea production (Linde 2013)

Biomass gasification processes for synthesis applications are in a pre-commercial development stage (Hannula 2013). The catalytic production of methanol from the mixture of carbon dioxide and hydrogen is shortly reported in chapter 2.1.2 (proceeding through only second reaction above).

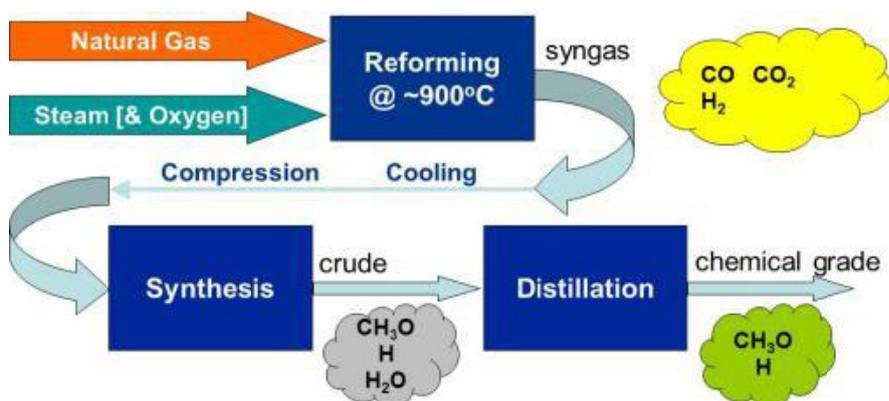


Figure 2 Simplified flow diagram of methanol production by steam reforming natural gas (Chesko 2014).

The global production of methanol in 2013 was 60 million metric tons. The global production capacity is higher, which is due to that the world biggest producer China operates their plants only at 45-50 % rates. The regional production of methanol in 2013 is shown in Figure 3 (Chesko 2014).

China is the biggest user of methanol (44 %, Figure 4). Nearly one third of methanol is used as a raw material in formaldehyde production. Methanol is increasingly used in energy applications (about 40 % of demand, fuel blending, biofuels and marine fuels). Traditional uses (formaldehyde, acetic acid, dimethyl terephthalate, methyl chloride) cover about 60 % of demand (Figure 1, Chesko 2014).

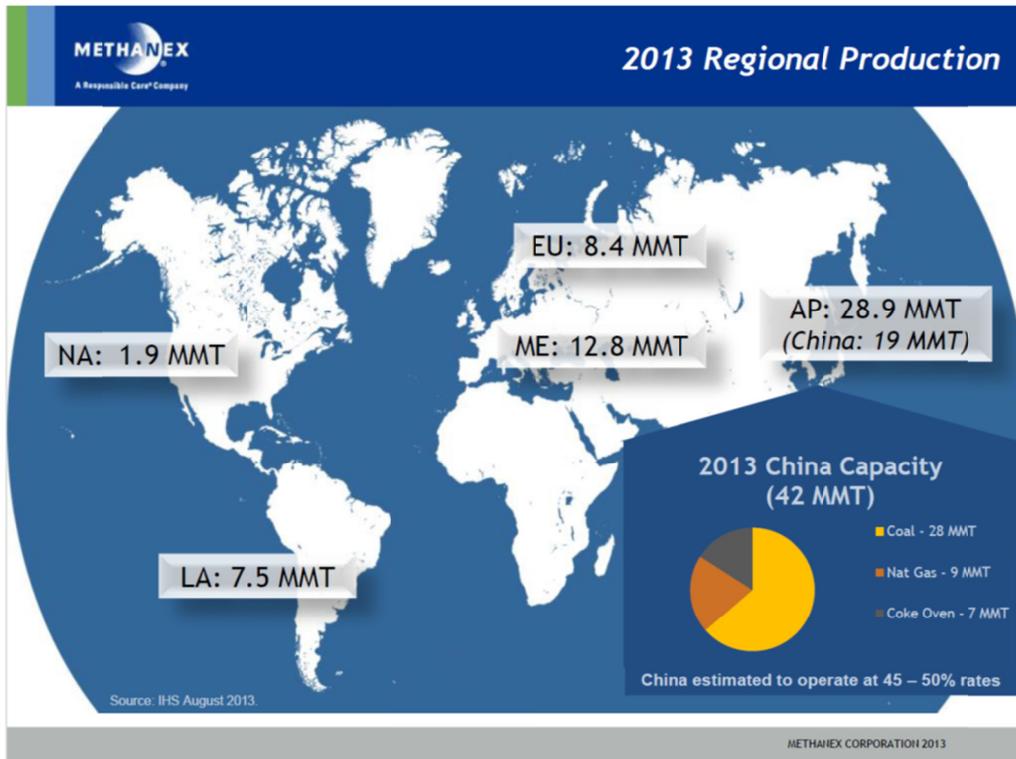


Figure 3 Regional methanol production in 2013 (Chesko 2014).

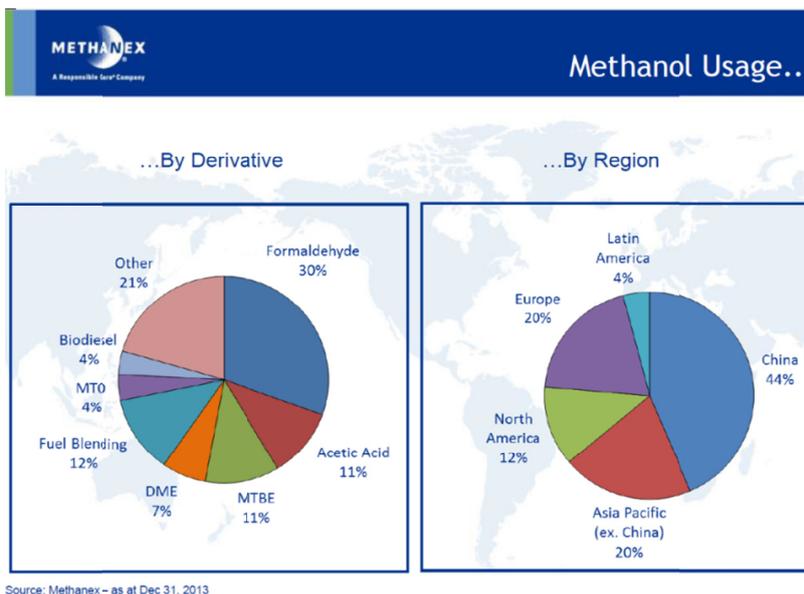


Figure 4 Methanol use by derivative and by region (Chesko 2014).

The estimated consumption of methanol up to 2017 in different purposes is given in Figure 5. Methanol spot price is now about 320 €/metric ton (Figure 6, Chesko 2014)

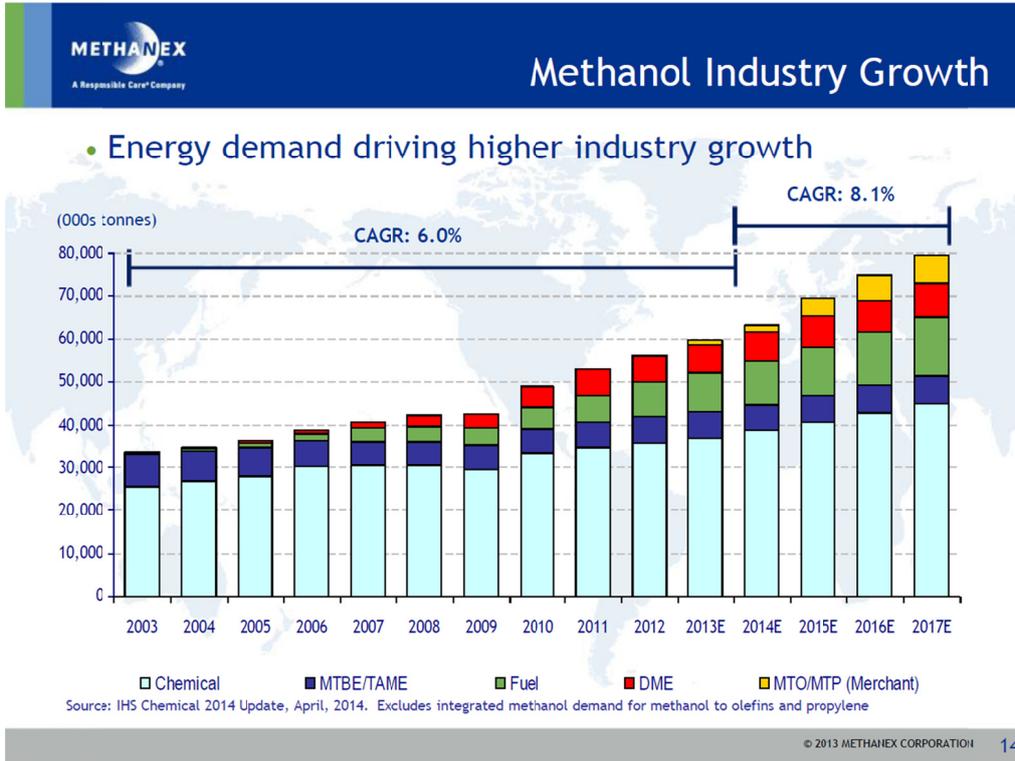


Figure 5 Methanol industry growth 2003-2017 (Chesko 2014).

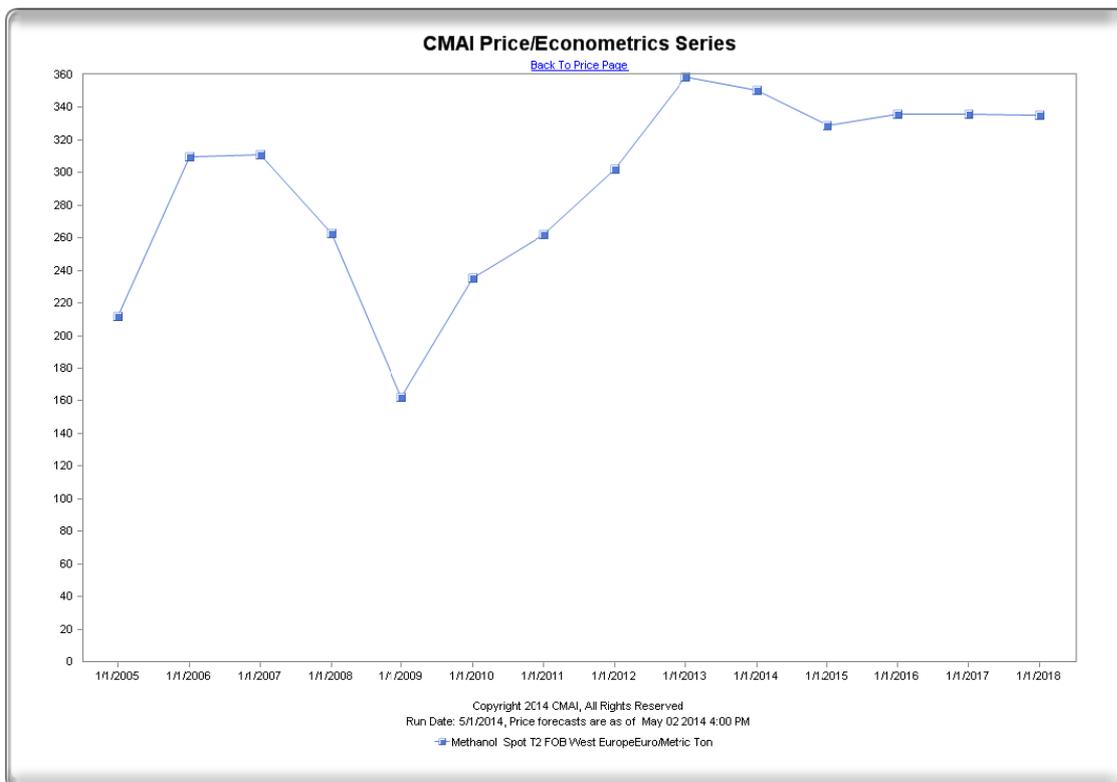


Figure 6 Methanol spot price (Chesko 2014).



(PB) estimates the thermal efficiency of the catalytic process is 75 % or better. CRI's preferred embodiment is probably a conventional geothermal power station, as it is low-emission source of electricity that still produces enough CO<sub>2</sub> (typically) to use as a feedstock for the methanol production process. As a replacement for fossil fuels, the potential market for CO<sub>2</sub> derived fuels is large and global. Consumption of fossil fuels for transport on 2007 was 2297 million metric tons of oil equivalent (GCCSI 2011).

The CRI methanol production process is described in Figure 7. All feedstock and utilities (electricity, carbon dioxide, steam, hot and cold water) are sustainably sourced from the local geothermal area and no fossil fuel is used in the production process. The process does not compete with food or feed production, has minimal land requirement and reaches 90 % reduction in GHG compared to gasoline (Sigurbjörnsson 2013).

### CRI production process

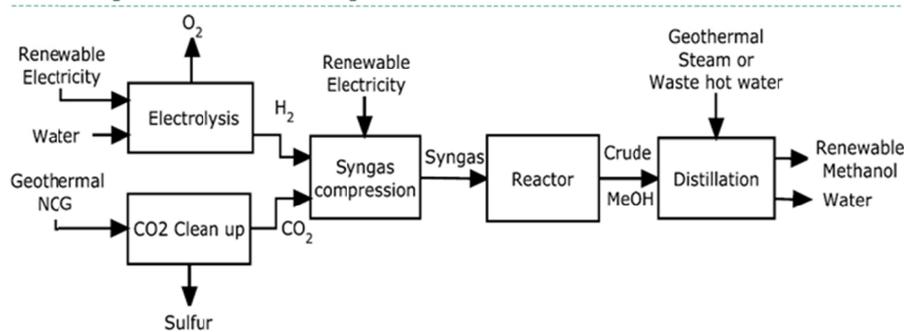


Figure 7 Carbon recycling International (CRI) methanol production process (Sigurbjörnsson 2013).

The pilot plant has been operated since 2007. The demonstration plant producing 2 million litres methanol was completed at the end of 2012. CRI plans to produce more than 5 million litres per year by 2014. Renewable methanol will be blended with gasoline and sold at gasoline stations in Iceland and abroad. CRI plans to construct also a larger plant in Iceland that will produce 50 million litres renewable methanol per year for export to other European countries ([www.carbonrecycling.is](http://www.carbonrecycling.is) 2015). The photo of 1.7 million litres methanol plant is given in Figure 8 (Sigurbjörnsson 2013).



Figure 8 Carbon recycling International's 1.7 million litres per year renewable methanol producing plant (Sigurbjörnsson 2013).

Mitsui Chemicals is operating a 100 t/a pilot plant producing methanol from  $\text{CO}_2$  and  $\text{H}_2$ .  $\text{CO}_2$  is captured from ethylene production, whilst  $\text{H}_2$  is produced from catalysed photolysis of water. Methanol is intended to be used in polymer synthesis, rather than liquid fuels (GCCSI 2011).

## 2.2 Synthesis gas

### 2.2.1 Industrial synthesis gas production and $\text{CO}_2$ routes for synthesis gas production

Synthesis gas, which is a mixture of carbon monoxide and hydrogen, is an important intermediate product (Figure 9, Bertau 2015) in manufacturing many chemicals and fuels. At the moment synthesis gas is industrially produced mainly by steam reforming of natural gas. The product gas from reforming is purified from impurities and the carbon monoxide and hydrogen ratio is adjusted to meet the stoichiometric requirement of the catalytic synthesis. Partial oxidation of methane is suitable for the production of heavier hydrocarbons and naphtha. In China methanol is produced via synthesis gas produced by gasification of coal. In Western countries coal gasification routes are not currently used, mainly because of economic and environmental reasons. In the future, it is predicted, that syngas will also be produced increasingly from renewable lignocellulosic feedstock via biomass gasification processes (Chesko 2014). More detailed information on the development of biomass synthesis gas technology is available in many reviews, for example in Hannula 2013. In this chapter only methane based conversion routes to synthesis gas is further discussed.

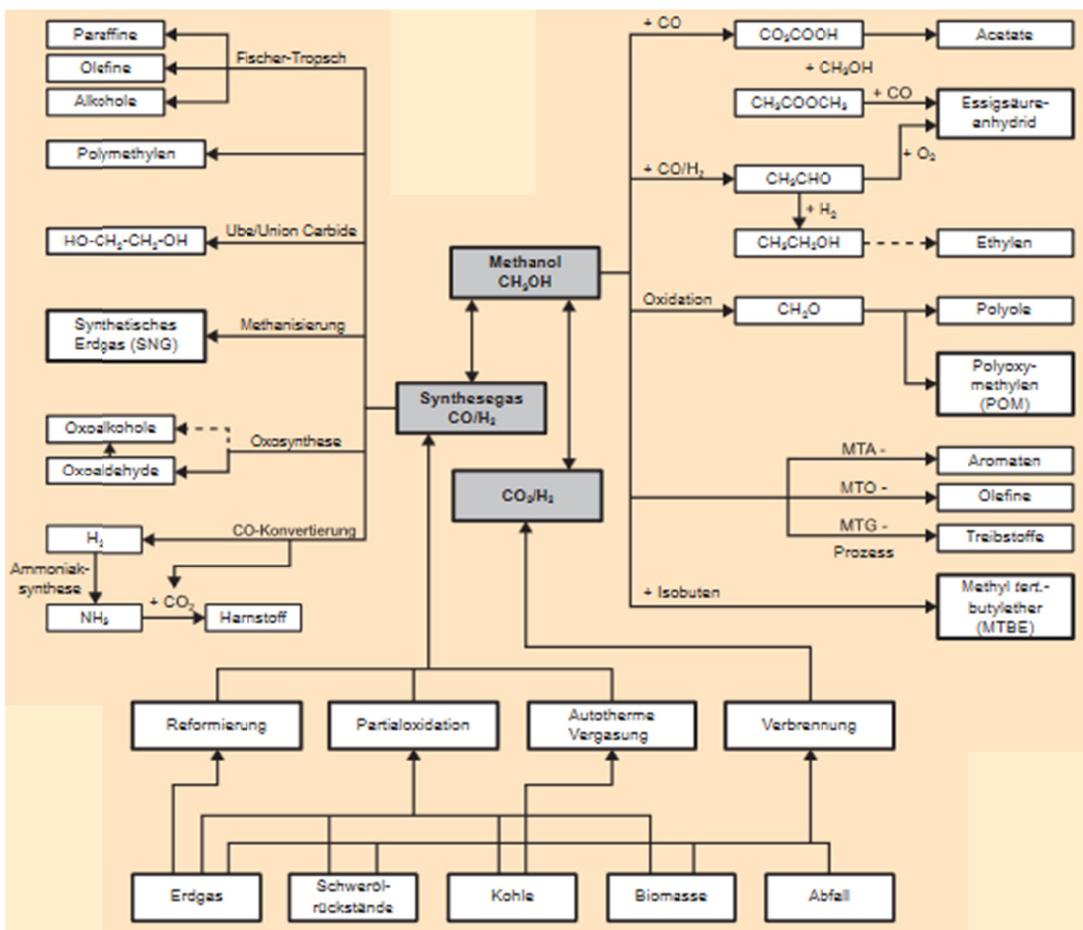
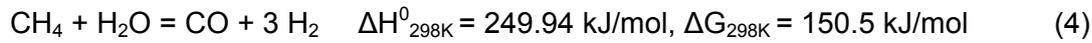


Figure 9 Synthesis gas and methanol can be utilized as a raw material of various chemicals and fuels (Bertau 2015).

The three processes that draw industrial attention in syngas production are steam reforming of methane (equation 4), partial oxidation of methane with oxygen or air (equation 5) and dry reforming of methane with carbon dioxide (equation 6):



Reforming of methane through steam or partial oxidation of methane with oxygen or air are well-established technologies with the advantages and disadvantages. Steam reforming of methane produces a higher ratio of syngas ( $\text{H}_2/\text{CO}=3$ ) compared to that required for Fischer-Tropsch or methanol synthesis ( $\text{H}_2/\text{CO}=2$ ). The process is energy intensive due to the endothermic nature and requires high investments of capital. Moreover steam reforming faces corrosion issues. Partial oxidation of methane is suitable for the production of heavier hydrocarbons and naphtha. The advantages of this process are high conversion rates, high selectivity and very short residence time. The exothermic nature of reaction has certain drawbacks that it induces hot spots on catalyst arising from poor heat removal rate and makes operation difficult to control. Cryogenic unit is necessary for the separation of oxygen from air (Usman 2015).

Dry reforming of methane offers valuable environmental benefits: biogas utilization, removal of GHG by conversion of methane with carbon dioxide to valuable syngas. Dry reforming of methane yields a lower syngas ratio ( $\text{H}_2/\text{CO}=1$ , equation 6 above), which is suitable for the synthesis of oxygenated chemicals and hydrocarbons from Fischer-Tropsch synthesis. Syngas from dry reforming has also been considered for storage of solar or nuclear energy through the chemical energy transmission system. Solar energy can convert feed gases (methane and carbon dioxide) to syngas that can be exported to places where energy sources are scarce. The energy stored in syngas is liberated by the backward reaction and utilized as an energy source (Usman 2015).

The production of syngas from dry reforming is governed by reverse water gas shift reaction (RWGS, equation 3) resulting in a syngas ratio less than unity ( $\text{H}_2/\text{CO} < 1$ ).



Dry reforming of methane suffers from carbon deposition problem induced by methane decomposition (equation 7) especially at temperatures higher than 550 °C and CO disproportionation reaction or Boudouard reaction (equation 8) especially at temperatures lower than 400 °C.



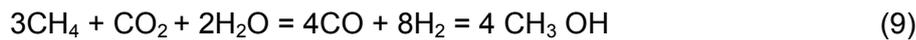
The tendency towards carbon deposition can be estimated by the ratio of O/C and H/C in the feed gas. The higher tendency towards carbon deposition will be observed in lower O/C and H/C ratio, which is the gas in dry reforming methane ( $\text{CH}_4/\text{CO}_2 = 1$ ) having O/C = 1 and H/C = 2. Reverse case was observed for steam reforming of methane ( $\text{CH}_4/\text{H}_2\text{O} = 1$ ) having O/C = 1 and H/C = 6 (Usman 2015).

Similarly, partial oxidation of methane ( $\text{CH}_4/0.5\text{O}_2$ ) showed a quite high ratio O/C = 1 and H/C = 4. Considering the aforementioned ratios, it was clear that dry reforming of methane has a higher tendency to towards carbon deposition compared to steam reforming or partial oxidation of methane. Thermodynamic studies on dry reforming reaction revealed that spontaneous reaction cannot be achieved below 640 °C and the side reactions took place at a significant rate between 633 °C and 700 °C: Therefore a higher temperature ( $T > 700$  °C)

was employed to minimize the effect of side reactions, which lead to reactor blockages and reduction in activity (Usman 2015). Djinic (2012) reported little higher temperatures than the previous report ( $> 750\text{ }^{\circ}\text{C}$ ).

Bimetallic (Ni-Pt, Ni-Rh, Ni-Ce, Ni-Mo, Ni-Co) and monometallic (Ni) catalysts are preferred for dry reforming comparing to noble metals (Rh, Ru, Ir and Pt) due to their low cost. Investigation of support materials indicated that ceria- zirconia mixtures,  $\text{ZrO}_2$  with alkali metals ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Y}^{2+}$ ) addition, MgO, SBA-15, ZSM-5,  $\text{CeO}_2$ ,  $\text{BaTiO}_3$  and  $\text{Ca}_{0.8}\text{Sr}_{0.2}\text{TiO}_3$  showed improved catalytic activities and decreased carbon deposition. The modifying effects of cerium (Ce), magnesium (Mg) and yttrium (Y) were significant for dry reforming of methane. MgO,  $\text{CeO}_2$  and  $\text{La}_2\text{O}_3$  promoters for metal catalysts supported on mesoporous materials and had the highest catalyst stability among the studied promoters. More about catalyst studies is given in this review article (Usman 2015). Other catalytic review studies for dry reforming are reported by Ma (2009), Lavoie (2014) and Budinan (2012).

In contrast to conventional syngas mixtures, George A. Olah developed a technology for methanol synthesis that generates syngas with a ratio  $\text{CO}/\text{H}_2 = 1:2$  called "metgas" in a single step process combining methane (or natural gas),  $\text{CO}_2$ , and steam in a 3:1:2 ratio. This process called bireforming (equation 9) is carried in a pressurized system at temperatures of 1073-1273 K and pressures of 0.5-4 MPa over a nickel-based catalyst (Olah 2013):



A different approach, useful for the conversion and utilization of  $\text{CO}_2$  for syngas production is called trireforming which is a synergetic combination of  $\text{CO}_2$  reforming (equation 6), steam reforming (equation 4) and partial oxidation (equation 5) (Dibenedetto 2014).

Trireforming can produce synthesis gas with  $\text{H}_2/\text{CO}$  molar ratio in the range of 1.5 - 2.0 and could eliminate carbon formation, which is a serious problem in the  $\text{CO}_2$  reforming (dry reforming) of methane.

The syngas produced could then with above methods be converted to hydrogen, methanol (a precursor for polymers), dimethyl carbonate (an automotive fuel additive and intermediate to polycarbonates), dimethyl ether (a fuel additive and aerosol propellant) or hydrocarbons, hence providing a long term or temporary sink for carbon (Song 2001a, 2001b, 2004).

## 2.3 Synthetic natural gas (SNG)

### 2.3.1 Synthetic natural gas from biomass or coal

Production of synthetic natural gas (SNG) is well established, but not much industrially applied. Besides the generation of electricity and liquid fuels, also the conversion of solid feedstock (coal, biomass) to synthetic or substitute natural gas (SNG) has been investigated in the past. SNG is a versatile energy carrier that is interchangeable to natural gas. The advantages of SNG are the high conversion efficiency, the already existing gas distribution infrastructure such as pipelines and the well-established and efficient end use technologies, e.g. CNG cars, heating, CHP power stations.

Coal and biomass have to be converted to SNG by thermochemical process via gasification and subsequent methanation, reaching an overall efficiency from biomass to SNG up to 65 %. The production of SNG via thermochemical process requires several conversion steps (Figure 10).

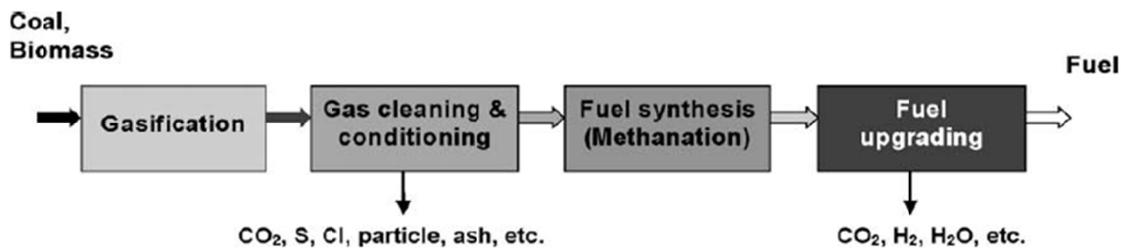


Figure 10 Simplified flow diagram for the production of SNG from biomass or coal.

The fuel synthesis itself is a heterogeneously catalysed process. In the hydrogenation of carbon monoxide reacts with hydrogen to methane in a so called methanation reaction (equation 10). Important side reaction is Boudouard reaction (equation 8), which can in certain circumstances poison the normally used nickel-based catalyst. The hydrogen to carbon monoxide molar ratio is normally over 3 in synthesis reactor. More about SNG synthesis is discussed in technology review (Kopyscinski 2010).



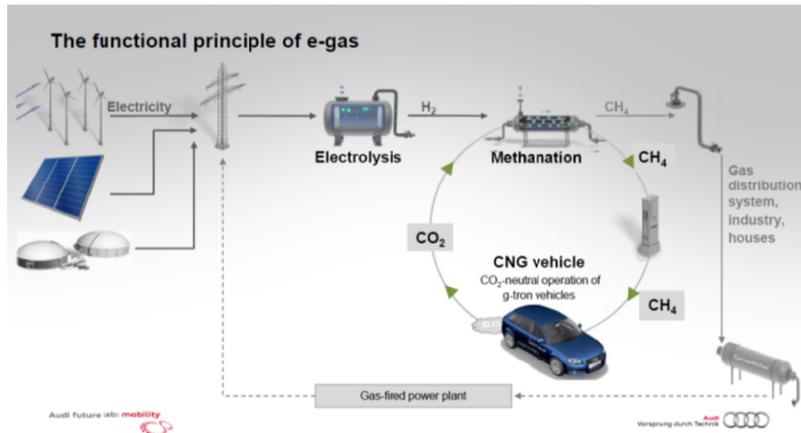
### 2.3.2 CO<sub>2</sub> routes for synthetic natural gas

Catalytic hydrogenation of CO<sub>2</sub> to methane, also called Sabatier reaction (equation 11), is an important catalytic process:



Hydrogenation of methane has been investigated using a number of catalytic systems based on VIII B metals (e.g. Ru and Rh) supported on various oxides (e.g. SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub> and CeO<sub>2</sub>). Supported nickel catalysts remain the most widely studied materials. Supports with high surface area, usually oxides, have been applied extensively for the preparation of metal catalysts. The nature of support plays a crucial role in the interaction between nickel and support, and thus determines catalytic performances toward activity and selectivity for CO<sub>2</sub> methanation (Wang 2011, Chang 2003)

Audi has built the e-gas plant in Werlte, Germany (start-up in fall 2013). In the first step plant uses surplus green electricity to break water down into oxygen and hydrogen. A second process is methanation, where hydrogen is reacted with CO<sub>2</sub> to produce synthetic methane or Audi e-gas. The Audi e-gas plant produces about 1000 metric tons of e-gas per year, chemically binding some 2800 metric tons CO<sub>2</sub>. The functional principle of e-gas plant and key performance indicators are given in Figure 11 (Otten 2014).



**Key Performance Indicators Audi e-gas plant (Werlte)**

Energy content e-gas (average)	13,85 kWh/kg	
Electricity input (prognosis)	26 – 29 GWh/a	
Power input electrolyzers	3 x 2 MW	
Efficiency „power to gas“ (without using heat)	54 %	
Max. H <sub>2</sub> output	1300 Nm <sup>3</sup> /h	
Max. H <sub>2</sub> storage time	60 min	
Max. e-gas output	325 Nm <sup>3</sup> /h	
Operation time (prognosis)	4.000 h/a	
e-gas output (prognosis)	1000 t/a	

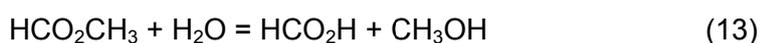
Figure 11 The functional principle of e-gas plant and key performance indicators (Otten 2014).

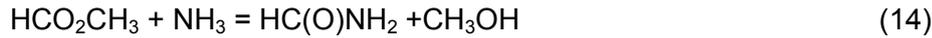
Using e-gas can be considered carbon neutral if the electricity used in the production plant was generated from renewable sources. Audi e-gas is practically identical to fossil based natural gas and is fed into existing natural gas network and distributed to filling stations. The amount of Audi e-gas is enough to power some 1500 Audi A3 Sportback g-tron cars, each of which can clock up to 15 000 kilometres of CO<sub>2</sub> neutral driving [Audi's e-gas project](#).

## 2.4 Formic acid

### 2.4.1 Formic acid industry outlook

Methyl formiate is formed, when methanol and carbon monoxide are combined in the presence of a strong base (equation 12). In industry this reaction is performed in the liquid phase at elevated pressures. Typical reaction conditions are 80 °C and 4.0 MPa. The most widely used base is sodium methoxide. Hydrolysis of the methyl formiate produces formic acid (equation 13). Efficient hydrolysis of methyl formiate requires of large excess of water. Some routes proceed indirectly by first treating the methyl formiate with ammonia to give formamide (equation 14), which is then hydrolysed with sulphuric acid. A disadvantage of this approach is the need to dispose of the ammonium sulphate by-product (equation 15). This problem has led some manufacturers to develop energy-efficient methods of separating formic acid from the large excess amount of water used in direct hydrolysis. In one these processes (used by BASF) the formic acid is removed from water via liquid-liquid extraction with organic base [https://en.wikipedia.org/wiki/Formic\\_acid](https://en.wikipedia.org/wiki/Formic_acid)





Formic acid is also a by-product of acetic acid production. The catalytic hydrogenation of  $\text{CO}_2$  to formic acid has long been studied (chapter 2.4.2).

A major use of formic acid is as a preservative and antibacterial agent in livestock feed. In Europe it is applied on silage (including fresh hay) to promote the fermentation of lactic acid and to suppress the formation of butyric acid. It also allows fermentation to occur quickly, and at lower temperature reducing the loss of nutritional value. Formic acid arrests certain decay processes and causes the feed to retain its nutritive value longer, and so it is widely used to preserve winter feed for cattle. In the poultry industry, it is sometimes added to feed to kill *E.coli* bacteria (instead of antibiotics). Use as a preservative for silage and (other) animal feed constituted 30 % of the global consumption in 2009. Formic acid is also significantly used in the production of leather, including tannin (23 % of the global consumption in 2009), and in dyeing and finishing of textile (9 % of the global consumption in 2009), because of its acidic nature. Use as a coagulant in the production of rubber constituted in 2009 6 % of the global consumption (Bizzari 2010).

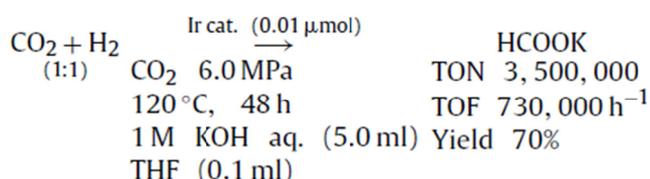
In 2009 the worldwide capacity of producing formic acid was 720 000 tonnes per annum, roughly equally divided between Europe (350 000 t/a, mainly in Germany) and Asia (370 000 t/a, mainly in China), while production was below 1 000 tonnes per annum in all other continents. It is commercially available in solutions of various concentrations between 85 and 99 w/w % (balance is water). As of 2009, the largest producers were BASF, Kemira, LC Industrial and Feicheng Acid Chemicals, with largest facilities in Ludwigshafen (200 000 metric tons/annum, BASF, Germany), Oulu (105 000, Eastman Chemical Company, formerly Kemira, Finland), Nakhon Pathom (n/a, LC Industrial) and Feicheng (100 000, Feicheng China). In 2010 the prices of formic acid ranged from €650/metric ton (equivalent to around \$800/metric ton) in Western Europe to \$1250/metric ton in United States (Bizzari 2010).

#### 2.4.2 $\text{CO}_2$ routes for formic acid

The syntheses of formic acid by the hydrogenation of carbon dioxide have been enthusiastically investigated with many transition metal compounds and some non-transition metal compounds. These reactions start with the insertion of carbon dioxide into a metal hydrogen bond. High turnover number (TON) and turnover frequency (TOF) values have been already been achieved in the production of formic acid by the hydrogenation of carbon dioxide in the presence of Ru and Rh metal compounds as the catalysts (Omae 2006, 2011, equation 16).



Recently formic acid was prepared by the reaction of carbon dioxide with hydrogen in the presence of transition metal compounds: Ru, Rh and Ir (Omae 2012). In 2009 a significant breakthrough in catalyst efficiency for the hydrogenation of carbon dioxide was reported by Nozaki (Tanaka 2010). This was achieved in the presence of an Iridium pincer compound and potassium hydroxide. Excellent TON (3,500,000) and TOF ( $150,000 \text{ h}^{-1}$ ) were obtained. The reaction is:



More about formic acid production R&D work of catalysts is discussed in reviews of Wang 2011 and Omae 2012.

To shift the reaction equilibrium, it is necessary to add a base (inorganic or organic) to the reaction system. Although homogeneous catalysts have been found to be efficient for  $\text{CO}_2$  hydrogenation to formic acid, they have some drawbacks such as separation of products and recycling the catalyst. Immobilization of a complex onto a supporting material improves the reusability and stability of the catalyst. The combination of a basic ionic liquid and a silica-supported ruthenium complex promoted  $\text{CO}_2$  hydrogenation to formic acid with satisfactory activity and selectivity (Zhang 2009).

Electro-reduction of  $\text{CO}_2$  is another possible route for formic acid production. Oxygen is a by-product in electro-reduction of  $\text{CO}_2$ . Process requires a lot of electricity (8 MWh/t  $\text{CO}_2$ ) and therefore the electricity needs to be generated by renewable energy to have any  $\text{CO}_2$  reduction effect. In other words electrolysis efficiency is 20 % when the energy content of the end product (formic acid) is considered. The technology is still in lab scale, and Global CCS Institute (2011) stated that the current process is not likely to be viable, as to break even on the cost of energy input alone it would require an electricity price no greater than US\$42/MWh, which Global CCS Institute said is unlikely for a renewable energy input.

More recently formic acid was reported as a useful hydrogen storage material because formic acid will be especially valuable in niche energy applications, such as portable devices (Figure 12, Omae 2012).

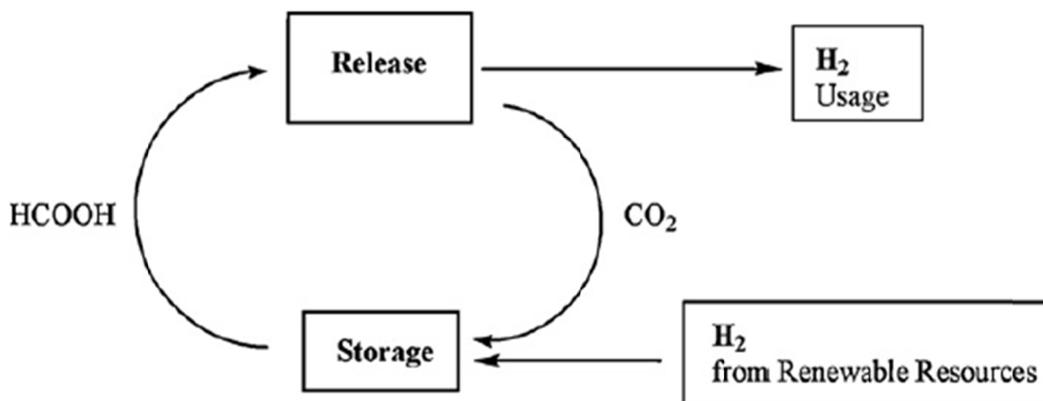


Figure 12 Catalytic cycle based hydrogen storage (Omae 2012).

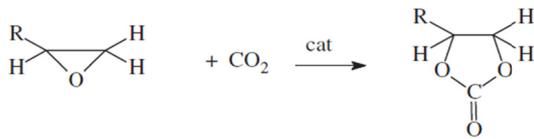
If formic acid as a liquid fuel can be shown to be commercially viable then demand for formic acid is likely to increase more significantly than current forecasts. This could result in current supply outstripping demand and provide an opportunity for entry to market. However, it is difficult to estimate likelihood of this (Global CCS Institute, 2011).

## 2.5 Cyclic carbonates

### 2.5.1 Industry outlook of cyclic carbonates

Cyclic carbonates (CC) are currently manufactured worldwide from  $\text{CO}_2$  and epoxides (reaction below), but current commercial processes utilise catalysts which require pure  $\text{CO}_2$  and high operating pressures and temperatures. Current commercial processes generate, rather than consume  $\text{CO}_2$ . The current global production is around 2 Mt per annum, but it has been estimated that this market could increase to 45 Mt per annum if the cost of their manufacture could be reduced by around 25 % (Styring 2011). The main drawback are the need for a high catalyst concentration, a high pressure (5 MPa of  $\text{CO}_2$ ), and a temperature

ranging 370 to 400 K. Many catalysts are used, for example alkyl ammonium, phosphonium-salts and alkali metal halides (Aresta 2010).



R= -H, ethene carbonate, equation 17  
 R= -CH<sub>3</sub>, propene carbonate, equation 18  
 Reactions need catalysts to proceed

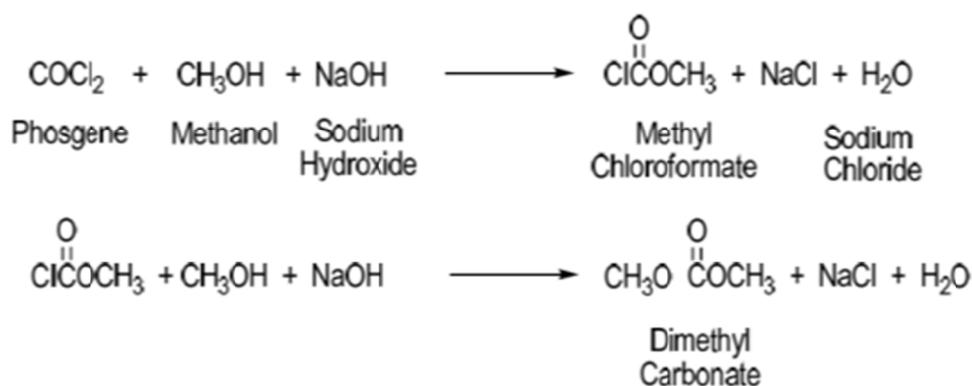
The Huntsman Corporation is one of world's largest producers, with a capacity of 33 000 t/a, covering approximately 50% of CC production worldwide (Aresta 2010). The estimate of Styring 2011 (2 Mt/a) seems to be too high for CC production. Jagadeesan 2015 and North 2010 estimate, that production of cyclic carbonates is 80000 t/a and 100 000 t/a, respectively. These estimates are near the above estimate of Aresta 2010. Free on Board (FOB) price in China for ethylene carbonate is 1350-1800 €/metric ton and for propylene carbonate is 1450-1550 €/metric ton for 99.5 % pure grade.

Cyclic carbonates are used as a polar solvents, precursor for polycarbonate synthesis, electrolytes in lithium secondary batteries, in the production of pharmaceuticals, as raw materials in various chemical reactions, in dimethyl carbonate synthesis (Dibenedetto 2014) and fuel additives (petrol, diesel, aviation fuel) (Styring 2011).

## 2.6 Dimethyl carbonate (DMC)

### 2.6.1 Dimethyl carbonate industry outlook

Historical industrial synthesis of dimethyl carbonate is phosgene method. The phosgenation of methanol was the most important method to produce DMC till 1980s. Under this method methanol is reacted with phosgene in the presence of 15-50 w-% aqueous alkali metal hydroxide and an inert, water-immiscible organic solvent. This reaction is carried out at temperatures ranging from -20 °C to +40 °C. Phosgene is a class A- poison and this method is not in use in Western countries (Kongpanna 2015).



Bayer process (equation 19) produces dimethyl carbonate by reacting methanol, carbon monoxide and oxygen in liquid state according to reaction (Kongpanna.2015):



As the catalyst, Cu(I)Cl and KCl in various ratios are usually employed (Tundo 2002). The process however suffers from low production rate, difficulties in downstream separation because of the existence of binary azeotropes in the system methanol – water- DMC and the need for corrosion resistant reactors. Nevertheless, the process has been licensed by Bayer for commercial production of DMC (Kongpanna 2015). The reaction temperature is known to

vary between 120 °C and 300 °C, but values between 120 °C and 180 °C is preferred. The reaction is carried out at atmospheric pressure. However to achieve sufficiently high reaction rate, it is advantageous to carry out the reaction at a higher pressure, preferably between 10 and 50 bar, with optimal between 12 and 32 bar (Krisfalussy 1996).

Lummus technology offers the Polimeri/Lummus process for the production of dimethyl carbonate (DMC). This process proceeds according to equation 19 (Bayer process). In the literature this process is the same than EniChem DMC process described by Aresta (Aresta 2010). The reactor runs under reasonable conditions (373-403 K, 2-3 MPa), with selectivity towards DMC in excess of 95 % (Aresta 2010). Methanol, CO and O<sub>2</sub> react in this process in the liquid phase in the presence of copper catalyst to yield DMC and water (Figure 13). The main by-product is CO<sub>2</sub>, with minor amounts of organics like dimethylether and methyl chloride. A small quantity of HCl is fed to reactor to maintain catalyst activity.

Unreacted gases, saturated with the organics, are fed to organics removal section. The clean gases – composed of CO, CO<sub>2</sub> and inerts – are subsequently fed to CO recovery unit where CO is recycled back to the reaction section and CO<sub>2</sub> is sent to an OSBL CO generation unit. The reaction section effluent, containing unreacted methanol, DMC, water, and traces of catalyst and HCl, is sent to the acid recovery section where catalysts and HCl are separated and recycled back to the reaction section. The remaining effluent is fed to the azeotropic distillation section. Methanol/DMC azeotrope is recycled back to the reaction section and DMC with water are fed to the final purification section to obtain DMC product.

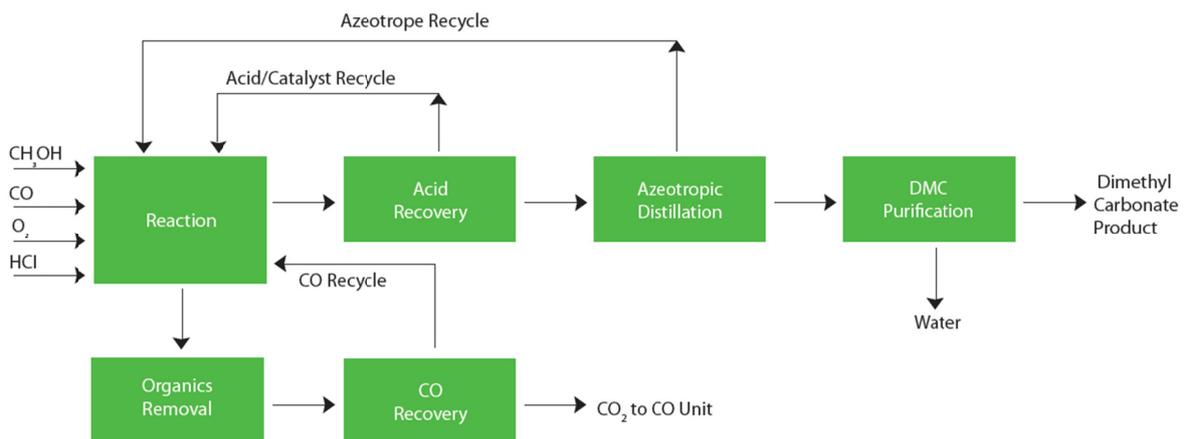


Figure 13 Block flow diagram of Polimeri/Lummus process ([www.CBI.com/lummus-technology](http://www.CBI.com/lummus-technology))

Typical overall material balance of Polimeri/Lummus process is given in Table 3. The quality of DMC product is shown in Table 3, too ([www.CBI.com/lummus-technology](http://www.CBI.com/lummus-technology))

Table 3 Overall material balance and DMC product quality of Polimeri/Lummus process ([www.CBI.com/lummus-technology](http://www.CBI.com/lummus-technology))

Typical Overall Material Balance		Typical DMC Product Quality	
Feeds	<i>MT/MT DMC Product</i>	Purity	99.8 wt.% min
Methanol (100% basis)	0.768	Color APHA	10 max.
CO (100% basis)	0.519	Acidity (as H <sub>2</sub> CO <sub>3</sub> )	50 ppm wt max.
O <sub>2</sub> (100% basis)	0.296	Chlorine (organics compd)	100 ppm wt max.
HCl (30 wt% solution)	0.023	Methanol	100 ppm wt max.
		Water	100 ppm wt max.
Main Products			
Dimethyl Carbonate	1.000		
CO <sub>2</sub> to CO unit	0.301		

Dimethyl carbonate is manufactured industrially by gas-phase methyl nitrite process of Ube Industries Ltd (Kongpanna 2015). The oxidative reactions using the alkyl nitrites as an oxidant have been developed by UBE (Tundo 2002). In the alkyl nitrite reactions, substrates such as CO and carbonyl-compounds are oxidized over palladium catalyst. The DMC, dialkyl oxalates and other useful chemicals are synthesized efficiently under moderate conditions by this type of alkyl nitrite reactions. In the case of DMC, methyl nitrate reacts with carbon monoxide to produce DMC and nitric oxide according to equation 20:



The gas-phase reactor technology utilizes heterogenous catalyst based on PdCl<sub>2</sub> and activated carbon. The process proceeds in a two-stage mode in which methanol is first reacted with NO at about 323 K to produce intermediate methyl nitrite and water. In the second stage, methyl nitrite is converted to DMC and NO by the addition of CO under catalytic conditions (383-423 K, 0.1-0.2 MPa). The NO is further recycled into first reactor. The selectivity of DMC lies in the range 90-95 % depending on CO and CH<sub>3</sub>ONO consumptions. Notably, the process not only eliminates the handling of slurries required by the EniChem process (Polimeri/Lummus process) but also prevent catalyst deactivation by water. Unfortunately both processes require the manipulation of toxic and hazardous reactants that hampers the large scale-up of this technology (Aresta 2010). Simplified process scheme is shown in Figure 14.

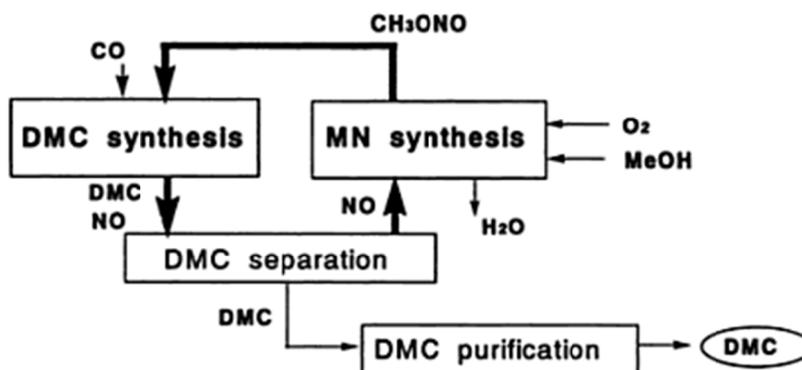


Figure 14. UBE's gas-phase DMC process

Ube Industries Ltd announced April 9, 2012 that it has reached agreement with Henan Zhonyuan Dahua Group Co., Ltd and High Chem Co., Ltd to establish a joint venture in China for the manufacturing dimethyl carbonate. The annual production capacity of plant (2013) is 100 000 tonnes/a. [http://www.ube-ind.co.jp/english/news/2012/20120409\\_01.htm](http://www.ube-ind.co.jp/english/news/2012/20120409_01.htm)

Catalyzed transesterification reaction between ethylene carbonate and methanol offers an alternative for “greening” DMC production (equation 21). In this Asahi Kasei process, the preferred catalyst is based on an anion-exchange resin operating under catalytic distillation conditions between 333 -353 K. This reactor design shifts the thermodynamic equilibrium towards complete conversion of ethylene carbonate, such that both yield and selectivity for DMC and monoethylene glycol are 99.5 %. The process is capable of supplying monoethylene glycol to the market, and DMC for captive use to produce DPC, C<sub>15</sub>H<sub>10</sub>O (Aresta 2010, Bonenfant 2008).



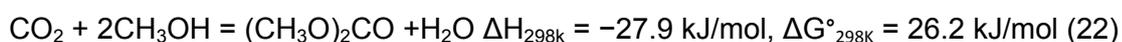
DMC is used in plastics and in pharmaceutical and agricultural chemicals and also as a non-toxic solvent in paints. There is growing demand in China for DMC used as a non-polluting additive for gasoline and notably diesel oil. In addition, demand for DMC used as an electrolyte solvent for lithium-ion rechargeable batteries is expected to grow rapidly, with global demand for eco-cars such as hybrid and electric vehicles increasing to significant levels <http://www.ube-ind.co.jp/english/news/2012/2012040>. Global dimethyl carbonate end users are polycarbonate 51 %, solvent 24 % (incl. lithium batteries) and others 25 %. Industrial grade purity is > 99.0 w-%, Pharmaceutical grade purity is >99.5 w-% and Li-battery grade is >99.9 w-%. China is the biggest user and producer of DMC [www.ChemSystems.com](http://www.ChemSystems.com). The FOB price in China varies from 700 to 1100 €/metric ton depending on the DME grade.

DMC is one of the organic chemicals, which production has grown a lot during last twenty years. The production has grown from 45 000 t/a in 1990 to 62 000 t/a 1997 and to 370 000 t/a 2007 (Bertau 2015). More recent production numbers was not found.

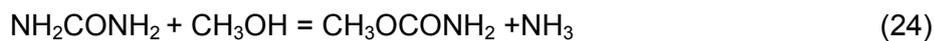
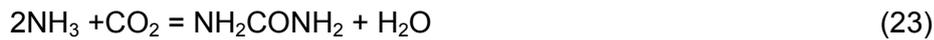
Despite the uncertainty with respect to very large scale applications (such as fuel additive/blending agent), there is significant growth demand for dimethyl carbonate into its various established/semi-established applications such as solvent use (especially as an electrolyte solvent), and plastic production industries ([www.ChemSystems.com](http://www.ChemSystems.com))

### 2.6.2 CO<sub>2</sub> routes for dimethyl carbonate

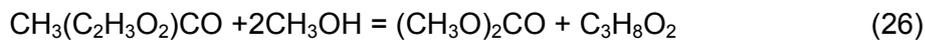
DMC from direct synthesis from CO<sub>2</sub> and methanol is still in the R&D stage (equation 22). For the direct use of CO<sub>2</sub> to produce DMC, it has been reported that CO<sub>2</sub> could react with methanol at critical temperature and critical pressure of CO<sub>2</sub>. The biggest problem is the limitation of reaction equilibrium, which blocks the reaction proceeding. Therefore, the development of dehydration systems for shifting the chemical equilibrium to the DMC side is required. For this purpose, the complete removal of water under practical reaction conditions is essential for achieving a high yield of DMC. Under mild conditions, a basic catalyst (ZrO<sub>2</sub>-MgO), a promoter (methyl iodide) and butylene oxide as a chemical trap were found to be an efficient catalytic system to shift the chemical equilibrium (ETA 2011). This direct reaction route results in high atom-efficiency to avoid the use of toxic reagents such as phosgene. However, industrial utilization of CO<sub>2</sub> in the direct DMC synthesis is still a significant challenge because CO<sub>2</sub> lies in a deep potential energy well of about – 400 kJ/mol that requires a huge amount of energy activation.



DMC can be synthesized from CO<sub>2</sub> via urea. This process, proposed as a new alternative, integrates the synthesis of urea and DMC, where CO<sub>2</sub> is used as a chemical feedstock. The process starts with the reaction between CO<sub>2</sub> and ammonia in the urea synthesizer, which is operated at 165-190 °C and 13.5-20.5 MPa (equation 22). The product stream is pumped to the purification section to remove water, excess CO<sub>2</sub> and ammonia from urea. The methanol is added for the alcoholysis reaction to produce DMC (equations 24 and 25) by using ionic liquid Et<sub>3</sub>NHCl-ZnCl or emimBr-ZnCl<sub>2</sub> (Kim 2010). It has been reported that the process involves a two-step reaction with methyl carbamate as the reaction intermediate according to reactions above.



One of the most promising route to effectively utilize CO<sub>2</sub> in DMC production is through cycloaddition of CO<sub>2</sub> to epoxides to form cyclic carbonates, which gives 100 % atom efficiency. Propylene carbonate is synthesized from propylene oxide and CO<sub>2</sub> at 130 °C and 2.0 MPa (equation 18). Subsequently, DMC is obtained through the transesterification of propylene carbonate and methanol (equation 26). Various types of catalysts can be used such as quaternary ammonium ion exchange resins with hydroxide counter ions. Also, verkade super bases can be effective at low catalyst loadings for the rapid transesterification of propylene carbonate with methanol under mild conditions and with high product selectivity (Williams 2009). For this this propylene glycol which is valuable chemical is obtained as a by-product.



Similar to the synthesis of propylene carbonate, ethylene carbonate is also produced from cycloaddition of CO<sub>2</sub> to ethylene oxide. The reaction conditions are relatively mild, i.e. 30 °C and 2.5 MPa in immobilized ionic liquid on amorphous silica (equation 17). Subsequent transesterification of ethylene carbonate with methanol produces DMC and ethylene glycol (equation 27). It has been reported that the conversion of ethylene carbonate to DMC is 81.2 % at 250 °C and 9.0 MPa. Various types of catalysts can be used, such as poly-4-vinyl pyridine as a novel base catalyst and DABCO-derived (1,4-diazobicyclo(2.2.2)octane) basic ionic liquids (Jagtap 2008).



### 3. Conclusions

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Carbon capture and utilisation (CCU) is an emerging option for utilizing CO<sub>2</sub> emissions from industrial operations. Main challenges to the chemical use of CO<sub>2</sub> are caused by the fairly inert nature of carbon dioxide, which leads to unfavourable kinetics and thermodynamics of CO<sub>2</sub> conversion. The thermodynamic limitations could be alleviated by adopting novel technological approaches. The use of catalytic membrane reactors, for example, may help to counteract the thermodynamic barrier and increase the yield and selectivity of the process.

The main part of the research (especially catalyst development work) for various reaction routes converting CO<sub>2</sub> into chemicals is currently carried out with lab-scale equipment. At the moment methanol seems the most promising product from CO<sub>2</sub> utilization point of view.

Using CO<sub>2</sub> as feedstock for chemicals production needs to be coupled with the use of renewable energy in order to ensure sustainable end-products. In order to keep climate warming under the 2 °C threshold, the greenhouse gas emissions must be in 2050 40 to 70 percent lower than emissions in 2010 (IPCC 2014). Power and transportation sectors are two largest sources of global CO<sub>2</sub> emissions.

The need for fuels is increasing with growing energy demand. However, fossil fuel resources are diminishing and fuel prices have experienced strong fluctuation in recent years. Therefore, it would be desirable to develop alternative fuels from renewable sources as well as new production processes for them.

In the power sector near-term solutions include photovoltaics, wind power, nuclear power and carbon capture and storage technologies (CCS). There is also need to use chemicals and fuels in energy storage to smooth the fluctuations in the renewable electricity production. Liquid chemicals or fuels are interesting products due to their higher volumetric energy density in comparison to gases, which might make them more suitable for various energy storage applications.

Transportation sector causes nearly one quarter of global-energy CO<sub>2</sub> emissions. The transportation sector emissions can be reduced by improvements in efficiency and change in vehicle fuel. Technology for the production of synthetic fuels from fossil feedstocks via synthesis gas has existed for almost a century. In the future synthetic fuels should be produced from biomass to limit overall CO<sub>2</sub> emissions. In this solution it is possible to use hydrogen from renewable electricity sources as a partial co-feed with biomass synthesis feed, which will lead to increased output of synthetic fuel in comparison to a plant operating with biomass alone. Biomass based gasification process can be also a source of pure carbon dioxide flow, which is needed in production of CO<sub>2</sub> based chemicals and fuels. Another solution in a longer term for the decarbonisation of synthetic fuels would be to manufacture them directly from carbon dioxide and renewable electricity. In the case of CO<sub>2</sub> to methanol production, for example, it is not easy to predict how technical development of process proceeds and when or if this route could be competitive with biomass gasification route. On the other hand, biomass resources are limited for transportation sector use. Bio-based methanol is both versatile fuel and interesting raw material for various chemicals and polymers. In any case the increasing share of renewable electricity in the energy supply mix is a positive backdrop for CO<sub>2</sub> chemicals and fuels that might lead to their breakthrough into markets, but this development is not yet visible in short term

The development and implementation of novel technologies is not only constrained by scientific and technical progress, but also by a number of political, social and economic factors. It is also necessary to promote the breakthrough of CO<sub>2</sub> based chemicals and fuels with the aid of political regulations and supports. Although many CCU technologies are still in the research phase, with the current estimated costs therefore high, strategic research can make these options more feasible.

## References

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Aresta, M. (Ed.), 2010. Carbon Dioxide as a Chemical Feedstock, Wiley-VCH, Weinheim. ISBN: 978-527-32475-0

Aresta, M., Dibenedetto, A., Angelini, A., 2014. Catalysis for the Valorization of Exhaust Carbon: From CO<sub>2</sub> to Chemicals, Materials, and Fuels. Technological Use of CO<sub>2</sub>. Chem. Rev., 114: 1709–1742. [dx.doi.org/10.1021/cr4002758](https://doi.org/10.1021/cr4002758)

Aresta, M. 2015. Plenary talk presented at the 13<sup>th</sup> International Conference on Carbon Dioxide Utilization (ICCDU XIII), July 5-9, 2015, Singapore

### [Audi's e-gas project.](#)

Bertau, M., Räuchle, K., Offertmanns, H., 2015. Methanol – die Basichschemikalie, Chem. Unsere Zeit, Wiley – VCH Verlag GmbH & Co KGaA, Weinheim. DOI:10.1002/cluz.201500689

Bizzari, S.N., Blagoev, June 2010. CEH Marketing Research Report: Formic acid (<http://www.sriconsulting.com/CEH/Public/Reports/659.2000/>). *Chemical Economics Handbook*, SRI Consulting. Retrieved July 2011.

Bonenfant, D., Kharoune, L., Sauve, S., Hausler, R., Niquette, P., Mimeault, M., 2008, Ind. Eng. Chem. Res., 47: 7610 - 7616.

Budiman, A.W., Song; S-H., Chang, T-S., Shin, C-H., Choi, M-J. , 2012. Dry Reforming of Methane over Cobalt Catalysts: A Literature Review of Catalyst Development, Catal Surv Asia 16:183-197

Chang, F.W., Kuo, M.S., Tsay, M.T., Hsieh, M.C., 2003, Appl. Catal. A, 309-320

Chesko, J., 2014, Methanol Industry Outlook, PROMSUS, May 2014

Dibenedetto, A., Angelini, A. and Styufano, P., 2014. Use of carbon dioxide as feedstock for chemicals and fuels: homogenous and heterogenous catalysis, J Chem Technol Biotechnol, 89: 334-353

Djinović, P., Osojnik, G., Črnivec, G, Erjavec, B, Pintar, A., 2012, Influence of active metal loading and oxygen mobility on coke-free dry reforming of Ni–Co bimetallic catalysts. Appl.Catal. B Environ.; 125:259–70

Eta, V., Mäki-Arvela, P., Wärnå, J., Salmi, T., Mikkola, J.-P., Murzin, D., 2011. Kinetics of dimethylcarbonate synthesis from methanol and carbon dioxide over ZrO<sub>2</sub>-MgO catalyst in the presence of butylene oxide as additive, Appl.Catal. A. Gen. 404: 39-46

Ganesh, I., 2014. Conversion of carbon dioxide into methanol – a potential liquid fuel: Fundamental Challenges and Opportunities (a review). Renewable and Sustainable Energy Reviews 31:221-257

GCCSI, 2011. Accelerating the uptake of CCS: industrial use of captured carbon dioxide. Global CCS Institute. <https://www.globalccsinstitute.com/publications/accelerating-uptake-ccs-industrial-use-captured-carbon-dioxide>

Hannula, I., Kurkela, E., 2013, Liquid transportation fuels via large-scale fluidised-bed gasification of lignocellulosic biomass, Espoo, VTT Technology 91. 114p. + app. 3 p.

[http://www.ube-ind.co.jp/english/news/2012/20120409\\_01.htm](http://www.ube-ind.co.jp/english/news/2012/20120409_01.htm)

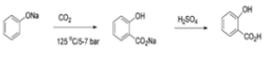
[https://en.wikipedia.org/wiki/Formic\\_acid](https://en.wikipedia.org/wiki/Formic_acid)

IPCC, 2005. IPCC Special Report on Carbon Dioxide Capture and Storage. Prepared by Working Group III of the Intergovernmental Panel on Climate Change. Metz, B., Davidson, O., de Coninck, H.C., Loos, M., Meyer, L.A. (Eds.). Cambridge University Press, Cambridge.

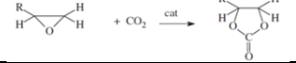
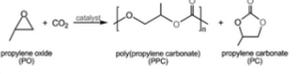
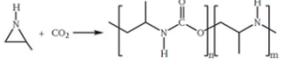
- IPPC, 2014. Summary of policymakers, in: O. Ederhofer, R. Pichs-Madruga, Y. Sokona, E. Farahani, S. Kadner, K. Seyboth, A. Adler, I. Baum, S. Brunner, P. Eickemeier, B. Kriemann, J. Savolainen, S. Schlmer, c. von Stechow, T. Zwickel, J.- Minx (Eds.), *Climate Change: Mitigation of Climate Change. Contribution of Working Group III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*, Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.
- Jadhav, S.G., Vaidya, P.D., Bhanage, B.M., 2014, Joshi, J.B. Catalytic carbon dioxide hydrogenation to methanol: A review of recent studies, *Chemical Engineering Research and Design* 92: 2557-2567
- Jagadeesan, D., Joshi, B., Pameswaran, P., 2015. Chemical utilisation of CO<sub>2</sub> –a challenge for the sustainable world, *Resonance*, February
- Jagtap, S.R., Bhor, M.D., Bhanage, B.M, 2008. Synthesis of ethylene carbonate via transesterification of ethylene carbonate with methanol using poly-4-vinyl pyridine as a novel base catalyst, *Catal. Commun.* 9: 1928-1931.
- Kim, D.-W., Kim, C.-W., Koh, J.-C., Park, D., 2010. Synthesis of dimethyl carbonate from ethylene carbonate and methanol using immobilized ionic liquid on amorphous silica, *J. Ind. Eng. Chem.* 16:474-478
- Kongpanna, P., Pavajarajarn, V., Gani; R., Assabumrungrat, S., 2015. Techno-economic evaluation of different CO<sub>2</sub>-based processes for dimethylcarbonate production. *Chemical Engineering Research and Design* 93: 496-510
- Kopyscinski, J., Schildhauer, T.J., Biollaz, S.M.A., 2010. Production of synthetic natural gas (SNG) from coal and dry biomass, A technology review from 1950-2009. *Fuel* 89: 1763 - 1783
- Krisfalussy, Z., Steude, H., Waldmann, H., Hallenberger, K., Wagner, W., Traencker, H.-J., 1996. Process for preparing dimethylcarbonate, US Patent 5,523,452 A.
- Lavoie, J-M., 2014. Review on dry reforming of methane, a potentially more environmentally-friendly approach to the increasing natural gas exploitation, *Frontiers in Chemistry*, Review Article, November, Volume 2, 17 p. [www.frontiersin.org](http://www.frontiersin.org) doi:10.3389/fchem. 2014.00081
- Liu, Y., Zhang, T., Wang, N, 2007, *Chem. Lett.* 36: 1182
- Ma, J., Sun, N., Zhang, X., Zhao, N., Xiao, F., Wei, W., Sun, Y., 2009. A short review of catalysis for CO<sub>2</sub> conversion, *Catalysis Today* 148: 221-231
- Mikkelsen, M., Jørgensen, M., Krebs, F.C., 2010. The teraton challenge. A review of fixation and transformation of carbon dioxide. *Energy Environ. Sci.*, 3: 43–81. DOI: 10.1039/b912904a
- Nexant, [www.ChemSystems.com](http://www.ChemSystems.com), Market report abstract
- North, M., Pasquale, R., Young, C., 2010. Synthesis of cyclic carbonates from epoxides and CO<sub>2</sub>, *Green Chem.* 12: 1524-1539
- Olah, G.A, 2013. Towards of independence through renewable methanol chemistry, *Angew. Chem. Int.* 52: 104-107
- Omae, I., 2006, *Cat.Today* 115: 33
- Omae, I., 2011, *Kagaku Kogyo* 62: 235, 478, 872
- Omae, I., 2012. Recent developments in carbon dioxide utilization for the production of organic chemicals – Review, *Coordination Chemistry Reviews* 256 1384-1405
- Otten, R., 2014. The first industrial PtG plant – Audi e-gas as driver for the energy turnaround, CEDEC Gas Day, Verona, 27th of May

- Otto, A., Grube, T., Schiebahn, S., Stolten, D. 2015, Energy Environ. Sci., DOI: 10.1039/C5EE02591E.
- Saeidi, S., Amin, N.A.S., Rahimpour, M.R, 2014. Hydrogenation of CO<sub>2</sub> to value-added products – A review and potential future developments. Journal of CO<sub>2</sub> Utilization 5 66-81
- Sigurbjörnsson, O, 2013. Recycling of Geothermal Carbon and Sulfur Emissions for Chemical production, Georg Waste to Value lecture series – April 17
- Song, C., 2001a. Tri-reforming: A new process for reducing CO<sub>2</sub> emissions. Chem. Innov. 31: 21
- Song, C., 2001b. Tri-reforming: a novel concept for CO<sub>2</sub> conversion to syngas with desired H<sub>2</sub>/CO using flue gas of power plants without CO<sub>2</sub> separation. Abstracts of the Seventh International Conference on Carbon Dioxide Utilization, Seoul, Korea, October 12-16, 121-122
- Song, C., Pan, W., 2004. Tri-reforming of methane: a novel concept for catalytic production of industrially useful synthesis gas with desired H<sub>2</sub>/CO ratios. Catalysis of Today 98 463-484
- Styring, P., Jansen, D., de Coninck, H., Reith, H., Armstrong, K. 2011. Carbon Capture and Utilisation in the green Economy - Using CO<sub>2</sub> to manufacture fuel, chemicals and materials. The Centre for Low Carbon Futures, Report no. 501. <http://co2chem.co.uk/carbon-capture-and-utilisation-in-the-green-economy>
- Tanaka, R., Yamashita, K., Nozaki, K., 2009, J. Am. Chem. Soc. 131:14168
- Teir, S., Bajamundi, C., Helaja, T., 2015. Travel report, ICDDU-XII, 5-9 July
- Tundo, P., Selva, M., 2002. The chemistry of dimethyl carbonate. Acc.Chem.Res. 35: 706-716
- Usman, M., Wan Daud, W.M.A, Abbas, H.F., 2015. Dry reforming of methane: Influence of process parameters - A review. Renewable and Sustainable Energy Reviews 45. 710-744
- Wang, W., Wang, S., Ma, X., Gong, J., 2011. Recent advances in catalytic hydrogenation of carbon dioxide. Chem.Soc. Rev. 40, 3703-3727.
- VCI and DECHEMA, 2009, Position Paper: Utilisation and Storage of CO<sub>2</sub>, Version 12: January 2009
- Williams, D. B.G., Sibiya, M.S., van Heerden, P.S., Kirk, M., Harris, R., 2009. Verkadesuper base-catalysed transesterification of propylene carbonate with methanol to co-produce dimethyl carbonate and propylene glycol. J. Mol. Catal. A: Chem. 304: 147-152.
- [www.CBI.com/lummus-technology](http://www.CBI.com/lummus-technology)
- [www.carbonrecycling.is](http://www.carbonrecycling.is) 2015
- [www.linde.com](http://www.linde.com) 2013
- Zhang, Z.F., Hu, S.Q., Song, J.L. Li, W.J. Yang, G.Y. and Han, B.X. 2009. Hydrogenation of CO<sub>2</sub> to Formic Acid promoted by a Diamine-Functionalized Ionic Liquid. ChemSusChem, 2: 234–238.

## **Appendix 1 CO<sub>2</sub> to chemicals (Excel table from Teir et al. 2015)**

Product	CCU process(es)	How produced now?	Current market (Mtpa)	Current market (CO2 Mtpa)	Future market (Mtpa)	Future market (CO2 Mtpa)	Reaction equations	Catalyst material	Process conditions (T, p)	Byproducts (incl. amounts)	Thermodynamic properties ( $\Delta H, \Delta G$ ) = [kJ/mol]	Post-processing
Methanol (CH3OH)	Current method (CO2 as additive)	From synthesis gas: $3CO + 9H_2 + CO_2 \rightarrow 4CH_3OH + H_2O$	60	10		>300	$3CO + 9H_2 + CO_2 \rightarrow 4CH_3OH + H_2O$	Cu/Zn oxides	225-280 C, 50-80 bar	Water		
Methanol (CH3OH)	Direct conversion into "Renewable" methanol	"	"	"	"	"	$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$	Cu/Zn/Zr oxides	225-280 C (a bit higher than in commercial route), 50-80 bar	Water	-58.5; 46.3 (at 250 C)	
Methanol (CH3OH)	Enzymatic production	"	"	"	"	"		Photocatalyst, eg. A@TiO2	1 bar, 37 C			
Urea (H2NCONH2)	Urea production	Haber-Bosch, consumes CO2, large energy requirement	180	132	210	154	$2NH_3 + CO_2 \rightarrow H_2NCOONH_4 \rightarrow H_2NCONH_2 + H_2O$	no catalyst	1: 150-250 bar, 150-200 C	H2O	-159.8; -21.1 (at 25 C)	Dehydration (reaction 2)
Urea (H2NCONH2)	Urea yield boosting	"	"	"	"	"	Surplus ammonia from the process is used with pure CO2 to produce more urea		"	"		"
Carbamates (RR'NCO2)	Carbamate from in situ generated carbamate ion + halide		6	1	11	4	$scCO_2 + BuX + Et_3NH \xrightarrow[100^\circ C, 2h]{Bu_4NH, K_2CO_3} Bu-O-C(=O)-N(Et)_3 + HX$	homogeneous metal catalyst (Sn, Ni)	100 C, super critical CO2	hydride		
Carbamates (RR'NCO2)	Carbamate from in situ generated carbamate ion + alcohol		"	"	"	"	$1-BuNH_2 + EtOH + CO_2 \xrightarrow[200^\circ C, 24h]{Bu_3NO, MgCOMe_2(2eq)} 1-BuNHCOOEt + H_2O$	organotin catalyst	200 C, high pressure CO2	water		
Formamides							$R_2NH + CO_2 + H_2 \rightarrow HCONR_2 + H_2O$					
Salicylic acid	Carboxylation	Kolbe-Schmitt-synthesis	0.06	0.02	0.1				125 C, 5-7 bar		$\Delta H=90.1$	Purification, acidification (reaction 2)
Carbon monoxide	reverse water shift reaction						$CO_2 + H_2 = CO + H_2O$	Cu, Fe	~600 C, 1 bar	water	36.4; 6.8 (at 600 C)	
Carbon monoxide	Reverse Boudouard reaction						$CO_2 + C \leftrightarrow 2CO$	No	~700 C		171.2; -0.2 (at 700 C)	
Synthesis gas (CO, H2)	Splitting of CO2 --> CO	steam ref (NG) or gasification (coal)					$CO_2 \rightarrow CO, + H_2 \rightarrow Syngas$					
Synthesis gas (CO, H2)	Dry reforming	steam ref (NG) or gasification (coal)					$CO_2 + CH_4 = 2H_2 + 2CO$	Ni, Co, noble metals	~800 C, 1 bar		259.6, -45.1 (at 800 C)	
Synthetic natural gas (CH4)	$3H_2 + CO = CH_4 + H_2O$	Catalytic hydrogenation of CO2					$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	Ni, Ru, Rh	300-450 C	water	-180.9; -40.6 (at 400 C)	
Formic acid (HCOOH)	Direct CO2 hydrogenation	$CH_3OH + CO \rightarrow HCO_2CH_3, HCO_2CH_3 + H_2O \rightarrow HCO_2H + CH_3OH$	1	0.9		>300	$H_2 + scCO_2 \xrightarrow[Et_3N, H_2O, 50^\circ C]{RuCl_2(PMe_3)_4} HCO_2H$	Ru complexes	<100 C, Supercritical CO2, P>150 bar		-29.7; 44.4 (at 80 C)	
Formic acid (HCOOH)	Electro-reduction of CO2 to produce formic acid (HCOOH) and O2	"	"	"	"	"						Formic acid used as a hydrogen carrier
Acetic acid (CH3COOH)							$CO_2 + CH_4 = CH_3COOH$	metal complexes			-11.9; 60.1 (at 80 C)	



Product	CCU process(es)	How produced now?	Current market (Mtpa)	Current market (CO2 Mtpa)	Future market (Mtpa)	Future market (CO2 Mtpa)	Reaction equations	Catalyst material	Process conditions (T, p)	Byproducts (incl. amounts)	Thermodynamic properties ( $\Delta H, \Delta G$ ) = [kJ/mol]	Post-processing
<b>Organic carbonates ((RO)2CO, total market)</b>				0.2		100	CO <sub>2</sub> → ROC(O)OR: alcoholysis of urea (CO <sub>2</sub> carrier) or direct carboxylation of alcohols: 2ROH + CO <sub>2</sub> → (RO)2CO + H <sub>2</sub> O	Al, Nb, Ce...		Water		Water removal, distillation
Acyclic carbonates (Dimethyl carbonate, DMC)		From methanol using phosgenes (COCl <sub>2</sub> + 2 CH <sub>3</sub> OH → CH <sub>3</sub> OCO <sub>2</sub> CH <sub>3</sub> + 2 HCl) or catalytic tech.	< 2	0.5	10	5	CH <sub>3</sub> OH + CO <sub>2</sub> → (CH <sub>3</sub> ) <sub>2</sub> CO + H <sub>2</sub> O	Ti, Sn complexes, organostannane	150 C, 60 bar	water		
Cyclic carbonates (ethene carbonate (EC), propene carbonate (PC), styrene carbonate (SC))	Direct carboxylation of alcohols	Carboxylation of epoxides	0.07-2			45		Many! Zu(OA <sub>2</sub> ), DMF, DAA, CeO <sub>2</sub>	30-100 bar, 100-130 C		EC -38.1; -0.2 (at 100 C)	
<b>Polymers, polycarbonates (total market)</b>		using monomers	5	1	10	3						
Polyethylene carbonate	Combine traditional feedstocks with CO <sub>2</sub>	"	45	0	50	25		zinc complexes		yes		
Polypropylene carbonate	Combine traditional feedstocks with CO <sub>2</sub>	"	80	0	90	45		zinc complexes (Zn(Oac) <sub>2</sub> )		yes		water removal
Polyurethane	Copolymers from Aziridines and CO <sub>2</sub>		10	<10					30-220 bar, 100 C			
<b>Inorganic carbonates (total market)</b>			200		400	100						
Calcium carbonate (CaCO <sub>3</sub> )	Slag2PCC	1. CaCO <sub>3</sub> → CaO + CO <sub>2</sub> , 2: CaO + H <sub>2</sub> O → Ca(OH) <sub>2</sub> , 3: Ca(OH) <sub>2</sub> + CO <sub>2</sub> → CaCO <sub>3</sub> + H <sub>2</sub> O	114	50.1			1: 2NH <sub>4</sub> Cl + CaO·SiO <sub>2</sub> + H <sub>2</sub> O → Ca <sub>2</sub> + + 2Cl <sup>-</sup> + 2NH <sub>4</sub> OH + SiO <sub>2</sub> , 2: Ca <sub>2</sub> + + 2Cl <sup>-</sup> + 2NH <sub>4</sub> OH + CO <sub>2</sub> → CaCO <sub>3</sub> + 2NH <sub>4</sub> Cl	No	20-50 C, normal flue gas pressure			
Sodium carbonates (Na <sub>2</sub> CO <sub>3</sub> )			50	15 (25% mined)		<1						
Magnesium carbonates (MgCO <sub>3</sub> )			3.5	mainly mined		>300	Mg <sub>3</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub> + 2CO <sub>2</sub> →					

Product	CCU process(es)	Product value (€/t)	Maturity	Power/steam/heat requirements	LCA (t CO2eq emitted per t CO2 used)	Other raw material requirements	Yield	Sensitivity to sulphur	Feasibility technical	Commercial viability
<b>Organic carbonates ((RO)2CO, total market)</b>										Water formation an issue
Acyclic carbonates (Dimethyl carbonate, DMC)										
Cyclic carbonates (ethene carbonate (EC), propene carbonate (PC), styrene carbonate (SC))	Direct carboxylation of alcohols	1300-2000				epoxide, olefins, etc				
<b>Polymers, polycarbonates (total market)</b>										
Polyethylene carbonate	Combine traditional feedstocks with CO2		Novomer pilot plant		5.5	epoxide				
Polypropylene carbonate	Combine traditional feedstocks with CO2		Novomer pilot plant		5.5	epoxide, propylene glycol				
Polyurethane	Copolymers from Aziridines and CO2		R&D (very little work)			aziridines	32-62%			
<b>Inorganic carbonates (total market)</b>										
Calcium carbonate (CaCO3)	Slag2PCC	100-200	Laboratory pilot at Aalto		-0.3		Up to 80% extraction of Ca, depending heavily on the slag			
Sodium carbonates (Na2CO3)										
Magnesium carbonates (MgCO3)										

<b>Colour codes (references):</b>
Mikkelsen 2010 and IPCC 2005
Styring 2011
GCCSI(2011)
Aresta(2010)
Aresta (2014)
Aresta (2015)