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**“The next Generation of Carbon for the Process Industry”**

Coordination and Support Action

Theme [SPIRE 5] – Potential use of CO<sub>2</sub> and non-conventional fossil natural resources in Europe as feedstock for the process industry

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***Report on fully integrated and intensified value chain concepts for process selection***

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# 1. Executive Summary

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A review of the products which can be synthesised using either carbon dioxide (CO<sub>2</sub>) or carbon monoxide (CO) has been conducted and this report presents the results of that review. In order to make the information more manageable, the report first covers products made using CO<sub>2</sub> and then products using CO. The products are classified into four groups: chemicals, chemicals/fuels, fuels and finally solid products. Within these groupings, the products have been further classified into chemical families so that similar products can be grouped together.

A total of 43 different products have been described which can be produced from CO<sub>2</sub>, utilising 71 different routes of synthesis. Similarly, 22 products have been identified which can be produced from CO, and these can be synthesised from 33 different chemical routes. Information about the potential products such as what it is used for and the size of the market, together with a description of the routes of synthesis, the nature of the chemical reactions which create them and the development status of the processes are provided in the text.

Following the text, tables of market and CO<sub>2</sub>/CO utilisation data are provided. The technology readiness level of each route of synthesis has been provided based upon the published literature or estimated based upon the description of commercial activity. The market for the majority of the products has been provided in terms of the total tonnage of product currently produced and sold and imported into the EU, together with the unit value and total value of this market. In addition to the market values, the amount of CO<sub>2</sub> or CO utilised per tonne of product has been provided, together with the total mass of CO<sub>2</sub> or CO assuming the total EU market is met by that production route. Finally the requirement for H<sub>2</sub> per tonne of product is provided together with a list of the other non-catalytic inputs required by the chemical reaction.

Methanol is often referred to as a "chemical building block", so to put this into context and to allow an appreciation of the range of products which can be produced from methanol, a simple list is provided. In a similar way, modern chemical plants have the ability to transform one type of carbonate monomer into another in order to produce multiple different polymers. The opportunity is therefore discussed that it may not be necessary to produce every different kind of monomer from CO<sub>2</sub> (or CO) in order for carbon recycling to have a major impact upon the sustainability of the chemical industries.

It is proposed that the information provided in this report, together with that provided in the review of industrial symbiosis which is to be submitted as deliverable 2.2, will be utilised to enable the selection of the most favourable products to be made from CO<sub>2</sub> and CO. This selection will be based upon market data, environmental impacts and potential symbiotic interactions between industries and will be presented as deliverable 2.3.

## 2. Introduction

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### 2.1 Objective

This report aims to:

- identify potential products which can be synthesised from CO<sub>2</sub> and CO;
- identify the routes/processes which can be utilised to produce these products;
- present the products and routes to those products in such a way as to enable the selection of those which offer the best economic and environmental outcomes.

This report (deliverable 2.1) does not include the selection of the products to produce from the CO or CO<sub>2</sub>. The selection will be made in deliverable 2.3, following a review of industrial symbiosis which is reported as deliverable 2.2.

This report is not intended to be a detailed study of the chemistry of carbon dioxide (CO<sub>2</sub>) and carbon monoxide (CO) reactions. However, the report does discuss different ways of producing products from CO/CO<sub>2</sub> together with other chemicals, so a knowledge of chemistry is required to understand these aspects. A brief introduction to explain the types of chemical reactions that these gases can undergo may assist the reader in understanding the nature of the CO<sub>2</sub> utilisation being discussed. In the context of the CarbonNext project, it is important to emphasise that CO<sub>2</sub> utilisation covers the transformation of CO<sub>2</sub> into other useful molecules so that the CO<sub>2</sub> molecule no-longer exists. We are not discussing the use of CO<sub>2</sub> in carbonating drinks, enhanced oil recovery or utilising CO<sub>2</sub> as a refrigerant for example.

The reactions that CO<sub>2</sub> undergoes when forming products can be grouped into two main classes:

1. **Carboxylation reactions** are essentially those in which the CO<sub>2</sub> molecule is incorporated into a new molecule without splitting both of the C=O bonds. As a consequence, such reactions do not require high levels of energy and can proceed at relatively low temperatures, resulting in carbonates (-CO<sub>3</sub>) or carboxylic acids (-COOH) for example. An example of such a reaction is the carboxylation of methane (CH<sub>4</sub>) by CO<sub>2</sub> to form acetic acid:  $O=C=O + CH_4 \Rightarrow CH_3COOH$ . We can see that bonds between the carbon and oxygen atoms from the CO<sub>2</sub> remain in the product.
2. **Reduction reactions** are reactions in which at least one of the C=O bonds from CO<sub>2</sub> has been completely broken down and the oxygen replaced with hydrogen, resulting in the formation of hydrocarbons which include most fuels. Examples of reduction reactions are when CO<sub>2</sub> is partially reduced to methanol (CH<sub>3</sub>OH) or completely reduced to methane (CH<sub>4</sub>). Such reactions tend to require high energy inputs such as high temperatures as well as a supply of H<sub>2</sub>.

Carbon monoxide (CO) is a more reactive molecule than CO<sub>2</sub> and consequently it undergoes chemical reactions more readily, making it already a widely used gas in industrial settings. Deliverable 1.1 of the CarbonNext project identified the iron and steel industry as the most important source of CO in Europe. CO is produced on purpose in the blast furnaces when a metal oxide ore is heated with coke, which is a form of pure carbon. Combustion of carbon in air initially leads to the formation of CO<sub>2</sub>, but in the presence of excess carbon, the CO<sub>2</sub> is reduced to CO. CO is a strong reducing agent, which means that it strips oxygen atoms from the metal oxide ore, so reducing the ore to a pure metal. By producing CO in this way, the iron ore is converted to pure iron for instance, but the excess CO becomes a significant component of the blast furnace gas.

Like CO<sub>2</sub>, CO can undergo reduction reactions where the oxygen is removed and hydrogen is added to produce hydrocarbons. Instead of the carboxylation reactions of CO<sub>2</sub>, CO undergoes carbonylation reactions where the CO is incorporated into another molecule.

## 2.2 Methods

The information presented in this report is based upon the scientific literature plus other published reports, company websites and various news sources. Company websites have been quoted with regard to claims of products arising from CO/CO<sub>2</sub>, news sources have occasionally been used to provide an overview of the current commercialisation status of different technologies.

In order to ease the evaluation of the many differing potential products that can be made from CO<sub>2</sub> and CO, they have been placed into four separate sections:

- **Chemicals** - mostly liquids and gases for utilisation by the chemicals, pharmaceuticals and plastics industries;
- **Chemicals/Fuels** - products which can be utilised as a chemical or a fuel (e.g. ethanol);
- **Fuels** - products whose use is almost exclusively as a fuel;
- **Solid Materials** - e.g. construction aggregates.

Within these groupings, the products have been further classified into chemical families, such as organic acids, olefins, polyols etc so that similar products can be grouped together and an example product given where multiple are possible. Information about the potential products, the nature of the chemical reactions which create them and the development status of the reactions are provided as text in each of the four sections listed above.

Following the text, each section provides a table which summarises the market and CO/CO<sub>2</sub> utilisation data to help the reader understand the potential economic and environmental impact of the different products and routes to those products. The tables present the potential product within the class of chemicals, a brief summary of the synthesis route and the overall reaction scheme. Alongside this, the technology readiness level (TRL) is provided to indicate at what stage of development the process is currently. Further details on the other indicators provided in the tables are described below.

### 2.2.1 Market size and value

In order to obtain an idea about the scale and value of the market for potential products which can be made from CO/CO<sub>2</sub>, and also the potential quantity of CO/CO<sub>2</sub> which could be utilised in making such products, the Eurostat databases were used. Prodcom – sold production, exports and imports by PRODCOM list (NACE Rev. 2) – annual data (DS-066341) for 2016 was used to obtain the quantities (tonnages) of the conventionally-produced chemicals produced within or imported into, the EU28 countries. The quantity imported was added to the quantity of production sold to obtain an idea of the scale of the market available. If the export quantity had been subtracted, this would have provided a measure of the level of consumption within the EU28. However, this was not done because by leaving the exports in the figures, the overall quantity of CO<sub>2</sub> which could be incorporated into products by EU manufacturers and the overall size of that market available, can be appreciated.

The same database was also used to provide information on the market value of the chosen products. Along with the quantity data described above, Prodcom also provides data on the value of the production, imports and exports. This value data for the sold production and imports to the EU28 was used together with the equivalent quantity data, to calculate the unit value (€/t) for each product. This was calculated based upon a weighted average, since the value per tonne for sold production and imports differed.

The Prodcom database did not provide data on fuels, so fuel quantity data was obtained from other Eurostat databases. The database “Supply, transformation and consumption of oil - annual data” (nrg\_102a) was used to obtain the most recent (2015) data on the quantities of gasoline, diesel and kerosene-type jet fuel produced and imported into the EU28. The relatively small quantities of biodiesel and bioethanol fuels were not included as this exercise is to estimate the impact of switching

from fossil-based resources. The "Complete Energy Balances – annual data (nrg\_110a)" database was used to obtain 2015 data on the quantities of natural gas produced and imported. This natural gas data was provided using the unit - tonnes of oil equivalent (toe). This was converted to tonnes of methane (CH<sub>4</sub>) using the standard assumption used by Eurostat that 1 toe = 41.868 GJ<sup>1</sup> and that CH<sub>4</sub> has a heat of combustion of 55.5 GJ/tonne<sup>2</sup> and therefore 1 tonne CH<sub>4</sub> = 1.326 toe. The Eurostat databases "Gas prices for household consumers" (nrg\_pc\_202) and "Gas prices for non-household consumers" (nrg\_pc\_203) provided an average gas price across the EU28 for 2016. Diesel and gasoline prices without taxes were obtained from Europe's Energy Portal<sup>3</sup> and jetfuel prices from the International Air Transport Association (IATA).<sup>4</sup>

## 2.2.2 CO/CO<sub>2</sub> utilisation potential

The quantity of CO/CO<sub>2</sub> potentially incorporated into each product was determined by multiplying the tonnes of CO<sub>2</sub> used per tonne of product by the quantity of product produced and sold plus the quantity imported. For example, Table 1 at the end of Section 3.1 of this report, reveals that synthesising benzene from CO<sub>2</sub> uses 3.38 tonnes of CO<sub>2</sub> per tonne of benzene produced. If all of the benzene currently produced and sold within the EU28, plus that imported (i.e. 6,808 kilotonnes (Kt) per year), was made from CO<sub>2</sub>, then the utilisation potential would be:

$$3.38 \text{ tCO}_2/\text{tproduct} \times 6,808 \text{ Kt product} = 23,011 \text{ Kt CO}_2 \text{ utilised}$$

In the cases where there are multiple routes to the production of a product, it may be that one route utilises more CO<sub>2</sub> than another route. In such circumstances, each route shows the EU CO<sub>2</sub> utilisation potential assuming that 100% of the market is met by using that route. In other words, the multiple routes are alternative scenarios, not additive.

At this stage it is important to recognise that the quantity of CO<sub>2</sub> utilised in making a product does not automatically mean that producing that product from CO<sub>2</sub> has a negative carbon balance. Other factors which need consideration include: the energy required to capture the CO<sub>2</sub> utilised; the energy required to produce any H<sub>2</sub> and other inputs needed during the process; the energy required to enable the reaction proceed. Also, whether the energy used was obtained from low carbon sources plays a big part in the overall carbon balance. This topic will be covered in detail as part of Work Package 4.2 where the value of life cycle assessment is discussed.

## 2.2.3 H<sub>2</sub> and other inputs

Many products synthesised from CO<sub>2</sub> and CO require H<sub>2</sub> to produce hydrocarbons. The production of H<sub>2</sub> has an environmental impact, so the amount of H<sub>2</sub> required per tonne of product is provided to enable comparison between products and routes to those products. Similarly, chemical inputs other than H<sub>2</sub> are required to synthesise many of the products, so these have also been listed in the tables.

Several of the chemical reactions require the initial CO/CO<sub>2</sub> to be converted into methanol prior to its subsequent transformation into the final product. In these cases, the H<sub>2</sub> required to produce the methanol from CO or CO<sub>2</sub> has been presented. However, as will be seen from the tables, there are multiple routes to produce methanol from CO and CO<sub>2</sub> which require differing amounts of H<sub>2</sub>. For this reason, the amount of H<sub>2</sub> required to produce products which are produced via methanol is presented as a range of values.

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<sup>1</sup> European Commission (2016). Eurostat statistics explained. Glossary: Tonnes of oil equivalent (toe). [http://ec.europa.eu/eurostat/statistics-explained/index.php/Glossary:Tonnes\\_of\\_oil\\_equivalent\\_\(toe\)](http://ec.europa.eu/eurostat/statistics-explained/index.php/Glossary:Tonnes_of_oil_equivalent_(toe)). Accessed September 2017.

<sup>2</sup> IEA, OECD and Eurostat (2004). Energy statistics manual. Available at: [http://ec.europa.eu/eurostat/ramon/statmanuals/files/Energy\\_statistics\\_manual\\_2004\\_EN.pdf](http://ec.europa.eu/eurostat/ramon/statmanuals/files/Energy_statistics_manual_2004_EN.pdf). Accessed September 2017.

<sup>3</sup> Europe's Energy Portal (2016). Fuel Prices. Available at <https://www.energy.eu/fuelprices/> Accessed October 2017.

<sup>4</sup> International Aviation Fuel Price Analysis. Available at: <http://www.iata.org/publications/economics/fuel-monitor/Pages/price-analysis.aspx> Accessed October 2017.

## 3. Products Utilising CO<sub>2</sub>

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From a thermodynamic standpoint, CO<sub>2</sub> is low in energy and is therefore relatively stable. This can be overcome by adding energy directly (in the form of heat, light or electricity), by reacting it with high-energy molecules (such as epoxides or H<sub>2</sub>), or by producing a product molecule which has an even lower energy content (mineralisation). Additionally, catalysts are often needed to overcome high kinetic barriers.

Despite the above challenges, CO<sub>2</sub> is currently utilised in the production of multiple products. Globally, in 2012, 157 million tonnes of urea, 605,000 tonnes of aromatic polycarbonates, 76,000 tonnes of aliphatic polycarbonates, 80,000 tonnes cyclic carbonates, 90,000 tonnes salicylic acid, 16,000 tonnes acetylsalicylic acid and 4000 tonnes of methanol were produced utilising CO<sub>2</sub>.<sup>5</sup>

The following four sections list the chemicals, chemicals/fuels, fuels and solid products which can be produced from CO<sub>2</sub>. Information about the products, the nature of the chemical reactions which create them and the development status of the processes needed to produce them is provided as text followed by a table summarising relevant information.

### 3.1 Chemicals

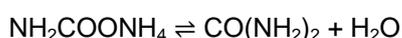
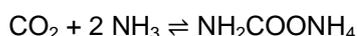
#### 3.1.1 Amides

##### Urea

Urea synthesis is currently the largest industrialised value-added product made from CO<sub>2</sub> utilisation, by quite some margin. Worldwide production stood at around 175 Mt/yr in 2015.<sup>6</sup> The majority of the urea produced is used as an agricultural fertilizer and this market is still expanding, but it is also used to produce the urea-formaldehyde and urea-melamine-formaldehyde resins used in glues, plywood and particle boards such as MDF.

##### Technologies/pathways:

The conventional, commercialised (TRL 9) two-step reaction pathway to synthesise urea is where CO<sub>2</sub> reacts with ammonia (NH<sub>3</sub>) to produce ammonium carbamate in a highly exothermic reaction. This then decomposes into urea and water in a slightly endothermic reaction (see reaction schemes below), so overall the reaction is exothermic and can proceed without the need for a catalyst.<sup>7</sup>



Urea is usually produced adjacent to an NH<sub>3</sub> production plant because large quantities of CO<sub>2</sub> are produced when natural gas is reformed to produce the H<sub>2</sub> for NH<sub>3</sub> production, and this CO<sub>2</sub> is utilised. In future, if the H<sub>2</sub> is produced from low-carbon sources such as water electrolysis rather than from steam methane reforming, then alternative source of CO<sub>2</sub> would be needed. However, incentives may be required to encourage the reuse of CO<sub>2</sub> arising from other industries.

Several commercial processes are currently used, which vary in how the CO<sub>2</sub> is captured and in details of how the reactions proceed. The most widely adopted are the Snamprogetti Urea technology,

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<sup>5</sup> Omae, I (2012). Recent developments in carbon dioxide utilization for the production of organic chemicals. *Coordination Chemistry Reviews* **256**: 1384-1405.

<sup>6</sup> International Fertilizer Association (2016). Available at: [http://www.fertilizer.org/en/doc\\_library/Statistics/PIT/urea\\_public.xlsx](http://www.fertilizer.org/en/doc_library/Statistics/PIT/urea_public.xlsx) Accessed September 2017.

<sup>7</sup> North M. (2015). What is CO<sub>2</sub>? Thermodynamics, Basic Reactions and Physical Chemistry. In *Carbon Dioxide Utilisation: Closing the Carbon Cycle*. Eds. Styring P, Quadrelli EA and Armstrong K. Elsevier.

the Stamicarbon CO<sub>2</sub> stripping process and Toyo Engineering Corp's Aces urea synthesis technology.<sup>8</sup>

During urea synthesis, one molecule of CO<sub>2</sub> is incorporated into one molecule of urea (i.e. a 1:1 stoichiometric ratio). Due to the difference in the mass of the two molecules, this means that 0.73 t of CO<sub>2</sub> is used to produce each tonne of urea. If all the urea produced within the EU28, plus that imported, incorporated 0.73 tCO<sub>2</sub> per tonne, then 3.97 Mt CO<sub>2</sub> would be utilised each year.

Future developments include increasing the CO<sub>2</sub> conversion efficiency, improving the overall thermal efficiency with specific energy consumption reductions.

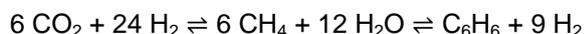
### 3.1.2 Aromatic hydrocarbons

#### Benzene, Toluene and Xylene

Benzene, toluene and xylene (BTX) are important aromatic compounds used for the production of synthetic fibres, resins, detergents and polymers, including polystyrene, polyurethane and polyesters. Production plus imports into the EU in 2016 was 6.8 Mt benzene, 1.3 Mt toluene and 2.6 Mt xylene (plus an additional 1.9 Mt mixed BTX). BTX components are produced conventionally by the steam cracking or catalytic reforming of naphtha.

#### Technologies/Pathways

1). Direct synthesis of benzene from CO<sub>2</sub> by methanation, followed by CH<sub>4</sub> dehydro-aromatisation:



This is achieved using two connected reactors, in a tandem catalysis reaction. The first reactor utilises a Ni/SiO<sub>2</sub> catalyst to form CH<sub>4</sub> which then passes to the second reactor where zeolite supported molybdenum (Mo/HZSM-5) catalyses the aromatisation reaction. Both reactors remained at atmospheric pressure, the first reached 400°C and the second at 700°C. A high CO<sub>2</sub> conversion of 92% was achieved.<sup>9</sup> TRL 2-4.

2). Indirectly via methanol in the Methanol-To-Aromatics (MTA) process developed by Mobil. Methanol can be converted to a range of aromatic compounds simultaneously using a zeolite catalyst (e.g. ZSM-5) at 370-540°C and 20-25 bar pressure. Compared to the methanol to olefins process, the temperature is lower and higher catalyst acidity is required. High conversion rates of 95–100% are achievable with an aromatics yield of 60–70% of which 80% are BTX, resulting in a total BTX yield of around 56%. TRL 7.

### 3.1.3 Aldehydes

#### Formaldehyde

Formaldehyde (together with paraformaldehyde) is conventionally synthesised by the oxidation of methanol on an industrial scale, 1 Mt/yr in Europe. It is primarily used in resins, plastics and paints, so if synthesised from CO<sub>2</sub>, it would offer the ability to sequester large quantities of CO<sub>2</sub> into long-life

<sup>8</sup> CEFIC/EUcheMs (2011/2012). Workshops Roadmaps for CO<sub>2</sub> Utilisation.

<sup>9</sup> Zhu *et al.* (2017). Tandem catalytic synthesis of benzene from CO<sub>2</sub> and H<sub>2</sub>. *Catal. Sci. Technol.* **7**: 2695-2699.

products. An example is urea-formaldehyde, a common insulating, fabric and wood glue material, made on a million-tonne per year scale.<sup>10</sup>

There are two potential routes to formaldehyde which utilise CO<sub>2</sub>:

1). Formaldehyde can be synthesised directly from CO<sub>2</sub> by hydrogenation to the intermediate formic acid, followed by further reduction to formaldehyde:



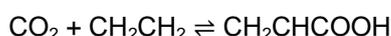
2). Alternatively, formaldehyde can be produced by the reduction of CO<sub>2</sub> using borane (boron trihydride) as the reductant, which is catalysed by a polyhydride ruthenium complex. The latter was done at atmospheric pressure and 25°C, but has only been achieved in the laboratory so far (TRL 1-3).<sup>11</sup>

### 3.1.4 Organic Acids

#### Acrylic acid

The European market for acrylic acid stands at around 1.3 Mt/yr, or 1.9 Mt/yr if methacrylic acid, its salts and esters are included. Acrylic acid is currently produced in a two-step process by the catalytic oxidation of propylene to acrolein, then to acrylic acid. However, it can be synthesised by the reaction of CO<sub>2</sub> with ethylene. This reaction could potentially be extended to produce methacrylic acid from propylene and adipic acid from butadiene – both of which are large volume chemicals (adipic acid is a precursor to nylon).

Researchers at BASF (the world's largest producer of acrylic acid) and Dow Chemicals have reported progress on the synthesis of acrylic acid from ethylene using metallo-lactone catalysts:

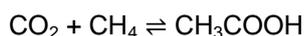


but research is still at lab scale (TRL 1-4).

#### Acetic acid

Acetic acid is widely used within the chemicals industry, both as a solvent and as a feedstock, and it is a major commodity chemical. One use is in the synthesis of acetate monomers for polymerisation into cellulose acetates and polyvinyl acetate (PVA), commonly found in glues and building materials such as plaster (representing a route that could lead to sequestration of CO<sub>2</sub> on a large scale).<sup>12</sup> It is currently made on a large scale in Europe (1.23 Mt/yr) with a market value of approximately €583M.

Acetic acid is commonly synthesised by the carbonylation of methanol using either the Cativa process using an iridium catalyst or the Monsanto process which utilises a rhodium catalyst. However, it can be synthesised by using the reaction of CO<sub>2</sub> with methane:



Current catalysts show low selectivity to acetic acid, so (as with the majority of the organic acids), the development of novel catalysts with higher yields and selectivities is required. The reaction could potentially be extended to produce propionic acid (CH<sub>3</sub>CH<sub>2</sub>COOH) and other useful organics

<sup>10</sup> Dowson and Styring (2015). Conversion of Carbon Dioxide to Oxygenated Organics. In *Carbon Dioxide Utilisation: Closing the Carbon Cycle*. Eds. Styring P, Quadrelli EA and Armstrong K. Elsevier.

<sup>11</sup> Bontemps *et al.* (2014). Ruthenium-Catalysed Reduction of Carbon Dioxide to Formaldehyde. *Journal of the American Chemistry Society* **136**: 4419-4425.

<sup>12</sup> Dowson and Styring (2015). Conversion of Carbon Dioxide to Oxygenated Organics. In *Carbon Dioxide Utilisation: Closing the Carbon Cycle*. Eds. Styring P, Quadrelli EA and Armstrong K. Elsevier.

Alternatively, LanzaTech, in collaboration with the Malaysian oil company Petronas, is developing a CO<sub>2</sub> to acetic acid process utilising the gas fermentation abilities of the acetogenic bacterium *Clostridium sp.*<sup>13</sup> This is discussed further under Ethanol in Section 3.2.1.

## Salicylic acid

Salicylic acid, the precursor to aspirin, is one of the products which is manufactured already by utilising CO<sub>2</sub> during production, and has done so since the late nineteenth century. Together with o-acetylsalicylic acid and its salts and esters, the EU market stands at around 43 Kt/yr. The sodium salt of phenol, sodium phenoxide, is carboxylated with CO<sub>2</sub> in the Kolbe-Schmidt reaction to form salicylic acid. This process is exothermic ( $\Delta H_f = -31$  KJ/mol) and like the reaction leading to the production of urea, it can proceed without the need for a catalyst.<sup>14</sup>

## Benzoic acid

The aromatic acids are a widely used class of chemicals which are currently mainly produced by the oxidation of liquid alkylaromatics. Production and imports into the EU28 of benzoic acid and its salts amounted to 190 Kt in 2016. They can, however, be synthesised by the reaction of CO<sub>2</sub> with benzene or substituted benzenes, but this appears only to be done at the lab scale.

***p*-Hydroxybenzoic acids** can be used as co-monomers in polycarbonates and polyesters, and also in liquid-crystalline polyesters which are used as high performance materials in the electronics industry. Esters of *p*-hydroxybenzoic acid (parabens) are used as preservatives in cosmetics and pharmaceuticals.

Like salicylic acid, *p*-hydroxybenzoic acid is produced commercially by the Kolbe-Schmitt reaction which utilises CO<sub>2</sub>, but when potassium phenolate is used instead of sodium phenolate, then the reaction yields *p*-hydroxybenzoic acid rather than salicylic acid.<sup>15</sup>

## Formic Acid

The European market for formic acid is currently around 490 Kt/yr with a market value of €267M. Formic acid is used as a preservative/antibacterial agent, defrosting agent, caustic, adhesive, used in leather tanning and rubber production. The methylester is used for production of dimethylformamide (DMF, solvent) and formamide). Formic acid can also be used as a fuel in fuel cells where it acts as an energy carrier with H<sub>2</sub> being the primary fuel.

There are two synthesis pathways from CO<sub>2</sub>:

1). Electrochemical reduction of CO<sub>2</sub>, there are few demonstration plants, DNV Norway produces around 350 kg/yr; Mantra Energy Alternatives Inc. is building a 35 t/yr plant in Vancouver. TRL 5-6 early demonstration phase. Work needed to find catalysts with long-term performance characteristics and low energy use; reactor configurations to be improved; develop cost-effective methods to concentrate formic acid solutions.<sup>16</sup>

2). Catalytic reduction of CO<sub>2</sub> (using H<sub>2</sub> produced from renewable sources) – combined with a catalyst for the reverse step this is proposed as a method to store/transport H<sub>2</sub>. Research at lab scale 2-3. Development needed to improve the stability and productivity of catalysts not based on noble metals.<sup>17</sup>

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<sup>13</sup> LanzaTech (2017). Chemicals Available at: <http://www.lanzatech.com/innovation/markets/chemicals/> Accessed September 2017.

<sup>14</sup> North M. (2015). What is CO<sub>2</sub>? Thermodynamics, Basic Reactions and Physical Chemistry. In *Carbon Dioxide Utilisation: Closing the Carbon Cycle*. Eds. Styring P, Quadrelli EA and Armstrong K. Elsevier.

<sup>15</sup> Peters *et al.* (2011). Chemical Technologies for Exploiting and Recycling Carbon Dioxide into the Value Chain. *ChemSusChem* **4**: 1216-1240.

<sup>16</sup> Perez-Fortes *et al.* (2016). Formic acid synthesis using CO<sub>2</sub> as a raw material: Techno-economic and environmental evaluation and market potential. *Int. J. Hydrogen Energy* **41**: 16444-16462.

<sup>17</sup> CEFIC/EUcheMs (2011/2012). Workshops Roadmaps for CO<sub>2</sub> Utilisation.

## Oxalic Acid

With the chemical formula HOOC-COOH, oxalic acid is the simplest dicarboxylic acid. Oxalic acid has a wide range of uses: fixing dyes to fabrics, precipitating rare earth metals to ease their extraction and as a bleaching/cleaning/rust removal agent. It is used for manufacturing esters and in the pharmaceutical industry it is used in the production of the antibiotics tetracycline, oxytetracycline and chlortetracycline. Glyoxylic acid can be obtained from the electroreduction of oxalic acid in water and glyoxylic acid is widely used in the fine chemicals industry.

Oxalic acid is currently produced by the oxidation of carbohydrates, ethylene glycol or propylene with nitric acid or nitric acid mixed with another acid. However, a process to avoid the use of the environmentally damaging nitric acid would be desirable.

By combining two CO<sub>2</sub> molecules, oxalic acid can be synthesised by the electrochemical reduction of CO<sub>2</sub> in a water-free aprotic media. This technique leads to 100% atomic efficiency, but requires the use of sacrificial anodes in an aprotic media. The technique yields a metallic oxalate which precipitates in the electrolyte and after separation needs to be converted into oxalic acid by recovering the metal allowing it to be recycled as the anode by using a conventional hydrometallurgical process. Reported yields are up to 85%, but deposition of the metallic oxalate leads to fouling of the cathode resulting in a continuous decrease in current efficiency.

The process is currently approximately at TRL 3-4. Further development work is needed to identify a non-degradable and easily recyclable electrolyte, plus reactor design improvements are required for future scale-up. An electrochemical reactor with sacrificial anodes needs to be developed which is designed for continuous metal feeding to the anode site without halting the process; designed with a geometry able to avoid the metallic oxalate deposition on the cathode; able to work at pressure up to 20 atm; able to operate at 1000 A/m<sup>2</sup> while maintaining a current efficiency of 80% or higher.

## Butyric acid

European production and imports of butyric, propanoic, pentanoic and chloroacetic acid combined are around 472 Kt/yr according to Prodcum data. Butyrate esters are used as food and perfume additives due to their pleasant aromas or tastes and butyric acid is found naturally in milk and is also produced during anaerobic fermentation processes.

Butyric acid is produced conventionally either chemically by the oxidation of butraldehyde, or biologically by the fermentation of starch by the anaerobic bacterium *Clostridium butyricum* or *C. tyrobutyricum* whose main products of fermentation is butyric acid and acetic acid. It can, however, be produced via gas fermentation by certain *Clostridium* species which are able to utilise CO<sub>2</sub> as their sole carbon source. This process does not appear to have been developed beyond the lab. See also Section 3.2.1 under Ethanol.

## 3.1.5 Olefins

### Ethylene & Propylene

Ethylene and propylene are produced in bulk from petrochemical feedstock. They act as chemical building blocks for many large-scale products including: polyethylene, polypropylene, styrene (via ethylbenzene), monoethylene glycol and other polyols such as polyethylene glycol (via ethylene/polyethylene oxide), acrylic acid, acrylonitrile, isopropylbenzene and downstream polymers including polyesters such as polyethylene terephthalate (PET) or polyurethanes. Further downstream products include PVC, polystyrene, polyacrylates, PMMA (plexiglass) and carbon fibres. Oxidation into acetone and further conversion into bisphenol A - further downstream products then include

polycarbonates and epoxy resins.<sup>18 19</sup> Reflecting this broad utility, nearly 11 Mt of ethylene is produced or imported into Europe per year, however, if polyethylene and other polymers of ethylene are included this rises to over 24 Mt/yr. For propylene the equivalent figure is 10 Mt, while if all forms of polypropylene is included then the figure is 27 Mt produced or imported per year.

#### Technologies/pathways:

Four pathways which utilise CO<sub>2</sub> have been identified, two produce ethylene directly while the remaining two produce it via methanol:

- 1). The direct conversion of CO<sub>2</sub> and renewable H<sub>2</sub> to light olefins is possible using modified Fischer-Tropsch catalysts. The synthol process developed by SASOL of South Africa uses CO and H<sub>2</sub> to produce a product high in olefins.
- 2). The selective electrocatalytic reduction of CO<sub>2</sub> to ethylene on copper(I) oxide films has been shown. The faradaic yields of ethylene can be systematically tuned by changing the thickness of the deposited overlayers on the electrodes. Films 1.7–3.6 µm thick exhibited the best selectivity, with faradic efficiencies of 34–39% for ethylene.<sup>20</sup>
- 3). Partial reduction of CO<sub>2</sub> to methanol, followed by the dehydration of two methanol molecules to form one molecule of dimethyl ether (DME), prior to conversion to olefins. Referred to as the Methanol-To-Olefin (MTO) process. Catalysts include silico-aluminophosphate (SAPO-34 or MTO-100) or zeolite systems. Several MTO technologies are licensed, UOP LLC & Norsk Hydro (; ExxonMobil; Lurgi & Statoil; SYN Energy Technology Co. & Lummus Technology. MTO has started to enter commercialisation with several plants built in China, but not in Europe that we are aware of.
- 4). An alternative route from methanol to propylene is to react ethylene with methanol to form propylene.

Current research efforts aimed at a direct electro-catalytic production of ethylene from CO<sub>2</sub> and water in a single step are all at early stages of development. While the general proof of concept has been shown, this technology is still at TRL 1-3. However, if it could be developed it would be significant as it omits the need of intermediate products such as methanol as feedstock for olefin synthesis. The direct F-T process needs to improve the stability and selectivity of the C<sub>2</sub>-C<sub>3</sub> olefins produced, catalysts require scale-up and pilot testing.

The overall TRL of the MTO processes are 8-9, but current implementation is based upon coal to methanol to olefins. Main development requirements lie in the methanol synthesis. Similarly the MTO process needs to improve catalyst stability and productivity. The energy demand of the entire chain from CO<sub>2</sub> to olefins is twice that of naphtha steam cracking, and it depends upon the availability of renewable H<sub>2</sub>.

## 3.1.6 Epoxides

### Ethylene oxide

Epoxides have a large market as monomers for polymers such as polycarbonates. One of its main uses is in the production of ethylene glycol (see below). Ethylene oxide alone account for 0.95 Mt/yr in Europe.

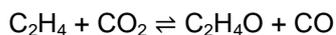
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<sup>18</sup> Dechema (2017). Low carbon energy and feedstock for the European chemical industry. Technology study commissioned by Cefic. Frankfurt.

<sup>19</sup> CEFIC/EUcheMs (2011/2012). Workshops Roadmaps for CO<sub>2</sub> Utilisation.

<sup>20</sup> Ren et al. (2015). Selective Electrochemical Reduction of Carbon Dioxide to Ethylene and Ethanol on Copper(I) Oxide Catalysts. *ACS Catalysis* 5: 2814 - 2821.

Ethylene oxide is generally produced by the direct oxidation of ethylene, but epoxides can be synthesised using CO<sub>2</sub> by the carboxylation of the olefin with the concomitant production of CO:



The reaction occurs if mediated by metal oxide catalysts.<sup>21</sup>

### 3.1.7 Polyols

Polyether polycarbonate polyols are covered in section 3.1.12 Polycarbonates (aliphatic)

#### Ethylene glycol and propylene glycol

European production and imports for ethylene glycol in 2016 was 1.94 Mt, and 0.76 Mt for propylene glycol (the market for all polyols was 5.4 Mt). Ethylene glycol is used as an antifreeze in coolants and heat transfer agents and as a precursor to polyesters such as polyethylene terephthalate (PET) used for plastic bottles. Similarly, propylene glycol is used in polyesters and polyurethanes as well as finding uses as a solvent in multiple applications.

Ethylene glycol is conventionally produced from ethylene, via ethylene oxide (with propylene glycol being produced via propylene oxide using the same route). However, the electrochemical reduction of CO<sub>2</sub> to polyols is possible:



Toshiba reports developing a highly efficient molecular catalyst that converts CO<sub>2</sub> into ethylene glycol, without producing other and unwanted by-products. The new catalyst can be used in electrochemical reactions powered by solar energy (often referred to as "artificial photosynthesis") to convert carbon dioxide and water into carbon compounds. Most artificial photosynthesis technologies use a two-step reduction conversion process, producing CO and formic acid. Others can achieve direct multi-step reduction, but tend to produce many by-products leading to separation problems. Toshiba's catalyst consists of an imidazolium salt applied to a metal surface and the resulting conversion is highly efficient, with the Faradaic efficiency reaching 87%.<sup>22</sup>

### 3.1.8 Carbonates (inorganic)

#### Sodium bicarbonate

Sodium bicarbonate has a wide variety of uses. In purified form is referred to as baking soda and baking powder where it is used in cookery. It is also used as a mild disinfectant, for pest control, to neutralise acid spills, as an antacid to treat acid indigestion, in medications and toothpastes and mouthwashes and as a cleaning agent. The EU market is 3.6 Mt/yr.

A CO<sub>2</sub> gas stream can be passed through an aqueous solution of sodium hydroxide to produce sodium carbonate, sodium bicarbonate or a mixture of the two. Further products can be achieved by combining chlorine with water to produce hypochlorous acid, allowing this to decay to hydrochloric acid, then using this to mix with the separated Ca<sub>2</sub>CO<sub>3</sub> to form CaCl. A demonstration plant operated by Carbonfree Chemicals in San Antonio, Texas, reports producing sodium bicarbonate, hydrochloric

<sup>21</sup> Aresta *et al.* (2016). State of the art and perspectives in catalytic processes for CO<sub>2</sub> conversion into chemicals and fuels: The distinctive contribution of chemical catalysis and biotechnology. *Journal of Catalysis* **343**: 2-45.

<sup>22</sup> Tamura *et al.* (2015). Electrochemical reduction of CO<sub>2</sub> to ethylene glycol on imidazolium ion-terminated self-assembly monolayer-modified Au electrodes in an aqueous solution. *Phys. Chem. Chem. Phys.* **17**: 26072-26078.

acid, sodium hydroxide and sodium hypochlorite (bleach) and expects to capture 75,000 tonnes CO<sub>2</sub> annually.<sup>23</sup>

### 3.1.9 Carbonates (cyclic)

Cyclic carbonates have been synthesised commercially since the 1950s and they are continually increasing in commercial importance as they have multiple applications. Ethylene carbonate is used as an electrolyte in lithium ion batteries, the market for which keeps on expanding. It is also used as a solvent in polyacrylonitrile spinning and as an educt for synthesis of various heterocycles. Propylene carbonate has similar applications and is also used as a plasticizer. Glycerol carbonate is an emerging green chemical which is useful as a solvent, a wetting agent in cosmetic formulations, a carrier in pharmaceutical formulations, for manufacturing intermediates such as glycidol, manufacturing of polyglycerols, synthesis of polycarbonates and blocked isocyanates. Its potential role in producing monomers useful in the manufacturing of non-isocyanate polyurethanes (so avoiding the use of the toxic isocyanate monomers) is also under investigation.

Currently market volumes are modest, however demand is expected to grow at 20% per year based upon the emerging market for sustainable chemicals. As an example, demand for glycerol carbonate is expected to be boosted by applications related to manufacture of non-isocyanate polyurethanes.

#### Technologies/pathways

Cyclic carbonates can be made from CO<sub>2</sub> following four different routes: the reaction between CO<sub>2</sub> and an epoxide (such as ethylene oxide), a diol (such as ethylene glycol), a monohalohydrin (such as 2-chloro-ethanol) or an olefin (such as ethylene).

**Epoxide route:** Although more complex carbonates are produced using phosgene, the simple but industrially important cyclic carbonates ethylene and propylene carbonate have been produced commercially using the reaction between the epoxides ethylene (or propylene) oxide and CO<sub>2</sub>. Since the 1950s.<sup>24</sup> Styrene oxide and cyclohexene oxide can also undergo the same reaction to their respective carbonates.

Due to the length of time in commercial production there has been a lot of research into the best catalysts to use. The range includes the traditional, simple phosphonium or ammonium salts, organometallic complexes, transition metals complexed by large macrocycles and ionic liquids. There are also pure heterogeneous catalysts based on metal oxides and supported versions of the salts and metal complexes mentioned above. Efforts continue to make catalysts faster, more selective, more robust toward impure sources of CO<sub>2</sub> and more active at low CO<sub>2</sub> pressures or concentrations.<sup>25</sup>

Regardless of the nature of the catalyst, a successful one will have some aspect of bifunctionality, i.e. both nucleophilic and electrophilic, or acidic and basic, or cationic and anionic. This bifunctionality plays a significant role in the activation and reaction of the epoxide. In general, the epoxide is activated by the cationic or electrophilic portion of the catalyst, the anion or the nucleophilic portion of the catalyst then opens the epoxide and CO<sub>2</sub> is inserted to give a linear carbonate. The catalyst causes the ring to close to form a cyclic carbonate.<sup>26</sup>

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<sup>23</sup> Carbonfree Chemicals (2017). Carbonfree Chemicals' Plant – information available at <http://www.carbonfreechem.com/carbonfree-chemicals-plant>, including several US patents available at <http://www.carbonfreechem.com/newsroom/patents>. Accessed September 2017.

<sup>24</sup> North M. (2012). Synthesis of cyclic carbonates from epoxides and carbon dioxide using bimetallic aluminium(salen) complexes. *ARKIVOC* 1: 610-628.

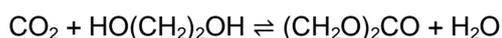
<sup>25</sup> CEFIC/EUcheMs (2011/2012). Workshops Roadmaps for CO<sub>2</sub> Utilisation.

<sup>26</sup> Heyn R.H. (2015). Organic Carbonates. In *Carbon Dioxide Utilisation: Closing the Carbon Cycle*. Eds. Styring P, Quadrelli EA and Armstrong K. Elsevier.

The key challenge to the epoxide route is the energy efficient synthesis of the starting epoxides - these are high energy containing reactants which are energy-intensive to produce. New synthetic routes for the direct synthesis of cyclic carbonates from olefins and CO<sub>2</sub> are possible.

**Diol route:** Carbon dioxide will react with diols to form 5-membered cyclic carbonates. The diols utilized in this reaction are primarily ethylene glycol, propylene glycol and glycerol, but the majority of reports study only the reaction of propylene glycol to propylene carbonate.

As shown in the reaction scheme below, the reaction of CO<sub>2</sub> with the diol involves the co-production of H<sub>2</sub>O and suffers from a small equilibrium constant, resulting in low product yields.



The effectiveness of the catalysts can be divided between those that show activity without the need for added water traps such as acetonitrile (MeCN) and those that require such equilibrium-shifting aids to observe any production of carbonate. Without the use of water traps such as MeCN, carbonate yields are commonly just a few percent, with the yields of ethylene carbonate often about half those propylene carbonate. Metal acetates form the most commonly studied catalysts for the synthesis of propylene carbonate in the presence of MeCN where yields of up to 19% are reported using Zn(OAc)<sub>2</sub>. Due to the problems discussed above, the glycol to carbonate route does not appear to have been developed beyond the small pilot plant stage.

Interestingly, the same reaction but in the reverse direction (where ethylene carbonate is hydrolysed back to monoethylene glycol) is the basis of the Omega process which Shell operates on a 750,000 tonne per annum scale and licenses to other manufacturers of ethylene glycol.<sup>27</sup>

**Monohalohydrin route:** CO<sub>2</sub> plus monohalohydrins (such as 2-chloro-ethanol, 3-chloro-1,2-propanediol) produce cyclic carbonates such as ethylene, propylene or glycerol carbonate. The technology has been shown to work at lab scale with yields of between 85-90% using tertiary amines as CO<sub>2</sub> fixation-activation agents, pressures up to 50 atm and temperatures up to 100°C. The monohalohydrin starting materials can be synthesized from diol and the corresponding hydrohalic acid. TRL 4-5.

The challenge is to decrease energy consumption by developing synthetic strategies at lower pressures (below 15 atm) and temperatures (below 80°C) while maintaining high yields. Also, developing an efficient catalyst separation process, so enabling the expensive catalysts to be recycled would aid progress towards feasibility demonstration at pilot plant scale.

**Olefin route:** Another, much less investigated reaction for cyclic carbonate synthesis is the direct oxidative carboxylation of an olefin such as ethylene. This reaction is effectively the synthesis of an epoxide from the required olefin, followed by a ring-forming carboxylation reaction. The challenge is in developing a system which allows both the epoxidation and then the carboxylation, to occur in a single reaction vessel.

Homogenous catalysts have been found that can convert styrene to its carbonate with a mixture of CO<sub>2</sub> and O<sub>2</sub>, with 20-30% yields of the carbonate were obtained, but the reaction was not selective with multiple products produced. While the homogeneous catalyst systems tend to exhibit good activities, their short lifetimes and issues of separation and recycling have led to the search for heterogeneous catalysts for the same reaction. Many of the heterogeneous catalysts that have been studied are binary systems based on an epoxide catalyst and a carboxylation catalyst.<sup>28</sup>

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<sup>27</sup> North M. (2015). What is CO<sub>2</sub>? Thermodynamics, Basic Reactions and Physical Chemistry. In *Carbon Dioxide Utilisation: Closing the Carbon Cycle*. Eds. Styring P, Quadrelli EA and Armstrong K. Elsevier.

<sup>28</sup> Heyn R.H. (2015). Organic Carbonates. In *Carbon Dioxide Utilisation: Closing the Carbon Cycle*. Eds. Styring P, Quadrelli EA and Armstrong K. Elsevier.

### 3.1.10 Carbonates (linear)

Linear carbonates such as dimethyl carbonate (DMC) are used as intermediates in the production of polycarbonates, as solvents in lithium ion batteries, lubricants and as a methylating agent in organic synthesis. The market is relatively small at around 2 Mt/yr globally (90 Kt/yr for DMC), but growing due to the increasing use of lithium ion battery technology. DMC is still being synthesised conventionally using the reaction between methanol and the toxic gas phosgene because the alternative processes available are more expensive, so new production routes are desirable.

Linear carbonates can be made directly from CO<sub>2</sub> and two alcohol molecules. The most studied example is between CO<sub>2</sub> and methanol to synthesise DMC:



The small equilibrium constant for such reactions lead to equilibrium yields for these reactions on the order of 1-2% product. Removal of the co-produced water is one way to increase the yield of the desired carbonate. Both physical and chemical water traps have been employed to remove the water and so shift the reaction equilibrium to the right with varying success. The two most studied catalytic systems for these reactions are the tin oxides and ceria-zirconia oxides, the former functioning as homogeneous catalysts and the latter as heterogeneous catalysts.<sup>29</sup> Further work is required to develop reactor technologies (in-situ water removal, catalytic distillation) to shift the reaction equilibrium and increase yields and to develop more productive catalysts.

### 3.1.11 Polycarbonates (aromatic)

Aromatic polycarbonates are produced conventionally by the reaction between phosgene and bisphenol-A. Both of these monomers are associated with safety questions, but utilising CO<sub>2</sub> provides an alternative to the use of phosgene. The EU market for polycarbonates (in primary forms and plates/sheets of product) is around 1.5 Mt/yr and worth around €3.9 billion according to Prodcum data.

The phosgene needed to produce aromatic polycarbonates can be replaced by diphenyl carbonate which in turn can be produced from dimethyl carbonate and phenol. This dimethyl carbonate can be prepared from ethylene carbonate and methanol, with the ethylene carbonate being synthesised from CO<sub>2</sub> plus ethylene oxide and the methanol also being made from CO<sub>2</sub> in a variety of potential routes (all described in the relevant sections in this report). Although this appears to be a long and arduous chain of reactions, the methanol and phenol intermediates are recycled within the process, so the only by-product is a highly pure anhydrous form of ethylene glycol which has significant commercial value.<sup>30</sup>

### 3.1.12 Polycarbonates (aliphatic)

Carbon dioxide can be made to react with an epoxide such as ethylene oxide, resulting in either a cyclic carbonate such as ethylene carbonate, or an aliphatic polycarbonate. Both reactions are highly exothermic and the product is dependent upon the catalyst used.

The commercial production of polycarbonates has developed relatively recently and most processes are still at pre-production stage. However, the market for aliphatic polycarbonates is potentially very large as they are transparent and have good impact resistance and so could replace many existing petrochemical derived polymers. In addition, low molecular weight polycarbonates can be used as

<sup>29</sup> Heyn R.H. (2015). Organic Carbonates. In *Carbon Dioxide Utilisation: Closing the Carbon Cycle*. Eds. Styring P, Quadrelli EA and Armstrong K. Elsevier.

<sup>30</sup> North M. (2015). What is CO<sub>2</sub>? Thermodynamics, Basic Reactions and Physical Chemistry. In *Carbon Dioxide Utilisation: Closing the Carbon Cycle*. Eds. Styring P, Quadrelli EA and Armstrong K. Elsevier.

replacements for polyether polyols which are one component of polyurethanes which have a global annual production in excess of 10 million tonnes.<sup>31</sup>

Carbon dioxide can be used directly as a component of a polymer or it can be used indirectly to produce a monomer which is then used to produce a polymer.

Ring opening copolymerisation of CO<sub>2</sub> and epoxides was discovered as a direct route to production of CO<sub>2</sub> based polymers 40 years ago. Upon reacting with CO<sub>2</sub>, the epoxide ring opens and forms a linear carbonate which can be made to copolymerise with other polycarbonates or polyether carbonates if a suitable catalyst is used in combination with the right reaction conditions. This repeating reaction forms polymers by the repetitive lining-up of the linear carbonate monomers.

The catalysts used include metal complexes of Co(III), Cr(III), Mn(III) or Al(III) coordinated by ligands such as salens or porphyrins. Co-catalysts of ionic compounds or Lewis bases are also utilised and some rare-earth compounds also exhibit very high carbonate selectivities in CO<sub>2</sub> co-polymerization.<sup>32</sup>

Detailed investigations of alternating epoxide/CO<sub>2</sub> copolymerization have led to improved understanding of the mechanisms of catalysis which has enabled the rational design of tailor-made catalysts. The resulting catalyst systems, optimised for the synthesis of alternating (aliphatic) polycarbonates, are very powerful, highly active as well as selective. Polymer molecular weights of up to several hundred kg/mol are reached while practically no cyclic carbonate is formed as side product during the synthesis. For the alternating copolymerization of propylene oxide and CO<sub>2</sub> to yield polypropylene carbonate, it has been reported that average molecular weights of 300 kg/mol have been achieved. Catalyst turnover frequencies as high as 26,000/hr have been achieved with special cobalt(III)-salen complexes.<sup>33</sup>

Many aliphatic polycarbonates are used as binders in ceramics, adhesives and pyrotechnics due to their thermal characteristics which prevent classic thermoplastic applications. For example, pure polypropylene carbonate (which contains 43 wt% CO<sub>2</sub>) has a glass transition point at around 40°C and decomposes directly to cyclic propylene at 250°C. However, it has mechanical properties such as high tensile strength plus elasticity which suit its new application as an impact modifier e.g., in polyhydroxybutyrate (PHB), polyvinyl chloride (PVC) or poly(methyl methacrylate) (PMMA, Plexiglas) formulations. Additionally, their biodegradability and hydrolytic cleavage make these materials interesting for biomedical and packaging applications.

Alicyclic polycarbonates (aliphatic and cyclic but not aromatic), such as poly(cyclohexene carbonate), typically exhibit higher glass transition and decomposition temperatures compared to aliphatic polycarbonates. This may enable them to be processed in the molten state which could allow for potential future use as engineering thermoplastics or resins.

Other direct CO<sub>2</sub> co-polymerization methods which have been explored include co-polymerisations of CO<sub>2</sub> with oxetanes (oxygen containing four-membered rings) to obtain aliphatic polycarbonates, however this route will not be discussed further here.

## Polyether carbonates and polyether carbonate polyols (Covestro process)

Using special catalyst classes results in the copolymerization of epoxide and CO<sub>2</sub> to yield polymers containing carbonate as well as ether forms. These polymers are referred as polyether carbonates.

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<sup>31</sup> North M. (2015). What is CO<sub>2</sub>? Thermodynamics, Basic Reactions and Physical Chemistry. In *Carbon Dioxide Utilisation: Closing the Carbon Cycle*. Eds. Styring P, Quadrelli EA and Armstrong K. Elsevier.

<sup>32</sup> Trott *et al.* (2016). Catalysts for CO<sub>2</sub>/epoxide ring-opening copolymerisation. *Phil. Trans. R. Soc. A*. **374**: 20150085.

<sup>33</sup> Langanke *et al.* (2015). Polymers from CO<sub>2</sub> - An Industrial Perspective. In *Carbon Dioxide Utilisation: Closing the Carbon Cycle*. Eds. Styring P, Quadrelli EA and Armstrong K. Elsevier.

The favoured catalytic systems for the synthesis of polyether carbonates are double metal cyanide complexes (DMC catalysts) and such catalysts with an unusual non-stoichiometric composition are also favoured for industrial synthesis of polyether polyols. There are extensive efforts to fully optimize these catalytic systems, but due to their amorphous and complex structure, determination of the relationship between structure and activity is proving difficult. It seems that not only the overall chemical composition (metal, ligands, dispersion agent, etc.) but also details of the preparation protocol (solvents, precipitation, drying, etc.) influence the catalytic performance.

In addition to the coordination of epoxide to various catalytic sites, CO<sub>2</sub> coordination also plays a crucial role. Polymerisations at higher CO<sub>2</sub> pressures result in more carbonate units in the polymer backbone, but the reaction rate decreases at the same time.

The polyether carbonates are highly thermally stable compared to the aliphatic polycarbonates - the decomposition temperature of polyether carbonate polyols reportedly exceeds 300°C. Such thermal properties, in combination with defined molecular structures and the ability to add chemically “active” end groups, offer a very broad field of potential applications.<sup>30</sup>

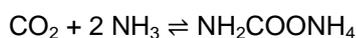
The most significant example of direct epoxide/CO<sub>2</sub> copolymerization to produce polyether carbonate polyols was achieved at Bayer (now Covestro) in their small commercial demonstration plant. Here, the exothermic epoxide ring opening provides the energy necessary for the CO<sub>2</sub> activation.

Due to the highly exothermic nature of the epoxide reaction, reactor and process design are important to allow- temperature control. One control option is to operate in a semi-batch mode with controlled epoxide feed. This allows the epoxide concentration to be kept low and so avoids the danger of thermal run-away. Another option is to utilise a continuous reactor which offers better heat removal, faster overall reaction rates and thus lower epoxide concentrations.

Polyether carbonate polyols are one of two raw materials required to produce polyurethanes, so the resulting polyurethane properties are influenced by the constituent polyols. Viscosity of the polyols is influenced by their CO<sub>2</sub> content and the resulting polyurethanes need to display appropriate thermal stability and strength characteristics.<sup>34</sup>

### 3.1.13 Carbamates (inorganic)

Carbamates are compounds derived from carbamic acid (NH<sub>2</sub>COOH). The inorganic compound ammonium carbamate (NH<sub>2</sub>COONH<sub>4</sub>) is produced as an intermediate in the production of urea when CO<sub>2</sub> reacts with ammonia.



Ammonium carbamate can be used as a substitute for ammonia in various applications such as in the denitrification of exhaust emissions, and is used as an ingredient in various agricultural pesticides. This production process using CO<sub>2</sub> is the current commercial route, so TRL 9.

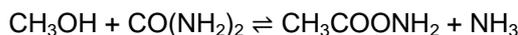
### 3.1.14 Carbamates (organic)

The EU market for organic carbamates (including cyclic and acyclic amides) is 1.2 Mt/yr. Carbamates are generally synthesised commercially by reacting an alcohol with urea, both of which can be

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<sup>34</sup> Langanke *et al.* (2015). Polymers from CO<sub>2</sub> - An Industrial Perspective. In *Carbon Dioxide Utilisation: Closing the Carbon Cycle*. Eds. Styring P, Quadrelli EA and Armstrong K. Elsevier.

produced from CO<sub>2</sub>. The simplest carbamate, methyl carbamate, is produced by reacting methanol and urea, often catalysed with boron trifluoride or cupric acetate:<sup>35</sup>



Methyl carbamate is used primarily as a reactive intermediate in the textile and polymer industries, but it also is used in the manufacture of some pharmaceuticals and insecticides.

The above reaction with methanol could also be performed on a polyol to produce a polycarbamate, which can subsequently be reacted with a polyaldehyde to create a three-dimensional polyurethane cross-linking structure. The catalyzed reaction can proceed at room temperature that makes the reaction suitable as a potential replacement for some isocyanate-derived products.

A carbamate can subsequently be reacted with a single aldehyde to produce hemiaminal, or two aldehydes to produce an aminal. The range of potential polycarbamate building blocks via aminal chemistry is wide, since the number of possible polyols is immense and the urea feedstock is relatively cost-effective.<sup>36</sup>

### 3.1.15 Dicarbamates

Dicarbamates are compounds which have two carbamate groups (-COONH<sub>2</sub>), a simple example being 1,2-ethanediol dicarbamate C<sub>2</sub>H<sub>4</sub>(COONH<sub>2</sub>)<sub>2</sub>. The potential market is large as it relates to the substitution of diisocyanates currently used in the manufacturing of polyurethanes. For example, methylene diphenyl diisocyanate (MDI) accounts for over 60% of total diisocyanate production worldwide and together with polymeric MDI, global MDI production was over 6 Mt in 2016. MDI could be substituted in many applications by 4,4'-diphenylmethane di(methyl carbamate).

Dicarbamates are formed by the reaction of CO<sub>2</sub> with diamines and an alcohol in the presence of a basic catalyst; or the reaction of CO<sub>2</sub> with diamines in the presence of a basic catalyst and the subsequent reaction of the product with an organic halide. The dicarbamate with the highest commercial potential, 4,4'-diphenylmethane di(methyl carbamate), can be produced by reacting MDA (methylene diphenyl diamine, an intermediate in the synthesis of MDI) with CO<sub>2</sub> and methyl bromide or methanol.

Alternatively, the thermal decomposition of dicarbamates can be used to produce isocyanates. Therefore there is hope that either the production of non-isocyanate polyurethanes from CO<sub>2</sub>-containing dicarbamates will be possible in future, or the isocyanates used will themselves contain CO<sub>2</sub>.

The synthesis of carbamates from CO<sub>2</sub> and amines and organic halides is reported in the literature at lab scale with variable yields up to 90% depending upon the starting material and the synthetic route. Specific processes for synthesising carbamates from useful diamines (such as hexamethylene diamine, isophorene diamine, toluene diamine, methylene diphenyl diamine) for polyurethane manufacturing must first be developed at lab scale, with more work required on catalyst screening and selection to achieve acceptable yields.<sup>37</sup>

<sup>35</sup> Sun *et al.* (2004). A Semi-continuous Process for the Synthesis of Methyl Carbamate from Urea and Methanol. *Chemical Engineering & Technology* 27: 435-439.

<sup>36</sup> Sonnenschein M.F. (2014). *Polyurethanes: Science, Technology, Markets and Trends*. Wiley.

<sup>37</sup> CEFIC/EUcheMs (2011/2012). *Workshops Roadmaps for CO2 Utilisation*.

### 3.1.16 Polycarbamates

#### Polyurethane

Polyurethane is produced conventionally by reacting an isocyanate (R-N=C=O) with a polyol (HO-R-OH) to form polymer chains of these two monomers which are joined together using carbamate links. Hence polyurethane is a polycarbamate, but it is not produced by polymerising carbamates. The market is vast, with polyurethanes in primary forms plus plates and sheets of polyurethanes amounting to 5 Mt in 2016, worth over €10 billion.

Since June 2016, Covestro (at Dormagen, Germany) has used CO<sub>2</sub> from a neighbouring chemical plant to produce a polyether polycarbonate polyol called Cardyon with a CO<sub>2</sub> content of 20%. The demonstration plant has an annual production capacity of 5000 tonnes (TRL 6-7). The polyol can be reacted with an isocyanate to produce flexible polyurethane foam<sup>38</sup>. Recticel (Belgium) launched the first commercial products using Cardyon onto the market at the end of 2016 – flexible foam mattresses and furniture<sup>39</sup>. More information concerning the synthesis of the polyether carbonates/polyether carbonate polyols by Covestro is provided in Section 3.1.12 of this report which covers the synthesis of aliphatic polycarbonates.

Saudi Aramco acquired the Converge polyol technology from Novomer Inc in 2016. It uses CO<sub>2</sub> to produce a sustainable alternative to petroleum-based polyols which are used for coatings, adhesives, sealants and elastomer applications such as in flexible and rigid foams – from car seats to building insulation panels. They claim they have 1/3 the carbon footprint of conventional polyether or polyester polyols, and when incorporated into polyurethane formulations they show performance improvements such as increased strength, abrasion, chemical and weather resistance<sup>40</sup>. Demonstration scale.

Other direct CO<sub>2</sub> co-polymerization methods have been explored including the co-polymerisation of CO<sub>2</sub> with aziridines, which are nitrogen containing three-membered rings (CH<sub>2</sub>)<sub>2</sub>NH, to obtain polycarbamates.<sup>41</sup> The production of polyurethane-amines in this way do not require a catalyst but have only been produced using supercritical CO<sub>2</sub> in the laboratory<sup>42</sup> so TRL 1-3.

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<sup>38</sup> Covestro (2017). Carbon dioxide is revolutionizing plastics production. <https://www.co2-dreams.covestro.com/> Accessed September 2017.

<sup>39</sup> Bioplastics Magazine.com (2016). Recticel to adopt use of new CO<sub>2</sub> based Cardyon polyol. Available at: <http://www.bioplasticsmagazine.com/en/news/meldungen/20160722-Recticel-to-adopt-use-of-new-CO2-based-cardyon-polyol.php> Accessed September 2017.

<sup>40</sup> Saudi Aramco (2016). Saudi Aramco acquires Novomer's polyol business and associated technologies, enhancing its downstream expansion strategy. Available at: <http://www.saudiaramco.com/en/home/news-media/news/acquires-novomers-polyol-business-downstream-expansion.html> Accessed September 2017.

<sup>41</sup> Langanke *et al.* (2015). Polymers from CO<sub>2</sub> - An Industrial Perspective. In *Carbon Dioxide Utilisation: Closing the Carbon Cycle*. Eds. Styring P, Quadrelli EA and Armstrong K. Elsevier.

<sup>42</sup> Ihata *et al.* (2005). Double stimuli-responsive behaviour of aliphatic poly(urethane-amine)s derived from supercritical carbon dioxide. *Chemical Communications* **17**: 2268-2270.

**Table 1. Potential chemical products with associated market and CO<sub>2</sub> utilisation data.**

Class	Product	Synthesis route	Overall reaction	TRL	EU28 prod. + plus imports [t/yr]	Unit value [€/t]	Market value [€M]	CO <sub>2</sub> used [t CO <sub>2</sub> /t product]	EU CO <sub>2</sub> utilisation [t/yr]*	H <sub>2</sub> requirement [t H <sub>2</sub> /t product]**	Other (non-catalytic) inputs
Amides	Urea	Current conventional pathway - reacting NH <sub>3</sub> and CO <sub>2</sub> to produce ammonium carbamate which then dehydrates to urea.	$\text{CO}_2 + 2 \text{NH}_3 \rightleftharpoons \text{NH}_2\text{COONH}_4 \rightleftharpoons \text{CO}(\text{NH}_2)_2 + \text{H}_2\text{O}$	9	5,410,342	452	2,444	0.733	3,965,780	0	Ammonia
Aromatic hydrocarbons	Benzene	CO <sub>2</sub> methanation followed by CH <sub>4</sub> dehydro-aromatisation	$6 \text{CO}_2 + 24 \text{H}_2 \rightleftharpoons 6 \text{CH}_4 + 12 \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_6 + 9 \text{H}_2$	2-4	6,807,829	533	3,627	3.38	23,010,462	0.62	-
		Methanol to aromatics (MTA) process resulting in the simultaneous production of all three BTX components.	$6 \text{CH}_3\text{OH} \rightleftharpoons \text{C}_6\text{H}_6 + 6 \text{H}_2\text{O} + 3 \text{H}_2$	7						0 - 0.62	Methanol
	Toluene	<i>as above</i>	$7 \text{CH}_3\text{OH} \rightleftharpoons \text{C}_6\text{H}_5\text{CH}_3 + 7 \text{H}_2\text{O} + 3 \text{H}_2$	7	1,262,684	459	580	3.35	4,229,991	0 - 0.61	Methanol
	Xylene	<i>as above</i>	$8 \text{CH}_3\text{OH} \rightleftharpoons \text{C}_6\text{H}_4(\text{CH}_3)_2 + 8 \text{H}_2\text{O} + 3 \text{H}_2$	7	2,563,662	552	1,414	3.32	8,511,358	0 - 0.60	Methanol
Aldehydes	Formaldehyde	Borane reduction of CO <sub>2</sub>	$2 \text{CO}_2 + 2 \text{H}_2 \rightleftharpoons 2 \text{CH}_2\text{O} + \text{O}_2$	1-3	1,056,418	252	266	1.467	1,549,765	0.067	-
		Hydrogenation to formic acid, then reduction to formaldehyde	$\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{HCOOH} \rightleftharpoons \text{CH}_2\text{O} + 0.5 \text{O}_2$	1-3							
Organic acids	Acetic acid	Oxidation of methane with CO <sub>2</sub>	$\text{CO}_2 + \text{CH}_4 \rightleftharpoons \text{CH}_3\text{COOH}$	3	1,231,867	473	583	0.73	899,263	0	Methane
		Gas fermentation of CO <sub>2</sub> by anaerobic bacteria	Reaction part of a complex metabolic pathway, but as CO <sub>2</sub> is the only carbon source: $2 \text{CO}_2 + 3 \text{H}_2 \rightleftharpoons \text{CH}_3\text{COOH} + 2 \text{OH}$	2-4				1.47	1,810,844	0.10	Nutrients
	Acrylic acid	Linear terminal alkenes react with CO <sub>2</sub> to produce linear chain carboxylic acids	$\text{CO}_2 + \text{C}_2\text{H}_4 \rightleftharpoons \text{CH}_2\text{CHCOOH}$	1-4	1,342,852	1,087	1460	0.61	819,140	0	Ethylene
	Benzoic acid	Aromatics (e.g. benzene) with CO <sub>2</sub> to form benzoic acid	$\text{CO}_2 + \text{C}_6\text{H}_6 \rightleftharpoons \text{C}_6\text{H}_5\text{COOH}$	1-3	190,601	1,092	208	0.361	68,807	0	Benzene
	<i>p</i> -hydroxy benzoic acid	Kolbe-Schmitt reaction: carboxylation of potassium phenoxide (K salt of phenol)	$\text{CO}_2 + \text{KOH} + \text{H}_2\text{O} + \text{KOC}_6\text{H}_5 \rightleftharpoons \text{HOC}_6\text{H}_4\text{COOH} + 2 \text{KOH}$	9	190,601 <sup>(1)</sup>	1,092	208	0.32	60,992	0	Potassium phenoxide

Class	Product	Synthesis route	Overall reaction	TRL	EU28 prod. + plus imports [t/yr]	Unit value [€/t]	Market value [€M]	CO <sub>2</sub> used [t CO <sub>2</sub> /t product]	EU CO <sub>2</sub> utilisation [t/yr]*	H <sub>2</sub> requirement [t H <sub>2</sub> /t product]**	Other (non-catalytic) inputs
	Butyric acid	Gas fermentation of CO <sub>2</sub> by anaerobic bacteria	Reaction part of a complex metabolic pathway, but as CO <sub>2</sub> is the only carbon source, then overall: $4 \text{ CO}_2 + 7 \text{ H}_2 \rightleftharpoons \text{C}_3\text{H}_7\text{COOH} + 6 \text{ OH}$	1-3	471,609	1,166	550	2.00	943,218	0.159	-
	Formic acid	Electrochemical reduction of CO <sub>2</sub>	$\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{HCOOH}$	5-6	490,069	545	267	0.96	470,466	0.043	-
		Catalytic reduction	$\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{HCOOH}$	2-3							
	Oxalic acid	Electrochemical reduction of CO <sub>2</sub>	$2 \text{ CO}_2 + \text{H}_2 \rightleftharpoons \text{HOOC-COOH}$	3-4	302,583 <sup>(2)</sup>	2,051	621	0.49	148,266	0.022	-
Salicylic acid (2-hydroxybenzoic acid)	Kolbe-Schmitt reaction: carboxylation of sodium phenoxide (Na salt of phenol)	$\text{CO}_2 + \text{NaOH} + \text{H}_2\text{O} + \text{NaOC}_6\text{H}_5 \rightleftharpoons \text{HOC}_6\text{H}_4\text{COOH} + 2 \text{ NaOH}$	9	42,703	3,497	149	0.319	13,622	0	Sodium hydroxide, sodium phenoxide	
Olefins	Ethylene	Direct using modified F-T catalysis	$2 \text{ CO}_2 + 6 \text{ H}_2 \rightleftharpoons \text{C}_2\text{H}_4 + 4 \text{ H}_2\text{O}$	2-4	24,505,336	873	21,382	3.14	76,946,755	0.43	-
		Direct electrochemical reduction of CO <sub>2</sub>	$2 \text{ CO}_2 + 8 \text{ H}_2\text{O} \rightleftharpoons \text{C}_2\text{H}_4 + 12 \text{ OH}$	1-3						0	-
		Methanol to olefin (MTO) process -condensation of CO <sub>2</sub> -derived methanol to DME followed by conversion to olefin	$\text{CH}_3\text{OH} + \text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{C}_2\text{H}_4 + 2 \text{ H}_2\text{O}$	8-9						0 - 0.57	Methanol
	Propylene	Methanol to olefin (MTO) process - methanol plus ethylene	$\text{CH}_3\text{OH} + \text{C}_2\text{H}_4 \rightleftharpoons \text{C}_3\text{H}_6 + \text{H}_2\text{O}$	8-9	27,123,818	913	24,774	3.14	85,168,789	0 - 0.19	Methanol, ethylene
		Methanol to olefin (MTO) process - condensation of CO <sub>2</sub> -derived methanol to DME followed by conversion to olefin	$6 \text{ CH}_3\text{OH} \rightleftharpoons 3 \text{ CH}_3\text{OCH}_3 + 3 \text{ H}_2\text{O} \rightleftharpoons 2 \text{ C}_3\text{H}_6 + 6 \text{ H}_2\text{O}$	8-9						0 - 0.57	Methanol
Epoxides	Ethylene oxide	Carboxylation of olefin	$\text{C}_2\text{H}_4 + \text{CO}_2 \rightleftharpoons (\text{CH}_2)_2\text{O} + \text{CO}$	2-4	947,849	700	663	1.0	947,849	0	Ethylene
Polyols	Ethylene glycol	Electrochemical reduction of CO <sub>2</sub>	$2 \text{ CO}_2 + 3 \text{ H}_2 \rightleftharpoons \text{HO}(\text{CH}_2)_2\text{OH} + \text{O}_2$	3-7	1,939,511	526	1,020	1.42	2,754,106	0.1	-
	Propylene	Electrochemical reduction of	$3 \text{ CO}_2 + 4 \text{ H}_2 \rightleftharpoons$	3-7	761,544	727	554	1.74	1,325,087	0.11	-

Class	Product	Synthesis route	Overall reaction	TRL	EU28 prod. + plus imports [t/yr]	Unit value [€/t]	Market value [€M]	CO <sub>2</sub> used [t CO <sub>2</sub> /t product]	EU CO <sub>2</sub> utilisation [t/yr]*	H <sub>2</sub> requirement [t H <sub>2</sub> /t product]**	Other (non-catalytic) inputs
	glycol	CO <sub>2</sub>	HO(CH <sub>2</sub> ) <sub>3</sub> OH + 2 O <sub>2</sub>								
Carbonates (inorganic)	Sodium bicarbonate	Two-step process, first carbonation of sodium hydroxide to sodium carbonate, then bicarbonation to sodium bicarbonate.	CO <sub>2</sub> + 2 NaOH ⇌ Na <sub>2</sub> CO <sub>3</sub> + H <sub>2</sub> O, Na <sub>2</sub> CO <sub>3</sub> + H <sub>2</sub> O + CO <sub>2</sub> ⇌ 2 NaHCO <sub>3</sub>	6-8	3,662,946	110	403	0.524	1,919,384	0	Sodium hydroxide
Carbonates (cyclic)	Ethylene carbonate	Carbonation of the epoxide ethylene oxide to ethylene carbonate	CO <sub>2</sub> + (CH <sub>2</sub> ) <sub>2</sub> O ⇌ (CH <sub>2</sub> ) <sub>2</sub> CO <sub>3</sub>	9	Unk	Unk	Unk	0.5	Unk	0	Ethylene oxide
		Diol (ethylene glycol) and CO <sub>2</sub>	CO <sub>2</sub> + HO(CH <sub>2</sub> ) <sub>2</sub> OH ⇌ (CH <sub>2</sub> ) <sub>2</sub> CO <sub>3</sub> + H <sub>2</sub> O	3-5							Ethylene glycol
		Monohalohydrins and CO <sub>2</sub>	CO <sub>2</sub> + ClCH <sub>2</sub> CH <sub>2</sub> OH ⇌ (CH <sub>2</sub> ) <sub>2</sub> CO <sub>3</sub> + HCl	4-5							2-chloro-ethanol
		Oxidative carboxylation of an olefin	CO <sub>2</sub> + C <sub>2</sub> H <sub>4</sub> + 0.5 O <sub>2</sub> ⇌ (CH <sub>2</sub> ) <sub>2</sub> CO <sub>3</sub>	1-3							Ethylene
Carbonates (linear)	Dimethyl carbonate	Carboxylation of alcohols (e.g. methanol to produce dimethyl carbonate)	CO <sub>2</sub> + 2 CH <sub>3</sub> OH ⇌ CH <sub>3</sub> OCOOCH <sub>3</sub> + H <sub>2</sub> O	3-7	Unk	Unk	Unk	0.49	Unk	0 - 0.18	Methanol
Poly-carbonates (aliphatic)	Poly-(propylene carbonate)	Carbonation of the epoxide propylene oxide to propylene carbonate in the presence of a catalyst which catalyses the polymerisation	CO <sub>2</sub> + CH <sub>3</sub> CHCH <sub>2</sub> O ⇌ -(CH <sub>3</sub> C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> CO)-	6-7	1,555,718	2,527	3,932	0.43	668,959	0	Propylene oxide
Poly-carbonates (aromatic)		Phosgene-free production using carbonation of ethylene oxide	CO <sub>2</sub> + (CH <sub>2</sub> ) <sub>2</sub> O ⇌ -(CH <sub>2</sub> CH <sub>2</sub> CO <sub>3</sub> )-	6-7				Unk			Unk
Carbamates (inorganic)	Ammonium carbamate	First step in the formation of urea	CO <sub>2</sub> + 2 NH <sub>3</sub> ⇌ NH <sub>4</sub> (H <sub>2</sub> NCO <sub>2</sub> )	9	Unk	Unk	Unk	0.56	Unk	0	Ammonia
Carbamates (organic)	Methyl carbamate	Reaction of alcohol (in this case methanol) with urea	CH <sub>3</sub> OH + CO(NH <sub>2</sub> ) <sub>2</sub> ⇌ CH <sub>3</sub> COONH <sub>2</sub> + NH <sub>3</sub>	9	1,191,873	2,585	3,082	0.59	703,205	0 - 0.11	Methanol, urea
Di-carbamates	Ethanediol dicarbamate	Diamine plus an alcohol reacts with CO <sub>2</sub> over a basic catalyst	2 CO <sub>2</sub> + C <sub>2</sub> H <sub>4</sub> (NH <sub>2</sub> ) <sub>2</sub> ⇌ (CH <sub>2</sub> COONH <sub>2</sub> ) <sub>2</sub>	1-3	> 6 Mt globally	Unk	Unk	0.30	Unk	0 - 0.05	Ethylene diamine, methanol
		Diamine reacts with CO <sub>2</sub> over a basic catalyst, the product then	2 CO <sub>2</sub> + C <sub>2</sub> H <sub>4</sub> (NH <sub>2</sub> ) <sub>2</sub> ⇌ (CH <sub>2</sub> COONH <sub>2</sub> ) <sub>2</sub>	1-3				0.30			Unk

Class	Product	Synthesis route	Overall reaction	TRL	EU28 prod. + plus imports [t/yr]	Unit value [€/t]	Market value [€M]	CO <sub>2</sub> used [t CO <sub>2</sub> /t product]	EU CO <sub>2</sub> utilisation [t/yr]*	H <sub>2</sub> requirement [t H <sub>2</sub> /t product]**	Other (non-catalytic) inputs
		reacts with an organic halide									organic halide
Poly-carbamates	Polyurethane	Carbonation of an epoxide yields polycarbonates for PU synthesis	$\text{CO}_2 + (\text{CH}_2)_2\text{O} \rightleftharpoons -(\text{CH}_2\text{CH}_2\text{CO}_3)-$	6-7	5,168,004	2,084	10,771			0	
		Co-polymerisation of CO <sub>2</sub> with 2-methylaziridine	$\text{CO}_2 + \text{C}_3\text{H}_6\text{NH} \rightleftharpoons -(\text{C}_3\text{H}_6\text{NHCOO})-$	1-3						0	

\*This assumes that all of the EU market for this product is synthesised using the route in question. If multiple possible routes to a product exist, each route shows the EU CO<sub>2</sub> utilisation potential if 100% of the market is met using that route, the multiple routes are not additive.

\*\* The H<sub>2</sub> requirement for products produced by biological fermentation in some instances may be provided in the form of metabolic reducing agents NADH, NADPH or FADH<sub>2</sub> rather than gaseous H<sub>2</sub>, but the mass of H<sub>2</sub> has been provided for consistency to allow comparison. The H<sub>2</sub> requirement for products produced from methanol includes the H<sub>2</sub> required for the production of the methanol and since there are a range of production routes utilising different amounts of H<sub>2</sub>, the total H<sub>2</sub> requirement is given as a range.

<sup>(1)</sup> Market data for *p*-hydroxybenzoic acid was not available, so data for benzoic acid was presented to give an indication of the market size and CO<sub>2</sub> utilisation potential. The true value for *p*-hydroxybenzoic acid will be a proportion of this.

<sup>(2)</sup> Market data for oxalic acid alone was not available, the data presented is for oxalic, azelaic, malonic, cyclonic, cyclenic or cycloterpenic polycarboxylic acids and salts (excluding butanedioic acid).

## 3.2 Fuels/Chemicals

### 3.2.1 Alcohols

#### Methanol

Methanol can be used directly as a transport fuel or converted to dimethyl ether (DME), methyl tert-butyl ether (MTBE) or oxygenated as polyoxymethylene dimethyl ether (POMDME) as a petroleum and diesel additive. It can also be used directly as a solvent, an antifreeze, for wastewater treatment and for alcohol denaturing (methylated spirits). However, its biggest use by far is to make other chemicals, around 40% of methanol is converted into formaldehyde and from there into other chemicals.<sup>43</sup> There are commercialised processes to produce urea-, melamin- and phenol-formaldehyde resins; Carbonylation to acetic acid (Monsanto and Cativa processes) and subsequent polymers via vinylacetate to PVA (for paints and adhesives) or to cellulose acetates (films, textiles). Section 3.5 of this report lists some of the products that methanol can be used to synthesise.

The market volume is already high - currently around 7.9 Mt/yr worth around €1.5 billion, but only 1 Mt is actually manufactured within Europe, the remaining 6.9 Mt is imported. The volume used is expected to increase as methanol starts to be used to produce olefins (see Section 3.1.5 of this report) and even higher market volumes could follow if methanol is used as a petroleum blend and/or as a method of storing or importing renewable energy.

#### Technologies/pathways:

The synthesis of methanol (CH<sub>3</sub>OH) from CO<sub>2</sub> has received more research interest than any other product, due to the central role that methanol plays as a commodity chemical and a potential fuel and energy store. In addition, methanol produced from CO<sub>2</sub> and H<sub>2</sub> is frequently referred to as a potential way of overcoming the difficulties with H<sub>2</sub> storage and distribution. The H<sub>2</sub> storage potential of methanol compares favourably to other storage media and methanol is a lot cheaper and easier to transport via pipeline or tanker than H<sub>2</sub>. Hydrogen can be released from methanol by methanol reforming or aqueous dehydrogenation techniques.<sup>44</sup> The wide range of chemical products that can be produced from methanol synthesised from CO<sub>2</sub> is covered in more detail in section 3.5 of this report. Due to the myriad of uses for methanol, multiple synthesis routes are under investigation.

Methanol can be synthesized from CO<sub>2</sub> using two different catalytic routes: the conversion of CO<sub>2</sub> to CO prior to hydrogenation (three routes), or the direct hydrogenation of CO<sub>2</sub>. The hydrogenation of CO is the conventional route to producing methanol (with the CO coming from steam reforming of methane) and commonly takes place over a Cu/ZnO catalyst (sometimes Cu/ZnO/Cr<sub>2</sub>O<sub>3</sub> or Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>). In practice, the syngas produced by steam reforming of methane contains more H<sub>2</sub> than is required by the reaction to produce methanol. A common method of dealing with this excess of H<sub>2</sub> is to inject CO<sub>2</sub> into the reaction vessel which reacts to form methanol in a similar way to CO. Using CO<sub>2</sub> as an additive in this way already utilises 6 million tonnes of CO<sub>2</sub> per year.<sup>45</sup>

In addition to the catalytic conversion options mentioned above, methanol can be produced electrochemically by CO<sub>2</sub> reduction and H<sub>2</sub>O oxidation, which can occur either in a fuel cell, a high temperature solid oxide cell or a photo-electric cell which utilises solar energy. Finally, an indirect route is possible by first converting CO<sub>2</sub> to methane and then producing methanol from the methane. Consequently, eight pathways to produce methanol from CO<sub>2</sub> have been identified and will be discussed here:

1). Reverse water gas shift reaction of CO<sub>2</sub> plus renewable H<sub>2</sub> to produce CO and water, followed by water removal and subsequent methanol synthesis using Fischer-Tropsch (F-T) type catalysts. TRL 7-

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<sup>43</sup> Maitlis (2013). Other Industrially Important Syngas Reactions. In *Greener Fischer-Tropsch Processes for Fuels and Feedstocks*. Eds. Maitlis and de Klerk. Wiley-VCH.

<sup>44</sup> Dowson and Styring (2015). Conversion of Carbon Dioxide to Oxygenated Organics. In *Carbon Dioxide Utilisation: Closing the Carbon Cycle*. Eds. Styring P, Quadrelli EA and Armstrong K. Elsevier.

<sup>45</sup> North M. (2015). What is CO<sub>2</sub>? Thermodynamics, Basic Reactions and Physical Chemistry. In *Carbon Dioxide Utilisation: Closing the Carbon Cycle*. Eds. Styring P, Quadrelli EA and Armstrong K. Elsevier.

8 for the reverse water gas shift reaction part of the process, but large-scale, low carbon H<sub>2</sub> production is expensive. This results in the costs for methanol production currently being a factor of 2 or more higher than when using the conventional route of steam reforming of natural gas to produce the necessary H<sub>2</sub>. CO<sub>2</sub> with low H<sub>2</sub>S concentrations (<0.1 ppm) is required for use with state-of-the-art catalysts, but purity is less critical for high-temperature solid oxide cells.

Mitsui Chemicals Inc. built the world's first CO<sub>2</sub> to methanol demonstration plant in Osaka in 2009. It produced around 100 tonnes methanol per year using CO<sub>2</sub> arising from ethylene production. According to their Corporate Social Responsibility Report 2016, the plant confirmed that methanol could be manufactured, but the supply of H<sub>2</sub> for the process was proving a major hurdle to further development.<sup>46</sup>

Carbon Recycling International (CRI) operates the only commercial CO<sub>2</sub> to methanol plant near Grindavik, Iceland, producing 5 million litres/yr of "Vulcanol". The CO<sub>2</sub> is captured from the flue gas of an adjacent geothermal power plant which emits geothermal steam and all energy used in the process is supplied by hydro and geothermal energy from the Icelandic grid.<sup>47</sup> In most cases, the hydrogenation of CO<sub>2</sub> to methanol is not financially competitive with the reduction of CO obtained from steam reforming of methane. This is because three molecules of H<sub>2</sub> are required to reduce one molecule of CO<sub>2</sub>, whilst only two are required to reduce each molecule of CO. However, the relatively inexpensive geothermal electricity available in Iceland allows the energy-demanding but more sustainable generation of H<sub>2</sub> by electrolysis of water.<sup>48</sup>

2). Dry methane reforming to produce syngas  $\text{CH}_4 + \text{CO}_2 \rightarrow 2 \text{CO} + 2 \text{H}_2$  followed by water gas shift reaction to adjust the H<sub>2</sub>:CO ratio, water removal, compression and subsequent methanol synthesis via Fischer-Tropsch catalysis. Further research is required before large scale implementation would be economic.

3). Combined steam and CO<sub>2</sub> reforming of methane (utilizing low quality natural gas), followed by water gas shift reaction to adjust the H<sub>2</sub>:CO ratio, water removal, compression and subsequent methanol synthesis. Currently at demonstration scale - Chiyoda Corp. (Japan).<sup>49</sup>

4). Direct catalytic hydrogenation of CO<sub>2</sub> to methanol, which actually forms a formic acid intermediate prior to further reduction and dehydration to methanol. As with many CO<sub>2</sub> reactions, catalysts are required to reduce the activation energy and increase the kinetics of the reaction whilst high temperatures enable higher energy products to be formed from lower energy reactants. Much work is ongoing, looking at catalysts which allow the reactions to proceed at temperatures which block the formation of undesirable by-products for instance. Some examples are Ir, Rh or Ru Homogeneous Catalysis or [Cu/Zn/Ga]OH photocatalysts which operate at 50-150°C and 20-30 atm whereas Cu/ZnO and Cu/Zn/SiO<sub>2</sub> catalysts operate at 250-300°C and 20-80 atm. The technique remains at the laboratory phase.

5). CO<sub>2</sub> electro-catalytic reduction to methanol combined with water electrolysis in an inverse methanol fuel cell. Methanol fuel cells currently operate by oxidising methanol in order to generate electricity, the idea is to reverse this process so that electricity is used to provide the energy necessary to perform what is essentially reverse combustion of methanol. Currently this field of research remains at lab scale and work is needed to develop electrodes and cells for direct selective conversion of CO<sub>2</sub> to methanol (e.g. without separate H<sub>2</sub> production). Before commercialisation, electrodes need to show increased selectivity, productivity and stability, and minimise/avoid the use of noble metals and other rare elements. Research is also required to enable the use of intermittent electrical energy provided by renewable sources; the development of membranes for these cells having low cross-over rate; improved cell engineering.

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<sup>46</sup> Mitsui Chemicals Group (2016). CSR Report 2016 available at: [http://www.mitsuichem.com/en/csr/report/pdf/csr2016web\\_e.pdf](http://www.mitsuichem.com/en/csr/report/pdf/csr2016web_e.pdf). Accessed September 2017.

<sup>47</sup> Carbon Recycling International (2016). World's Largest CO<sub>2</sub> Methanol Plant. Available at: <http://carbonrecycling.is/george-olah/2016/2/14/worlds-largest-co2-methanol-plant>. Accessed September 2017.

<sup>48</sup> North (2015). What is CO<sub>2</sub>? Thermodynamics, Basic Reactions and Physical Chemistry. In *Carbon Dioxide Utilisation: Closing the Carbon Cycle*. Eds. Styring P, Quadrelli EA and Armstrong K. Elsevier.

<sup>49</sup> Chiyoda Corporation (2017). CO<sub>2</sub> Reforming Process. Available at: [http://www.chiyoda-corp.com/technology/en/future/co2\\_reforming.html](http://www.chiyoda-corp.com/technology/en/future/co2_reforming.html). Accessed September 2017.

6). High temperature electrolysis in a solid oxide cell (SOC) can be used to electrolyse CO<sub>2</sub> to CO or steam to H<sub>2</sub>, or it can co-electrolyse the two simultaneously to produce syngas. Syngas can be converted to methanol following compression and subsequent catalytic synthesis using the techniques described above. The methanol produced can be utilised directly as a product, or used in a fuel cell to produce electricity. Solid oxide cells offer very efficient use of electricity and heat, with a near 100% electricity-to-syngas efficiency. They are currently operated only at lab/small pilot scale (TRL 3-5). The dominant costs are the electricity and the capital cost of the electrolyser, which increases for intermittent operation. In order for co-electrolysis to be more competitive, demonstration of durable operation at high current densities, and development of strategies for power management in intermittent operation are required.<sup>50</sup>

An SOC converts electrical energy into chemical energy and therefore can be thought of as an energy storage device since large scale storage of chemical compounds is significantly easier than storage of electricity. Such reasons suggest that this type of technology may have significant potential for future energy strategies.

7). Light energy absorbed by a semiconducting electrode can be used to drive a reduction/oxidation reaction (as an alternative to applying an electrical potential as in the electrochemical cell described above). Such a system is referred to as a photo-electrochemical cell (PEC) and involves the generation of a photopotential. While applying an electrochemical potential is not considered to be catalytic, the use of light energy to drive an otherwise unfavourable reaction is often described as 'photocatalysis'. However, photocatalysis is not true catalysis because it does not lower the kinetic barrier to a reaction, it simply uses light energy to overcome the kinetic barrier.

Using electrodes with a copper oxide thin film surface, CO<sub>2</sub> can be selectively reduced to methanol with a faradaic yield of 38%. Other products can be made by using different electrodes, the surface chemistry of which is critical to product formation, selectivity and yield.

In order to advance photoelectrochemical CO<sub>2</sub> utilisation and energy storage beyond the lab, the following challenges must be overcome: reliance upon expensive materials (e.g. noble metals or other expensive catalytic systems such as ionic liquid as electrocatalysts); energy efficiency; light absorption efficiency of the photosensitizer; understanding electrocatalysis mechanisms at semiconductor interfaces; reaction intermediates not well understood.<sup>51</sup>

8). This indirect route requires CO<sub>2</sub> to be reduced to CH<sub>4</sub>, before the latter is partially oxidised to CH<sub>3</sub>OH. However, the latter step proves difficult to control as over oxidation leads to the production of CO, CO<sub>2</sub> and H<sub>2</sub>O from the CH<sub>4</sub>. These by-products typically act to deactivate many catalysts used (Cu/Fe or Co/Fe ZSM zeolite, or Ag or Au WO photocatalysts), so a highly selective catalyst is required to prevent their formation in the first place. However, with temperatures of around 600°C required by such catalysts, in addition to the energy requirements of initially producing methane, commercialising this route will be challenging and it remains in the laboratory phase of development.

Although involving more process steps and energetically less favourable, the redeeming factor for the processes which utilise CO or methane as feedstock rather than CO<sub>2</sub> is that the infrastructure which currently utilises CO and CH<sub>4</sub> obtained from fossil sources could be used to use these products obtained from CO<sub>2</sub> conversion. The ability to utilise existing reactors and plants rather than to build new facilities offers significant economic benefits to any new process.<sup>52</sup>

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<sup>50</sup> Elder et al. (2015). High Temperature Electrolysis. In *Carbon Dioxide Utilisation: Closing the Carbon Cycle*. Eds. Styring P, Quadrelli EA and Armstrong K. Elsevier.

<sup>51</sup> Yan Y., Gu J., Zeitler E.L. and Bocarsly B.O. (2015). Photoelectrocatalytic Reduction of Carbon Dioxide. In *Carbon Dioxide Utilisation: Closing the Carbon Cycle*. Eds. Styring P, Quadrelli EA and Armstrong K. Elsevier.

<sup>52</sup> Dowson and Styring (2015). Conversion of Carbon Dioxide to Oxygenated Organics. In *Carbon Dioxide Utilisation: Closing the Carbon Cycle*. Eds. Styring P, Quadrelli EA and Armstrong K. Elsevier.

## Ethanol and butanol

The alcohols ethanol and butanol can be used directly as "drop-in" biofuels. In addition to their direct use as solvents, they can be used for the chemical synthesis of a number of other compounds: they can be dehydrated to produce olefins (ethylene, butylene) and subsequent conversion of these to polymers or higher value hydrocarbons (jet fuel); catalytic hydrogenation of acids (acetic, butyric) to the corresponding alcohols; use of the acids for the production of polymers, including cellulose-derived polymers (cellulose acetate, cellulose acetate butyrate); butyrate esters as flavouring/aroma compounds.

Ethanol is conventionally produced by the hydration of ethylene produced from fossil fuels, but it is also produced in industrial quantities by the yeast fermentation of plant biomass. The EU market for ethanol was 4.6 Mt plus an additional 1.3 Mt of denatured (methylated spirits). The market for all forms of butanol was much smaller at around 650 Kt in 2016.

### Technologies/pathways

Ethanol can be produced by the electrochemical reduction of CO<sub>2</sub> and both ethanol and butanol can be synthesised biologically utilising the gas fermentation ability of certain acetogenic bacteria.

1). The selective electroreduction of carbon dioxide to ethanol on copper(I) oxide films has identified that the faradaic yield of ethanol can be systematically tuned by changing the thickness of the deposited overlayers. Films 1.7–3.6 μm thick exhibited the best selectivity for these C<sub>2</sub> compounds, with faradic efficiencies of 9–16% for ethanol.<sup>53</sup>

2). The electrochemical conversion of CO<sub>2</sub> to ethanol at ambient temperature and pressure with a faradaic efficiency of 63% and selectivity of 84% was reported last year. The catalyst comprised of copper nanoparticles on an n-doped graphene electrode.<sup>54</sup> Both the above chemical conversion technologies remain at the laboratory level of development.

3). Fermentation of CO<sub>2</sub>/H<sub>2</sub> mixtures to C<sub>2</sub> compounds (acetate, ethanol) and C<sub>4</sub> compounds (butyrate, butanol) by acetogenic bacteria under anaerobic conditions.<sup>55</sup> In addition to CO<sub>2</sub>/H<sub>2</sub> mixtures, some members of this group can utilise other monocarbon compounds as substrates, including CO<sub>2</sub>-derived methanol. Although acetate/acetic acid is the main metabolic product of acetogenic bacteria (in general), other products can be formed such as butyrate/butyric acid and the alcohols ethanol and butanol. More work in this area has focussed on the fermentation of syngas to produce the biofuels bioethanol and biobutanol and other chemicals, with LanzaTech leading the development. Challenges include genetically engineering acetogenic species which can efficiently ferment CO<sub>2</sub>/H<sub>2</sub> and/or methanol to valuable products; optimizing the fermentation conditions; developing suitable bioreactors to handle gaseous substrates.<sup>56</sup>

Direct fermentation of CO<sub>2</sub> has two main challenges: the need for a source of H<sub>2</sub> (or reduction equivalents) and the gaseous nature and low water solubility of the substrates which results in low mass transfer and so low productivity. An alternative is to use CO<sub>2</sub>-derived methanol as a fermentation substrate as it is highly soluble in water which improves mass transfer and therefore productivity. This offers additional benefits as the fermentation of a liquid substrate is an easier engineering task; methanol doesn't require the supply of additional reduction equivalents as it effectively provides them itself; and the fermentation of methanol requires the presence of CO<sub>2</sub> as a co-substrate - reinforcing its utilisation as a feedstock. During a biological fermentation, in some cases the required H<sub>2</sub> is provided as a gas, but in other circumstances it is provided in the form of metabolic intermediates to enable the production of the reducing agents NADH, NADPH or FADH<sub>2</sub> which are used throughout metabolic

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<sup>53</sup> Ren *et al.* (2015). Selective Electrochemical Reduction of Carbon Dioxide to Ethylene and Ethanol on Copper(I) Oxide Catalysts. *ACS Catalysis* **5**: 2814 - 2821.

<sup>54</sup> Song *et al.* (2016). High Selectivity Electrochemical Conversion of CO<sub>2</sub> to Ethanol Using a Copper Nanoparticle/N-Doped Graphene Electrode. *ChemistrySelect* **1**: 6055-6061.

<sup>55</sup> Durre and Eikmanns (2015). C1-carbon sources for chemical and fuel production by microbial gas fermentation. *Current Opinions in Biotechnology*. **35**: 63 - 72.

<sup>56</sup> CEFIC/EUcheMs (2011/2012). Workshops Roadmaps for CO<sub>2</sub> Utilisation.

pathways as reducing equivalents. However, for consistency, in the tables accompanying this section it has been assumed that the reducing agent is supplied as gaseous H<sub>2</sub>.

Bioethanol and biobutanol production from syngas has developed further than when produced from CO<sub>2</sub>, which is not reported beyond laboratory phase development. Production from syngas is covered in the Section 4 of this report which covers products produced from carbon monoxide.

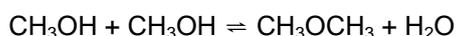
### 3.2.2 Esters

#### Dimethyl ether

A gas at room temperature, dimethyl ether (DME) has a high energy density of 63.4 KJ/litre (compared to methane at 36.4 KJ/l), so it is of interest as a fuel since it can perform similarly to liquefied petroleum gas (LPG) or propane. DME also has the potential to enable vehicle emissions targets to be met more easily since it ignites under compression and could be used as a diesel fuel additive. In addition to its potential as a fuel, DME is currently used as a feedstock for the production of dimethyl sulphate, it can be converted into acetic acid and is used as a laboratory reagent and solvent. Another small-scale but important use is as a replacement for chlorofluorocarbons as a propellant in aerosol canisters

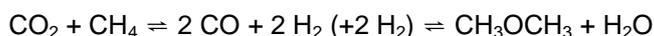
Three routes to DME production from CO<sub>2</sub> have been identified:

1). DME is conventionally produced by condensing two methanol molecules over an acidic alumina catalyst at 200-300°C:



For this process to be a CO<sub>2</sub> utilisation route, we must assume that the methanol had been produced from CO<sub>2</sub>. However, this implies that syngas was first converted to methanol before the methanol was converted to DME, whereas it would be more energy efficient to convert the syngas directly to DME.

2). In an alternative lab development, DME can be produced from CO<sub>2</sub> by the dry reforming of methane and CO<sub>2</sub> to produce syngas, add more H<sub>2</sub> and then react over a Cu-ZnO-Al<sub>2</sub>O<sub>3</sub>Zeolite catalyst at 260°C and 40 atm in an F-T type reaction:<sup>57</sup>



3). A single-step CO<sub>2</sub> hydrogenation process using a bifunctional catalyst which produces methanol and causes its dehydration in the same reactor is possible:



The process is still at the laboratory stage (TRL 1-3) with development work on the catalysts still ongoing.<sup>58</sup>

<sup>57</sup> Dowson and Styring (2015). Conversion of Carbon Dioxide to Oxygenated Organics. In *Carbon Dioxide Utilisation: Closing the Carbon Cycle*. Eds. Styring P, Quadrelli EA and Armstrong K. Elsevier.

<sup>58</sup> Aresta *et al.* (2016). State of the art and perspectives in catalytic processes for CO<sub>2</sub> conversion into chemicals and fuels: The distinctive contribution of chemical catalysis and biotechnology. *Journal of Catalysis* **343**: 2-45.

**Table 2. Potential chemical/fuel products with associated market and CO<sub>2</sub> utilisation data.**

Class	Product	Synthesis route	Overall reaction	TRL	EU28 prod. + imports [t/yr]	Unit value [€/t]	Market value [€M]	CO <sub>2</sub> used [t CO <sub>2</sub> /t product]	EU CO <sub>2</sub> utilisation [t/yr]*	H <sub>2</sub> requirement [t H <sub>2</sub> /t product]**	Other (non-catalytic) inputs	
Alcohols	Butanol	Gas fermentation of syngas produced from CO <sub>2</sub> by the anaerobic bacterium <i>Clostridium sp.</i>	Reaction part of a complex metabolic pathway, but as CO <sub>2</sub> is the only carbon source, then overall: $8 \text{ CO}_2 + 12 \text{ H}_2 \rightleftharpoons 2 \text{ C}_4\text{H}_9\text{OH} + 14 \text{ OH}$	2-4	649,068	548	356	2.38	1,544,782	0.162	Nutrients	
	Ethanol	Electrochemical reduction	$2 \text{ CO}_2 + 9 \text{ H}_2\text{O} \rightleftharpoons \text{C}_2\text{H}_5\text{OH} + 12 \text{ OH}$	1-3	5,904,504	575	3396	1.91	11,277,603	0	-	
		Electrochemical conversion using copper nanoparticle n-doped graphene electrode	$2 \text{ CO}_2 + 9 \text{ H}_2\text{O} \rightleftharpoons \text{C}_2\text{H}_5\text{OH} + 12 \text{ OH}$	1-3							-	
		Gas fermentation of syngas produced from CO <sub>2</sub> by the anaerobic bacterium <i>Clostridium autoethanogenum</i> .	$4 \text{ CO}_2 + 9 \text{ H}_2 \rightleftharpoons 2 \text{ C}_2\text{H}_5\text{OH} + 6 \text{ OH}$ (simplified - actual reaction part of a complex biochemical pathway).	2-4							0.196	-
	Methanol	Reverse water gas shift of CO <sub>2</sub> and renewable H <sub>2</sub> to produce CO and water, remove water, add more H <sub>2</sub> , then use F-T reactions to produce methanol.	$2 \text{ CO}_2 + 4 \text{ H}_2 \rightleftharpoons 2 \text{ H}_2\text{O} + 2 \text{ CO} (+ 2 \text{ H}_2) \rightleftharpoons \text{CH}_3\text{OH} + \text{CO}$	7-9	7,891,386	187	1476	2.75	21,701,312	0.25	-	
		Dry reforming of CH <sub>4</sub> and CO <sub>2</sub> to produce syngas, followed by water gas shift reaction to adjust the CO:H <sub>2</sub> ratio, water removal, compression and subsequent methanol synthesis via F-T.	$\text{CO}_2 + \text{CH}_4 \rightleftharpoons 2 \text{ CO} + 2 \text{ H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{CO}$	6-7							0	Methane
		CO <sub>2</sub> /steam reforming of CH <sub>4</sub> , followed by water gas shift reaction to adjust the CO:H <sub>2</sub> ratio, water removal, compression and subsequent methanol synthesis via F-T.	$\text{CO}_2 + \text{H}_2\text{O} + \text{CH}_4 \rightleftharpoons 2 \text{ CO} + 2 \text{ H}_2 (+ \text{H}_2\text{O}) \rightleftharpoons \text{CH}_3\text{OH} + \text{CO}$	5-7							0	Methane
		Direct catalytic hydrogenation of CO <sub>2</sub> to formic acid intermediate, followed by dehydration	$\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{HCOOH} + 2 \text{ H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O}$	1-3							0.188	-

Class	Product	Synthesis route	Overall reaction	TRL	EU28 prod. + imports [t/yr]	Unit value [€/t]	Market value [€M]	CO <sub>2</sub> used [t CO <sub>2</sub> /t product]	EU CO <sub>2</sub> utilisation [t/yr]*	H <sub>2</sub> requirement [t H <sub>2</sub> /t product]**	Other (non-catalytic) inputs	
		Electrocatalytic hydrogenation of CO <sub>2</sub> to methanol (combined with water electrolysis) in a reverse methanol fuel cell.	$\text{CO}_2 + 2 \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{OH} + 1.5 \text{O}_2$	1-3	7,891,386	187	1476	1.375	10,850,656	0	-	
		High temperature solid oxide cells use CO <sub>2</sub> and water to produce H <sub>2</sub> and CO, followed by compression and subsequent catalytic methanol synthesis.	$\text{CO}_2 + 2 \text{H}_2\text{O} \rightleftharpoons \text{CO} + 2 \text{H}_2 + \text{O}_2 \rightleftharpoons \text{CH}_3\text{OH}$	3-5							-	
		Photo-electrochemical cell	$\text{CO}_2 + 2 \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{OH} + 1.5 \text{O}_2$	1-3							-	
		Two-step process, first convert CO <sub>2</sub> to CH <sub>4</sub> via Sabatier reaction, then partially oxidise CH <sub>4</sub> to CH <sub>3</sub> OH	1). $\text{CO}_2 + 4 \text{H}_2 \rightleftharpoons \text{CH}_4 + 2 \text{H}_2\text{O}$ 2). $\text{CH}_4 + 0.5 \text{O}_2 \rightleftharpoons \text{CH}_3\text{OH}$	2-4						0.25	-	
Ethers	Dimethyl ether	Dry reforming of CH <sub>4</sub> and CO <sub>2</sub> to produce a syngas, plus additional H <sub>2</sub> .	$\text{CO}_2 + \text{CH}_4 \rightleftharpoons 2\text{CO} + 2\text{H}_2 (+ 2 \text{H}_2) \rightleftharpoons \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}$	1-3	Unk	Unk	Unk	0.96	Unk	0.09	-	
		Single-step process using a bifunctional catalyst which produces methanol and causes its dehydration in the same reactor.	$2 \text{CO}_2 + 6 \text{H}_2 \rightleftharpoons \text{CH}_3\text{OCH}_3 + 3 \text{H}_2\text{O}$	1-3						1.91	0.261	-
		Condensation then dehydration of CO <sub>2</sub> derived methanol in the presence of a solid acid catalyst	$\text{CH}_3\text{OH} + \text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}$	9						1.91	0 - 0.35	Methanol

\* This assumes that all of the EU market for this product is synthesised using the route in question. If multiple possible routes to a product exist, each route shows the EU CO<sub>2</sub> utilisation potential if 100% of the market is met using that route, the multiple routes are not additive.

\*\* The H<sub>2</sub> requirement for products produced by biological fermentation in some instances may be provided in the form of metabolic reducing agents NADH, NADPH or FADH<sub>2</sub> rather than gaseous H<sub>2</sub>, but the mass of H<sub>2</sub> has been provided for consistency to allow comparison. The H<sub>2</sub> requirement for products produced from methanol includes the H<sub>2</sub> required for the production of the methanol and since there are a range of production routes utilising different amounts of H<sub>2</sub>, the total H<sub>2</sub> requirement is given as a range.

## 3.3 Fuels

### 3.3.1 Liquid hydrocarbons

#### Gasoline and diesel fuel

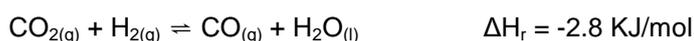
In 2015, European produced and/or imported 146 Mt of gasoline worth around €100 billion and 384 Mt of diesel fuel worth €247 billion.

#### Technologies/pathways

There are several routes by which CO<sub>2</sub> can be converted into hydrocarbon fuels, some routes have been termed direct and others indirect. Indirect routes initially involve reacting CO<sub>2</sub> with CH<sub>4</sub> to form CO and H<sub>2</sub> (syngas) in a process termed dry methane reforming. The syngas is then systematically reacted using Fischer-Tropsch (F-T) catalysts to produce long chain hydrocarbons, or converted to methanol which can subsequently be converted in methanol-to-hydrocarbon type reactions. This indirect process utilises a systematic sequence of reactions which occur in multiple reaction vessels, or zones of vessels. Such a process allows the reaction conditions to be optimized in the different reaction zones and relatively simple catalysts can be utilised.

Direct routes initially react CO<sub>2</sub> with H<sub>2</sub> in what is termed the reverse water gas shift reaction to create CO and H<sub>2</sub>O. These, together with unreacted CO<sub>2</sub> and H<sub>2</sub> form a mixture which is then reacted over F-T catalysts in the same reaction vessel to produce hydrocarbons. The single reactor employed by the direct routes needs to use a more complex catalyst with multiple functionalities to allow multiple reactions to proceed to completion. It has been suggested that direct hydrocarbon formation may occur from CO<sub>2</sub> without going via the intermediate CO.

The two equations below give the reaction enthalpies (ΔH<sub>r</sub>) of the reduction of CO<sub>2</sub> to CO with and without the presence of H<sub>2</sub>. The thermodynamic advantage of having the oxygen atom forming stable H<sub>2</sub>O as a co-product rather than unstable 0.5 O<sub>2</sub> is that the formation of low enthalpy H<sub>2</sub>O reduces the overall reaction enthalpy from being highly endothermic to slightly exothermic.



Due to the formation of water during the F-T reactions, the formation of the linear hydrocarbon chains which make up the liquid fuels is exothermic:



despite the fact that the reactions only proceed at high temperatures (200-350°C) and pressures (15-60 bar).

#### **Indirect routes**

The F-T process is flexible and the following product types can be produced: alkanes, carboxylic acids, esters, alcohols, ethers, alkenes, aldehydes and ketones. While the F-T process results in a broad range of hydrocarbons, it can also be optimised to be selective and this is dependent upon reaction or process conditions such as temperature, pressure, syngas ratio, reactor technology and catalyst choice.

From the perspective of generating fuel-based hydrocarbons, F-T may be operated in two distinctly different high and low temperature regimes. The high-temperature processes (300-350°C) using an Fe catalyst can be used to generate gasoline range hydrocarbons and low molecular weight olefins. The

<sup>59</sup> Zennaro *et al.* (2012). Syngas: The Basis of Fischer-Tropsch. In *Greener Fischer-Tropsch Processes for Fuels and Feedstocks*. Eds. Maitlis and de Klerk. Wiley-VCH.

low temperature regime is operated at 200-240°C with either Fe or Co catalysts. Under these operation conditions linear waxes are produced in large quantities from which hydrocarbons in the diesel fuel range can be produced via secondary reactions such as hydrocracking.

**Methanol-To-Gasoline (MTG) process:** To enable the transformation of CO<sub>2</sub> into high value fuels suitable for petrol or diesel engines, research into converting methanol into hydrocarbons (especially those with suitable octane or cetane ratings to act as fuels for petrol or diesel vehicles), is gaining interest. The MTG process was developed by Mobil in the 1970s and involves using a zeolite-supported catalyst to polymerise methanol, via DME, into long-chain hydrocarbons (methanol is dehydrated to DME, then converted to light olefins (C<sub>2</sub>-C<sub>4</sub>), to higher olefins, isoparaffins, aromatics and polycyclic aromatics). Stopping at the 2nd step and collecting the light olefins is the MTO (Methanol-To-Olefins) process described previously in this report. The favoured catalyst for gasoline-range hydrocarbons is ZSM-5 (an aluminosilicate zeolite).<sup>60</sup> The process requires pressures of 10-20 atm and temperatures of 300-400°C to generate around 82% gasoline by weight, conditions which are comparable to the Fischer-Tropsch syngas process. The octane rating of the product fuel varies but it can approach that of conventional petrol, although cyclic hydrocarbons are normally absent. Unfortunately a high portion of the cost of the fuel is due to the need to periodically burn off carbon deposits which build up on the catalysts and reduce their lifetime.

As described above, the first step in the MTG process is the formation of DME, so the energetic shortcut of syngas to DME (rather than syngas to methanol then methanol to DME) is important. By going directly from syngas to DME avoids the methanol synthesis, isolation and purification steps. However, this process is currently limited to producing short-chain (C<sub>2</sub>-C<sub>6</sub>) hydrocarbons and olefins by catalysis using Fe-MnO/Si molecular sieves at 300-400°C at 20 atm. Such compounds have limited use as fuels, but they do provide routes for CO<sub>2</sub> utilisation towards bulk plastics such as polyethylene and polypropylene.<sup>61</sup>

### Direct routes

When using an Fe-based catalyst for the F-T reactions the products are produced in a typical product distribution for the CO<sub>2</sub> derived process, but when Co-based catalysts are used, CH<sub>4</sub> is greatly favoured as a product. While Fe-catalysts can be used for both indirect and direct processes, its product selectivity in the direct process suffers adversely. As a consequence, additives must be utilised to improve it. Potassium may be used as an additive which facilitates improved CO<sub>2</sub> conversion and reduced methane production. It has therefore been hypothesised that potassium acts to enhance the chemisorption of CO<sub>2</sub> with reduced hydrogen adsorption leading to preferential -CH<sub>2</sub>- formation as opposed to CH<sub>4</sub>. Cerium (IV) oxide has also shown significant promise as an additive in this process as it appears to enhance reverse water gas shift activity at low temperature.

As with the indirect process, it is also possible to convert CO<sub>2</sub> by MTG reactions in a direct single reactor. However, such processes are not as popular as those employing F-T, but they are of interest as methanol can be generated quite readily from CO<sub>2</sub>.

The biggest drawback of reactions employing CO<sub>2</sub> as a feedstock is the reaction thermodynamics. Water is cogenerated in both F-T and MTG processes during the synthesis, which helps the thermodynamics of the reaction (see below), but in the MTG process the generated H<sub>2</sub>O competes with methanol for adsorption at active sites, hence limiting the maximum rate of reaction.

By using a relatively small number of different chemical reactions, CO<sub>2</sub> can be used to make liquid-fuel products much like those obtained from petrochemical processes. A major advantage of CO<sub>2</sub>-derived fuels is that they lack contamination by sulphur, nitrogen and metals. Additionally, if waxes generated in Fischer-Tropsch are processed to produce diesel fuel, this has the advantage of being cleaner and without the troublesome residue molecules found in heavier oil feed stocks, which minimises the need for pre-treatment processes.

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<sup>60</sup> France et al. (2015). The Indirect and Direct Conversion of CO<sub>2</sub> into Higher Carbon Fuels. In *Carbon Dioxide Utilisation: Closing the Carbon Cycle*. Eds. Styring P, Quadrelli EA and Armstrong K. Elsevier.

<sup>61</sup> Dowson and Styring (2015). Conversion of Carbon Dioxide to Oxygenated Organics. In *Carbon Dioxide Utilisation: Closing the Carbon Cycle*. Eds. Styring P, Quadrelli EA and Armstrong K. Elsevier.

Further work needs to be done to examine the potential of enhancing the reverse water-gas shift reaction at lower temperatures. Also, consider selectively poisoning catalyst H<sub>2</sub> adsorption/dissociation sites as this may enable greater control over the amounts of species present on the catalyst, which would result in a potentially more favourable ratio between the species leading to the generation of longer chained hydrocarbons.<sup>62</sup>

In May 2017, German company Sunfire reported producing three tons of synthetic crude oil substitute (called Blue Crude) in its power-to-liquids demonstration plant in Dresden.<sup>63</sup> Just two months later it was reported that a partnership between Nordic Blue Crude, Sunfire and Climeworks is planning to build a commercial plant in Norway to produce 8000 tonnes per year of the synthetic oil. The product consists of a mixture of various hydrocarbons which can be used as a raw material to make waxes, petrol, diesel or kerosene. Steam electrolysis will be used to produce H<sub>2</sub>, then CO<sub>2</sub> will be reduced to CO before undergoing a F-T process to produce the mixed hydrocarbon product. The CO<sub>2</sub> will be partly extracted on-site from the ambient air by using Direct Air Capture technology developed by the Swiss company Climeworks. Exploitation of the waste heat from the Sunfire F-T process will be used to increase efficiency of the CO<sub>2</sub> capture.<sup>64</sup>

In 2016, INFRA opened a demonstration gas-to-liquids plant in Texas which produces 100 barrels per day (b/d) of synthetic crude. The company hopes to run the plant on a commercial basis.<sup>65</sup>

A methanol to gasoline demonstration plant opened in China in 2009. Using ExxonMobil technology, it produced 2,500 b/d. In 2011 two additional MTG units were commissioned to produce 12,500 b/d each.<sup>66</sup> This suggests that the technology is at a TRL of around 6-8.

## Jetfuel

In 2015, European production plus imports of kerosene-type jetfuel amounted to almost 64 Mt, worth €31 billion.

LanzaTech and Vigin Atlantic have developed a biological gas fermentation process in which anaerobic bacteria ferment CO to produce ethanol which can then be transformed to a kerosene-type jetfuel. This process could utilise CO<sub>2</sub> if the CO<sub>2</sub> was first converted to syngas, but since this process is essentially transforming CO, to avoid duplication it is described in Section 4 of this report.

## 3.3.2 Gaseous hydrocarbons

### Methane

Methane, in the form of natural gas, is used in high quantities for heating and electricity generation. In 2015, European production plus imports was 339 Mt worth €193 billion. Synthetically produced methane (sometimes called synthetic natural gas or SNG) is often referred to as Power-to-Gas or Power-to-Methane as it can be considered as an energy storage option for intermittent power from renewable sources. One benefit is that methane storage can use the existing gas storage and distribution infrastructure. Several large scale plants were developed and installed in the 1970s during the oil crisis, but since that time, CO<sub>2</sub> methanation has not attracted serious attention until recently.

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<sup>62</sup> France et al. (2015). The Indirect and Direct Conversion of CO<sub>2</sub> into Higher Carbon Fuels. In *Carbon Dioxide Utilisation: Closing the Carbon Cycle*. Eds. Styring P, Quadrelli EA and Armstrong K. Elsevier.

<sup>63</sup> Sunfire (2017). Sunfire produces sustainable crude oil alternative. Available at: <http://www.sunfire.de/en/company/press/detail/sunfire-produces-sustainable-crude-oil-alternative>. Accessed September 2017.

<sup>64</sup> Sunfire (2017). First commercial plant for the production of blue crude planned in Norway. Available at: <http://www.sunfire.de/en/company/press/detail/first-commercial-plant-for-the-production-of-blue-crude-planned-in-norway>. Accessed September 2017.

<sup>65</sup> INFRA (2017). M100 USA. Available at: <http://en.infratechnology.com/projects/m100-usa/> Accessed October 2017.

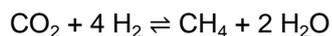
<sup>66</sup> ExxonMobil (2017). Synthetic Fuels. <http://corporate.exxonmobil.com/en/company/worldwide-operations/catalysts-and-licensing/synthetic-fuels>. Available at: Accessed October 2017.

The hydrogenation of carbon dioxide to methane is exothermic ( $\Delta H_f = -253$  kJ/mol), and provided the required hydrogen can be obtained without the use of fossil fuels, this offers a potentially sustainable source of gaseous fuel. However, it has not yet been widely commercialised.<sup>67</sup>

#### Technologies and pathways:

Three routes to CH<sub>4</sub> from CO<sub>2</sub> have been identified:

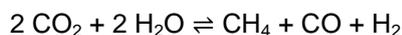
1). CO<sub>2</sub> methanation (via the Sabatier reaction) has been recognised since the beginning of the last century.<sup>68</sup>



As can be seen from the reaction stoichiometry above, water is formed during the reaction which needs to be removed to obtain pure methane. The loss of hydrogen by water formation is an unavoidable drawback in the production of CH<sub>4</sub>, but the reaction is exothermic due to this water production (as explained previously). The gas feed stream for methanation needs to be very pure, which results in the only impurities in the dehydrated CH<sub>4</sub> being CO<sub>2</sub>, H<sub>2</sub> and small quantities of higher hydrocarbons. Water is removed by drying the resulting gas stream, while small quantities of H<sub>2</sub> and CO<sub>2</sub> can be usually tolerated in the SNG and the hydrocarbons can even be used to adapt the heating value of the product. For easier transport and storage, natural gas can be liquefied by cooling it to -162°C. Condensing gas requires it to be very clean: prior to condensation it must be treated to remove other condensates, CO<sub>2</sub>, H<sub>2</sub>O, sulphur and mercury compounds. As SNG contains significantly less of these impurities than natural gas, liquefaction is easier and cheaper.<sup>69</sup>

Carmaker Audi opened a demonstration plant in Werlte, Germany in 2013 to produce 1000 tonnes of synthetic gas (marketed as e-gas) per year. The plant uses wind power to run an electrolyser to produce H<sub>2</sub> and utilises waste CO<sub>2</sub> arising from an adjacent biogas plant (which in turn utilises waste heat arising from the methanation process).<sup>70</sup>

2). Electrocatalytic reduction of CO<sub>2</sub> produces methane and CO:



The CO<sub>2</sub> is reduced in an aqueous acidic solution using a cobalt protoporphyrin catalyst immobilized on a graphite electrode. The efficiency and selectivity are reported to be good but CO is the main reduction product with CH<sub>4</sub> appearing as a by-product.<sup>71</sup> Still in early phases of development.

3). Fermentation of CO<sub>2</sub> by methanogenic bacteria can produce methane. The reaction is part of a complex metabolic pathway, but assuming CO<sub>2</sub> is the only carbon source, then overall it will be equivalent to:  $\text{CO}_2 + 4 \text{H}_2 \rightleftharpoons \text{CH}_4 + 2 \text{H}_2\text{O}$

Audi, in collaboration with Weissman, opened a second demonstration plant in 2016 to produce synthetic methane. This plant in Allendorf, Germany uses biological fermentation of CO<sub>2</sub> to form methane.<sup>72</sup>

<sup>67</sup> North (2015). What is CO<sub>2</sub>? Thermodynamics, Basic Reactions and Physical Chemistry. In *Carbon Dioxide Utilisation: Closing the Carbon Cycle*. Eds. Styring P, Quadrelli EA and Armstrong K. Elsevier.

<sup>68</sup> Strangeland *et al.* (2017). CO<sub>2</sub> methanation: the effects of catalysts and reaction conditions. *Energy Procedia* **105**: 2022 – 2027.

<sup>69</sup> Dechema (2017). Low carbon energy and feedstock for the European chemical industry. Technology study commissioned by Cefic. Frankfurt.

<sup>70</sup> European Power to Gas (2013). Audi opens renewable energy E-gas plant in Germany. Available at: <http://www.europeanpowertogas.com/blog/623> Accessed September 2017.

<sup>71</sup> Shen *et al.* (2015). Electrocatalytic reduction of carbon dioxide to carbon monoxide and methane at an immobilised cobalt protoporphyrin.

<sup>72</sup> Audi (2016). New method for producing the synthetic fuel Audi e-gas. Available at: <https://www.audi-mediacycenter.com/en/press-releases/new-method-for-producing-the-synthetic-fuel-audi-e-gas-5722> Accessed October 2017.

An alternative approach is taken by a consortium led by RAG of Austria, which is Europe's fourth largest gas storage operator. The "Underground sun conversion" project pumps CO<sub>2</sub> together with renewable H<sub>2</sub> into existing underground gas storage reservoirs. A natural methanation process by unspecified micro-organisms reportedly converts the gases to CH<sub>4</sub> within an acceptable timeframe.<sup>73</sup>

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<sup>73</sup> Underground Sun Conversion (2017). Project Description. Available at: <http://www.underground-sun-conversion.at/en/project/project-description.html>. Accessed September 2017.

**Table 3. Potential fuel products with associated market and CO<sub>2</sub> utilisation data.**

Class	Product	Synthesis route	Overall reaction	TRL	EU28 prod. + imports [t/yr]	Unit value [€/t]	Market value [€M]	CO <sub>2</sub> used [t CO <sub>2</sub> /t product]	EU CO <sub>2</sub> utilisation [t/yr]*	H <sub>2</sub> requirement [t H <sub>2</sub> /t product]**	Other (non-catalytic) inputs
Liquid hydrocarbons	Diesel	Syngas produced from CO <sub>2</sub> and H <sub>2</sub> undergoes F-T reactions to produce linear waxes. Hydrocracking converts to synthetic diesel	$12 \text{ CO}_2 + 36 \text{ H}_2 \rightleftharpoons \text{C}_{12}\text{H}_{24} + 24 \text{ H}_2\text{O}$	7-8	384,086,000	643	247,271	3.14	1,206,030,040	0.43	-
	Gasoline	Syngas produced from CO <sub>2</sub> and H <sub>2</sub> undergoes F-T reactions to produce gasoline-range hydrocarbons	$8 \text{ CO}_2 + 25 \text{ H}_2 \rightleftharpoons \text{C}_8\text{H}_{18} + 16 \text{ H}_2\text{O}$	7-8	146,243,000	684	100,042	3.09	451,890,870	0.44	-
		Methanol to Gasoline process, via DME and olefins	$8 \text{ CH}_3\text{OH} + \text{H}_2 \rightleftharpoons \text{C}_8\text{H}_{18} + 8 \text{ H}_2\text{O}$	6-8						0.02 - 0.58	Methanol
	Jetfuel - kerosene type (C <sub>8</sub> H <sub>18</sub> - C <sub>16</sub> H <sub>34</sub> , average C <sub>12</sub> H <sub>26</sub> )	Gas fermentation of syngas produced from CO <sub>2</sub> by anaerobic bacteria to produce ethanol. This then undergoes oligomerisation and dehydration/hydrogenation to produce hydrocarbons suitable for use as kerosene-type aviation fuel ( <i>LanzaTech - Virgin Atlantic process</i> )	Two-stage reaction, the first part of a complex biochemical pathway which can be simplified to: $4 \text{ CO}_2 + 9 \text{ H}_2 \rightleftharpoons 2 \text{ C}_2\text{H}_5\text{OH} + 6 \text{ OH}$ . The second step synthetically converts the bioethanol to suitable hydrocarbons: $6 \text{ C}_2\text{H}_5\text{OH} + \text{H}_2 \rightleftharpoons \text{C}_{12}\text{H}_{26} + 6 \text{ H}_2\text{O}$	5-7	63,928,000	488	31,215	3.11	198,816,080	0.329	Nutrients
Gaseous hydrocarbons	Methane	CO <sub>2</sub> methanation (Sabatier reaction)	$\text{CO}_2 + 4 \text{ H}_2 \rightleftharpoons \text{CH}_4 + 2 \text{ H}_2\text{O}$	6-7	338,511,000	571	193,229	2.75	930,905,250	0.5	-
		Electrocatalytic reduction of CO <sub>2</sub> over a cobalt catalyst	$2 \text{ CO}_2 + 2 \text{ H}_2\text{O} \rightleftharpoons \text{CH}_4 + \text{CO} + \text{H}_2$	1-3				5.5	1,861,810,500	0	-
		Gas fermentation by the anaerobic bacterium <i>Clostridium sp.</i>	Reaction part of a complex metabolic pathway, but assuming CO <sub>2</sub> is the only carbon source, then overall: $\text{CO}_2 + 3 \text{ H}_2 \rightleftharpoons \text{CH}_4 + 2 \text{ OH}$	4-6				2.75	930,905,250	0.375	Nutrients

\* This assumes that all of the EU market for this product is synthesised using the route in question. If multiple possible routes to a product exist, each route shows the EU CO<sub>2</sub> utilisation potential if 100% of the market is met using that route, the multiple routes are not additive.

\*\* The H<sub>2</sub> requirement for products produced by biological fermentation in some instances may be provided in the form of metabolic reducing agents NADH, NADPH or FADH<sub>2</sub> rather than gaseous H<sub>2</sub>, but the mass of H<sub>2</sub> has been provided for consistency to allow comparison. The H<sub>2</sub> requirement for products produced from methanol includes the H<sub>2</sub> required for the production of the methanol and since there are a range of production routes utilising different amounts of H<sub>2</sub>, the total H<sub>2</sub> requirement is given as a range.

## 3.4 Solid materials

### 3.4.1 Carbonates (mineral)

Converting gaseous CO<sub>2</sub> into solid mineral carbonates (termed mineral carbonation or carbon mineralisation) is a desirable option as the carbon is sequestered indefinitely rather than temporarily. Magnesium and calcium silicates such as olivine and serpentine are naturally abundant (wollastonite is less so) and can undergo carbonation to form magnesium or calcium carbonates (limestone). These can be used as aggregates for construction, liming agents to neutralise soil acidity, for land reclamation/remediation projects. The tonnages of aggregates used throughout Europe is vast - Prodcum data suggests that the total tonnage of crushed stone of a kind used for concrete aggregates, road metalling or railway ballast; pre-coated aggregates; plus limestone flux and limestone used for the manufacture of lime or cement comes to 777 Mt/yr. Even at a unit cost of less than €10/t, this comes to a value of €7.5 billion per year.

There is the potential to produce higher value materials such as pure Ca/Mg carbonates and high surface area silica which could be used as fillers in papers, plastics and construction materials. Worldwide, there are enough suitable minerals to store hundreds of thousands of Gtonnes of carbon and the reactions can utilise untreated flue gases rather than pure CO<sub>2</sub> streams. However, even though the mineralisation reactions are exothermic and therefore thermodynamically favourable (for olivine  $\Delta H = -89$  KJ/mol CO<sub>2</sub>, for serpentine  $\Delta H = -64$  KJ/mol CO<sub>2</sub>), the kinetics prove difficult as the reactions happen very slowly. Over the past couple of decades, work has progressed to try to accelerate the process (sometimes called engineered weathering) by grinding and dissolving the minerals in aqueous solutions in single-step and two-step reaction processes which have been developed. However, issues exist with the carbon balance of the process once the energy required for the quarrying and transport of the minerals is taken into account, so the technologies have not been widely adopted to-date.<sup>74</sup>

Techniques for injecting high pressure CO<sub>2</sub> into geological deposits of the relevant minerals, i.e. *in-situ* mineralisation, are not discussed as that is a technique only for the potential storage of CO<sub>2</sub> rather than its utilisation.

### Cement and concrete products

The same carbonation process as occurs with natural minerals can be made to occur to processed mineral products. CarbonCure, based in Canada, have commercialised the process of injecting CO<sub>2</sub> into wet concrete as it is being mixed. This leads to the transformation of the calcium oxides already present within the cement into calcium carbonate nanoparticles within the concrete matrix, which reportedly increases the strength of the resulting concrete.<sup>75</sup> It is used to produce pre-cast concrete blocks as well as ready-mixed concrete.

The market for cements and mortars is 185 Mt/yr, worth €14billion. The market for ready-mixed concrete plus concrete blocks and pre-fabricated concrete structural components is around 750 Mt/yr worth €40 billion.

### Industrial wastes

Another source of material for potential carbonation are industrial wastes such as fly ash, steel slags and cement kiln dusts. Such wastes are currently costly to dispose of, but contain higher levels of cations present as reactive oxides than which occur in natural minerals. This makes these wastes ideal for carbonation reactions and worldwide supplies are estimated to enable in the order of several hundred Mt CO<sub>2</sub> storage per year. As with natural minerals, the carbonates produced have potential

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<sup>74</sup> Gadikota G and Park A-HA (2015). Accelerated carbonation of Ca- and Mg-bearing minerals and industrial wastes using CO<sub>2</sub>. In *Carbon Dioxide Utilisation: Closing the Carbon Cycle*. Eds. Styring P, Quadrelli EA and Armstrong K. Elsevier.

<sup>75</sup> Carboncure (2017). Technology. Available at: <http://carboncure.com/technology/> Accessed September 2017.

for use as construction aggregates, so long as a consistent product can be produced from a waste which may vary in composition.

Carbon8 Systems, the UK company which developed the process, now operate two commercial plants in the UK which produce carbonate pellets for use as construction aggregates as Carbon8 Aggregates, with planning permission for a third. Additionally, the process has been utilised by many companies across Europe for stabilising and treating different wastes, including Cemex in Heidelberg to treat cement kiln dust, Lafarge to treat steel slag, EoN to treat air pollution control residues, BP and Shell for oil drill cuttings and it has been used for quarry fines, contaminated soils, MSW incinerator bottom ash<sup>76</sup>.

Calera (USA) produce cement products which they use to create cement boards for construction. They utilise industrial wastes containing calcium hydroxide ( $\text{CO}_2 + \text{Ca(OH)}_2 \rightleftharpoons \text{CaCO}_3 + \text{H}_2\text{O}$ ) or sodium hydroxide and calcium chloride ( $\text{CO}_2 + 2 \text{NaOH} + \text{CaCl}_2 \rightleftharpoons \text{CaCO}_3 + 2 \text{NaCl} + \text{H}_2\text{O}$ ) to produce calcium carbonate for their cement boards. Two pilot plants produce up to two tonnes of  $\text{CaCO}_3$  containing products per day<sup>77</sup>.

Carbon Clean Solutions (UK) recently announced the successful commissioning of a project in Tamil Nadu, India, where a coal-fired power plant has become the site of the first industrial installation to re-use all its  $\text{CO}_2$  emissions. The unsubsidised project will ensure 60,000 metric tons of  $\text{CO}_2$  are captured each year at a cost of \$30 per tonne. The captured  $\text{CO}_2$  will then be used by Indian firm, Tuticorin Alkali Chemicals & Fertilizers for soda ash production, a compound commonly used in glassmaking.<sup>78</sup>

### Agricultural fertiliser

The European market for fertilisers is large (over 24 Mt/yr for all types) and if just those classed on Prodcom as "nitrogenous", plus "animal or vegetable" and "other" fertilisers are included (i.e. the 13.6 Mt of NPK fertilisers are excluded), the market still stands at 10.3 Mt/yr which is worth around €2.4 billion.

CCm Research (UK) are developing an agricultural fertiliser synthesised from pellets of cellulosic biomass such as agricultural wastes, mineral solutions and waste  $\text{CO}_2$ .<sup>79</sup> An aqueous solution of ammonia and calcium nitrate is used to capture  $\text{CO}_2$  from flue gas, which reacts to form a solution containing ammonium nitrate and calcium carbonate. This is used to soak the cellulosic biomass pellets which then are dried to form pellets of cellulose and ammonium nitrate with a  $\text{Ca}_2\text{CO}_3$  coating. Extensive field trials appear to show that the fertiliser pellets perform well so an industrial pilot plant is under development.<sup>80</sup>

## 3.4.2 Pure carbon

A number of advanced carbon-based materials are produced from pure carbon, these include carbon fibres, carbon nanotubes and graphene. Advanced carbon-based materials have a wide range of uses in the aviation, automotive, and renewable energy sectors and are extremely desirable due to their superior performance when compared to traditional materials. The market for these products is rapidly expanding with growth rates exceeding 10% per annum. However, current production routes to these products are typified by extremely high temperatures and pressures, leading to large emissions

<sup>76</sup> Carbon8 Systems (2017). Using carbon dioxide to give waste value. Available at: <http://c8s.co.uk/> Accessed September 2017.

<sup>77</sup> Calera (2017). The Process and Scale-up. Available at: <http://calera.com/beneficial-reuse-of-co2/process.html>. Accessed September 2017.

<sup>78</sup> Carbon Clean Solutions (2016). First Fully Commercial CCSU Plant Launches Capturing  $\text{CO}_2$  at \$30 per tonne. Available at: <http://www.carboncleansolutions.com/media-center/news/article/2016/11/first-fully-commercial-ccsu-plant-launches-capturing-co2-at-30-per-tonne> Accessed September 2017.

<sup>79</sup> Innovate UK (2016). CCm Research develops carbon dioxide utilisation process for value added materials. Available at: <https://www.ktn-uk.co.uk/perspectives/ccm-research-develops-carbon-dioxide-utilisation-process-for-value-added-materials> Accessed September 2017.

<sup>80</sup> CCm Research (2017). Using waste to create valuable products and a better environment (video). Available at: <https://www.ktn-uk.co.uk/perspectives/ccm-research-develops-carbon-dioxide-utilisation-process-for-value-added-materials> Accessed September 2017.

footprints. New routes via CO<sub>2</sub> are an emerging research area at low TRL (1-2). Although, the current market for these products is small, the price per tonne of product is extremely high. The small production quantities would only utilise a small amount of CO<sub>2</sub>, however the superior properties of the materials could lead to significant reductions in avoided CO<sub>2</sub> emissions. Other pure carbon products include synthetic diamonds which have superior conductivity and hardness over natural diamonds and are therefore highly desirable for industrial applications.

Carbon nanofibers have been synthesised using CO<sub>2</sub> dissolved in molten carbonates at George Washington University<sup>81</sup> and are an emerging area of interest for CO<sub>2</sub> utilisation. These fibres could be used in applications such as Li-ion batteries, building materials and composites. Routes to longer length fibres and nanotubes are a target research area. Synthetic diamonds can be synthesised by the reduction of solid CO<sub>2</sub> at 440°C and 800 atm for 12 hrs in the presence of metallic sodium.<sup>82</sup>

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<sup>81</sup> Ren *et al.* (2015). One-Pot Synthesis of Carbon Nanofibres from CO<sub>2</sub>. *Nano Letters* **15**: 6142-6148.

<sup>82</sup> Chen *et al.* (2003). Diamond Formation by Reduction of Carbon Dioxide at Low Temperatures. *Journal of American Chemical Society* **125**: 9302 - 9303.

**Table 4. Potential solid material products with associated market and CO<sub>2</sub> utilisation data.**

Class	Product	Synthesis route	Overall reaction	TRL	EU28 prod. + imports [t/yr]	Unit value of product [€/t]	Market value [€M]	CO <sub>2</sub> used [t CO <sub>2</sub> /t product]	EU CO <sub>2</sub> utilisation [t/yr]*	H <sub>2</sub> requirement [t H <sub>2</sub> /t product]	Other (non-catalytic) inputs
Carbonates (mineral)	Calcium/magnesium carbonates - construction aggregates	Single-step direct aqueous mineralisation of calcium/magnesium silicates.	2 CO <sub>2</sub> + Mg <sub>2</sub> SiO <sub>4</sub> (olivine) ⇌ 2 MgCO <sub>3</sub> + SiO <sub>2</sub> <b>or</b> 3 CO <sub>2</sub> + Mg <sub>3</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub> (serpentine) ⇌ 2 MgCO <sub>3</sub> + 2 SiO <sub>2</sub> + 2 H <sub>2</sub> O	3-4	777,209,041	9.69	7,531	0.53	411,920,792	0	Naturally occurring Ca or Mg silicates (e.g. olivine or serpentine)
		Two-step mineralisation to improve mineral dissolution and carbonate formation.	As above, but mineral dissolution increased by acidic conditions.	3-4							
		As above, but using alkaline industrial wastes (high in reactive Ca/Mg oxides).	CO <sub>2</sub> + CaO ⇌ CaCO <sub>3</sub>	9				0.44	341,971,978		
	Cement-like products	Captured flue gases react with alkaline industrial brines to produce carbonates and bicarbonates.	CO <sub>2</sub> + Ca <sup>2+</sup> + 2 OH <sup>-</sup> ⇌ CaCO <sub>3</sub> + H <sub>2</sub> O	6-8	185,166,311	76.42	14,150	0.53	98,138,145	0	Waste alkaline brines
	Concrete products	CO <sub>2</sub> injected into concrete to form calcium carbonate nanoparticles within the concrete	CO <sub>2</sub> + CaO ⇌ CaCO <sub>3</sub>	9	754,825,440	54.23	40,934	0.44	332,123,194	0	Concrete
	Mineral fertiliser	Captured CO <sub>2</sub> forms a carbonate coating around biomass pellets	CO <sub>2</sub> + Ca(NO <sub>3</sub> ) <sub>2</sub> + NH <sub>3</sub> + H <sub>2</sub> O ⇌ 2 NH <sub>4</sub> NO <sub>3</sub> + CaCO <sub>3</sub>	7-8	10,301,330	233.69	2,407	Unk <sup>(1)</sup>	Unk <sup>(1)</sup>	0	Biomass, Ca(NO <sub>3</sub> ) <sub>2</sub> , NH <sub>3(aq)</sub>
Pure carbon	Carbon fibre	Electrocatalytic conversion of CO <sub>2</sub> dissolved in molten carbonates	CO <sub>2</sub> ⇌ C + O <sub>2</sub>	2	16,650	31,651	527	3.67	16,106	0	-
	Nanotubes		CO <sub>2</sub> ⇌ C + O <sub>2</sub>	2	Unk	Unk	Unk	3.67	Unk	0	-
	Graphene		CO <sub>2</sub> ⇌ C + O <sub>2</sub>	2	481 <sup>(2)</sup>	Unk	Unk	3.67	1,765	0	-
	Diamonds	Reduction of solid CO <sub>2</sub> in the presence of metallic sodium	CO <sub>2</sub> ⇌ C + O <sub>2</sub>	1-2	Unk	Unk	Unk	3.67	Unk	0	-

\* This assumes that all of the EU market for this product is synthesised using the route in question. If multiple possible routes to a product exist, each route shows the EU CO<sub>2</sub> utilisation potential if 100% of the market is met using that route, the multiple routes are not additive.

<sup>(1)</sup> The mineral:biomass ratio of the fertiliser product is unknown, therefore the amount of CO<sub>2</sub> utilised is unknown.

<sup>(2)</sup> Value for global production, not European.

## 4. Products Utilising CO

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### 4.1 Overview of current uses

Carbon monoxide can either be used alone or as a synthesis gas (syngas). Syngas is a mixture of gases, mostly CO and H<sub>2</sub>, but it may also contain impurities such as CO<sub>2</sub>, O<sub>2</sub> and CH<sub>4</sub>. In Europe, syngas is mainly produced via steam methane reforming, or alternatively via autothermal reforming using oxygen rather than steam. It is sometimes used in turbine engines that employ natural gas as a fuel, but its use as a fuel is limited by the fact that its energy density is 50% lower than that of CH<sub>4</sub>. In general, its main use is as a fundamental chemical building block within the chemical industry. Here it has multiple potential uses as a feedstock for the production of basic inorganic and organic chemicals, polymers, hydrocarbons and synthetic fuels, as we shall see shortly. The large potential of syngas is due to the inherent flexibility in its CO:H<sub>2</sub> ratio which is due to the ability to adjust the ratio to the needs of the subsequent chemistry by using the water gas shift reaction. Other important features of syngas are the intrinsic high chemical energy content of both CO and H<sub>2</sub> and the large number of catalysts and reaction processes available.<sup>83</sup>

Approximately 50% of the carbon used in the chemistry of steelmaking leaves the process as CO. Since CO is potentially useful, any produced as an industrial by-product is usually re-used in a production process. However, if it cannot be re-used it is generally flared because CO is toxic and should not be simply released to atmosphere. In the steel industry the CO is generally either flared or, due to its energy content, used for heat and/or power generation within the steel plant. In either case, the CO is combusted and the resulting CO<sub>2</sub> is emitted. The following sections describe the chemical products which could be synthesized if it was utilised chemically rather than combusted.

There is a significant amount of overlap between the products that can be synthesised from CO<sub>2</sub> and those which can be synthesised from CO. For instance, many of the chemical pathways discussed in the previous section required the CO<sub>2</sub> to be converted to CO before the products were synthesised. Three of the routes to synthesise methanol from CO<sub>2</sub> which were reviewed in the previous section involved the preliminary production of CO from CO<sub>2</sub> by the reverse water gas shift, or dry reforming of methane and CO<sub>2</sub>, or steam reforming of CH<sub>4</sub> and CO<sub>2</sub>. In these cases, these products and/or routes are mentioned only briefly to avoid repetition. As discussed above, CO is already recognised as a useful feedstock within the petrochemicals industry, so many of the production routes mentioned in the following sections are already commercialised. However, in such processes the CO utilised is usually generated from fossil fuels, either from steam reformation of methane or gasification of coal. The opportunity exists to fill this requirement for CO by utilising that which is produced as a by-product from the steel industry.

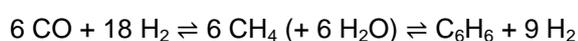
## 4.2 Chemicals

### 4.2.1 Aromatic hydrocarbons

#### Benzene, toluene and xylene

There are two routes to the production of BTX components from CO:

1). The direct synthesis of benzene can be achieved by CO methanation followed by CH<sub>4</sub> dehydro-aromatisation:




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<sup>83</sup> France et al. (2015). The Indirect and Direct Conversion of CO<sub>2</sub> into Higher Carbon Fuels. In *Carbon Dioxide Utilisation: Closing the Carbon Cycle*. Eds. Styring P, Quadrelli EA and Armstrong K. Elsevier.

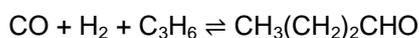
The basis of the reaction is identical to that previously described for CO<sub>2</sub>, the only difference being the first step which produces methane from CO rather than from CO<sub>2</sub>. The subsequent dehydration and aromatisation of the resulting methane is the same reaction as was described for CO<sub>2</sub> and remains at the same late lab stage of development.

2). Indirectly via methanol in the same Methanol-To-Aromatics (MTA) process developed by Mobil described in Section 3 (TRL 7). Section 4.2.1 describes the production of methanol from CO.

## 4.2.2 Aldehydes

### Butanal

Oxygenated hydrocarbons such as aldehydes were originally identified as by-products of F-T reactions. An olefin formed during the F-T process may react with H<sub>2</sub> and CO in what is called a hydroformylation (or oxo synthesis) reaction. If the olefin was propylene, the result is the aldehyde butanal.

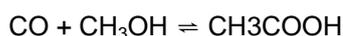


This reaction, which is generally conducted in an aqueous solution of the rhodium catalyst, is the main commercial production route for butanal today. The commonest product of this reaction is *n*-butanal, but the branched chain version, isobutanal can be produced by using special ligands on the rhodium catalyst.<sup>84</sup> The European market for butanol is about 225 Kt/yr, the majority of which is used as feedstock or intermediates within the chemical industry.

## 4.2.3 Organic acids

### Acetic acid

Acetic acid is currently synthesised commercially by the carbonylation (addition of CO) of methanol:



In the Cativa process developed by BP an iridium catalyst is used, whereas in the Monsanto process a rhodium catalyst is used. Both processes similar reactions conditions (temperatures of 150-200°C and pressures of 30-60 atm) but the Cativa process can be operated at low water levels which saves energy when it comes to the removal of water to produce the anhydrous acid. TRL 9.

A biological synthesis route is also possible using the ability of Clostridia to ferment CO, however this technique remains in the laboratory.

### Butyric acid

Butyric acid is produced conventionally by the industrial bacterial fermentation of starch, but it can also be produced in the lab via gas fermentation by the anaerobic bacterium *Clostridium sp.* which utilises CO as a feedstock.<sup>85</sup>

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<sup>84</sup> Maitlis (2013). Other Industrially important Syngas Reactions. In Greener Fischer-Tropsch Processes for Fuels and Feedstocks. Wiley-VCH.

<sup>85</sup> Drzyzga *et al.* (2015). New challenges for syngas fermentation: towards production of biopolymers. *Journal of Chemical Technology and Biotechnology* **90**: 1735 - 1751.

Using bacteria as biocatalysts for syngas fermentation offers advantages over traditional mineral-based catalysts for syngas transformation: biological catalysts can operate at temperatures and pressures which are closer to standard environmental conditions than chemical catalysts, which typically use very high temperatures and at least 10 atm pressure; biological catalysts are often less sensitive to the ratio of CO to H<sub>2</sub> in syngas compared with traditional catalysts and biological catalysts are less sensitive to trace amounts of contaminants which would poison traditional catalysts.

## Formic acid

Formic acid is currently commonly produced from carbonylation of methanol in the presence of a strong base such as sodium methoxide. The resulting methyl formate ester is subsequently cleaved with sodium hydroxide or a large excess of water.<sup>86</sup> TRL 9.

## Propiolactone

Lactones are the cyclic esters of a hydroxycarboxylic acids and around 43 Kt are produced in Europe each year. Propiolactone readily polymerizes to polypropiolactone, even at room temperature. Water causes its hydrolysis to 3-hydroxypropionic acid (hydracrylic acid) and the principal use of propiolactone is as an intermediate in the synthesis of other chemical compounds. It was once widely used as an intermediate in the production of acrylic acid and its esters, but that has been largely displaced by cheaper alternatives.

Propiolactone is produced conventionally by the reaction of formaldehyde with ketene, but the US green chemistry company Novomer has developed a method of synthesising it by the carbonylation (addition of CO) of the epoxide ethylene oxide. Since this route is potentially significantly cheaper than conventional routes of production, Novomer hope that the resulting propiolactone will again be used to produce acrylic acid and its esters, and also as a precursor to the production of succinic acid, succinic anhydride and butanediol.<sup>87</sup> The technology is currently at the stage of a continuous automated process at lab scale (4-5 Kg/day) - TRL 4-5.

## 4.2.4 Esters

### Methyl formate

Methyl formate is the methyl ester of formic acid, which is produced during the carbonylation of methanol in the presence of sodium methoxide. The total European market for formic acid, its salts and esters is around 490 Kt/yr, so methyl formate will be a fraction of that market. The process is used commercially by BASF and is 96% selective towards methyl formate, however the CO used needs to be very dry as the catalyst is sensitive to the presence of water in syngas. The ester is produced as an intermediate during the production of formic acid, as mentioned previously, but it is also used to synthesize formamide, dimethyl formamide and some agrochemicals and pharmaceuticals.<sup>88</sup>

## 4.2.5 Olefins

### Ethylene and propylene

Olefins can be produced from CO indirectly via the Methanol-To-Olefin (MTO) process that was described in Section 3.1.5. Section 4.2.1 describes the production of methanol from CO.

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<sup>86</sup> Peters *et al.* (2011). Chemical Technologies for Exploiting and Recycling Carbon Dioxide into the Value Chain. *ChemSusChem* 4: 1216-1240.

<sup>87</sup> Novomer (2017). CO Business Overview. Available at: <http://www.novomer.com/co-business-overview> Accessed October 2017.

<sup>88</sup> Maitlis (2013). Other Industrially Important Syngas Reactions. In *Greener Fischer-Tropsch Processes for Fuels and Feedstocks*. Eds. Maitlis and de Klerk. Wiley-VCH.

## 4.2.6 Dienes

### 1,3-Butadiene

1,3-butadiene is currently produced as a by-product when steam-cracking crude oil or naphtha during the production of ethylene and propylene. It is of commercial interest because it can be polymerised to form a synthetic rubber and its largest use is for making automobile tyres. However, in addition to synthetic rubber, butadiene is one of the chemicals at the heart of the chemicals industry. Over the past few years, cheap shale gas has started to replace crude oil as the feedstock for ethylene and propylene production. Shale gas has a much lower proportion of 4-carbon hydrocarbons than oil and as a consequence, the price of butadiene is rising quickly. Europe uses almost 2.5 Mt 1,3-butadiene and isoprene per year, worth just over €1 billion.

The polyol 2,3-butanediol is a natural product of *Clostridium* Sp. fermentation and it can be used as a precursor in the industrial production of 1,3-butadiene (2,3-Butanediol = 1,3-butadiene + water). It therefore seems likely that 2,3-butanediol will be one of the next commercial products from syngas fermentation, as the respective enzymes from *Clostridium autoethanogenum* have been identified and their genes have already been expressed in *Escherichia coli*.<sup>89</sup> LanzaTech is in the process of commercialising the production of 2,3-butanediol in collaboration with Invista and SK Innovation. However, the same partners are also looking at a single step process to 1,3-butadiene rather than the 2-step process via 2,3-butanediol, so the production of 2,3-butanediol may not be required.<sup>90</sup>

## 4.2.7 Linear carbonates

### Dimethyl carbonate

DMC (CH<sub>3</sub>OCOOCH<sub>3</sub>) is still produced in some locations by the reaction of the toxic gas phosgene with methanol, which produces the intermediate methyl chloroformate. Various alternative routes have replaced the use of phosgene in Europe, one of the most common involving reacting CO with methanol in the presence of oxygen. A single-step liquid-phase reaction catalysed by CuCl<sub>2</sub> was developed by EniChem (Italy) and is used commercially in Europe. An alternative two-step process is also close to commercialisation:

Ube Industries (Japan) opened a demonstration plant in 1992 producing 3000 t/yr DMC using vapour-phase direct oxidative carbonylation to produce DMC from CO and methanol. CO and methyl nitrite react to form DMC and nitric oxide, which together with methanol are oxidised back to methyl nitrite and water in a separate nitrite regenerator. The overall reaction is the oxidation of CO and methanol to DMC and water (with dimethyl oxalate CH<sub>3</sub>COOCOOCH<sub>3</sub> as a by-product). The reaction is catalysed by using a PdCl<sub>2</sub>/CuCl<sub>2</sub> catalyst on activated carbon. In 2016, Ube licensed the technology to CNSG Anhui Hong Sifang Co. Ltd of China to build a 100,000 t/yr DMC production facility.<sup>91</sup>

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<sup>89</sup> Durre and Eikmanns (2015). C1-carbon sources for chemical and fuel production by microbial gas fermentation. *Current Opinions in Biotechnology*. **35**: 63 - 72.

<sup>90</sup> LanzaTech (2017). Chemicals. Available at: <http://www.lanzatech.com/innovation/markets/chemicals/> Accessed October 2017.

<sup>91</sup> Ube Industries (2016). Ube Industries Licenses DMC Technology and Agrees to Establish Joint Venture for High-Purity DMC. Available at: [http://www.ube-ind.co.jp/ube/en/news/2015/20160316\\_01.html](http://www.ube-ind.co.jp/ube/en/news/2015/20160316_01.html). Accessed October 2017.

## 4.2.8 Carbamates (organic)

Methyl carbamate ( $\text{CH}_3\text{COONH}_2$ ) can be produced indirectly from CO by the reaction of methanol ( $\text{CH}_3\text{OH}$ ) with urea ( $\text{CO}(\text{NH}_2)_2$ ). This reaction is identical to that already described in Section 3.1.14, so shall not be repeated again here.

Section 4.2.1 describes the production of methanol from CO.

Table 5. Potential chemical products with associated market and CO utilisation data.

Class	Product	Synthesis route	Overall reaction	TRL	EU28 prod. + imports [t/yr]	Unit value [€/t]	Market value [€M]	CO used [t CO/t product]	EU CO utilisation [t/yr]*	H <sub>2</sub> requirement [t H <sub>2</sub> /t product]**	Other (non-catalytic) inputs
Aromatic hydrocarbons	Benzene	CO methanation followed by CH <sub>4</sub> dehydro-aromatisation	$6 \text{ CO} + 18 \text{ H}_2 \rightleftharpoons 6 \text{ CH}_4 + 6 \text{ H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_6 + 9 \text{ H}_2$	2-4	6,807,829	533	3627	2.15	14,636,832	0.46	-
		Methanol to aromatics (MTA) process involving reacting methanol over a zeolite catalyst resulting in the simultaneous production of all three BTX components.	$6 \text{ CH}_3\text{OH} \rightleftharpoons \text{C}_6\text{H}_6 + 6 \text{ H}_2\text{O} + 3 \text{ H}_2$	7						0.31 - 0.46	Methanol
	Toluene	as above	$7 \text{ CH}_3\text{OH} \rightleftharpoons \text{C}_6\text{H}_5\text{CH}_3 + 7 \text{ H}_2\text{O} + 3 \text{ H}_2$	7	1,262,684	459	580	2.13	2,689,517	0.30 - 0.46	Methanol
	Xylene	as above	$8 \text{ CH}_3\text{OH} \rightleftharpoons \text{C}_6\text{H}_4(\text{CH}_3)_2 + 8 \text{ H}_2\text{O} + 3 \text{ H}_2$	7	2,563,662	552	1414	2.11	5,409,327	0.30 - 0.45	Methanol
Aldehydes	Butanal	Hydroformylation of propylene	$\text{CO} + \text{H}_2 + \text{C}_3\text{H}_6 \rightleftharpoons \text{CH}_3(\text{CH}_2)_2\text{CHO}$	9	225,430	682	154	0.39	87,918	0.03	Propylene
Organic acids	Acetic acid	Conventional carbonylation of methanol (Monsanto and Cativa processes)	$\text{CO} + \text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{COOH}$	9	1,231,867	473	583	0.47	578,977	0.07 - 0.10	Methanol
		Gas fermentation by the anaerobic bacterium <i>Clostridium sp.</i>	Reaction part of a complex metabolic pathway, but as CO is the only carbon source, then overall: $2 \text{ CO} + 2 \text{ H}_2 \rightleftharpoons \text{CH}_3\text{COOH}$	1-3				0.93	1,145,636	0.067	Nutrients
	Butyric acid	Gas fermentation by the anaerobic bacterium <i>Clostridium sp.</i>	Reaction part of a complex metabolic pathway, but as CO is the only carbon source, then overall: $4 \text{ CO} + 5 \text{ H}_2 \rightleftharpoons \text{C}_3\text{H}_7\text{COOH} + 2 \text{ OH}$	1-3	471,609	1166	550	1.27	598,943	0.114	Nutrients
	Formic acid	CO and methanol, subsequent cleavage of methylester with water to produce formic acid	$\text{CO} + \text{CH}_3\text{OH} \rightleftharpoons \text{HCOOCH}_3 (+ \text{H}_2\text{O}) \rightleftharpoons \text{HCOOH} + \text{CH}_3\text{OH}$	9	490,069	545	267	0.61	298,942	0.09 - 0.13	Methanol
	Propio-lactone	Carbonylation of epoxide ethylene oxide	$\text{CO} + \text{C}_2\text{H}_4\text{O} \rightleftharpoons \text{CH}_2\text{CH}_2\text{CO}_2$	4-5	43,690 <sup>(1)</sup>	24,011	1049	0.39	17,039	0	Ethylene oxide
Esters	Methyl	Carbonylation of methanol	$\text{CO} + \text{CH}_3\text{OH} \rightleftharpoons \text{HCOOCH}_3$	9	490,069 <sup>(2)</sup>	545	267	0.47	230,333	0.07 - 0.10	Methanol

Class	Product	Synthesis route	Overall reaction	TRL	EU28 prod. + imports [t/yr]	Unit value [€/t]	Market value [€M]	CO used [t CO/t product]	EU CO utilisation [t/yr]*	H <sub>2</sub> requirement [t H <sub>2</sub> /t product]**	Other (non-catalytic) inputs
	formate										
Olefins	Ethylene	Methanol to olefin (MTO) process (condensation of CO-derived methanol to DME followed by conversion to olefin)	$\text{CH}_3\text{OH} + \text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{C}_2\text{H}_4 + 2 \text{H}_2\text{O}$	8-9	24,505,336	872	21,382	1.00	24,505,336	0.14 - 0.21	Methanol
	Propylene	Methanol to olefin (MTO) process (methanol plus ethylene)	$\text{CH}_3\text{OH} + \text{C}_2\text{H}_4 \rightleftharpoons \text{C}_3\text{H}_6 + \text{H}_2\text{O}$	8-9	27,123,818	913	24,774	2.00	54,247,636	0.10 - 0.14	Methanol, ethylene
		Methanol to olefin (MTO) process (condensation of CO <sub>2</sub> -derived methanol to DME followed by conversion to olefin)	$6 \text{CH}_3\text{OH} \rightleftharpoons 3 \text{CH}_3\text{OCH}_3 + 3 \text{H}_2\text{O} \rightleftharpoons 2 \text{C}_3\text{H}_6 + 6 \text{H}_2\text{O}$	8-9	27,123,818	913	24,774	2.00	54,247,636	0.29 - 0.43	Methanol
Dienes	1,3-Butadiene	Gas fermentation of CO by the anaerobic bacterium <i>Clostridium</i> via 2,3-butanediol	Reaction part of a complex metabolic pathway, but as CO is the only carbon source, then overall: $4 \text{CO} + 5 \text{H}_2 \rightleftharpoons \text{C}_4\text{H}_{10}\text{O}_2 (+ \text{O}_2) \rightleftharpoons \text{C}_4\text{H}_6 + 2 \text{H}_2\text{O}$	6-7	2,486,932	473	1,177	2.07	5,147,949	0.19	Nutrients
Carbonates (linear)	Dimethyl carbonate	Carbonylation of methanol in the presence of O <sub>2</sub>	$\text{CO} + 2 \text{CH}_3\text{OH} + 0.5 \text{O}_2 \rightleftharpoons \text{CH}_3\text{OCOOCH}_3 + \text{H}_2\text{O}$	8	Unk	Unk	Unk	0.31	Unk	0.09 - 0.13	Methanol, oxygen
Carbamate (organic)	Methyl carbamate	Reaction of alcohol (in this case methanol) with urea	$\text{CH}_3\text{OH} + \text{CO}(\text{NH}_2)_2 \rightleftharpoons \text{CH}_3\text{COONH}_2 + \text{NH}_3$	9	1,191,873	2,585	3,082	0.37	440,993	0.05 - 0.08	Methanol, urea

\* This assumes that all of the EU market for this product is synthesised using the route in question. If multiple possible routes to a product exist, each route shows the EU CO<sub>2</sub> utilisation potential if 100% of the market is met using that route, the multiple routes are not additive.

\*\* The H<sub>2</sub> requirement for products produced by biological fermentation in some instances may be provided in the form of metabolic reducing agents NADH, NADPH or FADH<sub>2</sub> rather than gaseous H<sub>2</sub>, but the mass of H<sub>2</sub> has been provided for consistency to allow comparison. The H<sub>2</sub> requirement for products produced from methanol includes the H<sub>2</sub> required for the production of the methanol and since there are a range of production routes utilising different amounts of H<sub>2</sub>, the total H<sub>2</sub> requirement is given as a range.

<sup>(1)</sup> Propiolactone is not on Prodcum, so the production and import figures for all lactones were used in order to give an idea of the scale of the market.

<sup>(2)</sup> Prodcum grouped together formic acid, its salts and esters. As methyl formate is an ester of formic acid, the same market and valuation data was used as for formic acid.

## 4.3 Chemicals/fuels

### 4.3.1 Alcohols

#### Butanol

Two chemical routes to utilise CO in butanol were identified:

1). The commercial production of butanal (butyraldehyde) by the hydroformylation (addition of CO and H<sub>2</sub>) of propylene was described above. The commonest commercial route to butanol is simply to hydrogenate the butanal produced in this way. This allows n-butanol or isobutanol to be produced depending upon which form of butanal was synthesised in the hydroformylation step. TRL 9.

2). Isobutanol has been reported to be produced selectively in a laboratory reactor when syngas is passed over zirconia and isobutene can be produced when zirconia dioxide is used.

Isobutanol and isobutene are intermediates in the synthesis of the gasoline additives methyl-*tert*-butyl ether (MTBE) and ethyl-*tert*-butyl ether (ETBE). Environmental concerns have led to a switch from MTBE to ETBE and the latter also has some advantages over ethanol as a gasoline additive in that it does not absorb moisture from the air or encourage gasoline to evaporate.

In addition to the two chemical synthesis routes described above, butanol can also be produced biologically by utilising the gas fermentation abilities of acetogenic bacteria such as *Clostridium* sp. As described previously in Section 3, Clostridia can be used to produce butanol from CO<sub>2</sub>, but fermentation techniques using CO as the carbon source are more advanced. However, as the market for bio-butanol is less advanced than the market for bio-ethanol, the leading player in the field, LanzaTech, appears to be focussing its efforts on ethanol at present. The TRL for butanol appears to be around 3-5.

As mentioned in section 3, during a biological fermentation, in some cases the required H<sub>2</sub> is provided as a gas, but in other circumstances it is provided in the form of metabolic intermediates to enable the production of the reducing agents NADH, NADPH or FADH<sub>2</sub> which are used throughout metabolic pathways as reducing equivalents. However, for consistency, in the tables following this section it has been assumed that the reducing agent is supplied as gaseous H<sub>2</sub>.

#### Ethanol

Both chemical and biological routes to ethanol production from CO have been under development.

Research into chemical routes has included modification of the catalysts and reaction conditions of Fischer-Tropsch processes to enable the synthesis of oxygenated products other than methanol. The use of rhodium and rare earth oxides allows the synthesis of significant proportions of ethanol, but process issues have hindered development.

A demonstration plant run by Snamprogetti, Enichem and Haldor Topsoe (SEHT) in Italy produced 400 t/day between 1982 and 1987 using a modified methanol synthesis catalyst. A series of adiabatic reactors operated at 260-420°C and pressures of 180-260 atm to produce mixed alcohols for use as gasoline additives.

Alternatively, Lurgi built a pilot plant in Germany in 1990 for its Octamix process which used a low temperature and pressure methanol synthesis catalyst. The process operated at 350°C and 100 atm

which resulted in 21-28% CO conversion and 66-79% selectivity to alcohol products - but selectivity to methanol was 41-58% whereas to ethanol it was only 1-9%.<sup>92</sup>

Finally, a more recent example is Range Fuels (USA) who reportedly built a commercial-scale facility to produce syngas from the gasification of biomass, then used this to produce a mixture of alcohols using a molybdenum catalyst. Unfortunately the company failed in 2011 and the facility closed.<sup>93</sup>

Currently, biological routes appear to be more promising, with gas fermentation of CO: Until last year, INEOS Bio operated a plant in Vero Beach, Florida (Indian River BioEnergy Center). It began production in 2013 with a planned capacity of 8 million gallons (30.3 million l) of ethanol per year plus 6 MW of renewable power. However it experienced problems and closed last year, blaming the market for ethanol. LanzaTech (Chicago, Illinois) has operated a demonstration plant in cooperation with BaoSteel (Shanghai, China), which had a capacity of 100 000 gallons (378 541 l) per year, and another one with the Shougang Group (China).<sup>94</sup>

The steelmaker ArcelorMittal and LanzaTech are together building a commercial scale production plant to produce 47,000 tonnes of ethanol (dubbed "Steelanol") per year from waste CO arising from the steelmaking process. The facility is located at ArcelorMittal's steel plant in Ghent, Belgium and will utilise LanzaTech's biological gas fermentation process in which CO is used as a feedstock by the anaerobic bacterium *Clostridium autoethanogenum* which ferments it to produce ethanol.<sup>95</sup> Similar bioethanol production plants are also under construction at steelworks in China and South Africa.<sup>96</sup> TRL 6-8.

## Methanol

Two routes to the synthesis of methanol from CO have been identified:

1). Methanol is produced conventionally by producing syngas from steam reforming of methane. The CO and H<sub>2</sub> present in the syngas then undergo F-T type reactions at high temperature and pressure (240-260°C at 50-100 atm) over a catalyst of copper/zinc oxide on an alumina support. TRL 9.

2). An alternative process is desirable in order to reduce the energy costs associated with F-T chemistry. A 2-step process is possible in which CO first undergoes a methanation reaction to form methane, which is then subsequently partially oxidised to CH<sub>3</sub>OH.<sup>97</sup>

The second step is challenging as there is a tendency for methanol to become over-oxidised because methanol is more easily oxidised than methane. High-temperature reaction systems tend to favour total oxidation, which suggests that the catalysts for methane activation should be active at low temperatures. Enzymatic-inspired metal-exchanged zeolite systems apparently fulfil this need, however, methanol yield is currently low and a catalytic process cannot yet be established. This reaction pathway therefore remains at lab stage development.<sup>98</sup>

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<sup>92</sup> Maitlis (2013). Other Industrially Important Syngas Reactions. In *Greener Fischer-Tropsch Processes for Fuels and Feedstocks*. Eds. Maitlis and de Klerk. Wiley-VCH.

<sup>93</sup> Muhler and Kaluza (2015). Syngas to Methanol and Ethanol. In *Fuel Production with Heterogenous Catalysis*. Ed. Jacinto Sa. CRC Press.

<sup>94</sup> Durre and Eikmanns (2015). C1-carbon sources for chemical and fuel production by microbial gas fermentation. *Current Opinions in Biotechnology*. **35**: 63 - 72.

<sup>95</sup> LanzaTech (2015). ArcelorMittal, LanzaTech and Primetals Technologies Announce Partnership to Construct Breakthrough \$87 Biofuel Production Facility. Available at: <http://www.lanzatech.com/arcelormittal-lanzatech-primetals-technologies-announce-partnership-construct-breakthrough-e87m-biofuel-production-facility/> Accessed September 2017.

<sup>96</sup> LanzaTech (2017). Swayana Brings Carbon Recycling to South Africa. Available at: <http://www.lanzatech.com/swayana-brings-carbon-recycling-south-africa/> Accessed September 2017.

<sup>97</sup> Dowson and Styring (2015). Conversion of Carbon Dioxide to Oxygenated Organics. In *Carbon Dioxide Utilisation: Closing the Carbon Cycle*. Eds. Styring P, Quadrelli EA and Armstrong K. Elsevier.

<sup>98</sup> Alayon *et al.* (2012). Catalytic Conversion of Methane to Methanol Using Cu-Zeolites. *Chimia* **66**: 668-674.

## 4.3.2 Ethers

### Dimethyl ether

Two routes from CO to DME are possible:

- 1). The conventional route involving the condensation of two molecules of CO-derived methanol.
- 2). A single-step process using a bifunctional catalyst which produces methanol and causes its dehydration in the same reactor is possible:



The reaction is catalysed by a Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> HZSM-5 zeolite catalyst at 260°C and 40 atm in an F-T type reaction. However, the process remains still at the laboratory stage (TRL 2-4) with development work still needed.

**Table 6. Potential chemical/fuel products with associated market and CO utilisation data.**

Class	Product	Synthesis route	Overall reaction	TRL	EU28 prod. + imports [t/yr]	Unit value [€/t]	Market value [€M]	CO used [t CO/t product]	EU CO utilisation [t/yr]*	H <sub>2</sub> requirement [t H <sub>2</sub> /t product]**	Other (non-catalytic) inputs
Alcohols	Butanol	Gas fermentation of CO by the anaerobic bacterium <i>Clostridium sp.</i>	$8 \text{ CO} + 8 \text{ H}_2 \rightleftharpoons 2 \text{ C}_4\text{H}_9\text{OH} + 6 \text{ OH}$ (simplified - actual reaction part of a complex biochemical pathway)	3-5	649,068	548	356	1.51	980,093	0.108	Nutrients
		Two-steps: hydroformylation of propylene to form butanal, followed by hydrogenation to butanol.	1). $\text{CO} + \text{H}_2 + \text{C}_3\text{H}_6 \rightleftharpoons \text{CH}_3(\text{CH}_2)_2\text{CHO}$ 2). $\text{CH}_3(\text{CH}_2)_2\text{CHO} + \text{H}_2 \rightleftharpoons \text{C}_4\text{H}_9\text{OH}$	9				0.38	246,646	0.03	Propylene
		Isobutanol produced selectively by passing syngas over Zr catalyst.	$4 \text{ CO} + 8 \text{ H}_2 \rightleftharpoons \text{C}_4\text{H}_{10}\text{O} + 3 \text{ H}_2\text{O}$	1-3				1.51	980,093	0.22	-
	Ethanol	Modified F-T process using high pressures (SEHT)	$2 \text{ CO} + 4 \text{ H}_2 \rightleftharpoons \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}$	4-6	5,904,504	575	3396	1.22	3,601,747	0.174	-
		Moderate pressure modified F-T process (Lurgi - Octamix)	$2 \text{ CO} + 4 \text{ H}_2 \rightleftharpoons \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}$	4-6							
		Gas fermentation of CO by the anaerobic bacterium <i>Clostridium autoethanogenum</i> .	$4 \text{ CO} + 7 \text{ H}_2 \rightleftharpoons 2 \text{ C}_2\text{H}_5\text{OH} + 2 \text{ OH}$ (simplified - actual reaction part of a complex biochemical pathway)	6-8						0.152	Nutrients
Methanol	CO and H <sub>2</sub> react over a Cu/ZnO catalyst	$\text{CO} + 2 \text{ H}_2 \rightleftharpoons \text{CH}_3\text{OH}$	9	7,891,386	187	1476	0.88	6,944,420	0.13	-	
	Two-step process, first convert CO to CH <sub>4</sub> via methanation reaction, then partially oxidise CH <sub>4</sub> to CH <sub>3</sub> OH	1). $\text{CO} + 3 \text{ H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$ 2). $\text{CH}_4 + 0.5 \text{ O}_2 \rightleftharpoons \text{CH}_3\text{OH}$	2-3						0.19		
Ethers	Dimethyl ether	Condensation then dehydration of CO-derived methanol in the presence of a solid acid catalyst	$\text{CH}_3\text{OH} + \text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}$	9	Unk	Unk	Unk	1.22	Unk	0.17 - 0.26	Methanol
		Bifunctional catalyst allows conversion to methanol then dehydration to DME in a single vessel	$2 \text{ CO} + 4 \text{ H}_2 \rightleftharpoons 2 \text{ CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}$	2-4	Unk	Unk	Unk		Unk	0.17	-

\* This assumes that all of the EU market for this product is synthesised using the route in question. If multiple possible routes to a product exist, each route shows the EU CO<sub>2</sub> utilisation potential if 100% of the market is met using that route, the multiple routes are not additive.

\*\* The H<sub>2</sub> requirement for products produced by biological fermentation in some instances may be provided in the form of metabolic reducing agents NADH, NADPH or FADH<sub>2</sub> rather than gaseous H<sub>2</sub>, but the mass of H<sub>2</sub> has been provided for consistency to allow comparison. The H<sub>2</sub> requirement for products produced from methanol includes the H<sub>2</sub> required for the production of the methanol and since there are a range of production routes utilising different amounts of H<sub>2</sub>, the total H<sub>2</sub> requirement is given as a range.

## 4.4 Fuels

### 4.4.1 Gasoline and diesel fuel

Carbon monoxide can be reacted using Fischer-Tropsch catalysts to produce long chain hydrocarbons, or converted to methanol which can subsequently be converted in methanol-to-hydrocarbon type reactions. These were discussed in detail in Section 3.3.1 and so shall not be repeated again here.

### 4.4.2 Jetfuel

LanzaTech have developed a biological gas fermentation process in which CO is used as a feedstock by the anaerobic bacterium *Clostridium autoethanogenum* which ferments it to produce ethanol. Working with the airline Virgin Atlantic, LanzaTech has developed a process whereby the ethanol then undergoes oligomerisation and dehydration/hydrogenation to produce hydrocarbons suitable for use as a kerosene-type aviation fuel. In February 2017 LanzaTech and Virgin Atlantic announced that they had synthesised 1500 litres of jetfuel from ethanol which was produced by gas fermentation of CO captured from a steel plant.<sup>99</sup>

### 4.4.3 Methane

Methane can be produced from CO chemically or biologically.

The first commercial synthetic gas plant opened in 1984. The Great Plains Synfuel Plant in North Dakota (USA) produces syngas by gasification of coal, then produces synthetic natural gas (CH<sub>4</sub>) by hydrogenation of CO and H<sub>2</sub> over a nickel catalyst.<sup>100</sup> China has many such facilities. By simply switching the CO source from the gasification of coal for the purpose of producing CO, to recycling CO arising from steelworks, the carbon balance of the process would be transformed.

Biologically, methane can be produced during the anaerobic gas fermentation of CO by several different methanogenic strains of bacteria. However, the technology has not been developed beyond lab scale as it appears that methanogenic growth whilst utilising CO as the sole substrate is not very efficient. Only three strains actually grow while producing methane, so further development work engineering the metabolism of suitable bacteria is required before further progress can be made.<sup>101</sup>

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<sup>99</sup> LanzaTech (2017). Low Carbon Fuel Project Achieves Breakthrough. Available at: <http://www.lanzatech.com/low-carbon-fuel-project-achieves-breakthrough-lanzatech-produces-jet-fuel-waste-gases-virgin-atlantic/> Accessed September 2017.

<sup>100</sup> National Energy Technology Laboratory (2017). SNG from Coal: Process & Commercialization. Available at: <https://www.netl.doe.gov/research/coal/energy-systems/gasification/gasifipedia/great-plains> Accessed October 2017.

<sup>101</sup> Diender et al. (2015). Pathways and Bioenergetics of Anaerobic Carbon Monoxide Fermentation. *Frontiers in Microbiology*. 6: 1275, doi: 10.3389/fmicb.2015.01275

Table 7. Potential fuel products with associated market and CO utilisation data.

Class	Product	Synthesis route	Overall reaction	TRL	EU28 prod. + imports [t/yr]	Unit value [€/t]	Market value [€M]	CO used [t CO/t product]	EU CO utilisation [t/yr]*	H <sub>2</sub> requirement [t H <sub>2</sub> /t product]**	Other (non-catalytic) inputs
Liquid hydrocarbons	Diesel	CO and H <sub>2</sub> undergoes F-T reaction at 200-240°C to produce linear waxes. Hydrocracking converts to synthetic diesel.	$12 \text{ CO} + 24 \text{ H}_2 \rightleftharpoons \text{C}_{12}\text{H}_{24} + 12 \text{ H}_2\text{O}$	7-8	384,086,000	643	247,271	2.00	768,172,000	0.29	-
	Gasoline	CO and H <sub>2</sub> undergoes F-T reaction at 300-350°C to produce gasoline-range hydrocarbons.	$8 \text{ CO} + 17 \text{ H}_2 \rightleftharpoons \text{C}_8\text{H}_{18} + 8 \text{ H}_2\text{O}$	7-8	146,243,000	684	100,042	1.96	286,636,280	0.3	-
		Methanol to Gasoline process, via DME and olefins.	$8 \text{ CH}_3\text{OH} + \text{H}_2 \rightleftharpoons \text{C}_8\text{H}_{18} + 8 \text{ H}_2\text{O}$	6-8						0.30 - 0.44	Methanol
	Jetfuel - kerosene type (C <sub>8</sub> H <sub>18</sub> - C <sub>16</sub> H <sub>34</sub> , average C <sub>12</sub> H <sub>26</sub> )	Gas fermentation of syngas by the anaerobic bacterium <i>Clostridium autoethanogenum</i> to produce ethanol. This then undergoes oligomerisation and dehydration/hydrogenation to produce hydrocarbons suitable for use as kerosene-type aviation fuel ( <i>LanzaTech - Virgin Atlantic process</i> )	Two stage reaction, the first being part of a complex biochemical pathway which can be simplified to: $2 \text{ CO} + 4 \text{ H}_2 \rightleftharpoons \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}$ The second, synthetically converts the bioethanol to suitable hydrocarbons: $6 \text{ C}_2\text{H}_5\text{OH} + \text{H}_2 \rightleftharpoons \text{C}_{12}\text{H}_{26} (+ 6 \text{ H}_2\text{O})$	5-7	63,928,000	488	31,215	1.98	126,577,440	0.259	Nutrients
Gaseous hydrocarbons	Methane	CO methanation over a nickel catalyst.	$\text{CO} + 3 \text{ H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$	9	338,511,000	571	193,229	1.75	592,394,250	0.38	-
		Gas fermentation of syngas by the anaerobic bacterium <i>Clostridium sp.</i>	$2 \text{ CO} + 5 \text{ H}_2 \rightleftharpoons 2 \text{ CH}_4 + 2 \text{ OH}$ (simplified - actual reaction part of a complex biochemical pathway)	1-2						0.313	Nutrients

\* This assumes that all of the EU market for this product is synthesised using the route in question. If multiple possible routes to a product exist, each route shows the EU CO<sub>2</sub> utilisation potential if 100% of the market is met using that route, the multiple routes are not additive.

\*\* The H<sub>2</sub> requirement for products produced by biological fermentation in some instances may be provided in the form of metabolic reducing agents NADH, NADPH or FADH<sub>2</sub> rather than gaseous H<sub>2</sub>, but the mass of H<sub>2</sub> has been provided for consistency to allow comparison. The H<sub>2</sub> requirement for products produced from methanol includes the H<sub>2</sub> required for the production of the methanol and since there are a range of production routes utilising different amounts of H<sub>2</sub>, the total H<sub>2</sub> requirement is given as a range.

## 5. Potential products from methanol

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The only carbon containing compounds currently synthesised on a scale  $\geq$  100 million t/yr are urea and ethylene. However, methanol is both an important chemical building block and a potential liquid fuel, either directly or after dehydration to dimethyl ether. The potential demand for methanol is therefore much greater than that of the other chemicals discussed. Of course, when the methanol is used as a fuel, the carbon is converted back into carbon dioxide, but if the carbon dioxide is originally obtained from non-fossil fuel sources then the process is carbon neutral overall.<sup>102</sup>

Methanol can be synthesised from both  $\text{CO}_2$  and  $\text{CO}$  and is itself used in the synthesis of many different chemical compounds. For this reason, methanol is commonly referred to as a "commodity chemical" and a "chemical building block". By synthesising methanol from waste  $\text{CO}$  or  $\text{CO}_2$ , rather than from steam reformed methane as per the conventional route, it becomes possible to indirectly substitute fossil carbon with carbon derived from  $\text{CO}_2$  into a multitude of plastics, polymers and carbon containing chemicals.

The list of chemical products which can be made from methanol is extensive. The previous sections included a few products which were synthesised via methanol, because they are widely recognised as being products which can utilise  $\text{CO}$  or  $\text{CO}_2$ . However, there are many more and a list of just some of them are provided below. These chemicals, which can be synthesised from methane, have been grouped under the main routes of synthesis. The list is not exhaustive, it simply aims to give an idea of the scope of what is possible.<sup>103 104</sup>

Conversion of methanol to ethylene/propylene and subsequent olefin polymerization:

- Polyethylene
- Polypropylene
- Polyolefin-copolymers

Conversion to ethylene/propylene and then into vinyl chloride, styrene, acrylic acid and derivatives, acrylonitrile, and subsequent polymerization:

- Polyvinylchloride
- Polystyrene
- Poly(methyl)acrylates
- Polyacrylonitrile
- Acrylonitrile butadiene styrene

Conversion to ethylene/propylene and then into ethylene oxide, ethylene glycol, propylene oxide and subsequent polymerization:

- Polyester
- Polyether
- Polyurethanes

Conversion to propylene, oxidation to acetone, further conversion into bisphenol A and subsequent polymerization:

- Aromatic polycarbonates
- Epoxy resins

Conversion of methanol to formaldehyde by partial oxidation (dehydrogenation/oxidation) over silver catalysts and subsequent (co)polymerization, reaction with acetylene or urea:

- Polyformaldehyde
- Polyoxymethylene
- POM-Copolymers

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<sup>102</sup> North (2015). What is  $\text{CO}_2$ ? Thermodynamics, Basic Reactions and Physical Chemistry. In *Carbon Dioxide Utilisation: Closing the Carbon Cycle*. Eds. Styring P, Quadrelli EA and Armstrong K. Elsevier.

<sup>103</sup> Langanke *et al.* (2015). Polymers from  $\text{CO}_2$  - An Industrial Perspective. In *Carbon Dioxide Utilisation: Closing the Carbon Cycle*. Eds. Styring P, Quadrelli EA and Armstrong K. Elsevier.

<sup>104</sup> Dowson and Styring (2015). Conversion of Carbon Dioxide to Oxygenated Organics. In *Carbon Dioxide Utilisation: Closing the Carbon Cycle*. Eds. Styring P, Quadrelli EA and Armstrong K. Elsevier.

- 1,4-Butynediol-derived polymers
- Urea-based polymers

Carbonylation of methanol using an iridium containing catalyst (Cativa process) to acetic acid, then reacted with ethylene:

- Vinyl acetate monomer
- Polyvinyl acetate

Transesterification of triglycerides with methanol:

- Biodiesel (methyl esters)

Reaction of methanol with CO in the presence of oxygen:

- Dimethyl carbonate,

Polymerisation of methanol via DME to long chain hydrocarbons:

- Gasoline

Halogenation of methanol creates the halomethanes:

- Methyl iodide
- Methyl bromide

React methanol with ammonia in the presence of an aluminosilicate catalyst:

- monomethylamine
- dimethylamine
- trimethylamine

React methanol with isobutylene over an acidic ion exchange resin (or in the presence of sulphuric acid):

- Methyl-*tert*-butyl-ether (MTBE)

Gasification of methanol to produce syngas (CO and H<sub>2</sub>), followed by reduction of CO (methanation):

- Methane

## 6. Future outlook and potential impact

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### 6.1 Hydrogen production

The requirement for low-carbon H<sub>2</sub> is common to many of the CO/CO<sub>2</sub> utilisation routes discussed. For this reason, some objectives for future development of H<sub>2</sub> from electrolysis of water have been included below.

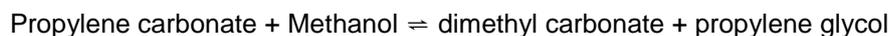
Water electrolysis is currently not competitive with methane steam reforming for the production of H<sub>2</sub>. In the short term the electrolysis equipment needs to be available at lower costs and capable of higher efficiency; it needs to be capable of coping with the intermittent, fluctuating energy supplied by renewables; the technologies need to be scaled-up to provide larger units; electrodes need to be developed with low content of noble metals and other rare elements; and development of high temperature electrolysers (solid oxide fuel cells) and related electrodes needs to be accelerated.

Over the longer term water photolysis needs further development at lab scale, with concomitant development of highly efficient, corrosion-resistant, photo-electrode materials and processing technologies. Again, electrodes without noble metals and other rare elements should be investigated and pilot/demonstration facilities for high temperature electrolysers and their integration with concentrated solar power units should be progressed.<sup>105</sup>

### 6.2 Carbonates

Carbonates are increasing in popularity as solvents for a variety of applications and use as a reagent in the synthesis of high volume polymers such as polycarbonates or polyurethanes also makes them in demand. They are considered to be relatively "green" solvents for a variety of applications, such as in paints, since they are biodegradable and have low ecotoxicity. However, this environmentally friendly profile is not maintained when the current industrial synthesis of these chemicals are considered. DMC is still often produced from phosgene, and even the current non-phosgene routes such as methanol oxycarbonylation have environmental issues. Similarly, cyclic carbonates are readily made from epoxides, the synthesis of which is energy intensive, and these chemicals are not considered environmentally friendly. Making carbonates sustainably from CO<sub>2</sub> would result in that CO<sub>2</sub> carbon atom ending up in a vast variety of products.

It may not be necessary to develop industrial processes to synthesise each of the commercially relevant carbonates from CO<sub>2</sub>. Viable commercial production of only one carbonate, linear or cyclic, is necessary. Due to the non-specificity of the transesterification reaction for carbonates, it is likely that all industrially relevant carbonates could be obtained from any carbonate produced from CO<sub>2</sub>. An example of a transesterification reaction for carbonates is below. The propylene glycol product could be cycled back to propylene carbonate by the addition of another CO<sub>2</sub> molecule.



In such a scenario, the glycol would be recycled whereas the CO<sub>2</sub> would remain in the final carbonate product. Such transesterification reactions are already used in commercial chemical plants where a cyclic carbonate is formed via the mature epoxide/CO<sub>2</sub> route. After transesterification to the desired carbonate (primarily DMC), the glycol by-product is sold as a second product instead of recycling back into a carbonate for further transesterification. While this may be satisfactory in the short term, to achieve sustainable outcomes the co-produced alcohol or glycol would need to be recycled back to carbonate (utilising extra CO<sub>2</sub>).<sup>106</sup>

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<sup>105</sup> CEFIC/EUcheMs (2011/2012). Workshops Roadmaps for CO<sub>2</sub> Utilisation.

<sup>106</sup> Heyn R.H. (2015). Organic Carbonates. In *Carbon Dioxide Utilisation: Closing the Carbon Cycle*. Eds. Styring P, Quadrelli EA and Armstrong K. Elsevier.

## 7. Conclusion

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This report described 43 products which can be produced from CO<sub>2</sub>, utilising 71 different routes of synthesis. Similarly, 22 products which can be produced from CO were described, along with the 33 different chemical routes from which they can be synthesised. The technology readiness level of each route of synthesis was provided, based upon the published literature or estimated from the description of commercial activity. The market for the majority of the products was provided in terms of the total tonnage of product currently produced and sold and imported into the EU, together with the unit value and total value of this market. In addition to the market values, the amount of CO<sub>2</sub> or CO utilised per tonne of product was provided, together with the total mass of CO<sub>2</sub> or CO assuming the total EU market is met by that production route. Finally the requirement for H<sub>2</sub> per tonne of product was provided together with a list of the other non-catalytic inputs required by the chemical reaction.

Methanol is frequently talked of as a "chemical building block", so to put this into context and to gain an appreciation of the range of products which can be produced from methanol, a list was provided. In a similar way, the ability of modern chemical plants to transform one type of carbonate monomer to another in order to produce multiple polymers is extensive. It therefore may not be necessary to produce every different kind of monomer from CO<sub>2</sub> (or CO) in order for carbon recycling to have a major impact upon the sustainability of the chemical industries.

The information provided in this report, together with that provided in the review of industrial symbiosis submitted as deliverable 2.2, will be utilised to enable a selection of the most favourable products to be made. This selection will be based upon market data, environmental impacts and potential symbiotic interactions between industries and will be presented as deliverable 2.3.

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