Project no. 723678

ñThe next Generation of Carbon for the Process Industryò

Coordination and Support Action

Theme [SPIRE 5] ï Potential use of CO_2 and non-conventional fossil natural resources in Europe as feedstock for the process industry

Deliverable *2.3*: *Selection of most relevant processes for further investigation*

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1. Executive Summary

This report describes the selection of the products to be further assessed in the CarbonNext project and the process used to choose them. The products are selected together with the route(s) used to synthesise those products from carbon dioxide (CO_2) and carbon monoxide (CO). The selection is made from the lists of products and routes identified in deliverable 2.1. The aim is to select products which will enable the replacement of fossil-derived carbon used in the European process industries with carbon from CO_2 and CO by 2030.

To select products and routes which would achieve this aim, it was decided that:

- the CO/CO_2 utilisation process must have a high technology readiness level (TRL) to ensure that uptake by 2030 is possible,
- the market value of the products needs to be significant,
- the CO/CO_2 utilisation potential needs to be significant to ensure that the amount of fossil-sourced carbon being replaced is worthwhile,
- the products should not require other non-catalytic chemical inputs which contain fossil-sourced carbon, as this would limit the impact of utilising the alternative carbon source.

The selection was carried out by assessing these four criteria for each product/route using a qualitative approach (i.e. ranking them as high, medium or low) and choosing the products which had a combination of the most favourable traits.

Carbon mineralisation products were assessed as part of this process and they have great potential, both as commercial products and for carbon storage. However, it is considered that mineralisation products are not consistent with the aims of the CarbonNext project - which is to select feedstocks sourced from alternative carbon sources which will end the current reliance of the process industries upon feedstocks derived from fossil-sourced carbon. For this reason, only chemicals and fuels have been selected for further investigation in this project.

Fourteen products were selected for further analysis, nine of which can be synthesised from CO_2 or from CO: ethylene, propylene, benzene, xylene, methanol, dimethyl ether, gasoline, diesel fuel and methane. In addition, 1,3-butadiene, dimethyl carbonate, ethanol and kerosene-type jetfuel were selected from those produced from CO and ethylene carbonate from those synthesised from CO_2.

2. Introduction

2.1 Objective

Deliverable 2.1 identified routes which can be utilised to produce products that can be synthesised from carbon dioxide (CO_2) and carbon monoxide (CO). This report aims to:

- assess which of these routes offer the best economic and environmental outcomes (i.e. they have the required traits) to replace fossil-derived carbon used in the European process industries by 2030
- make a shortlist of the routes to be analysed in Work Package 4 of CarbonNext, which will assess the business case and environmental impacts of these routes under different scenarios

2.2 Methods

In deliverable 2.1, potential products that can be made from CO_2 or CO were identified from the literature. The products, together with their routes of synthesis, were placed into four groupings:

- **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 were further classified into chemical families, such as organic acids, olefins, polyols, etc. so that similar products could be grouped together and an example product given where multiple were possible. In this way, every possible chemical entity which could be produced from CO_2 or CO was not identified, i.e. ethylene oxide was provided as an example of an epoxide, where others may potentially be possible.

Products identified utilising CO_2 included 27 chemicals (produced using 39 routes), 4 chemicals/fuels (15 routes), 4 fuels (7 routes) and 8 solid products (10 routes). Products identified utilising CO included 14 chemicals (using 17 routes), 4 chemicals/fuels (10 routes) and 4 fuels (8 routes).

2.2.1 Aims

It is not possible to simply select the most favourable products/routes without first determining what the aim of the selection is. Within the context of the CarbonNext project:

> The aim is to replace the fossil-derived carbon used in the European process industries with carbon from CO_2 and CO within the near future (by 2030). Doing this will minimise the import of fossil carbon (especially oil) by reducing the dependency of the process industries upon chemical feedstocks derived from petrochemicals.

To meet the above aim, products and routes to products were selected to maximise the impact that fossil-carbon replacement would have upon the process industries. Therefore it was determined that:

- The Technology Readiness Level (TRL) of the process must be high (at demonstration stage or beyond) for this to be achievable within the selected timeframe (by 2030).
- Products which have a medium to high market value were selected, as they need to be economically viable to be adopted.
- The CO/CO_2 utilisation potential should be significant so that the amount of carbon being replaced is meaningful.
- The products should not require other non-catalytic chemical inputs which contain fossil-sourced carbon in order to maximise the replacement of fossil-sourced carbon.

2.2.2 Selection Process

Deliverable 2.1 provided tables which summarised data to illustrate the potential economic and environmental impact of the different products and routes to those products. This impact data included:

1. Technology Readiness Levels (TRLs) published in the scientific literature, trade journals or provided on commercial websites were used to describe how close to market the products and processes are.

2. Measures of the EU market value of chemicals, alcohols and mineralisation products were obtained from the Eurostat Prodcom database.
3. The CO/CO_2 utilisation potential of the product was calculated by the author using stoichiometric reaction formulae (tonnes of CO_2 utilised per tonne of product multiplied by the EU market size).
4. Other non-catalytic chemical inputs into the synthesis reactions were examined to determine whether they contain carbon or not and if so, whether they can be produced from CO_2 or CO.

Of the data provided in the tables of deliverable 2.1, only the H_2 requirement of the product synthesis process has not been used during the selection process. However, this will be used when the environmental impact of the selected routes are assessed in Work Package 4 of the CarbonNext project.

2.2.3 Ranking of impact data

To enable comparison of the potential impacts of the different products and/or routes of synthesis, the impact data described above were ranked using a simple scale from 1 to 3 (1 being highly desirable, 2 desirable and 3 undesirable). Table 1 shows how the indicators were ranked. To aid visual identification in tables 2-8 provided as appendices, the measures ranked as 1 are coloured green, those ranked 2 are amber, and those ranked with an undesirable 3 are coloured red. Using "traffic light" colours in this way, it is hoped that the reader can more easily distinguish products displaying more desirable (green) features from products with more undesirable (red) features.

Regarding the other sources of carbon within the product, it was deemed more desirable if all of the carbon contained within a product is sourced from CO/CO_2 than if a proportion of the carbon came from fossil feedstock. Therefore, if the additional carbon-containing chemical can be synthesised from CO/CO_2 then it is given a more favourable ranking than a chemical which can only be synthesised from fossil carbon.

	Ranking		
Indicators	**3**	**2**	**1**
TRL	1 - 3	4 - 6	7 - 9
Market value	<1 úb/yr	1 - 10 úb/yr	>10 úb/yr
CO/CO_2 utilisation potential	<1 Mt/yr	1 - 10 Mt/yr	>10 Mt/yr
Other sources of fossil carbon in the product	Yes and it cannot be made from CO or CO_2	Yes, but it can be made from CO or CO_2	No

Table 1. Ranking of the indicators used to select the routes which have the best traits to replace fossil-derived carbon by 2030. Higher rankings (red) are less desirable than lower rankings (green).

2.2.4 Selection process

Products and processes were limited to those with a TRL ranking of 1, (i.e. a TRL of 7 or above) to give confidence that the selected processes can be brought to commercialisation without delay; a market value ranking of 1, 2 or unknown, a CO/CO_2 utilisation ranking of 1, 2 or unknown and another source of carbon in the product of 1 or 2. A small proportion of the identified products were not included on the Prodcom database which meant that the market size/value was unknown and the CO/CO_2 utilisation could not be calculated. To stop this from preventing a product from being selected, unknown values were selected as described above. In practice, only two products were selected with unknown data, as will be described in the results section below.

3. Selection of Products and Processes Utilising CO_2

Tables 2-5 show all 43 products (71 routes) which can be synthesised from CO_2 and are presented in Appendix 1. The products and processes are listed in the same order as in deliverable 2.1 to ease comparisons. The rankings are colour-coded red, amber and green as described in section 2.2.3. This then allows the reader to see how all the products faired and not just those selected for further investigation.

3.1 Selection

Using the technique described in Section 2, the chemical products identified (in no particular order) were: ethylene, propylene, ethylene carbonate, benzene, xylene, urea and ammonium carbamate. The routes identified to produce these products were:

1. **Ethylene** - via the methanol to olefin (MTO) process whereby CO_2-derived methanol undergoes condensation then dehydration to form dimethyl ether before conversion to ethylene.
2. **Propylene** - via a very similar MTO process as for ethylene described above.
3. **Propylene** - via a variation of the MTO process where methanol reacts with ethylene to form propylene.
4. **Ethylene carbonate** - via carbonation of the epoxide ethylene oxide.
5. **Benzene** - via the methanol to aromatics (MTA) process developed by Mobil involving reacting methanol over a zeolite catalyst resulting in the simultaneous production of benzene, xylene and toluene.
6. **Xylene** - as above.
7. **Urea** - current/conventional pathway reacting ammonia and CO_2 in a 2-step reaction to produce ammonium carbamate which then dehydrates to urea.
8. **Ammonium carbamate** - first step in the production of urea.

The process to produce urea (included above) involves reacting ammonia with CO_2 to produce ammonium carbamate (also included above) which then dehydrates to form urea. This process is by far the largest commercial example of CO_2 utilisation globally and is well understood with multiple commercialised process variations. For this reason, urea and ammonium carbamate will not be selected for further analysis as both the economic viability and environmental impacts of the process are already well understood. The remaining five

chemicals (ethylene, propylene, ethylene carbonate, benzene and xylene) with the six routes described above, will move forward for further analysis.

The chemical/fuel products identified were dimethyl ether and methanol, produced by the following routes:

1. **Dimethyl ether** - condensation then dehydration of CO_2-derived methanol.
2. **Methanol** - via high temperature solid oxide cells which use CO_2 and water to produce H_2 and CO, followed by compression and subsequent catalytic methanol synthesis.
3. **Methanol** - dry reforming of CH_4 and CO_2 to produce syngas, followed by water gas shift reaction to adjust the $CO:H_2$ ratio, water removal, compression and subsequent methanol synthesis via Fischer-Tropsch synthesis.
4. **Methanol** - reverse water gas shift of CO_2 and renewable H_2 to produce CO and water, remove water, add more H_2, then use Fischer-Tropsch reactions to produce methanol.
5. **Methanol** - CO_2/steam reforming of CH_4, followed by water gas shift reaction to adjust the $CO:H_2$ ratio, water removal, compression and subsequent methanol synthesis via Fischer-Tropsch synthesis.

Both DME and methanol (including all four synthesis routes for methanol) will be selected for further analysis.

The fuel products identified were gasoline, methane and diesel fuel, with the following routes:

1. **Gasoline** - via the methanol to gasoline (MTG) process whereby CO_2-derived methanol undergoes condensation then dehydration to form dimethyl ether, is then converted to olefins and finally to gasoline-range hydrocarbons.
2. **Gasoline** ï syngas produced from CO_2 and H_2 undergoes Fischer-Tropsch reactions at 300-350°C to produce gasoline-range hydrocarbons.
3. **Methane** - via CO_2 methanation (the Sabatier reaction).
4. **Diesel fuel** - whereby syngas produced from CO_2 and H_2 undergoes Fischer-Tropsch reactions at 200-240°C to produce linear waxes. Hydrocracking converts to synthetic diesel.

The three products (gasoline, methane and diesel fuel) and the four routes identified above will be selected for further analysis.

The solid materials products identified were construction aggregates, cement products, concrete products and mineral carbonate fertiliser. The production routes were:

1. **Construction aggregates** - via direct aqueous mineralisation/carbonation of alkaline industrial wastes (high in reactive Ca/Mg oxides) to produce calcium and magnesium carbonates.
2. **Cement-like products** - where captured flue gases react with alkaline industrial brines to produce carbonates and bicarbonates.
3. **Concrete products** - where CO_2 injected into liquid concrete reacts to form calcium carbonate nanoparticles within the concrete matrix.
4. **Mineral carbonate fertiliser** - CO_2 is reacted with aqueous ammonia and calcium nitrate to form ammonium nitrate and calcium carbonate. This is dried to form a coating over pellets made from waste biomass from a biogas plant (digestate) for use as agricultural fertiliser.

The four solid materials identified above have great potential as commercial products, all have high TRLs or are already commercialised. Additionally, carbon mineralisation has the potential to play a role in climate change mitigation as the only class of products which can permanently store CO_2 and potentially, in the future, they may be accepted within the EU Emissions Trading System [SCOT Project Briefing Paper 2016[1]]. However, despite the promising outlook for these products, it has been concluded that the mineralisation products described above are not consistent with our understanding of the aims of the CarbonNext project ï which is to select feedstock sourced from alternative carbon sources which will end the current reliance of the process industries upon feedstock derived from fossil-sourced carbon. For this reason, only the chemicals, chemical/fuels and fuels will be taken for further analysis in this project.

In conclusion, 10 products (produced via 15 routes) have been selected from those synthesised from CO_2: five chemicals (ethylene, propylene, benzene, xylene and ethylene carbonate); two chemical/fuels (methanol and dimethyl ether); and three fuels (gasoline, diesel and methane).

It should be noted that the impacts of new technologies, economic and policy changes associated with producing these products will be assessed in Deliverable 3.3. The results of

[1] SCOT Project (2016). SCOT Project Briefing Paper: EU-ETS to Incentivise CO_2 Utilisation? Available at: http://www.scotproject.org/images/Briefing%20paper%20EU%20ETS%20final.pdf Accessed January 2018.

that review may further reduce the list of products/routes which are assessed for environmental impacts and business case in Work Package 4.

3.2 Potential over the longer term

The selection above lists the products/routes which are believed to provide the greatest potential by 2030. The potential over a longer term is necessarily more subjective as it requires an understanding of the potential market of products in the future.

One product widely suggested to have massive future potential is carbon fibres, which is already starting to replace steel in the aerospace, automotive and wind power sectors and this could spread to other construction sectors [Engineering.com[2]]. The current relatively modest market for carbon fibres meant that they were not selected using the technique described above, which relied upon there being a large market size and therefore market value and CO_2 utilisation potential.

The pervasive use of methanol within the chemicals industry is well documented and there have been suggestions for a "methanol economy", most notably by Olah [Olah, 2005[3]; Olah *et al*, 2009[4]], which describe the role that CO_2-derived methanol could play in the fuels, chemicals and energy storage sectors. Whilst already a high-volume product, if methanol were to be widely used as a fuel, its market size and importance would increase multiple-fold.

Deliverable 2.1 described the potential of carbonates in producing high-value polymers such as polycarbonates and polyurethanes (without the use of environmentally damaging phosgene) as well as being used as solvents. It was also mentioned that the polymer industry already has the ability to convert carbonates from cyclic to linear forms and *vice versa*. Therefore, the production of either cyclic carbonates (such as ethylene carbonate) or

[2] Engineering.com (2016). Carbon Fibre May Be the Future of Automotive and Aerospace Manufacturing. Available at: https://www.engineering.com/AdvancedManufacturing/ArticleID/13848/Carbon-Fiber-May-Be-the-Future-of-Automotive-and-Aerospace-Manufacturing.aspx. Accessed January 2018.

[3] Olah, George A (2005). Beyond Oil and Gase: The Methanol Economy. *Angewandte Chemie International Edition* **44**: 2636-2639.

[4] Olah, George A; Goeppert, Alain; & Prakash G.K. Surya (2009). Chemical Recycling of Carbon Dioxide to Methanol and Dimethyl Ether: From Greenhouse Gas to Renewable, Environmentally Carbon Neutral Fuels and Synthetic Hydrocarbons. *Journal of Organic Chemistry* **74**: 487-498.

linear carbonates (such as dimethyl carbonate) from CO_2 could have a significant impact upon the carbon balance of the feedstock used in the polymer sector.

Of the 10 products produced from CO_2 which were selected for further analysis above, ethylene carbonate was one of just two (the other being dimethyl ether) that did not have market data on Prodcom and so were selected with unknown market value and CO_2 utilisation values. The fact that ethylene carbonate is believed to have high future potential supports its selection. Likewise, the fact that methanol had already been selected for further analysis before its future potential was taken into consideration emphasises the strength of this product.

4. Selection of Products and Processes Utilising CO

Tables 6-8, showing the 22 products (35 routes) which can be synthesised from CO are presented in Appendix 2. As with the tables for CO_2 utilisation, the products and processes are listed in the same order as in deliverable 2.1 to ease comparisons. The rankings are colour-coded red, amber and green as described in section 2.2.3. This then allows the reader to see how all the products faired and not just those selected for further investigation.

4.1 Selection

Using the technique described in section 2, the chemical products selected for further analysis (in no particular order) are: ethylene, propylene, 1,3-butadiene, benzene, xylene and dimethyl carbonate. The routes selected are:

1. **Ethylene** - methanol to olefin (MTO) process (condensation of CO-derived methanol to DME followed by conversion to olefin)
2. **Propylene** - MTO process
3. **Propylene** - variation of the MTO process using methanol plus ethylene.
4. **1,3-butadiene** - gas fermentation of CO by the anaerobic bacterium *Clostridium* sp. leading to production of 2,3-butanediol.
5. **Benzene** - methanol to aromatics (MTA) process developed by Mobil involving reacting methanol over a zeolite catalyst resulting in the simultaneous production of benzene, xylene and toluene.
6. **Xylene** - as above
7. **Dimethyl carbonate** - carbonylation of methanol in the presence of O_2.

The chemical/fuel products selected for further analysis are ethanol, methanol and dimethyl ether. The selected routes are:

1. **Ethanol** - via gas fermentation of CO by the anaerobic bacterium *Clostridium autoethanogenum*.
2. **Methanol** - CO and H_2 react over a Cu/ZnO catalyst.
3. **Dimethyl ether** - condensation then dehydration of CO-derived methanol in the presence of a solid acid catalyst.

The fuel products selected for further analysis are: gasoline, diesel fuel, methane and kerosene-type jetfuel. The routes selected are:

1. **Gasoline** - via the methanol to gasoline (MTG) process via dimethyl ether and olefins and finally to gasoline-range hydrocarbons.
2. **Gasoline** ï CO and H_2 undergo Fischer-Tropsch reactions at 300-350°C to produce gasoline-range hydrocarbons.
3. **Diesel fuel** - CO and H_2 undergo Fischer-Tropsch reactions at 200-240°C to produce linear waxes, then hydrocracking converts this to synthetic diesel.
4. **Methane** - CO methanation over a nickel catalyst.
5. **Jetfuel (kerosene type)** - Fischer-Tropsch reactions to produce kerosene-type hydrocarbons.

In conclusion, 13 products (produced via 15 routes) have been selected from those synthesised from CO_2: seven chemicals (ethylene, propylene, 1,3-butadiene, benzene, xylene, ethylene carbonate and dimethyl carbonate); three chemical/fuels (ethanol, methanol and dimethyl ether); and four fuels (gasoline, diesel, jetfuel and methane).

4.2 Potential over the longer term

The selection above lists the products and routes which will enable the replacement of fossil-derived carbon used in the European process industries with carbon from CO by 2030. The potential over a longer term is, as mentioned before, more subjective.

A forward- looking view is important. For example, tyre manufacturers are interested in alternative production pathways for 1,3-butadiene (C_4H_6), especially those which could be marketed as being sustainable or low carbon. 1,3-butadiene (the monomer polymerised to produce the synthetic rubber used to make automobile tyres) is currently produced as a by-product when steam-cracking crude oil or naptha during the production of ethylene and propylene. However, 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 lower proportion of 4-carbon hydrocarbons than oil and as a consequence, the price of butadiene has risen markedly in the past few years.

5. Conclusions

Overall, 14 products were selected for further analysis: 10 products/15 routes were selected from the 43 products identified which can be synthesised from CO_2 and 13 products/15 routes were selected from the 22 products identified which can be synthesised from CO. There is significant overlap between the two lists, with nine products coming from both CO_2 and CO: ethylene, propylene, benzene, xylene, methanol, dimethyl ether, gasoline, diesel fuel and methane. In addition, ethylene carbonate was selected from those produced from CO_2 and four additional products from those synthesized from CO: 1,3 butadiene, dimethyl carbonate, ethanol and kerosene-type jetfuel.

Of the routes identified in Deliverable 2.1, those utilising CO are generally at a higher TRL than those utilising CO_2. This is due to due to the fact that CO is an energy carrier and is therefore routinely used as a feedstock in the chemicals industry, which is why many production pathways are already commercialised. As a consequence, a higher proportion of the routes utilising CO were selected in this exercise than utilising CO_2.

The review of industrial symbiosis involving gaseous CO and CO_2 streams reported in Deliverable 2.2 shows that in addition to these gas streams being potentially available from the steel-production sector, CO_2 is also available in suitable quantities arising from the chemicals sectors and bio-based sectors such as fermentation/brewing and anaerobic digestion/biogas production facilities. Indeed, the widespread involvement of companies from these sectors in the research projects described in that report suggest that they are keen to find uses for such gas streams. This may reflect a combination of public pressure to provide products with reduced environmental impact and the effect of economic instruments such as the EU-ETS. It is assumed that policy enhancements to allow CCU inclusion into the EU Emissions Trading Scheme and RED (Renewable Energy Directive), for instance, would only add to the enthusiasm of industrial companies to get involved in symbiotic relationships with other companies who could utilise their unwanted gas streams. Physical proximity is beneficial as it reduces the required pipeline distances, making industrial/chemical parks ideal for such relationships as they may contain sources of CO_2 co-located with process industries able to utilise it.

6. Appendix 1. Tables of Potential Products Utilising Carbon Dioxide

Table 2. Potential chemical products utilising CO_2 with rankings and weightings.

Product	Synthesis route	TRL ranking	Market value ranking	CO_2 utilisation ranking	Other carbon in product ranking
Urea	Reacting NH_3 and CO_2 to produce ammonium carbamate which dehydrates to urea.	1	2	2	1
Benzene	CO_2 methanation followed by CH_4 dehydro-aromatisation	3	2	1	1
	Methanol to aromatics process.	1	2	1	1
Toluene	*as above*	1	3	2	1
Xylene	*as above*	1	2	2	1
Formaldehyde	Borane reduction of CO_2	3	3	2	1
	Hydrogenation to formic acid, then reduction to formaldehyde	3	3	2	1
Acetic acid	Oxidation of methane with CO_2	3	3	3	2
	Gas fermentation	3	3	2	1
Acrylic acid	Linear terminal alkenes react with CO_2 to produce linear carboxylic acids	3	2	3	2
Benzoic acid	Benzene reacts with CO_2 to form benzoic acid	3	3	3	2
p-hydroxy benzoic acid	Kolbe-Schmitt reaction	1	3	3	3
Butyric acid	Gas fermentation	3	3	3	1
Formic acid	Electrochemical reduction of CO_2	2	3	3	1
	Catalytic reduction	3	3	3	1
Oxalic acid	Electrochemical reduction of CO_2	3	3	3	1
Salicylic acid (2-hydroxy benzoic acid)	Kolbe-Schmitt reaction	1	3	3	3
Ethylene	Direct using modified F-T catalysis	3	1	1	1
	Direct electrochemical reduction of CO_2	3	1	1	1
	Methanol to olefin process (condensation of methanol to DME then	1	1	1	1

Product	Synthesis route	TRL ranking	Market value ranking	CO_2 utilisation ranking	Other carbon in product ranking
	conversion to olefin)				
Propylene	Methanol to olefin process (methanol plus ethylene)	1	1	1	2
	Methanol to olefin process (condensation of methanol to DME then conversion to olefin)	1	1	1	1
Ethylene oxide	Carboxylation of ethylene	3	3	3	2
Ethylene glycol	Electrochemical reduction of CO_2	2	2	2	1
Propylene glycol	Electrochemical reduction of CO_2	2	3	2	1
Sodium bicarbonate	Carbonation of NaOH to Na_2CO_3, then bicarbonation to $NaHCO_3$.	1	3	2	1
Ethylene carbonate	Carbonation of ethylene oxide to ethylene carbonate	1			2
	Ethylene glycol and CO_2	2			2
	Monohalohydrin and CO_2	2			3
	Oxidative carboxylation of an ethylene.	3			2
Dimethyl carbonate	Carboxylation of methanol	2			1
Poly (propylene carbonate)	Carbonation of propylene oxide to propylene carbonate in presence of a catalyst which catalyses the polymerisation.	1	2	3	2
Polycarbonate (aromatic)	Phosgene-free production using ethylene oxide	1	2	3	2
Ammonium carbamate	First step in the formation of urea	1			1
Methyl carbamate	Reaction of methanol with urea	1	2	3	2
Ethanediol dicarbamate	Diamine plus an alcohol reacts with CO_2 over a basic catalyst	3			3
	Diamine reacts with CO_2 over a basic catalyst, the product then reacts with an organic halide	3			3
Polyurethane	Carbonation of an epoxide yields polyols for PU synthesis.	1	1	3	3
	Co-polymerisation of CO_2 with aziridine	3	1		3

Table 3. Potential chemical/fuel products utilising CO_2 with rankings and weightings.

Product	Synthesis route	TRL ranking	Market value ranking	CO_2 utilisation ranking	Other carbon in product ranking
Butanol	Gas fermentation	3	3	2	1
Ethanol	Electrochemical reduction	3	2	1	1
	Electrochemical conversion using copper nanoparticle n-doped graphene electrode	3	2	1	1
	Gas fermentation	3	2	1	1
Methanol	Reverse water gas shift, then F-T reactions.	1	2	1	1
	Dry reforming of CH_4 and CO_2, water gas shift, then F-T reactions.	1	2	1	2
	CO_2/steam reforming of CH_4, water gas shift, then F-T reactions.	1	2	1	2
	Direct catalytic hydrogenation of CO_2 to formic acid intermediate, followed by dehydration	3	2	1	1
	Electrocatalytic hydrogenation of CO_2 (combined with water electrolysis) in a reverse methanol fuel cell.	3	2	1	1
	High temperature solid oxide cell uses CO_2 and water to produce H_2 and CO, followed by catalytic methanol synthesis.	1	2	1	1
	Photo-electrochemical cell	3	2	1	1
	Two-step process, first convert CO_2 to CH_4 via Sabatier reaction, then partial oxidation of CH_4	3	2	1	1
Dimethyl ether	Dry reforming of CH_4 and CO_2 to produce a syngas, plus additional H_2.	3			2
	Single-step process using a bifunctional catalyst which produces methanol and causes its dehydration in the same reactor.	3			1
	Condensation then dehydration of CO_2 derived methanol in the presence of a solid acid catalyst	1			1

Table 4. Potential fuel products utilising CO_2 with rankings and weightings.

Product	Synthesis route	TRL ranking	Market value ranking	CO_2 utilisation ranking	Other carbon in product ranking
Diesel	F-T reactions to produce linear waxes, then hydrocracking.	1	1	1	1
Gasoline	F-T reactions to produce gasoline-range hydrocarbons	1	1	1	1
	Methanol to Gasoline process, via DME and olefins	1	1	1	1
Jetfuel - kerosene type	Gas fermentation to produce ethanol. Then oligomerisation and dehydration/hydrogenation.	2	1	1	1
Methane	CO_2 methanation (Sabatier reaction)	1	1	1	1
	Electrocatalytic reduction of CO_2 over a cobalt catalyst	3	1	1	1
	Gas fermentation	2	1	1	1

Table 5. Potential solid material products utilising CO_2 with rankings and weightings.

Product	Synthesis route	TRL ranking	Market value ranking	CO_2 utilisation ranking	Other carbon in product ranking
Construction aggregates	Single-step direct aqueous mineralisation of calcium/magnesium silicates.	3	2	1	1
	Two-step mineralisation to improve dissolution and carbonate formation.	3	2	1	1
	As above, but using alkaline industrial wastes.	1	2	1	1
Cement-like products	Flue gases react with alkaline industrial brines.	1	1	1	1
Concrete products	CO_2 injected into concrete to form calcium carbonate nanoparticles within the concrete.	1	1	1	2
Mineral carbonate fertiliser	Carbonate coated biomass pellets	1	2		1
Carbon fibres	Electrocatalytic conversion of CO_2 dissolved in molten carbonates	3	3	3	1
Nanotubes		3			1
Graphene		3			1
Synthetic diamonds	Reduction of solid CO_2 at for 12 hrs	3			1

7. Appendix 2. Tables of Potential Products Utilising Carbon Monoxide

Table 6. Potential chemical products utilising CO with rankings and weightings.

Product	Synthesis route	TRL ranking	Market value ranking	CO utilisation ranking	Other carbon in product ranking
Benzene	Methanation then dehydroaromatisation	3	2	1	1
	Methanol to aromatics	1	2	1	2
Toluene	*as above*	1	3	2	2
Xylene	*as above*	1	2	2	2
Butanal	Hydroformylation of propylene	1	3	3	2
Acetic acid	Carbonylation of methanol	1	3	3	2
	Gas fermentation	3	3	2	1
Butyric acid	Gas fermentation	3	3	3	1
Formic acid	CO and methanol, subsequent cleavage of methyl ester to formic acid	1	3	3	2
Propio-lactone	Carbonylation of ethylene oxide	2		3	2
Methyl formate	Carbonylation of methanol	1	3	3	2
Ethylene	Methanol to olefin (meOH condensation to DME then conversion to olefin)	1	1	1	2
Propylene	Methanol to olefin (meOH plus ethylene)	1	1	1	2
	Methanol to olefin (condensation of meOH to DME then conversion to olefin)	1	1	1	2
1,3-Butadiene	Gas fermentation	1	2	2	1
Dimethyl carbonate	Carbonylation of methanol in the presence of O_2	1			2
Methyl carbamate	MeOH with urea	1	2	3	2

Table 7. Potential chemical/fuel products utilising CO with rankings and weightings.

Product	Synthesis route	TRL ranking	Market value ranking	CO utilisation ranking	Other carbon in product ranking
Butanol	Gas fermentation	2	3	3	1
	Hydroformylation of propylene to butanal then hydrogenation to butanol.	1	3	3	2
	Isobutanol produced selectively by Zr catalyst.	3	3	3	1
Ethanol	Modified F-T process using high pressures (SEHT)	2	2	2	1
	Modified F-T process (Lurgi-Octamix)	2	2	2	1
	Gas fermentation	1	2	2	1
Methanol	Reaction over a Cu/ZnO catalyst	1	2	2	1
	Methanation then partial oxidation	3	2	2	1
Dimethyl ether	Condensation then dehydration of meOH	1			2
	Bifunctional catalyst allows conversion to methanol then dehydration to DME	3			1

Table 8. Potential fuel products utilising CO with rankings and weightings.

Product	Synthesis route	TRL ranking	Market value ranking	CO utilisation ranking	Other carbon in product ranking
Diesel	F-T reaction to produce linear waxes, then hydrocracking.	1	1	1	1
Gasoline	F-T reaction at 300-350°C to produce gasoline-range hydrocarbons.	1	1	1	1
	Methanol to Gasoline process, via DME and olefins.	1	1	1	2
Jetfuel - kerosene type	Gas fermentation to ethanol, then oligomerisation and dehydration/ hydrogenation	2	1	1	1
	F-T reaction to produce kerosene-type hydrocarbons	1	1	1	1
	MTG-type reactions (referred to as syngas to gasoline plus, or STG+)	2	1	1	2
Methane	Methanation over a nickel catalyst.	1	1	1	1
	Gas fermentation	3	1	1	1