



Project no. 723678



## **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

### **Deliverable 5.3: *Stakeholder Pathway Selection Tool***

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# 1. Executive Summary

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This report describes a tool designed to enable stakeholders to select products which can be synthesised from carbon dioxide (CO<sub>2</sub>) and/or carbon monoxide (CO) and/or the routes, pathways, and technologies which can be utilised to synthesise such products. The pathways selected are those which offer the most favourable outcomes to a series of nine economic and environmental indicators which are weighted by the user to suit the priorities and aims of the stakeholder.

The focus of this tool is solely upon the CO/CO<sub>2</sub> conversion technologies. The costs and energy requirements of capturing and transporting the CO/CO<sub>2</sub> and producing and transporting any H<sub>2</sub> required by the process are not covered. However, the amount of H<sub>2</sub> required by the products and the pathways to produce them is included within the selection.

Many CO<sub>2</sub> conversion technologies have a high energy demand and this is a major contributor to both the economic and the environmental impacts of most CO<sub>2</sub>-derived products. The energy requirement tends to be less for CO conversion since the CO molecule itself has a higher energy content. All forms of energy (even renewables) have a carbon footprint, so the carbon intensity of the energy used in any energy-demanding process plays a big part in the overall carbon balance. Obtaining figures for the direct energy requirement of many of the identified products and pathways is challenging due to them being confined to either lab-based research or pilot/demonstrator plants where commercial confidentiality limits data availability. This tool aims to utilise readily-available data which can be used as a proxy for energy use so that stakeholders can use it, together with other data, as indicators of the economic and environmental impacts of the CO/CO<sub>2</sub> conversion reactions.

The selection tool has been produced using Microsoft Excel, and has been designed to be as simple as possible so that the user can not only see how it works, but add and delete data as they see fit. It is provided not as a finished product, but rather as a tool which can evolve as the data it uses changes.

## 2. Introduction

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This report describes a technology selection tool designed to enable stakeholders to select:

- products that can be synthesised from carbon dioxide (CO<sub>2</sub>) and/or carbon monoxide (CO) which best suit the priorities of the stakeholder

and/or

- pathways which can be utilised to synthesise such products, which offer the best economic and environmental outcomes which suit the priorities of the stakeholder.

The products and/or pathways are selected based upon a mix of economic and environmental indicators and the requirements of the stakeholder are determined by the stakeholder assigning a relative priority to the various indicators included in the tool<sup>1</sup>.

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.

Three additional factors play an important role:

1. The energy required to capture and transport the CO<sub>2</sub> utilised.
2. The energy required to produce and transport any hydrogen needed during the process.
3. The energy required to enable the conversion reaction itself to proceed.

The first two factors listed above are outside the scope of this report in that the different CO<sub>2</sub> capture and H<sub>2</sub> production technologies are not discussed and compared. The focus of this report is solely upon the CO/CO<sub>2</sub> conversion pathways. As identified in the deliverables of CarbonNext Work Package 4, many CO<sub>2</sub> conversion pathways, especially those involving reduction reactions, have a high energy demand which can be a major contributor to both the economic and the environmental impacts of CO<sub>2</sub>-derived products. This is less significant for CO conversion routes since the CO molecule itself has a higher energy content.

The production of all forms of energy (even electricity from renewable sources) releases greenhouse gases, so the carbon intensity of the energy used in any process with a high energy demand plays a big part in the overall carbon balance of that process. The value of life cycle assessment to obtain a definitive measure of the carbon balance of a process is well recognised, but the complexity and therefore time required to conduct such an assessment is significant. The calculations necessary to perform even a coarse-grid LCA approach to allow comparison between different products and technologies, such as was used in Deliverables 4.2 and 4.4 are still too demanding for a technology selection tool such as that being developed here. What is required is high-level, readily-available data which stakeholders can access and use as an indicator of the economic and environmental impacts of the CO/CO<sub>2</sub> conversion reactions.

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<sup>1</sup> These are Technology Readiness Level, EU 28 market size, market value, EU CO<sub>2</sub> utilisation potential, H<sub>2</sub> needed, reaction enthalpy, reaction temperature, reaction pressure and further (non-catalytic) inputs.

## 3. Methodology

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### 3.1 Background

The methodology used in this selection process was developed during the production of prior deliverables for CarbonNext. A brief paragraph on the relevant deliverables will enable the reader to better understand how the methodology was developed.

CarbonNext deliverable 2.1 provided a list of technologies and potential products which can be produced from CO<sub>2</sub> and CO. The list was presented in the form of tables which summarised the potential economic and environmental impact of the different products and routes to those products. 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. Measures of the EU market size (EU28 production plus imports) and value (market value and unit value/t) were obtained from the Eurostat Prodcom database. The CO/CO<sub>2</sub> utilisation potential (t CO/CO<sub>2</sub> used/t product multiplied by market size) and the H<sub>2</sub> requirement (t H<sub>2</sub>/t product) of the process were calculated by the author using stoichiometric reaction formulae. The production of H<sub>2</sub> in a sustainable and low-carbon way (such as by the electrolysis of water), has a high energy requirement, so the amount of H<sub>2</sub> required/t product was provided to enable comparison between products and routes to those products. Finally, chemical inputs other than H<sub>2</sub> are required to synthesise many of the potential products of interest and these were listed in the tables.

For the selection technique used in deliverable 2.3, those additional chemical requirements were assessed as to whether they contain carbon or not and if so, whether they can be produced from CO<sub>2</sub> or CO. If the additional carbon-containing chemical can be synthesised from CO<sub>2</sub> (or CO) then it was deemed to be more favourable in terms of recycling carbon and moving the chemicals industry away from fossil carbon feedstock than a chemical which can only be synthesised from fossil sources.

The selection process used in deliverable 2.3 used just four pieces of data: the TRL of the process, the market value of the product, the CO/CO<sub>2</sub> utilisation potential of the product and whether other non-catalytic chemical inputs using fossil carbon were required. These four items were ranked according to their desirability and products in which all four items were ranked favourably were selected.

The selection methodology used to develop the tool described here uses additional data to take better account of the energy usage. As before, it ranks the data as a way of normalising it, but then it allows the stakeholder to use weightings to prioritise the data to reflect their aims and priorities.

### 3.2 Additional data on energy use

Compared to the indicators introduced in deliverable 2.3, the tool includes data on reaction enthalpy, temperature and pressure as described below.

### 3.2.1 Reaction enthalpy

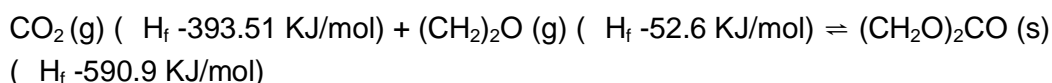
Published data concerning the amount of energy required to transform CO<sub>2</sub> or CO into various products is limited for most processes. Some of the reactions of interest have only been conducted in a laboratory and so the electricity requirements are unknown. Reaction pathways which are further developed and are in pilot, demonstration or even early commercial phases are generally shrouded in commercial confidentiality. For this reason, and to enable a consistent approach, we have referred to the basic thermodynamic properties of the reactants and products to estimate the amount of energy inputs required.

The energy absorbed or evolved as a reaction proceeds is referred to as the enthalpy of the reaction ( $H_r$ ). This value is the difference between the energy (or enthalpy) required for the formation of the products compared to the enthalpy required for the formation of the reactants. In practice, the enthalpy of the reaction is derived from the sum of ( ) the enthalpy of formation ( $H_f$ ) of the products minus the sum of the enthalpy of formation of the reactants. The overall calculation is therefore:

$$H_r = H_f \text{ products} - H_f \text{ reactants}$$

A positive  $H_r$  implies that the reaction is endothermic and needs additional energy to enable it to proceed, a negative  $H_r$  suggests it is exothermic and heat will be generated as the reaction proceeds.

As an example, the reaction of CO<sub>2</sub> with ethylene oxide to form ethylene carbonate is given below:



Using the equation provided above:

$$H_r = (-590.9) - (-393.5 + -52.6) = -144.8 \text{ KJ/mol}$$

The above reaction to form ethylene carbonate is exothermic (the  $H_r$  is negative) and it also has a negative free energy suggesting that the equilibrium position of the reaction will be towards the products. Despite this, the reaction does not proceed spontaneously and a catalyst is required to reduce the activation energy of the reaction so that it can proceed. However, since the activation energy does not affect the overall enthalpy change of the reaction, the use of a catalyst also does not affect the overall enthalpy change of the reaction.

Calculations of this type have been performed for all of the reactions reviewed (where data was available) to provide an indication of the amount of energy required for the reactions to proceed. The enthalpy of formation ( $H_f$ ) values used were obtained from standard texts<sup>2 3</sup>.

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<sup>2</sup> CRC Handbook of Chemistry and Physics. CRC Press, London. Standard Thermodynamic Properties of Chemical Substances. Available at: [http://www.update.uu.se/~jolkkonen/pdf/CRC\\_TD.pdf](http://www.update.uu.se/~jolkkonen/pdf/CRC_TD.pdf). Accessed September 2017.

The tables forming the appendices of this report contain the calculated reaction enthalpies as a resource for interested parties.

### 3.2.2 Reaction temperature and pressure

In addition to the calculated enthalpy of the reactions, the published temperature and pressures required for the reactions to proceed have been recorded as an alternative measure, or proxy, for energy use. This is because even though some reactions involving CO and CO<sub>2</sub> are exothermic, they still require high temperature and pressures to proceed - a relevant example being the Fischer-Tropsch reactions whereby CO is converted to a range of liquid hydrocarbons over a cobalt catalyst. By recording the temperature and pressures of the reactions in addition to the enthalpy, a better idea of the energy requirements of a process is obtained.

It is proposed that the reaction temperature alone should not be used as a measure of the energy usage of a process, but that all three indicators should be used together. One reason for this is that a reaction may initially require a high energy input to achieve the high reaction temperature required for the chemical transformation to begin. However once the reaction starts, it may be exothermic and so generate enough heat to keep the reaction vessel at the required temperature. Indeed, some exothermic processes required cooling once the reaction has begun. The impact of reaction enthalpy, temperature and pressure are therefore not straightforward and as a consequence they should be used together as an indicator of the energy requirement rather than alone.

One way of utilising the reaction enthalpy data could be to convert the enthalpy value measured in KJ/mole of product to electrical energy in KWh/t of product. This can then be converted to Kg CO<sub>2</sub> equivalent per KWh electrical energy by using reference conversion factors for electricity carbon intensity, as is done when conducting life cycle assessments. In a similar way, a calculation of the compression energy required to achieve the required pressures within the reaction vessel could be conducted to convert the pressure value to electrical energy and then to climate impact as above.

However, whilst potentially providing impact values relevant to climate change, we are mindful that the purpose of this tool is to produce a method of selecting between different products or technologies. Determination of the climate change impact of a reaction enthalpy or a required operating pressure of a reaction vessel may be of interest, but the risk is that it does not reflect the uncertainties involved. For instance, as shown above, the reaction enthalpy for ethylene carbonate from ethylene oxide was exothermic, yet the reaction only proceeds spontaneously if certain reaction conditions are met. With this in mind, it could be misleading to calculate the climate impacts of endothermic reaction enthalpies without taking into consideration such factors. For this reason, it was decided that the enthalpy, temperature and pressure values should be used simply as an indicator of energy usage, with high values ranked as undesirable and low temperatures/pressures and exothermic

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<sup>3</sup> Chemistry-Reference.com (2017). Available at: <http://chemistry-reference.com/standard%20thermodynamic%20values.pdf> Accessed September 2017.

enthalpy values ranked as desirable. In this way, we are not attributing more significance to the individual values than they deserve.

### 3.3 Ranking

To enable comparison of the potential impacts of the different synthesis pathways, the indicators described above were ranked using a simple scale of 1 to 3 (1 undesirable, 2 desirable and 3 highly desirable). Table 1 shows how the indicators were ranked. To aid visual identification in the tables provided in the appendix, the measures ranked highly desirable (3) are coloured green, those ranked less desirable (2) are amber, and those ranked an undesirable (1) are coloured red. The "traffic light" colours are used in this way to enable the reader to more easily distinguish products displaying more desirable (green) features from products with more undesirable (red) features.<sup>4</sup>

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<sub>2</sub> than if a proportion of the carbon came from fossil feedstock. Therefore, if the additional carbon-containing chemical can be synthesised from CO/CO<sub>2</sub> then it is given a more favourable ranking than a chemical which can only be synthesised from fossil carbon.

Ranking of indicators	1	2	3
TRL	1 - 3	4 - 6	7 - 9
Market size	<1 Mt/yr	1 - 10 Mt/yr	>10 Mt/yr
Market value	<1 " b/yr	1 - 10 " b/yr	>10 " b/yr
CO/CO <sub>2</sub> utilisation potential	<1 Mt/yr	1 - 10 Mt/yr	>10 Mt/yr
H <sub>2</sub> reliance	>0.25 tH <sub>2</sub> /t product	0.01 - 0.25 tH <sub>2</sub> /t	0 tH <sub>2</sub> /t product
Reaction enthalpy	>100 KJ/mol	0 - 100 KJ/mol	exothermic
Reaction temperature	>250°C	51 - 250°C	1-50°C
Reaction pressure	>30 atm	6 - 30 atm	1 - 5 atm
Other sources of fossil carbon in product	Yes and cannot be made from CO <sub>2</sub>	Yes, but can be made from CO <sub>2</sub>	No

**Table 1. Ranking of the indicators used to select the most favourable products and production routes. Higher rankings (red) are less desirable than the low rankings (green).**

<sup>4</sup> note that this is a different approach to that taken in CarboNnext deliverable 2.3 where desirable features were assigned a low ranking. The reason for this change is explained in section 3.5 weighting.



### 3.4 Weighting

Without weightings, the system treats the ranking of each measure described above as being of equal importance. However, if someone is looking to develop a CO<sub>2</sub> derived product in the short term, then the TRL of a process is a vital indicator of whether this is likely to be possible. In such circumstances a high weighting should be applied to the TRL, which will result in the pathways with a high TRL as being ranked as highly desirable. Alternatively, someone may be looking towards the longer term development of future products and so the current TRL of a process is less significant. In that case, a lower weighting would be applied to TRL resulting in that aspect having a reduced impact upon the overall scores being used for selection.

The weightings are applied by the stakeholder, the data and rankings are already provided in the spreadsheet. It is more intuitive to apply higher weightings to the indicators considered to be important by the stakeholder and low weightings to those deemed to be of low priority to the stakeholder. As these weightings are multiplied by the ranking, this approach requires the rankings to be high for desirable and low for undesirable indicators. This ensures that a high overall score is achieved for indicators of significance to the stakeholder and a low overall score for indicators which are less or not significant to the stakeholder.

### 3.5 The selection process

The ranking of an aspect for a pathway is multiplied by the weighting to give a score, then the average score for all available indicators is calculated for each pathway. The higher the average score, the more closely the pathway meets the priorities of the stakeholder. The average score is used rather than the sum of the scores because in a proportion of the cases, data for some of the indicators was not available.

#### **Data availability**

For example, the market size and value for the chemical ethylene carbonate was not available at the time of writing and therefore the total CO<sub>2</sub> utilisation potential for the EU could not be calculated. Similarly, the sources used to identify the enthalpy of formation ( $H_f$ ) for the products and reactants, which were in turn used to calculate the reaction enthalpy ( $H_r$ ), did not include ethanediol dicarbamate, which meant that the enthalpy of the reaction could not be calculated. Additionally, the H<sub>2</sub> requirement of products which are made via methanol depends upon the process used to synthesise the methanol which can range from no H<sub>2</sub> requirement to a high requirement. In such cases this measure was simply left out and the average score of the other eight measured determined rather than using all nine. Overall, in over 80% of the 104 products and processes included in the spreadsheets, data was available for either eight or nine of the nine measures.

Tables listing the products and pathways identified in Deliverable 2.1 are presented in the appendices to this report. Available data for the nine indicators is provided as a reference and the data fields are colour-coded red, amber and green to indicate the rankings applied as described in Table 1 above.

The user is free to tailor the list of products and pathways to their specific interests and/or requirements by simply adding or removing product pathways as desired. The only limitation to adding additional potential products to the list is the availability of the data which is used to select from the list.

To apply weightings to the nine ranked indicators, the user should consider that the weightings assigned should reflect their aims or priorities. For instance:

- If utilisation of the most CO/CO<sub>2</sub> is a priority, then assign a high weighting to the CO/CO<sub>2</sub> utilisation potential so that products/technologies which have the potential to utilise a large quantity of CO/CO<sub>2</sub> are scored highly.
- If the supply of sustainable/low carbon H<sub>2</sub> is likely to be a barrier, then assign a high weighting to H<sub>2</sub> reliance so that products which require no or low H<sub>2</sub> are scored highly.
- If the goal is to identify the best solutions for the long-term, then assign a low weighting to TRL so that this measure is not a strong determinant in the selection process.
- If replacing fossil carbon is a priority, then other sources of fossil carbon in product+ should be assigned a high weighting.
- Some companies may see themselves competing in the market for bulk chemicals or fuels whereas others may be more comfortable in the speciality chemicals sector. The market size and market value measures can be weighted appropriately to indicate such preferences.
- If electricity prices are of significant concern, then a larger weighting may be applied to the energy measures of reaction temperature, pressure and enthalpy than if the producer had access to a cheaper source of electricity (onsite generation for instance).

Weightings should be applied to all of the indicators used, but the scale of the weighting is at the discretion of the user. It is suggested that the user changes the weightings to see how this changes the outcome.

## 3.6 How to use the tool

The accompanying selection tool is composed of a spreadsheet with three tabs: a list of the pathways from CO<sub>2</sub>, an equivalent list of pathways from CO, and an interactive selector+tab.

### Pathway tabs

The lists provided in the two Pathways+tabs are structured in exactly the same way as each other. The only difference between the two is the products and pathways listed in columns A-D which are split into the categories: chemicals, chemicals/fuels, fuels and solid materials (the latter for CO<sub>2</sub> only). Data relating to the nine indicators described in Table 1 above are provided in columns E to AG, along with a column ranking that measure and a column for adding the weighting for that measure. For example, data relating to the EU28 market size of the product (obtained from Prodcom) is provided in column H. Column I alongside it ranks that data using the 1-3 scale described above. Both of these columns have been colour-coded red for the unfavourable ranking of 1, orange for the mid-ranking of 2 and green for

the favourable ranking of 3. Column J alongside this is the weightings are assigned by the user for that aspect. The spreadsheet has been provided with all nine indicators set with an initial weighting of 2.

#### **Interactive selector tab**

The **Interactive selector** tab is where the user can change the weightings assigned and see the results. The nine indicators are listed in column A and column B allows the weightings to be increased or decreased (as reflected in column C). The results, i.e. the **Best pathways** for CO<sub>2</sub> are listed in columns E, F and G, whereas the results for CO can be seen by scrolling along to columns H, I and J. As the weightings are changed, the user will see the order of the pathways listed in the results (**Best pathways list**) change as the spreadsheet automatically calculates the sum of the weighted rankings and this is divided by the number of available indicators per product/pathway to give a mean score per pathway. The pathways with the highest scores are the most favourable, in terms of the measures used.

The user does not need to make any changes to the data within the **Pathway** tabs, only the **Interactive selector** tab needs to be changed to reflect the preference of the stakeholder. However, the selector tool uses the data within the pathways tabs, so by updating the data as required or by adding new pathways or deleting others, the user has the ability to make the tool more useful and relevant to their situation.

## 4. Conclusion

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In summary, a selection tool has been produced using straightforward spreadsheets within Microsoft Excel. The tool has been designed to be as simple as possible so that the user can not only see how it works, but add and delete data as they see fit. It is not a provided as a finished product, but rather it will need to constantly evolve as the data it uses is updated.

As already mentioned, the weightings are left to the user to assign, to suit their requirements. It is recommended that users try out different weightings to see how the product selection changes. It is also suggested that the boundaries between the rankings could be altered and products can be assigned different rankings as technology develops. For instance, the TRL of a process may be listed on the spreadsheet at a low level, but users may be aware of recent developments which may have increased this closer to the point of commercial interest. Market data for the EU28 was used to populate the spreadsheet, but users are free to change this to reflect another region or a specific country if preferred. Other data may well be available to users which better measure the potential impacts of a product or pathway which would improve and refine the selection tool.

## 5. Appendix

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### 5.1 Potential products from CO<sub>2</sub>

**Table 2.** Potential chemicals from CO<sub>2</sub> with economic and environmental measures and rankings.

**Table 3.** Potential chemical/fuels from CO<sub>2</sub> with economic and environmental measures and rankings.

**Table 4.** Potential fuels from CO<sub>2</sub> with economic and environmental measures and rankings.

**Table 5.** Potential solid materials from CO<sub>2</sub> with economic and environmental measures and rankings.

**Table 2. Potential chemicals from CO<sub>2</sub> with economic and environmental measures and rankings.**

Class	Product	Pathway	TRL	Market size (t/yr)	Market value (€M/yr)	CO <sub>2</sub> utilisation potential (t/yr)	H <sub>2</sub> reliance (t H <sub>2</sub> /t product)	Reaction enthalpy (KJ/mol)	Reaction temperature (°C)	Reaction pressure (atm or bar)	Other carbon in product
Amides	Urea	React NH <sub>3</sub> and CO <sub>2</sub> to produce ammonium carbamate which then dehydrates to urea	9	5,410,342	2,444	3,965,780	0	-133.2	170-185	145	No
Aromatic hydrocarbons	Benzene	CO <sub>2</sub> methanation followed by CH <sub>4</sub> dehydro-aromatization	2-4	6,807,829	3,627	23,010,462	0.62	2410.1	700	1	No
		MTA process - react methanol over a zeolite catalyst	7	6,807,829	3,627	23,010,462	0 - 0.62	-231.8	370-540	20-25	Methanol
	Toluene	<i>as above</i>	7	1,262,684	580	4,229,991	0 - 0.61	-315.6	370-540	20-25	Methanol
	Xylene	<i>as above</i>	7	2,563,662	1,414	8,511,358	0 - 0.60	-398.8	370-540	20-25	Methanol
Aldehydes	Formaldehyde	Borane reduction of CO <sub>2</sub>	1-3	1,056,418	266	1,549,765	0.067	284.9	25	1	No
		Hydrogenation to formic acid, then reduction to formaldehyde	1-3	1,056,418	266	1,549,765	0.067	284.9	25	70	No
Organic acids	Acetic acid	Catalytic oxidation of CH <sub>4</sub> with CO <sub>2</sub>	3	1,231,867	583	899,263	0	-15.8	400	1	Methane
		Gas fermentation	2-4	1,231,867	583	1,810,844	0.1	N/A	37	1	No
	Acrylic acid	Linear terminal alkene reacts with CO <sub>2</sub> to produce linear carboxylic acid	1-4	1,342,852	1,460	819,140	0	-42.7	100	10	Ethylene
	Benzoic acid	Benzene reacts with CO <sub>2</sub> to form benzoic acid	1-3	190,601	208	68,807	0	-40.5	70	57	Benzene
	<i>p</i> -hydroxy-benzoic acid	Kolbe-Schmitt reaction	9	190,601	208	60,992	0	?	125	100	Potassium phenoxide
	Butyric acid	Gas fermentation	1-3	471,609	550	943,218	0.159	N/A	37	1	No
	Formic acid	Electrochemical reduction of CO <sub>2</sub>	5-6	490,069	267	470,466	0.043	-31.5	25	1	No
		Catalytic reduction	2-3	490,069	267	470,466	0.043	-31.5	50	100	No
	Oxalic acid	Electrochemical reduction of CO <sub>2</sub>	3-4	302,583	620	148,266	0.022	-34.7	25	1	No
Salicylic acid (2-hydroxy-benzoic acid)	Kolbe-Schmitt reaction	9	42,703	149	13,622	0	?	125	100	Sodium phenoxide	
Olefins	Ethylene	Direct using modified F-T catalysis	2-4	24,505,336	21,382	76,946,755	0.43	-303.9	300-350	15-60	No
		Direct electrochemical reduction of CO <sub>2</sub>	1-3	24,505,336	21,382	76,946,755	0	366.2	25	1	No

**Table 2. Potential chemicals from CO<sub>2</sub> with economic and environmental measures and rankings (continued).**

Class	Product	Pathway	TRL	Market size (t/yr)	Market value (€M/yr)	CO <sub>2</sub> utilisation potential (t/yr)	H <sub>2</sub> reliance (t H <sub>2</sub> /t product)	Reaction enthalpy (kJ/mol)	Reaction temperature (°C)	Reaction pressure (atm or bar)	Other carbon in product
Olefins (continued)	Ethylene	MTO process: condensation of methanol to DME followed by conversion to olefin	8-9	24,505,336	21,382	76,946,755	0 - 0.57	-41.2	400-450	1	No
	Propylene	MTO process: methanol plus ethylene	8-9	27,123,818	24,774	85,168,789	0 - 0.19	-79.2	400-450	1	Ethylene
		MTO process: condensation of methanol to DME followed by conversion to olefin	8-9	27,123,818	24,774	85,168,789	0 - 0.57	-120.4	400-450	2	Methanol
Epoxides	Ethylene oxide	Carboxylation of ethylene	2-4	947,849	663	947,849	0	178.0	325	24	Ethylene
Polyols	Ethylene glycol	Electrochemical reduction of CO <sub>2</sub>	3-5	1,939,511	1,020	2,754,106	0.1	327.0	25	1	No
	Propylene glycol	Electrochemical reduction of CO <sub>2</sub>	3-5	761,544	554	1,325,087	0.11	679.5	25	1	No
Carbonates (inorganic)	Sodium bicarbonate	Carbonation of NaOH to Na <sub>2</sub> CO <sub>3</sub> , then bicarbonation to NaHCO <sub>3</sub>	6-8	3,662,946	403	1,919,384	0	-254.9	60	1	No
	Calcium carbonate		6-7	5,544,934	576	2,439,771	0	-179.0	20	1	No
Carbonates (cyclic)	Ethylene carbonate	Carbonation of ethylene oxide to ethylene carbonate	9	?	?	?	0	-144.8	190-200	80	Ethylene oxide
		Diol (ethylene glycol) and CO <sub>2</sub>	3-5	?	?	?	0	-23.2	150	66	Ethylene glycol
		Monohalohydrins and CO <sub>2</sub>	4-5	?	?	?	0	5.7	100	50	2-Chloro-ethanol
		Oxidative carboxylation of ethylene	1-3	?	?	?	0	-249.8	120	50	Ethylene
Carbonates (linear)	Dimethyl carbonate	Carboxylation of methanol to produce dimethyl carbonate	2-4	?	?	?	0 - 0.18	220.7	150-170	50	Methanol
Poly-carbonates (aliphatic)	Poly (propylene carbonate)	Carbonation of propylene oxide to propylene carbonate in the presence of a polymerisation catalyst	6-7	1,555,718	3,932	668,959	0	-97.1	190-200	80	Propylene oxide

Table 2. Potential chemicals from CO<sub>2</sub> with economic and environmental measures and rankings (continued).

Class	Product	Pathway	TRL	Market size (t/yr)	Market value (€M/yr)	CO <sub>2</sub> utilisation potential (t/yr)	H <sub>2</sub> reliance (t H <sub>2</sub> /t product)	Reaction enthalpy (kJ/mol)	Reaction temperature (°C)	Reaction pressure (atm or bar)	Other carbon in product
Poly-carbonates (aromatic)		Phosgene-free production using ethylene oxide	6-7	1,555,718	3,932	668,959	0	-144.8	?	?	Ethylene oxide
Carbamates (inorganic)	Ammonium carbamate	First step in the formation of urea	9	?	?	?	0	637.5	150-170	145	No
Carbamates (organic)	Methyl carbamate	Reaction of methanol with urea	9	1,191,873	3,082	703,205	0 - 0.11	12.5	130-150	1-13	Methanol, urea
Dicarbamates	Ethanediol dicarbamate	Diamine plus an alcohol reacts with CO <sub>2</sub> over a basic catalyst	1-3	?	?	?	0 - 0.05	?	?	?	Ethylene diamine, methanol
		Diamine reacts with CO <sub>2</sub> over a basic catalyst, the product then reacts with an organic halide	1-3	?	?	?	0	?	?	?	Ethylene diamine, organic halide
Polycarbamates	Polyurethane	Carbonation of an epoxide yields polyols for PU synthesis.	6-7	5,168,004	10,771	671,841	0	?	100	15-90	Ethylene oxide
		Co-polymerisation of CO <sub>2</sub> with aziridine	1-3	5,168,004	10,771	?	0	?	100	3-22	Aziridine



**Table 3. Potential chemical/fuels from CO<sub>2</sub> with economic and environmental measures and rankings.**

Class	Product	Pathway	TRL	Market size (t/yr)	Market value (€M/yr)	CO <sub>2</sub> utilisation potential (t/yr)	H <sub>2</sub> reliance (t H <sub>2</sub> /t product)	Reaction enthalpy (KJ/mol)	Reaction temperature (°C)	Reaction pressure (atm or bar)	Other carbon in product
Alcohols	Butanol	Gas fermentation	2-4	649,068	356	1,544,782	0.162	N/A	37	1	No
	Ethanol	Electrochemical reduction	1-3	5,904,504	3,396	11,277,603	0	322.0	25	1	No
		Electrochemical conversion using copper nanoparticle n-doped graphene electrode	1-3	5,904,504	3,396	11,277,603	0	322.0	25	1	No
		Gas fermentation	2-4	5,904,504	3396	11,277,603	0.196	N/A	37	1	No
	Methanol	Reverse water gas shift then use Cu/ZnO catalysis to produce methanol	7-9	7,891,386	1,476	21,701,312	0.25	437.5	150-900	1-50	No
		Dry reforming of CH <sub>4</sub> and CO <sub>2</sub> , followed by water gas shift reaction then catalytic methanol synthesis	6-7	7,891,386	1,476	10,850,656	0	118.8	650-1000	1	Methane
		CO <sub>2</sub> /steam reforming of CH <sub>4</sub> , followed by WGS then catalytic methanol synthesis	6-7	7,891,386	1,476	10,850,656	0	404.7	700-1000	3-25	Methane
		Direct catalytic hydrogenation of CO <sub>2</sub> to formic acid, followed by dehydration	1-3	7,891,386	1,476	10,850,656	0.188	-131.4	250-300	20-80	No
		Electrocatalytic hydrogenation of CO <sub>2</sub> with electrolysis in a reverse methanol fuel cell	1-3	7,891,386	1,476	10,850,656	0	154.5	50-150	1-3	No
		High temperature solid oxide cell uses CO <sub>2</sub> and water to produce H <sub>2</sub> and CO, followed by catalytic methanol synthesis	7	7,891,386	1,476	10,850,656	0	726.1	500-1000	1	No
Photo-electrochemical cell		1-3	7,891,386	1,476	10,850,656	0	154.5	25	1	No	
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		2-4	7,891,386	1,476	10,850,656	0.25	154.5	200-500	10-30	No	
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> .	1-3	?	?	?	0.09	-1.5	260	40	Methane
		Single-step process producing methanol then dehydrating it in the same reactor	1-3	?	?	?	0.261	-254.5	225	40	No
		Condensation then dehydration of CO <sub>2</sub> -derived methanol using a solid acid catalyst	9	?	?	?	0 - 0.35	8.2	250	17	Methanol

**Table 4. Potential fuels from CO<sub>2</sub> with economic and environmental measures and rankings.**

Class	Product	Pathway	TRL	Market size (t/yr)	Market value (€M/yr)	CO <sub>2</sub> utilisation potential (t/yr)	H <sub>2</sub> reliance (t H <sub>2</sub> /t product)	Reaction enthalpy (KJ/mol)	Reaction temperature (°C)	Reaction pressure (atm or bar)	Other carbon in product
Liquid hydrocarbons	Diesel	F-T reactions to produce linear waxes, then hydrocracking	7-8	384,086,000	247,271	1,206,030,040	0.429	-2364.0	200-240	15-60	No
	Gasoline	F-T reactions to produce gasoline-range hydrocarbons	7-8	146,243,000	100,042	451,890,870	0.44	-1633.3	300-350	15-60	No
		Methanol to Gasoline process, via DME and olefins	6-8	146,243,000	100,042	451,890,870	0.02 - 0.58	-582.9	300-400	10-20	Methanol
	Jetfuel (kerosene type)	Gas fermentation to produce ethanol. Then oligomerisation and dehydration/hydrogenation	5-6	63,928,000	31,215	198,816,080	0.329	-400.3 or -73.5	250	100-200	No
Gaseous hydrocarbons	Methane	CO <sub>2</sub> methanation (Sabatier reaction)	6-7	338,511,000	193,229	930,905,250	0.5	-253.0	200-500	10-30	No
		Electrocatalytic reduction of CO <sub>2</sub> over a cobalt catalyst	1-3	338,511,000	193,229	1,861,810,500	0	1173.3	0-40	1-10	No
		Gas fermentation	4-6	338,511,000	193,229	930,905,250	0.375	N/A	37	1	No

**Table 5. Potential solid materials from CO<sub>2</sub> with economic and environmental measures and rankings.**

Class	Product	Pathway	TRL	Market size (t/yr)	Market value (€M/yr)	CO <sub>2</sub> utilisation potential (t/yr)	H <sub>2</sub> reliance (t H <sub>2</sub> /t product)	Reaction enthalpy (KJ/mol)	Reaction temperature (°C)	Reaction pressure (atm or bar)	Other carbon in product
Mineral carbonates	Construction aggregates	Single-step direct aqueous mineralisation of calcium/magnesium silicates.	3-4	777,209,041	7,531	411,920,792	0	-140.6	20	1	No
		Two-step mineralisation to improve dissolution and carbonate formation.	3-4	777,209,041	7,531	411,920,792	0	-140.6	20	1	No
		As above, but using alkaline industrial wastes.	9	777,209,041	7,531	341,971,978	0	-179.0	20-60	1-3	No
	Cement-like products	Flue gases react with alkaline industrial brines.	6-8	185,166,311	14,150	98,138,145	0	-639.9	20	1	No
	Concrete products	CO <sub>2</sub> injected into concrete to form calcium carbonate nanoparticles within the concrete.	9	754,825,440	40,934	332,123,194	0	-179.0	20	1	Concrete
	Mineral carbonate fertiliser	Carbonate coated biomass pellets	8	10,301,330	2,407	?	0	?	20	1	Cellulosic biomass
Pure carbon	Carbon fibres	Electrocatalytic conversion of CO <sub>2</sub> dissolved in molten carbonates	2	16,650	527	61,106	0	?	730	1	No
	Nanotubes		2	Unknown	?	?	0	?	750	1	No
	Graphene		2	481 globally	?	?	0	?	850	1	No
	Synthetic diamonds	Reduction of solid CO <sub>2</sub> at for 12 hrs	1-2	Unknown	?	?	0	?	440	800	No

## 5.2 Potential products from CO

**Table 6.** Potential chemicals from CO with economic and environmental measures and rankings.

**Table 7.** Potential chemical/fuels from CO with economic and environmental measures and rankings.

**Table 8.** Potential fuels from CO with economic and environmental measures and rankings.

Table 6. Potential chemicals from CO with economic and environmental measures and rankings.

Class	Product	Pathway	TRL	Market size (t/yr)	Market value (€M/yr)	CO utilisation potential (t/yr)	H <sub>2</sub> reliance (t H <sub>2</sub> /t product)	Reaction enthalpy (KJ/mol)	Reaction temperature (°C)	Reaction pressure (atm or bar)	Other carbon in product
Aromatic hydrocarbons	Benzene	Methanation followed by dehydro-aromatisation	2-4	6,807,829	3,627	14,636,832	0.46	711.99	700	1	No
		MTA process	7	6,807,829	3,627	14,636,832	0.31 - 0.46	-231.81	370-540	20-25	Methanol
	Toluene	<i>as above</i>	7	1,262,684	580	2,689,517	0.30 - 0.46	-315.59	370-540	20-25	Methanol
	Xylene	<i>as above</i>	7	2,563,662	1,414	5,409,327	0.30 - 0.45	-398.8	370-540	20-25	Methanol
Aldehydes	Butanal	Hydroformylation of propylene	9	225,430	154	87,918	0.03	-148.7	130-160	100-200	Propylene
Organic acids	Acetic acid	Carbonylation of methanol	9	1,231,867	583	578,977	0.07 - 0.10	-134.6	150-200	30-60	Methanol
		Gas fermentation	1-3	1,231,867	583	1,145,636	0.067	N/A	37	1	No
	Butyric acid	Gas fermentation	1-3	471,609	550	598,943	0.114	N/A	37	1	No
	Formic acid	CO and methanol, subsequent cleavage of methyl ester to formic acid	9	490,069	267	298,942	0.09 - 0.13	-314.5	80	40	Methanol
	Propiolactone	Carbonylation of ethylene oxide	4-5	43,690	?	17,039	0	-166.84	60	58	Ethylene oxide
Esters	Methyl formate	Carbonylation of methanol	9	490,069	267	230,333	0.07 - 0.10	-36.57	80	40	Methanol
Olefins	Ethylene	MTO process: condensation of methanol to DME followed by conversion to olefin	8-9	24,505,336	21,382	24,505,336	0.14 - 0.21	-41.2	400-450	1	Methanol
		Propylene	MTO process: methanol plus ethylene	8-9	27,123,818	24,774	54,247,636	0.10 - 0.14	-79.2	400-450	1
		MTO process: condensation of methanol to DME followed by conversion to olefin	8-9	27,123,818	24,774	54,247,636	0.29 - 0.43	-240.8	400-450	2	Methanol
Dienes	1,3-Butadiene	Gas fermentation to produce 2,3-butanediol	6-7	2,486,932	1,177	5,147,949	0.19	N/A	37	1	No
Carbonates (linear)	Dimethyl carbonate	Carbonylation of methanol in the presence of O <sub>2</sub>	8	?	?	?	0.09 - 0.13	-62.27	240-260	50-100	Methanol
Carbamates (organic)	Methyl carbamate	Reaction of methanol with urea	9	1,191,873	3,082	440,993	0.05 - 0.08	12.45	130-150	1-13	Methanol, urea

**Table 7. Potential chemical/fuels from CO with economic and environmental measures and rankings.**

Class	Product	Pathway	TRL	Market size (t/yr)	Market value (€M/yr)	CO utilisation potential (t/yr)	H <sub>2</sub> reliance (t H <sub>2</sub> /t product)	Reaction enthalpy (KJ/mol)	Reaction temperature (°C)	Reaction pressure (atm or bar)	Other carbon in product
Alcohols	Butanol	Gas fermentation	3-5	649,068	356	980,093	0.108	N/A	37	1	No
		Hydroformylation of propylene to butanal, then hydrogenation to butanol	9	649,068	356	246,646	0.03	-236.6	170	20	Propylene
		Isobutanol produced selectively over Zr catalyst	1-3	649,068	356	980,093	0.22	-750.2	360-420	100	No
	Ethanol	Modified F-T process using high pressures (SEHT)	4-6	5,904,504	3,396	7,203,495	0.174	-342.4	260-420	180-260	No
		Moderate pressure modified F-T process (Lurgi - Octamix)	4-6	5,904,504	3,396	7,203,495	0.174	-342.4	350	100	No
		Gas fermentation	6-8	5,904,504	3,396	7,203,495	0.152	N/A	37	1	No
	Methanol	Reaction over a Cu/ZnO catalyst	9	7,891,386	1,476	6,944,420	0.13	-128.5	240-260	50-100	No
		Methanation followed by partial oxidation	2-3	7,891,386	1,476	6,944,420	0.19	-128.5	180-240	1	No
Ethers	Dimethyl ether	Condensation then dehydration of methanol	9	?	?	?	0.17 - 0.26	8.2	250	17	Methanol
		Bifunctional catalyst allows conversion to methanol then dehydration to DME	2-4	?	?	?	0.17	-248.9	260	40	No

**Table 8. Potential fuels from CO with economic and environmental measures and rankings.**

Class	Product	Pathway	TRL	Market size (t/yr)	Market value (ÖM/yr)	CO utilisation potential (t/yr)	H <sub>2</sub> reliance (t H <sub>2</sub> /t product)	Reaction enthalpy (KJ/mol)	Reaction temperature (°C)	Reaction pressure (atm or bar)	Other carbon in product
Liquid hydrocarbons	Diesel	F-T reaction at 200-240°C to produce linear waxes. Hydrocracking converts to synthetic diesel	7-8	384,086,000	247,271	768,172,000	0.29	-2330.2	200-240	15-60	No
	Gasoline	F-T reaction at 300-350°C to produce gasoline-range hydrocarbons	7-8	146,243,000	100,042	286,636,280	0.3	-1610.7	300-350	15-60	No
		MTG process, via DME and olefins	6-8	146,243,000	100,042	286,636,280	0.30 - 0.44	-582.5	300-400	10-20	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 to produce ethanol, then oligomerisation and dehydration/hydrogenation to produce suitable hydrocarbons	5-6	63,928,000	31,215	126,577,440	0.259	(-400.3) or (-73.5)	370	250	No
		F-T reaction to produce kerosene-type hydrocarbons	9	63,928,000	31,215	126,577,440	0.294	(-2454.9) or (-2128.1)	200-240	15-60	No
		MTG-type reactions (syngas to gasoline plus, or STG+)	5-6	63,928,000	31,215	126,577,440	0.294-0.436	(-912.5) or (-585.7)	300-400	10-20	Methanol
Gaseous hydrocarbons	Methane	CO methanation over a nickel catalyst	9	338,511,000	193,229	592,394,250	0.38	-250.2	180-240	1	No
		Gas fermentation	1-2	338,511,000	193,229	592,394,250	0.313	N/A	37	1	No