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Abstract

This report evaluates post-capture CO_2 management options for the cement industry. A number of possible CCU products are evaluated according to metrics such as the energy demand, the technology readiness level and the market size.

Six scenarios were proposed and evaluated in this report, in order to illustrate of the options available for the reference CEMCAP cement plant.

1) CCS1: CO_2 capture from a cement plant in Belgium and injection in a saline aquifer in the Dutch continental shelf is estimated to cost 114 €/ton CO_2 avoided.
2) CCS2: CO_2 capture from a cement plant in costal Germany and injection in a saline aquifer in the Norwegian continental shelf is estimated to cost 153 €/ton CO_2 avoided. The difference between these two scenarios show the impact of the transportation mode and the distance between source and sink on the CO_2 cost.
3) CCS3: mineralization to $MgCO_3$ is expected to between 150 and 400 €/ton CO_2 avoided. The process efficiency, the transportation of rock and $MgCO_3$, as well as the heat demand,

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play an important role in the final cost. Further process developments and an optimized chain can bring the costs significantly down;

4) CCS1+U1: blue ethanol production using 3,1% of the emitted CO_2 requires 50 MW excess renewable power. The remaining fraction of the captured CO_2 (86,9%) is sequestered using CCS1. The total CCUS cost is 111 €/ton of CO_2 avoided (3% reduction as compared to CCS1) when blue ethanol replaces green ethanol from sugarcane. In case of replacement of green ethanol from wheat, the cost drops to 96 €/ton of CO_2 avoided (16% reduction as compared to CCS1).
5) CCS1+U2: by using 7,5% of the emitted CO_2, 288 kt/y of blue polyol are produced. 82,5% of the CO_2 is stored via CCS1. This configuration may lead to a positive business case, depending on the spread between the polyol market price and that of propylene oxide. If both prices are set as 1400 €/ton (zero spread), the CCUS chain leads to a profit of 18 €/ton CO_2 captured.
6) CCS1+U3: purifying 6,5% of the emitted CO_2 to food-grade (blue CO_2) and placing it in the food market lowers the integrated CCUS cost as long blue CO_2 replaces fossil-derived CO_2: in that case, the cost drops to 108 €/ton CO_2 captured. If green CO_2 is available (e.g. from fermentation), the CCUS option actually leads to a higher cost than CCS1: 120 €/ton CO_2 avoided.

Polyol and ethanol are representative of other CO_2 utilization routes, and the overall conclusions derived for these processes can be extended to high value specialties and fuels, respectively.

CO_2 utilization should always be considered in combination with storage. The fraction of the CO_2 that is utilized in a full scale CCUS implementation in a cement plant is expected to be lower than 10%.

High added-values products may lead to positive business cases. However. the number of cement plants that could benefit from this option will be strongly limited by the product's market.

The utilization of CO_2 to replace CO_2 intensive raw materials or products (e.g. ethanol from wheat or propylene oxide) lead to improved costs when the basis of calculation is CO_2 avoided. LCA should be conducted for the different technological routes, in order to take this important factor into consideration.

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1 INTRODUCTION

CO_2 is an abundant raw material that can be used as such – for instance as a working fluid, a supercritical solvent or a refrigerant; or as a feedstock for the production of chemicals or fuels. Although high purity CO_2 can be obtained, e.g. from ammonia production plants, it is typically available at low concentrations, around 10% by volume.
Driven by a green agenda and governments' commitment to reduce carbon footprint, many novel carbon capture and utilization (CCU) technologies to convert CO_2 into fuels, minerals or value-added chemicals have been reported.
Some representative products obtainable from CO_2 are shown in Figure 1-1, which highlights the carbon oxidation state and the nature of the atom it is bonded to. As shown in this figure, the carbon atom in CO_2 is in a high oxidation state (+4), which indicates it is a highly stable molecule. Reducing the oxidation state of the carbon atom requires energy and therefore, the processes of CO_2 utilization are typically energy intensive.

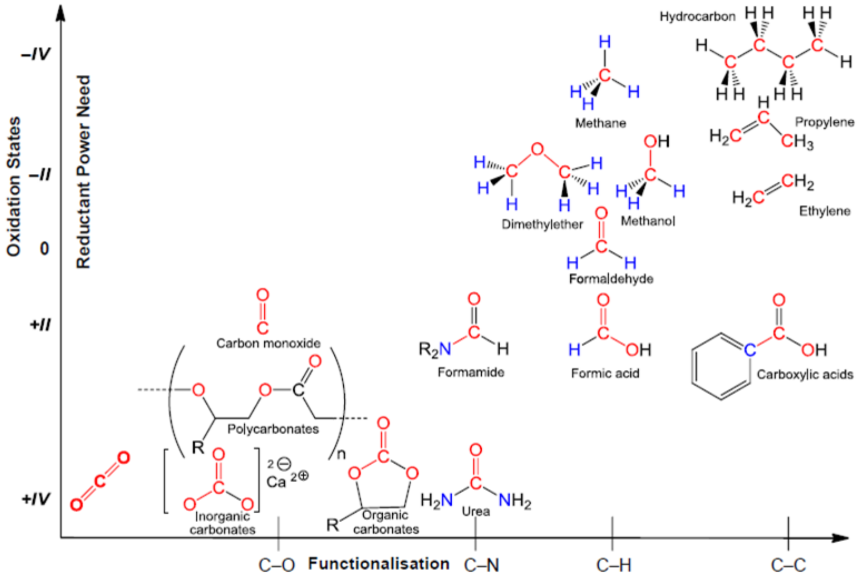

Figure 1-1: Products obtainable from CO_2 utilization reactions. Source: [1]

The current utilization of CO_2 (conversion into chemicals and other nonchemical applications) ranges around 200 Mt/y, with a possibility for escalating in the short-term to a maximum of 300 Mt/y CO_2. If the conversion of larger volumes is to be achieved, then the chemicals market will not suffice, and fuels – which have a much bigger market – or inorganic carbonates – which can be either utilized or disposed of – must be targeted as products. [2] Inorganic carbonates offer the opportunity of providing durable storage for the required time-scale of hundreds of thousands to millions of years, as their disposal leads to permanent fixation of the utilized CO_2 in the form of the carbonate.
As can be seen in Figure 1-1, producing drop-in fuels from CO_2 (e.g., methane, liquid hydrocarbons) requires a high degree of reduction, with the carbon molecule being hydrogenated. As a result, these processes are highly energy intensive. As a result, alternative fuels such as methanol, dimethyl ether and formic acid are proposed.
In a recent roadmap, the potential of CO_2 utilization in carbonate aggregates (for concrete), fuels, concrete, methanol and polymers adds up to 7 Gt/y by 2030. These 5 utilization routes are

forecasted to create a market of 800 billion US dollars. In this scenario, CCU accounts for the removal of 10% of the emitted CO_2 [3]. The potential for CO_2 utilization is shown in Figure 1-2.

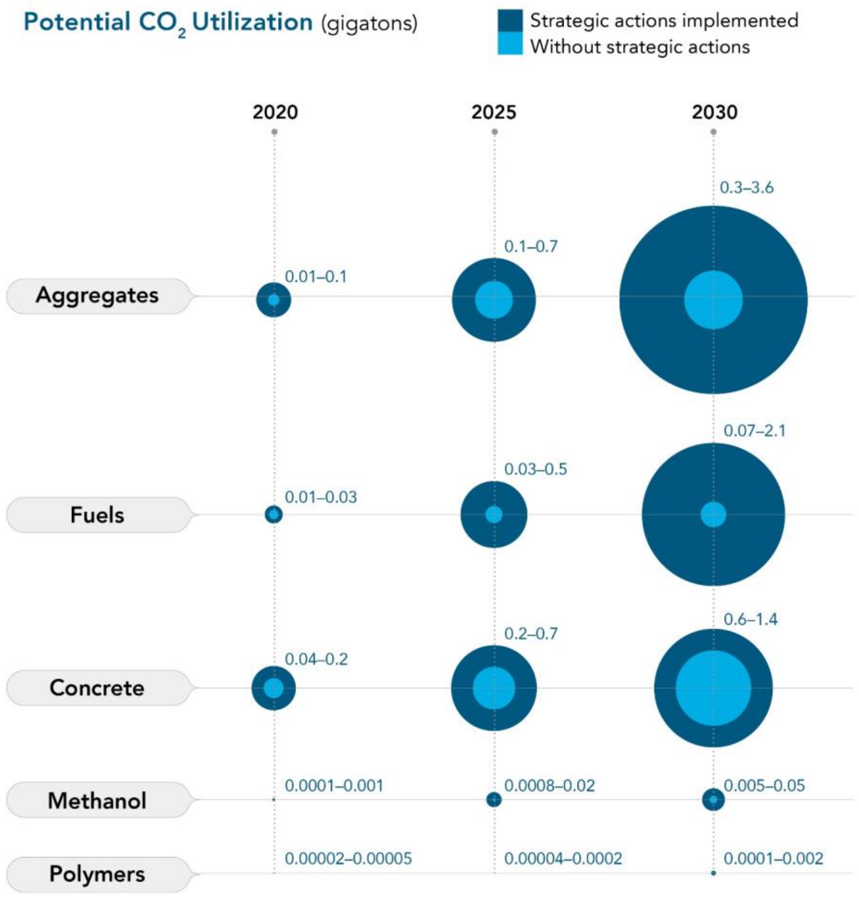

Figure 1-2: Potential CO_2 utilization in 2020, 2025 and 2030. Source: [3]

As the quantity of CO_2 avoided by CCU is limited by the product(s) demand, and given that the global emissions from the energy sector stood at 32.1 Gt in 2016 [4], carbon storage has to be complementary to CCU processes in order to achieve a significant decarbonisation through carbon capture.

The potential for CO_2 utilization in the production of any given product is a function of:

1) The energy demand (thermodynamic barrier, conversion, selectivity, efficiencies);
2) The technology readiness level (TRL) – defined in Table 2-1;
3) The market size.

For instance, methane has a very large market, and the technology for methane production from CO_2 and renewable hydrogen is nearly commercial. However, the thermodynamic barrier for converting CO_2 into CH_4 is high, which makes this process very energy intensive. Therefore, the feasibility of producing methane from CO_2 is dependent on whether a low-cost (or free) energy/hydrogen source is available (methane is discussed in detail in item 4.4).

On the other hand, while producing cyclic organic carbonates from CO_2 is much more favorable thermodynamically, these products have only a niche market, and the TRL level of sustainable routes is low (cyclic carbonates are discussed in detail in item 6.1).

Table 1-1: TRL level definitions

TRL	DEFINITION
TRL 1	basic principles observed
TRL 2	technology concept formulated
TRL 3	experimental proof of concept
TRL 4	technology validated in lab
TRL 5	technology validated in relevant environment
TRL 6	technology demonstrated in relevant environment
TRL 7	system prototype demonstration in operational environment
TRL 8	system complete and qualified
TRL 9	actual system proven in operational environment

This report aims at identifying CCUS processes that can lead to lowering the CO_2 emissions of the cement industry.

1.1 Characteristics of the cement industry

Cement, a mixture of calcium silicates, aluminates and aluminoferrite, is produced from a mixture of raw materials, in special limestone ($CaCO_3$). The cement industry is one of the major sources of CO_2, with emissions of 1.88 Gt in 2006, corresponding to about 5-6% of global anthropogenic emissions. About 60% of these emissions come from mineral decomposition (limestone to lime, CaO), and the remainder is from fuel combustion. In its roadmap for cement industry emission reductions, the IEA points to CCUS as the major contributor to emission reductions (56% by 2050, or 1.05 Gt of CO_2 per year) to be deployed from 2020 on [5].

1.1.1 Reference cement plant

The CO_2 concentration in cement plant flue gases is relatively high (20 to 25 mol%[1]). Typical capacities of cement plants are between 1 and 3 Mton/year. [6]. Within CEMCAP, a cement reference plant was defined based on the Best Available Technique (BAT) standard as defined in the European BREF-Document for the manufacture of cement. The reference cement plant exhibits a clinker capacity of 3,000 t/d, which corresponds to a yearly clinker production of 1 Mt of clinker, or a cement production of 1.36 Mt per year. The specific CO_2 emissions are 850kg/ton clinker, or 625 kg/ton cement. For more information on the reference cement plant, please refer to “D3.2: CEMCAP framework for comparative techno-economic analysis of CO_2 capture from cement plants”, which is publicly available online [7].

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[1] Concentrations are reported in a dry basis unless stated otherwise.

1.1.2 CCUS in the cement industry

The IEA target of reducing the emissions of CO_2 by 1.05 Gt/year is equivalent to capturing and sequestrating or utilizing 100% of the CO_2 produced in 1240 reference plants. Post-combustion capture plants are normally dimensioned to capture 90% of the CO_2 in the flue gas – in this case, achieving the IEA target would require that full scale CO_2 capture plants are installed in 1373 cement BAT plants. The best CCUS option for each cement plant is dependent on the plant location, as the local market demands and local availability of geological storage sites, for instance, will influence the economics of the CCUS chain.

There are different options for CO_2 capture, leading to different CO_2 qualities. Post-combustion and oxy-fuel are the options relevant for the cement industry [8]. Post-combustion capture typically uses amine scrubbing and produces CO_2 at high quality (99.9 mol% dry basis), while in oxy-combustion, the flue gas CO_2 concentration increases to typically 80 mol%. The calcium looping technology is under development for post-combustion capture in the cement industry. Within CEMCAP, a pilot scale test for calcium looping in a cement plant has been performed, thus bringing the technology up to TRL 6 [9]. The calcium looping technology also produces high quality CO_2.

Therefore, in a BAT cement plant,CO_2 is available at 2 different concentrations: 20-25% mol before capture and nearly 100 mol% after capture (amine scrubbing/calcium looping). For the oxy-fuel case, 80 mol% CO_2 is available.

1.2 Scope and structure of this report

This report gives a description of the many options of utilization and sequestration of CO_2. The report is divided in three parts, as illustrated in Figure 1-3.

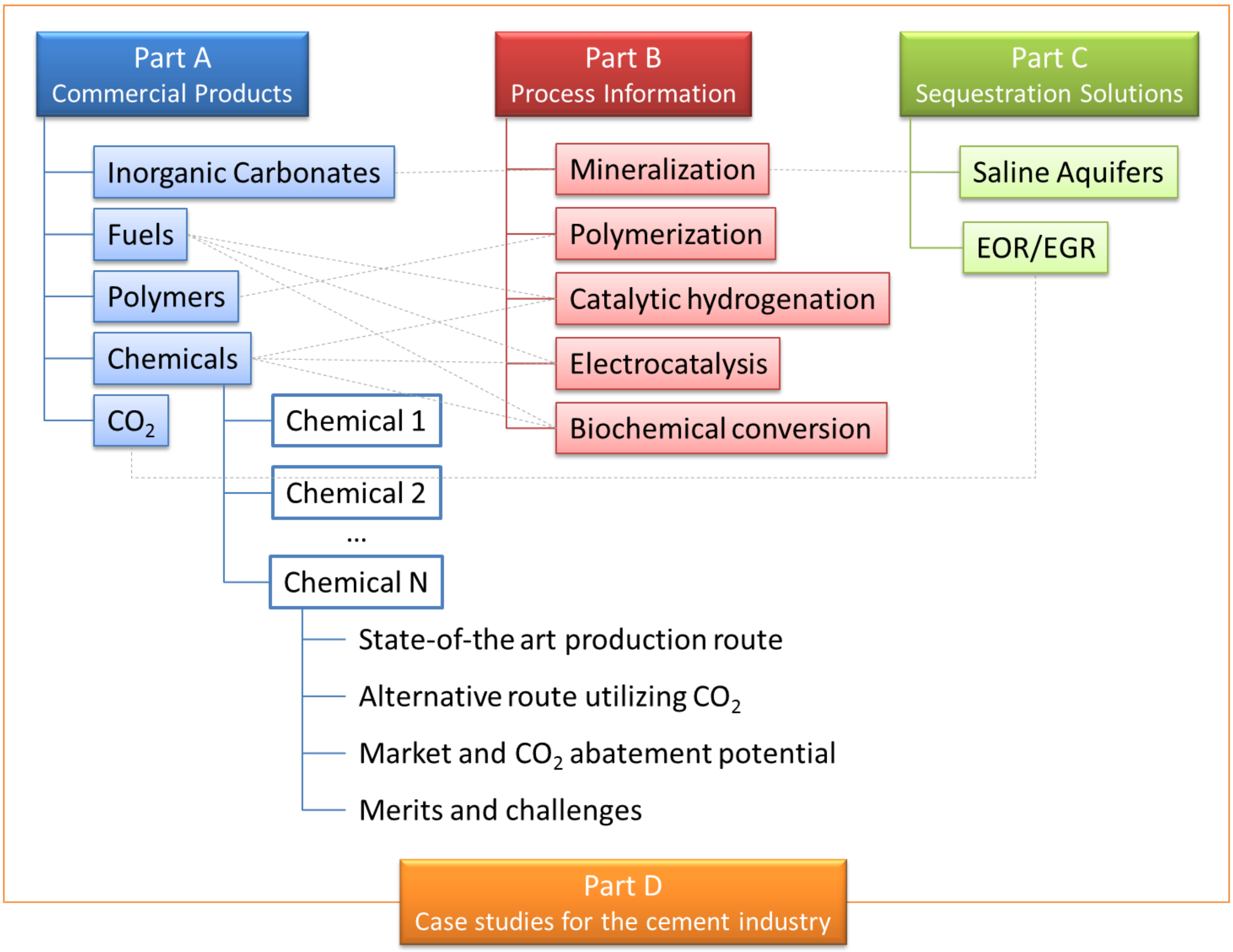

Figure 1-3: Structure of this report

Part A describes commercial products that are obtainable via CO_2 utilization. The products, mostly shown in Figure 1-1, are divided into 5 categories:

- *Inorganic carbonates*, such as calcium and potassium carbonates;
- *Fuels*, such as hydrocarbons, biodiesel, methanol and dimethylether;
- *Polymers*, such as polycarbonates and polyurethanes;
- *Chemicals*, including both specialties such as organic carbamates, and bulk such as ethylene; and
- *CO_2*, as a product on its own, such as food-grade CO_2.

For each product, a short market analysis is performed. The state-of-the-art technology of production and the alternative routes via CO_2 utilization are described. The product global market and the potential for CO_2 uptake are given, and these information are connected to the cement industry data in order to evaluate the merits and challenges of each product. Part A includes Chapters 2 to 7.

While the technological pathways for each product are specifically addressed in part A of the report, part B presents general descriptions of some of the researched technologies, namely

electrochemical conversion, catalytic hydrogenation and mineralization. Part B includes Chapters 8 to 11.
In part C of the report, the technological routes to CO_2 sequestration are discussed. The formation of inorganic carbonates is re-valuated from a sequestration perspective, and EOR I also discussed. Part C is discussed in chapter 12, and part D (chapter 13) presents case studies for the cement industry.

1.3 Approach

The data presented in this report is obtained by means of extensive literature review on each product/technology.

1.3.1 CO_2 uptake potential

Two terms are used in this report to describe CO_2 utilization, namely abatement and uptake potentials. The *CO_2 uptake potential* (CUP) of a certain technological route is defined by stoichiometry.

$$CUP(Mton/year) = \frac{CO_2\ consumed\ (kg)}{product\ (kg)} Product\ market\ (\frac{Mton}{year})$$

Hence, if 1 kg of product contains 0,4 kg of CO_2, and the product market is 2 Mton/year, then the CO_2 uptake potential is 0,8 Mton/year.

It should be highlighted that the CUP metric does not take into consideration the CO_2 emissions associated with the processes involved. Hence, producing methanol by CO_2 hydrogenation has a fixed CUP, regardless whether renewable fossil-derived hydrogen is used.

1.3.2 CO_2 abatement potential

The potential of a certain CCU route to lower the net emissions of CO_2 (herein referred to as *CO_2 abatement potential*, CAP) is very dependent on the technological route itself, and must be assessed by means of a life cycle analysis (LCA). Whereas LCA are generally not available for the routes evaluated in this report, some authors have performed partial analysis of the CO_2 emissions associated to factors such as energy consumption (e.g., heated reactors). Whenever available, the CAP metric is reported. It should be noticed, however, that different authors have used different methods to evaluate the CAP, making it a non-standardized metric.

CO_2-based fuels may displace conventional fossil fuel use, thus leading to CO_2 abatement. On the other hand, it should be assessed whether it is likely that CO_2-based fuels compete against other, more effective climate mitigation technologies and processes. In such case, treating all forms of CO_2 uptake technologies as *de facto* CO_2 abatement could have detrimental impacts on efforts to reduce emissions on the long-term [10].

Performing a LCA is beyond the scope of the present report. The indicative sink factor is used as a metric for duration of CO_2 storage in the product, as defined by the Zero Emissions Platform [10].

2 PART A: COMMERCIAL PRODUCTS (CCU)

Commercial CO$_2$ utilization is currently found in beverage carbonation, food industry, medical applications, urea synthesis, rubber/plastics or to mix gases/aerosols, among others. Meanwhile, CCU to fuels is still under development. Iceland has the first semi-commercial plant, which runs on geothermal energy to produce methanol from CO$_2$ (see item 4.1 for details). Table 2-1 gives an overview of existing CCU technologies discussed in this report and the associated TRL levels. The different colors indicate different maturity levels: red for $\text{TRL} \leq 5$; orange for $5 < \text{TRL} < 7$; and green $\text{TRL} \geq 8$.

Table 2-1: TRL of CCU technologies. Adapted from: [11]

CCU category	**Technology/application**	**TRL**
Fuels	Renewable methanol production	9
	Renewable methane production	9
	Production of “crude oil”	6
	Formic acid production	3-5
	Algae cultivation for biodiesel production	3-5
Minerals	Mineral carbonation	3-7
	Aggregates production	9
	CO$_2$ concrete curing (carbonated concrete)	9
Polymers	Polymer processing (polycarbonates)	9
	Polymer processing (polyols for polyurethanes)	9
Chemicals	Formic acid production	3-5
	Cyclic carbonates	3
Other existing commercial applications	Food and beverage applications	9
	Horticulture	9
	Other industrial uses	9

The Global Roadmap for Implementing CO$_2$ Utilization [3] has identified 180 actively engaged actors currently developing end-products from CO$_2$, including start-ups, mid-sized companies, corporations, consortia and research institutes. As can be seen in Figure 2-1, 70 of these actors are engaged in developing chemical intermediates. This is a logical finding, since chemicals intermediates normally have high added-value. In comparison, 28 actors target fuels, and 24 focus on building materials, such as carbonate aggregates and concrete curing. Algae cultivation (and processing for either biofuels or food additives) is under development by 21 actors, whereas 15 actors focus on polymers.

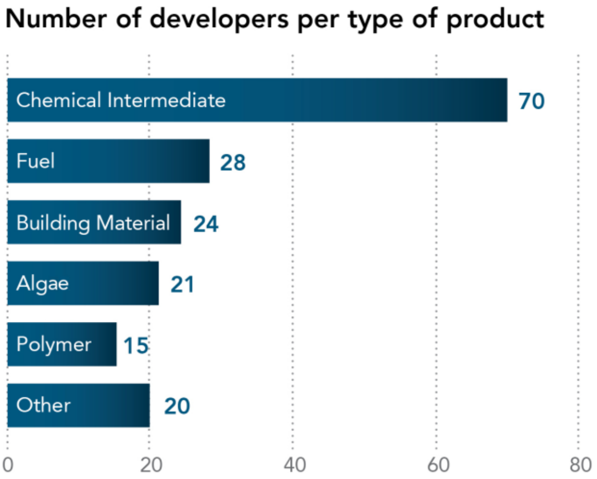

Figure 2-1: Number of developers per type of product. Source: [3]

In the following chapters, mineral carbonates, fuels, polymers, chemicals and purified CO_2 are discussed.

3 MINERAL CARBONATES

The products discussed in this chapter are calcium carbonate, construction aggregates and carbonated concrete.

3.1 Calcium carbonate ($CaCO_3$)

3.1.1 State-of the art technology for $CaCO_3$ production

The following process descriptions are based on information from the British Calcium Carbonates Federation [12]. Commercial calcium carbonate grades, in the form of powders, granules and slurries, are produced through the extraction and processing of natural ores or synthetically through chemical precipitation.

Ground calcium carbonate, commonly referred to as GCC, is primarily based on limestone, chalk and marble stone. The production process maintains the carbonate very close to its original state, ending up in a finely ground product delivered either in dry or slurry form (water based suspension). Generally, the processing includes washing, sorting of undesirable contaminants, grinding, size classification of particles and possibly drying. Depending on the circumstances and intended uses, the order and necessity of those different steps vary. Surface treatment of GCC is another aspect of adding value to the basic material. Such coatings aim to match the surface tension of calcium carbonate fillers with that of the compounds (e.g. thermoplastics) in which they are incorporated.

Precipitated Calcium Carbonate (PCC) is produced through a recarbonisation process or as a by-product of some bulk chemical processes. In the recarbonisation method, limestone is converted into calcium oxide (lime) and carbon dioxide by calcination at high temperatures. After calcination the lime is slaked with water and the resulting milk of lime is purified and re-carbonised with the carbon dioxide obtained directly from the calcination process.

This produces a water-based suspension of $CaCO_3$. A cake comprising up to 60% solid matter (depending on particle diameter) is then obtained by filtration. This filter cake is then dried and subsequently grinded. Depending on the chemical composition of the milk of lime used and on the purifying stages during production, food and pharmaceutical grades as well as technical grades can be produced. The fineness of the grain, as well as the morphology of the PCC crystals can be modified during the process by controlling temperature, concentration and time. There are three main crystal morphologies: Calcite, Aragonite, and Vaterite. Within each morphology, several crystal forms are possible. This opens up interesting possibilities of tailoring PCC products to specific use applications.

3.1.2 $CaCO_3$ production via CO_2 mineralization

3.1.2.1 PCC from calcium-rich ash waste stream: TRL 3

PCC can be produced via CO_2 mineralization using calcium-rich ash, a waste from the power industry containing ca. 32 wt% of free CaO [13]. A schematic of the continuous PCC production process is shown in Figure 3-1. The process operates at atmospheric pressure and room temperature, and was demonstrated to generate a crystalline product with $CaCO_3$ content from 91.6wt% to 99wt% and mean particle diameter in the range of 3.7 to 7.5 µm, depending on the gas-to-liquid ratio in the mineralization reactor.

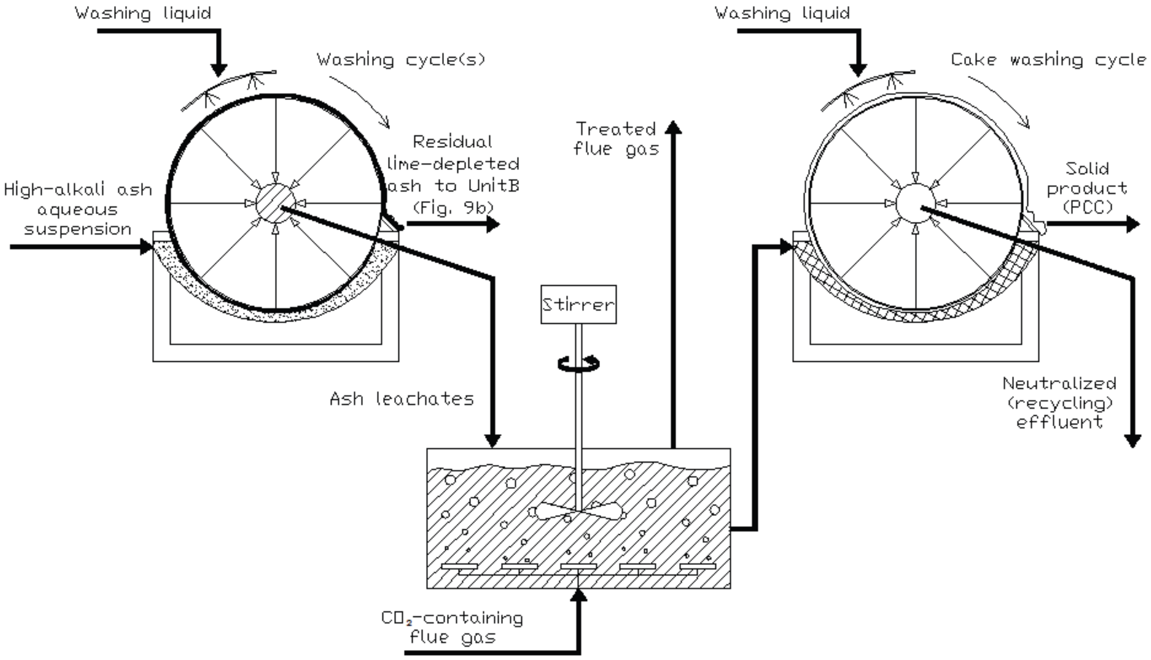

Figure 3-1: Simplified schematic of the continuous PCC production process on the basis of waste oil shale ash. Source: [14]

The power sector is responsible for producing large amounts (ca. 7 Mt/year) of calcium-rich waste ash in Estonia. The present waste ash management strategy is to hydraulically transport the residue for deposition in ash fields. The Baltic Thermal and Estonian Electric Power Plant ash fields near Narva are Estonia's largest waste handling sites and cover a total of 13 km^2. It is estimated that each tone of ash can bind up to 290 kg of CO_2. [13]. Hence, the ashes of the Estonian power sector would be enough to mineralize the CO_2 emissions from 2,4 reference cement plants.

3.1.2.2 Calera calcium carbonate powder – TRL 7

Calera Corporation has designed, constructed and operated two pilot plants to utilize the flue gas from coal-fired power plants to produce calcium carbonate. The flue gas is contacted in a scrubber with an aqueous alkaline solution that effectively removes the CO_2 (capture step) and a calcium source that results in the formation of the calcium carbonate product (PCC). After drying, the product. The company is currently looking to license its technology [15].

3.1.3 $CaCO_3$ market and potential for CO_2 uptake

The global calcium carbonate market is moderately concentrated. The top three players accounted for more than 35% of the market in 2012. Calcium carbonate is commercialized in two different forms: ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC). The paper industry is the main consumer of calcium carbonate (ca. 40% of the market), followed by the plastics industry (ca. 20%), paints & coatings, and adhesives & sealants. [16]. The global market of GCC was 75 million tonnes, and that of PCC was 14 M tonnes in 2012. The market is estimated to reach 98.7 million tons by 2020, which is equivalent to 43.4 millions

of tons of CO_2, or 4% of the IEA CO_2 emissions reduction target (of 1.05 Gt). This number represents the total emissions of 51 reference cement plants.
GCC prices vary widely, from ca. 25 to 350 €/ton, depending on the product particle size distribution. PCC prices are higher, varying between 350 to 520 €/ton. [17]

3.1.4 $CaCO_3$: merits and challenges

Merits
CO_2 mineralization requires solid processing technology, which the cement industry is familiar with.

Challenges
PCC and GCC have limited markets

3.2 Magnesium carbonate ($MgCO_3$)

3.2.1 State-of the art technology for $MgCO_3$ production

Magnesium carbonate is an ore used for production of a wide range of industrial minerals and compounds, as well as magnesium metal and its alloys. Magnesium carbonate is produced by mining. It occurs in two physical forms: cryptocrystalline (amorphous) and macrocrystalline.

3.2.2 $MgCO_3$ production via CO_2 mineralization

A number of processes are described in chapter 11. Demonstration projects are summarized in item 12.1.3, and the application to a reference cement plant is described in item 13.4.

3.2.3 $MgCO_3$ market and potential for CO_2 uptake

Commercial products are various forms of magnesia (MgO), such as calcinated-, fused-, and dead burned magnesia. When crude magnesite is heated to between 700°-1000°C, CO_2 is liberated, and calcinated magnesia (MgO) is obtained. Because of its ability to absorb heavy metals and ions, calcinated magnesia is useful in water treatment. When calcined magnesia is heated to between 1530°-2300°C, the non-reactive product exhibits exceptional stability and strength at high temperatures. This product known as 'dead-burned' or sintered magnesia is mainly used as a refractory material. Finally, when magnesia is heated in excess of 2800°C in an electric arc furnace, 'fused magnesia' is produced, and can be used in the manufacture of premium grade refractory bricks used in the high wear hot spots of Basic Oxygen Furnaces, electric arc or similar furnaces. [18]
The world magnesia market is estimated between 8 and 10 million tonnes per year. Dead-burned magnesia has a market share of 78%,while fuse magnesia responds for 22% of the market. The supply is concentrated in China (49%) and Russia (17%).
The current $MgCO_3$ market does not offer a potential for CO_2 uptake under the "commercial application" category. However, mineralization to $MgCO_3$ has a potential for CO_2 uptake for geological sequestration, as described elsewhere in this report (please refer to chapter 11, and items 12.1.3 and 13.4).

3.2.4 $MgCO_3$: merits and challenges

Merits
CO_2 mineralization requires solid processing technology, which the cement industry is familiar with. Long term sequestration period, indicative sink factor: 40-75% [10].

Challenges
Magnesite ($MgCO_3$) has limited market, and that is for the production of magnesia (MgO). However, when the oxide is produced, the captured CO_2 is emitted. Therefore, for effective sequestration, $MgCO_3$ cannot be utilized, and the claim that $MgCO_3$ has a market value is not valid. Other uses for $MgCO_3$ are being developed.

3.3 Aggregate

Construction aggregate, or simply "aggregate", is a broad category of coarse to medium grained particulate material used in construction, including sand, gravel, crushed stone, slag, recycled concrete and geosynthetic aggregates. [19] Aggregates are used as a means of stabilizing and reinforcement.

3.3.1 State-of-the-art technology for aggregate production

Aggregates are the most mined materials in the world, being produced in quarries. Preferably, limestone, granite, marble or other quality stone bedrock deposits are quarried for aggregate production. Wherever those deposits are not available, natural sand and gravel are mined for use as aggregate. [19]

3.3.2 Aggregate production via CO_2 mineralization – TRL 9

The accelerated carbonation of hazardous wastes is a controlled accelerated version of the naturally occurring process. The solid waste mixture is carbonated under a gaseous CO_2-rich environment, which promotes rapid stiffening of the product into a structural medium within minutes. [20]
Carbon-negative construction aggregates are manufactured by Carbon8 using this route. The company uses a CO_2 mineralization route that has been developed as a treatment for industrial wastes and contaminated soils. The first commercial plant is in operation at the Lignacite site in Brandon, UK (Figure 3-3). Lignacite uses the aggregates to manufacture a carbon-negative building block, ‘The Carbon Buster’ (see Figure 3-2), since 2013. The first production line was commissioned in February 2012 and a second line added in 2014 giving a total capacity for the plant of over 65,000 tonnes of aggregate product per year. [21], [22]

Figure 3-2: Lignacite's Carbon Buster. Source: [22]

Figure 3-3 Carbon8 aggregate plant at the Lignacite site in Brandon, UK. Source: [21]

The reaction takes place at ambient pressure and temperature. Purified CO_2 (>90 wt%) is preferable, but CO_2 rich gas streams with a minimum of 20wt% CO_2 could be used in the reaction [23]. This means that cement flue gas could be used without the need of a capture step.

3.3.3 Aggregate market and potential CO_2 uptake

Through 2017, worldwide sales of construction aggregates are forecast to expand 5.8 percent per year to 53.2 billion metric tons, from which more than 50% are crushed stones [24]. According to the CO_2 utilization roadmap, aggregates have the highest potential for CO_2 utilization amongst all the possible products in 2030: up to 3.6 Gton of CO_2. [3] This potential surpasses the target CO_2 emission reduction target of the cement industry.

3.3.4 Aggregate merits and challenges

Merits
The process involves solids handling, which is familiar to the cement industry. The product has its application in the construction business. The market size is relevant, and the IEA emission reduction target could potentially be achieved. Recycling waste materials as produce aggregates avoids mining for primary aggregates, which has multiple benefit to the environment. Long term sequestration period, indicative sink factor: 40-75% [10].

Challenges
As an accelerated version of a naturally occurring process (taking minutes instead of decades), the CO_2 uptake by aggregates production doesn't necessarily lead to CO_2 abatement over the product life cycle. On the other hand, avoiding mining for primary aggregates and recycling

waste instead has been shown to lead to lower CO_2 emissions [25]. A LCA is needed in order to evaluate the net effect.

3.4 Carbonated concrete

Concrete is the most consumed man-made material in the world. A typical concrete is made by mixing Portland cement (PC), water, and aggregate. Carbonated concrete differs from the traditional concrete in the chemical process used for the concrete curing (setting and hardening).

3.4.1 State-of-the-art technology for concrete production

Concrete production typically begins by mixing the dry (cement, sand and crushed stone) and the liquid (water and chemical additives) components of the concrete. Portland cement (PC) is commonly used. The water and chemical additives control the flow behavior of the concrete mixture while it is in the plastic stage. After mixing, the material can be formed into the final concrete part shape by casting, extrusion, rolling and pressing.

Concrete is cured in a series of hydration reactions which release of a significant amount of heat. These hydration reactions are responsible for the setting and hardening of concrete. The hydration of the calcium silicate components of Portland cement begins immediately after contact with water, but proceeds at a relatively slow pace. The curing of PC-based concrete can last up to 28 days, and roughly 70% of the cement particles are hydrated (under normal curing conditions and without chemical accelerators). [26] Addition of accelerators make the curing process much faster, and curing periods of less than 24 hours are achieved [27].

3.4.2 Carbonated concrete production via CO_2 mineralization

Solidia Cement™ is a cement composed primarily of low-lime, calcium silicate phases such as wollastonite/pseudowollastonite ($CaO \cdot SiO_2$). This contrasts with the high-lime phases that comprise ordinary Portland cement. Solidia cement is cured through a carbonation process, with $CaCO_3$ and SiO_2 as reaction products (for more details on the mineralization process refer to chapter 11). The curing of Solidia Cement™-based concrete is dependent on the diffusivity of gaseous CO_2 throughout the material, being a relatively fast process. Curing periods are comparable to that of curing by hydration using accelerators. [26] Carbon Cure™ also uses a CO_2 curing technology to produce carbonated cement.

3.4.3 Carbonated concrete market and potential CO_2 uptake

Solidia Cement™-based concrete can consume up to 300 kg of CO_2 per ton of cement during the curing process [26] resulting in about 48% reduction in CO_2 emission as compared to concrete from a BAT cement plant.
The concrete market was estimated in 20-30 billion metric tons in 2015, and the carbonated concrete market is forecasted to grow up to 16.5 billion metric tons by 2030 [3]. The cement content in concrete is variable, but assuming 10 wt% composition leads to ca. 0,5 Gt CUP in 2030.

3.4.4 Carbonated concrete merits and challenges

Merits

The product has its application in the construction business. The market size is relevant, and the IEA emission reduction target could potentially be achieved. Medium term sequestration period, indicative sink factor: 10-40% [10].

Challenges

Cement carbonation is a natural process. Over its lifetime, cement materials will be exposed to air and reacts with the available CO_2. Estimates indicate that this process was responsible for a cumulative uptake of 4,5 GtC between 1930 and 2013, thus offsetting 43% of the CO_2 emission from cement production over the same period [28]. Therefore, the production of carbonated concretes accelerates the CO_2 uptake process, but it does not necessarily leads to CO_2 abatement.

4 FUELS

The world's energy requirement is expected to reach about 28 TW in the year 2030. The Department of Energy of the USA predicted that if the solar irradiance of 1% of the Earth's surface is converted into storable energy (i.e., a liquid fuel) with 10% efficiency, it would provide a resource base of 105 TW. The current liquid fuels such as gasoline and diesel fulfil all the requirements for suitable energy storage, except emission of greenhouse gases [29].
The relevance of a fuel can be measured by the amount of energy that it is able to store both by weight and volume (gravimetric and volumetric energy densities). Figure 4-1 shows that the actual energy density of electricity storing batteries is very low when compared to that of liquid hydrocarbons and alcohols [29]. Other important factors to consider are the practicality of handling, transportation and storage, and safety handling parameters. The added bonus of a fuel's compatibility with the current energy infrastructure, so called drop-in fuels, is particularly relevant to shorten the timeframe of technology deployment. As strongly advocated by Surya Prakash, Goeppert and Olah, methanol and its associated product dimethyl ether (DME) rank high among these potential liquid fuels derived from renewable energy sources and using CO_2 chemistry [1].

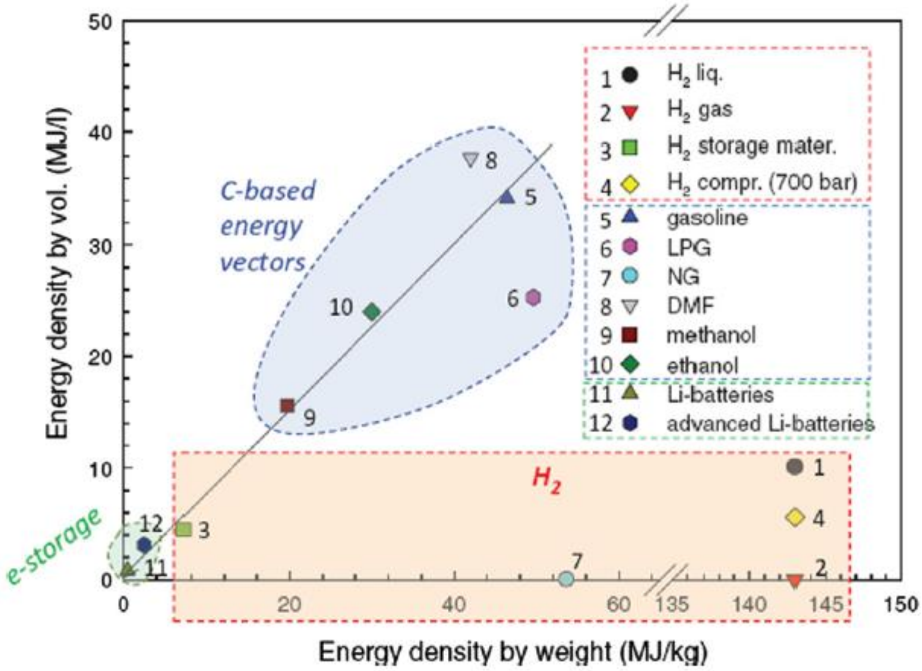

Figure 4-1: Energy density of liquid and gaseous fuels, as well as Li-batteries. Source: [29]

The CO_2-based liquid fuels market is under development, as can be seen in Figure 4-2. Carbon Recycling International (CRI), Sunfire and Mitsui Chemical are the most important players in this field. LanzaTech is also presented as a major player, but it should be emphasized that LanzaTech's technology converts CO – and not CO_2 – to ethanol.

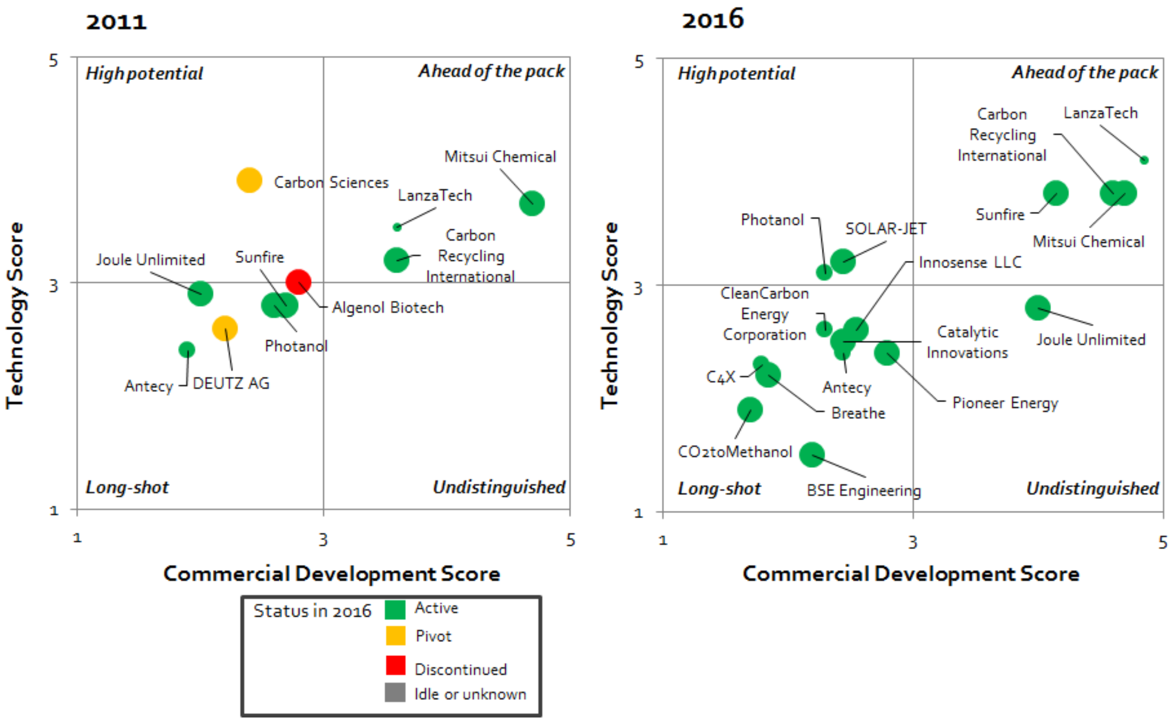

Figure 4-2: Liquid CCU fuels market in 2011 and 2016. Source: [3]

4.1 Methanol

Methanol, besides being a fuel, is a major intermediary in the chemical industry. By volume, methanol is one of the top five chemical commodities distributed worldwide, and is used for central feedstock productions such as formaldehyde and acetic acid. Since the late seventies, substantial research has looked at establishing methanol-to-olefin routes [1].

4.1.1 State-of-the art technology for methanol production

Methanol is commercially produced from synthesis gas ($CO + CO_2 + H_2$) using $CuO/ZnO/Al_2O_3$ catalysts [30]. Syngas is produced by natural gas reforming, so this is a fossil-fuel based technology.

4.1.2 Technologies for methanol production utilizing CO_2

4.1.2.1 Hydrogenation of CO_2 to methanol: TRL 8

The first studies of the CO_2-based methanol synthesis were carried out as early as the mid-90s and described the catalytic and reaction system in terms of reaction kinetics, mechanism, catalyst development and scale-up [31].
Methanol can be produced from CO_2 hydrogenation according to the following reactions. Eq. 1 and Eq. 2 describe the methanol formation reactions, while Eq. 3 is the reverse water-gas-shift (rWGS) reaction, that occurs in parallel.

$$CO + 2H_2 = CH_3OH \quad \Delta H^0_{298} = -90.7\ kJ/mol_{CO} \qquad \textit{Eq. 1}$$

$$CO_2 + 3H_2 = CH_3OH + H_2O \quad \Delta H^0_{298} = -49.5\ kJ/mol_{CO_2} \qquad Eq.\ 2$$

$$CO_2 + H_2 = CO + H_2O \quad \Delta H^0_{298} = +41.2\ kJ/mol_{CO_2} \qquad Eq.\ 3$$

The catalytic hydrogenation of CO_2 to methanol produces much more water than during the commercial production of methanol via synthesis gas. Furthermore, the thermodynamics for methanol production from H_2 and CO_2 are not as favorable as those for production of methanol from syngas. For example, the equilibrium yield of methanol from CO_2 at 200ºC is slightly less than 40% whereas the yield from CO is greater than 80% [30].

Using a H_2/CO_2 ratio equal to 3, the equilibrium CO_2 conversion is 27% and the methanol selectivity is 68% at 250ºC and 50 bar. High pressure, ca. 300 bar, is required to achieve high CO_2 conversion (>80%) at 125ºC.

In spite of the difficulties imposed by thermodynamics, after decades of efforts in exploiting effective catalyst materials and developing advanced reactors, catalytic CO_2 hydrogenation has become technically competitive with the industrial production of methanol from syngas [32]. Cu, Zn, Cr, and Pd are commonly used to minimize by-product formation (i.e. hydrocarbons) and maximize methanol yield and selectivity. Among these, Cu/ZnO catalyst is well-known for its high activity and selectivity for the methanol synthesis reaction. A support such as Al_2O_3 can further increase the activity and selectivity [30]. Such catalyst is commercially available. Improved catalysts based on Cu/ZnO containing various additives in addition to alumina (ZrO_2, Ga_2O_3, and SiO_2) have been reported. These additives improve the specific activity, active surface area (dispersion), thermal stability, and long-term stability (sintering of support and active phases), but water tolerance is generally not discussed [33].

A conceptual process flowsheet for the production of methanol via catalytic hydrogenation of CO_2 is given in Figure 4-3.

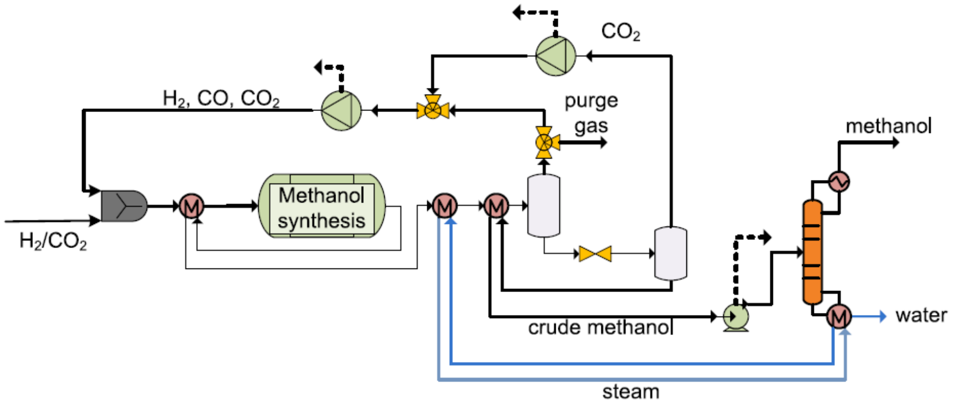

Figure 4-3: Process flowsheet Methanol production via CO_2 catalytic hydrogenation. Source: [34]

A novel process for methanol synthesis by CO_2 hydrogenation has been proposed to address the issue of high water content. The proposed process uses a stripper column to separate the products – methanol and water – from the reactant media, thus shifting the reactions depicted in Eq. 1 to Eq. 3 towards the products. Additionally, because of this process feature, the low-value water-saturated hydrogen obtained as a by-product in the chloralkali production becomes a feasible raw material for the hydrogenation. The process modification leads to significantly higher overall conversion of CO_2: from 95.2% to 99.8%, while lowering electricity and steam usage [35].

Further catalyst development may also help address the high water content issue. It has recently been showed that In_2O_3 catalysts inhibit the rWGS reaction, leading to higher methanol yield [36].

Pilot scale experiments: TRL 6

The MegaMethanol® process plants are commercially available for production of at least 5000 tonnes of methanol per day. The first Lurgi MegaMethanol® plant started up in fall 2004 [31], and since then nearly 20 licenses have been signed, with acceleration over the last months [37]. A pilot plant of Lurgi MegaMethanol® process, situated at Air Liquide Forschung und Entwicklung (ALFE) in Frankfurt, was used for evaluating the CO_2 hydrogenation to methanol. The MegaMethanol® technology is designed to convert syngas to methanol over a commercial Cu/ZnO catalyst (Süd-Chemie, Germany). The reactor has a heated jacket that is kept at 250ºC, operates at 70 bar and the gas hourly space velocity is 10500 h^{-1}. The recycle ratio is 3.6 [31].

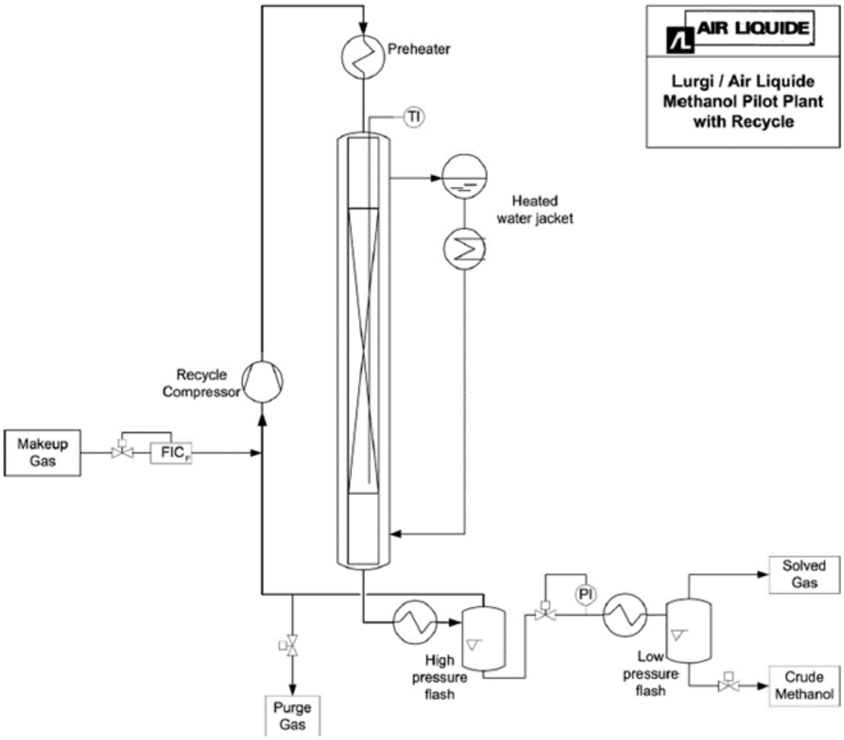

Figure 4-4: MegaMethanol® pilot plant in ALFE, Frankfurt. Source: [31]

For the CO_2 hydrogenation pilot runs, the same catalyst, jacket temperature and GHSV were used. The pressure was increased to 80 bar, and the recycle ratio was increased to 4.5. The H_2:CO_2 ratio was 3:1. The results of the pilot campaign are shown in Table 4-1, as compared to the results obtained in a reference campaign using standard syngas. As expected, the water content of the CO_2 hydrogenation was significantly higher. However, the formation of other by-products was lower.

In a direct comparison with syngas standard process, the CO_2 hydrogenation is not competitive under the given conditions. However, using a tuned catalyst or adapting the process so that water

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and methanol are separated from the recycled reactants could lead to more promising results. The CO_2 hydrogenation campaign lasted 700h, under which the productivity remained stable.

Table 4-1: Results from Megamethanol® pilot plant campaigns. Adapted from [31]

Process	Selectivity to Methanol (%)	Water content (%)	Other by-products (ppmw)	Temperature peak (ºC)
Standard syngas	87 (99.82)[a]	12.8	1800	283
CO_2:H_2 = 3:1	63.9 (99.96)[a]	36.1	390	ca. 260

[a] Excluding water and only taking the other by-products into account

Demonstration and commercial scale production of methanol from CO_2: TRL 7-9

Carbon Recycling International (CRI), in Iceland, operate a commercial scale methanol plant since 2011. The plant, connected to the Svartsengi geothermal power plant, has capacity of producing 4000 tons of methanol per year, by hydrogenating 5500 tons of CO_2 per year. A larger plant with capacity 40000 t/y is planned [38].

Figure 4-5: CRI's George Olah Renewable Methanol Plant in Svartsengi. World's Largest CO_2 Methanol Plant. Source: [39]

Mitsui Chemicals installed a plant with capacity of 100 t/y of methanol in Osaka. The plant synthetizes methanol from CO_2 (captured from factories nearby) and H_2 (from water photolysis). The methanol is used to produce olefins and aromatics. [40] Mitsui demonstrated the methanol synthesis under relevant industrial conditions in this plant in 2010.

Since then, Mitsui has been busy examining business models for improving commercialization accuracy. The company has concluded that securing hydrogen supplies is "a major hurdle" and is looking into biomass-derived hydrogen to overcome this problem [41].

4.1.3 Methanol Market and CO_2 uptake potential

Nobel laureate George Olah is an advocate of "the methanol economy" [42]. Methanol is a rather flexible product, being not only a fuel in itself, but also a precursor of many fuels and chemicals.

The current methanol market is 80 million metric tons (in 2016), and the increase in the use of methanol as fuel and in MTO technology is expected to expand the global demand to ca. 100 million metric tons by 2020 [43], as can be seen in Figure 4-6, and to up to 160 million metric tons by 2030 [3].

Source: IHS Chemical

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Figure 4-6: Methanol demand by region. Source: [43]

While some methanol derivatives already have large established markets (olefins, gasoline, formaldehyde), others are expected to gain space in the near future (DME in LPG blends and as diesel substitute). It is expected that by 2030, 30% of the produced methanol will be used as fuel [3].

The increasing methanol demand creates a great potential for producing sustainable methanol. Besides, methanol production is the most mature CO_2 utilization technology via hydrogenation. Therefore, it seems reasonable to expect that in the short-term the implementation of CO_2 utilization routes to produce fuels will include methanol production.

If the entire market of methanol (80 Mt/year) would be based on CO_2 hydrogenation, a total of 110 Mt of CO_2 would be utilized in the reaction. This is equivalent to 130 reference cement plants, of 10% of the target utilization.

The CO_2 utilization roadmap predicts a maximum CO_2 utilization for methanol production (as a chemical intermediate) of 50 Mt/year by 2030, or about 46% of the methanol total market [3]. This is equivalent to the CO_2 emissions of 59 reference cement plants. The total CO_2 utilization in fuels is projected up to 2,1 Gt/year in 2030. It is unclear which fraction of this total would be due to methanol, but the roadmap identifies methanol as the closest CO_2-based fuel achieve to production scale.

4.1.4 Methanol: merits and challenges

Merits

- Methanol is the easiest alcohol to synthetize from CO_2. The TRL level of CO_2 hydrogenation from methanol is high (7-8).
- Methanol already has an established market, which may grow substantially in case of the “methanol economy” development.
- Methanol production from CO_2 is expected to consume up to 2M ton/year by 2030 (methanol as a chemical intermediate).
- If the methanol is largely adopted as a fuel, it has the potential of mitigating 100% of the emissions of the cement industry.

Challenges

The production cost of methanol from coal or methane is 80 €/ton [2], whereas the methanol price in Europe is ca. 250-300 €/ton. On the other hand, the economic evaluation of methanol production via CO_2 hydrogenation leads to costs between 370 and 900 €/ton [44], using different sustainable hydrogen sources (see Figure 4-7). Therefore, producing methanol from sustainable hydrogen sources is still not economic. Scenarios with free hydrogen lead to positive business cases, with methanol costs between 130 and 180 €/ton [44]. The break-even hydrogen price is around 900 €/ton, which is close to the cost of hydrogen produced by steam methane reforming (see chapter 8).

The production of methanol via CO_2 hydrogenation can be either carbon neutral or lead to an abatement of ca. 0.5 ton CO_2 per ton methanol produced, depending on the source of electricity used to produce hydrogen (wind, solar, biomass and hydro)[44], as in depicted in Figure 4-7. The comparison to conventionally-produced hydrogen (SMR-H_2) evidences the potential of the sustainable routes. However, securing sustainable hydrogen sources is still a challenge [41].

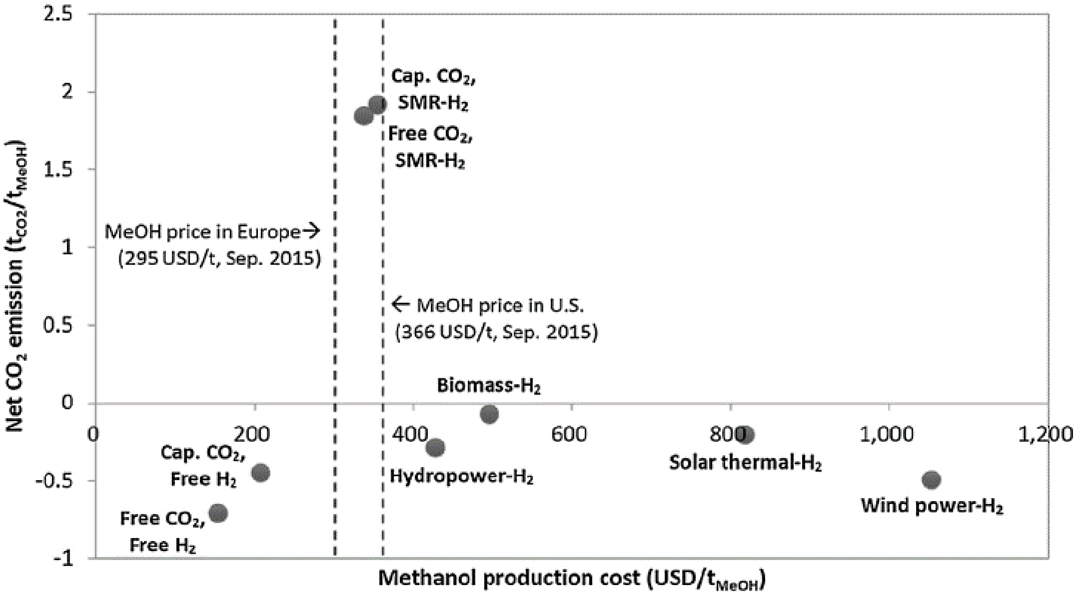


Figure 4-7: Methanol production net CO_2 emissions and costs. Source: [44]

Methanol has short term sequestration period, indicative sink factor: 0-10% [10].

4.2 Dimethyl ether (DME)

The first and simplest downstream product from methanol is obtained by dehydration: two molecules of methanol yielding one molecule of dimethyl-ether (DME). Historically, DME has been used as a propellant for aerosol sprays in personal-care products, paints, coatings, food products, and other applications. DME is also a clean-burning fuel, that can be used as a substitute for diesel or as a LPG supplement [31], [33].

4.2.1 State-of-the art technology for producing DME

The process for converting pure methanol into DME is well known since decades. Typically γ-Al_2O_3 is used as catalyst. Depending on the temperature and the water content of the reactor inlet typically temperatures of 250–400ºC are applied to achieve per-pass methanol conversions of 70–85%. The increased interest in DME offers opportunities for proposing process improvements specially for large scale production capacities (above 3000 t/d). The Lurgi MegaDME® technology was developed to achieve large single train capacity and high process and energy integration [31].

4.2.2 Technologies for DME production from CO_2

4.2.2.1 Methanol dehydration: TRL 9

Methanol dehydration to DME can be performed independently from the methanol production route. Therefore, the DME market can be a very interesting outlet for the CO_2-based methanol.

4.2.2.2 Direct DME production: TRL 3

Laboratory scale runs show that it’s possible to tune a hybrid catalyst so that CO_2 hydrogenation to methanol and subsequent methanol dehydration to DME can be performed in one unit operation, achieving CO_2 conversion up to 24% and high rate of methanol dehydration at 240ºC and pressure between 30 and 50 bar [45]. The relevant reactions can be represented as in Eq. 4 and Eq. 5, which evidences the consumption of 6 hydrogen molecules for each DME molecule formed. Moreover, the formation of 2 water molecules in the first reaction step is clearly detrimental to the second reaction step (dehydration) [46].

$$2CO_2 + 6H_2 \xleftrightarrow{Cu.ZnO} 2CH_3OH + 2H_2O \qquad \text{Eq. 4}$$

$$2CH_3OH = CH_3OCH_3 + 2H_2O \qquad \text{Eq. 5}$$

Studies on direct DME synthesis focus on the reaction conditions and fundamentals of catalysis (catalyst, promoters and support characterization) [45], [46], while the problem of water removal is addressed by proposing the integration of a water-selective membrane in the DME synthesis reactor [47].

4.2.3 DME market and CO_2 uptake potential

The global DME capacity has expanded from 10 kt/y in 1993 to 8 Mt/y in 2016. The growth was mainly driven by increasing demand in the Asia-Pacific region. China accounts for more than 80% of the global demand. Currently, the production facilities are concentrated in China, with few capacities in Japan, Germany, The Netherlands and the U.S [43], [48].
The International DME Association (http://www.aboutdme.org/) defines DME as the 21st century energy. There are prototypes of vehicles running on DME, including a Ford Mondeo and Volvo truck. In Japan, Fuel DME Production Co. Ltd. produces 80 thousand tons of DME per year. The company was established as a joint venture of nine companies (Mitsubishi Gas Chemical, ITOCHU, JAPEX, Taiyo Oil, Total Di-Methyl Japan, Toyota Tsusho, JGC, Mitsubishi Heavy Industries and Mitsubishi Chemical) aiming at promoting the wide-spread of DME as fuel.

Figure 4-8: Fuel DME production Co. produces 80 kton DME per year. Source: http://www.aboutdme.org/

Due to stoichiometric of Eq. 5, each tonne of CO_2 leads to the production of 523 kg of DME. Hence, the global CO_2 uptake potential is currently 15.3 Mt/year. This is equivalent to 18 reference cement plants, or 1.5% of the CO_2 utilization target. If DME becomes a drop-in fuel, this potential can be much increased.

4.2.4 DME: merits and challenges

Merits
DME can be synthetized from methanol using commercially available technology. Therefore, if green methanol is produced from CO_2, green DME can be easily obtained. The market of DME is small, but has the potential of growing quickly if it is adopted as a fuel or an additive to diesel. Prototype vehicles already run on DME.

Challenges
All the challenges related to hydrogen cost and availability debated in item 4.1.4 also apply to DME. The technology for producing DME directly from CO_2 and H_2 (process intensification) has low TRL level (3). Short term sequestration period, indicative sink factor: 0-10% [10].

4.3 Hydrocarbons (except methane)

Hydrocarbons generally occur as mixtures, not only in the nature, but also in the synthesis processes such as Fischer-Tropsch, or Methanol to Olefins/Gasoline. Therefore, hydrocarbons mixtures are treated as a single product in this report. As an exception, methane is discussed separately in item 4.4.

4.3.1 State-of-the-art production of hydrocarbons

Hydrocarbons occur naturally in crude oil and natural gas (fossil fuels), and are mainly produced by oil and gas exploration and processing. These activities are well-known and widely described in literature, and therefore are not discussed in this report.

4.3.2 Technologies for hydrocarbons production from CO_2

4.3.2.1 Synthesis of HCs via Fischer-Tropsch synthesis: TRL 3-6

The direct CO_2 hydrogenation to hydrocarbons is a combination of two reaction steps. First, CO_2 is reduced to CO via reverse water-gas shift (RWGS) and subsequent CO is hydrogenated to hydrocarbons via Fischer–Tropsch synthesis (FT) [49]. The indirect route differs from the direct one because separate reactors are used. The intermediate product in case of the indirect route is syngas and/or methanol. While the direct route has the potential to be more economic and environmentally benign due to process intensification, the indirect approach is preferred when targeting light paraffins as products [49].

The relative competition between CO and CO_2 is an important aspect to consider, and requires modifications to the traditional FT catalysts. Co-based catalysts form high amounts of methane, while Fe-based catalysts give better results, comparable with those obtainable when producing HCs from syngas [33]. The water formed in the reverse water-gas shift reaction inhibits the FT reactions, lowering the reaction rate. Therefore, removing H_2O in situ is also relevant for this technology[50].

The equilibrium conversion has been calculated to be 72%, but in general, actual conversion levels over iron catalysts reported range from 19% to 68%. The range of conversion levels can be explained by differences in the experimental conditions, reactor design and catalysts.

Similarly to FT technology, the catalysts for CO_2 hydrogenation to HCs can be tuned to maximize the selectivity towards desired products. For instance, addition of Mn or Cu to an iron catalyst suppresses methane formation and increases the alkene/alkane ratio. Addition of potassium has been demonstrated to increase CO_2 conversion and decrease the methane yield. While for FT larger amounts of K are known to poison the iron catalyst, in CO_2 hydrogenation it is beneficial to have a larger amount of this promoter [50]. K/Fe atomic ratio of 1 has been shown to selectively lead to olefins in the C2-C4 range [51].

It is noteworthy to mention that methane is thermodynamically the most favored HC product while selectivity to alkene in the C2–C5+ range of around 80% is commonly reported [50]. Recently, by the use of advanced nanocatalysts, the direct route was tuned to produce C5-C11 hydrocarbons (gasoline range) with a selectivity of 78% (conversion of 30%) [49].

Other process conditions, such as residence time and pressure will also influence on the quality and quantity of the obtained products. Elevated pressure favors long-chain products and lowers the olefin/paraffin ratio [50]. An example of the achieved CO_2 conversion and hydrocarbon distribution is given in Figure 4-9, as a function of the proximity of the two components in the multifunctional catalyst.

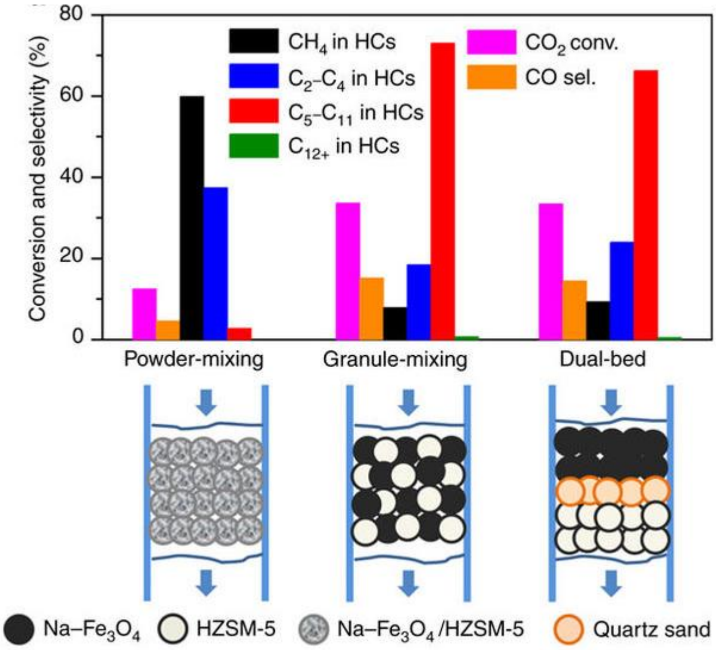


Figure 4-9: CO_2 conversion to hydrocarbons over Na-Fe3O4/HZSM-5 catalyst. Source: [49]

Sunfire's technology demonstration – TRL 6
Leading the market of hydrocarbon's production via CO_2 hydrogenation, Sunfire has developed and demonstrated a process for generating a synthetic crude oil which can be refined for producing waxes, gasoline, diesel and kerosene. Three tons of "blue crude" were produced in a plant in Dresden, via a power-to-liquid route, meaning that the hydrogen was obtained via water electrolysis. The plant operated for 1500h, consuming almost 10 tons of CO_2. The refined product (e-diesel) was successfully tested by the car manufacturer AUDI AG. In July 2017, the first commercial Blue Crude plant was announced. The operation is scheduled to start in 2020, producing 8000 tons of Blue Crude per year. The targeted price per liter is below 2 euros/liter. [52].

4.3.2.2 Indirect synthesis of HCs via methanol, multistage approach: TRL 9

The idea of converting methanol to hydrocarbons is not new, nor restricted to the CO_2 utilization theme. In fact, commercial technologies are available, as ExxonMobil's proprietary methanol-to-gasoline (MTG) technology, which produces ultra-low sulfur gasoline. In the MTG case, methanol is first produced from natural gas. Air Liquide markets and licenses its proven Lurgi MegaMethanol^{TM} technology combined with ExxonMobil's MTG. The combination of technologies is marketed under the trademark G2G^{TM} [37].
The methanol-to-olefins (MTO) process is an alternative approach to producing light olefins (ethylene and propylene) from methanol feedstock. UOP LLC and Norsk Hydro A/S commercialize an MTO technology that synthesizes olefins from methanol using a SAPO-34-type zeolite catalyst in a fluidized-bed reactor.
As previously discussed, Mitsui Chemicals installed a plant with capacity of 100 t/y of CO_2-derived methanol. The company intention is to use the methanol to produce olefins and aromatics. [40]

4.3.3 Hydrocarbons market and CO_2 uptake potential

Oil is the most traded commodity in the world. The current crude oil production is around 80 million barrels per day, which corresponds to about 11 million tonnes per day. CO_2 emissions due to oil use as a fuel were 3,3 Gt C/y in 2015 (Figure 4-10), which converts to 12,1 Gt CO_2/y. As can be clearly seen in the graph below, the oil-related emissions are much higher than those from the cement industry.

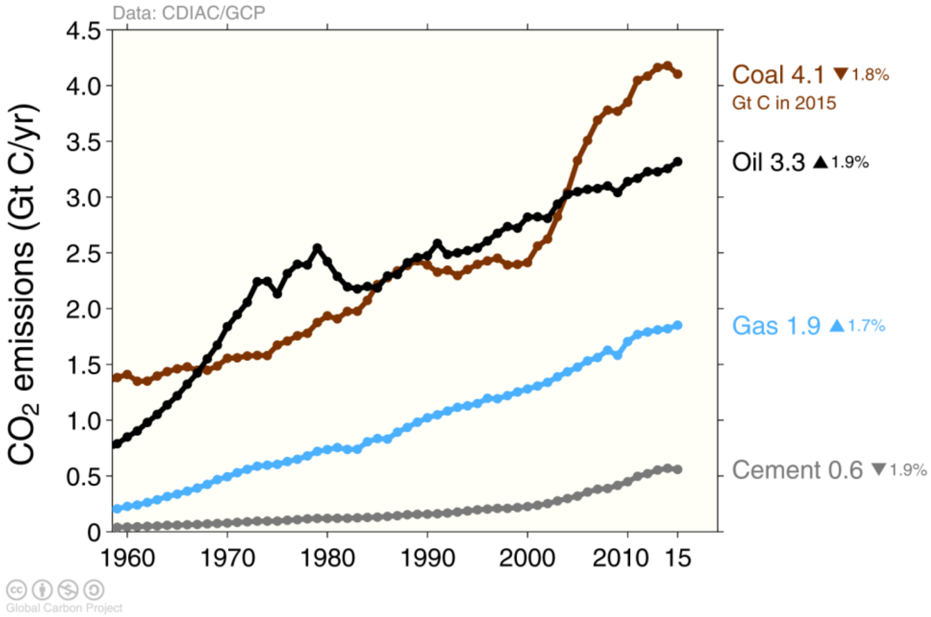


Figure 4-10: 2015 CO_2 emissions. Source: [53]

The Global Roadmap for Implementing CO_2 Utilization [3] predicts a maximum of 2,1 Gt/y of CO_2 being utilized for the production of fuels. By capturing 1.05 Gt CO_2/year (IEA target reduction for the cement industry) and converting it to hydrocarbons, about 470 Mt of hydrocarbons could be produced each year. This represents 12% of the hydrocarbons market. Of course that the range of hydrocarbons obtained from CO_2 hydrogenation is variable, from light hydrocarbons (C2-C5) to gasoline cut ones (C5-C11). While C5+ hydrocarbons are fuels, light olefins (ethylene, propylene and butylenes) are raw materials in the petrochemical industry, as illustrated in Figure 4-11, leading to polymers and chemicals.

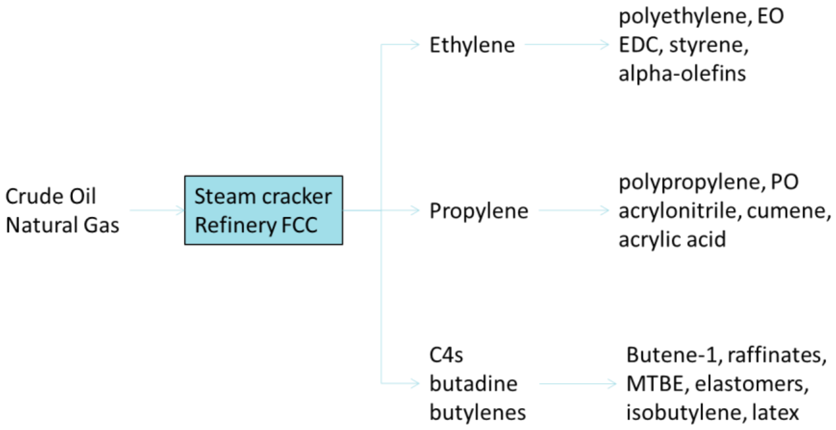


Figure 4-11: Product chain of light olefins (C2-C4)

4.3.4 Hydrocarbons: merits and challenges

Merits
Converting CO_2 or to products like gasoline, diesel or light alkanes has a clear advantage over any other utilization technological route: these products are drop-in fuels and chemicals that therefore face no challenges regarding infrastructure or public acceptance.

Challenges
In general, the production of hydrocarbons from CO_2 requires a more intensive use of the resources (energy, H_2, more reaction steps, etc.) as compared to producing oxygenated products like methanol. Thus, the production of HCs is in principle a less favorable route for the production of fuels. [33] As fuels, hydrocarbons have short term sequestration period, indicative sink factor: 0-10%. [10].

4.4 Methane

4.4.1 State-of-the-art production of methane

Methane is the main constituent of natural gas, and is produced in natural gas processing units. This activity is well-known and widely described in literature, and therefore is not discussed in this report.

4.4.2 Technologies for methane production from CO_2

The technology of storing electricity by producing hydrogen via water electrolysis and subsequently performing CO_2 hydrogenation to methane is kwon as Power-to-Gas (or PtG) PtG development has progressed significantly in Europe. Technology developers ETOGAS, Audi and Electrochea are near commercialization. A recent review shows the number of PtG projects distributed by country and technology, as seen in Figure 4-12.

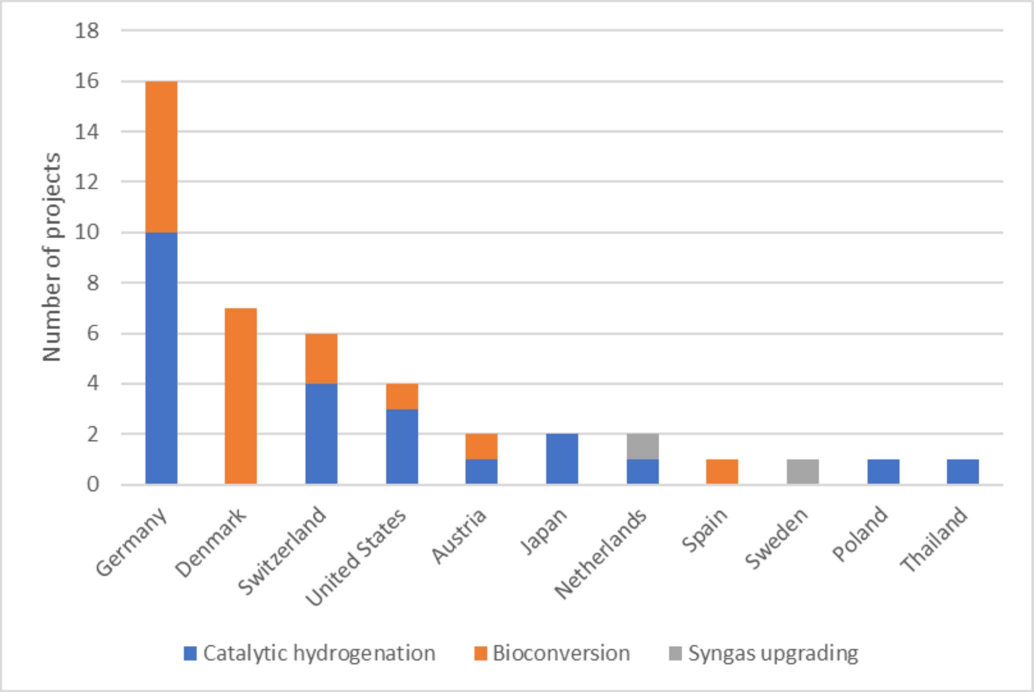


Figure 4-12: Existing PtG projects distributed by country and technology. Adapted from [54]

4.4.2.1 CO_2 catalytic hydrogenation: TRL 9

CO_2 hydrogenation to methane occurs via a different technological route as compared to other hydrocarbons, the Sabatier reaction (Eq. 6), and methane production is therefore treated separately in this report.

$$CO_2 + 4H_2 = CH_4 + H_2O \quad \Delta H^0_{298.15} = -164.747\ kJ/mol \qquad \text{Eq. 6}$$

In the past decades, extensive research on CO_2 hydrogenation to methane have been reported, aiming at designing active catalysts, such as supported Ni, Ru, Rh, Pd Co, Fe and Cu. Recently, it was demonstrated that nickel-impregnated metal-organic frameworks can have high activity, reaching CO_2 conversion of 47% at 280ºC, and 75% at 300ºC. In both conditions, the reaction was 100% selective towards methane [55].

Ni-based zeolite catalysts can be tailored to have an intensified sorption function, thus having a high affinity to water. This property can be used for the hydrogenation reaction benefit by actively removing the water obtained as by-product from the reaction centers.

ETOGAS – Audi e-gas: TRL 9 [54]

The Audi e-gas plant in Werlte (Germany), is the largest industrial PtG plant in the world (6 MWe). It is based in the catalytic methanation of pure hydrogen and carbon dioxide in a single isothermal fixed-bed reactor. The electrolysers are powered by an offshore wind park in the North Sea, with 4 turbines of 3,6 MW each. The high purity CO_2 is captured from a nearby biogas plant by amine scrubbing [54].

The PtG plant has a total efficiency of 54%, obtaining synthetic natural gas (SNG) with 13,85 kWh/kg. The renewable electricity is available for 4000h/y, leading to a production of 1000 t per year of SNG [54].

4.4.2.2 Biological conversion: TRL 8

In the BioCat Project a commercial-scale power-to-gas facility has been constructed. The facility uses an alkaline electrolyzer (1MW) and a biological methanation system (using a proprietary bioreactor developed by Electrochaea.dk ApS) to produce pipeline-grade renewable gas for injection and storage in a local gas distribution grid at 4 bar. In April 2016, BioCat started the methane production in the pilot plant [56].

In Electrochaea's biological methanation system, the hydrogen from the electrolyzer is combined with carbon dioxide, and this gas mixture is then introduced to a liquid phase methanation reactor. Over the course of the experimental testing phase in the BioCat Project, two sources of carbon dioxide were used: (i) raw biogas from an adjacent anaerobic digester with a composition of approximately 60% methane and 40% carbon dioxide, and (ii) a pure stream of CO_2 supplied by an on-site biogas upgrading system [56].

Inside the bioreactor, a culture of methanogenic archaea metabolizes the hydrogen and carbon dioxide to methane. Archaea are single-celled organisms (prokaryotes) that have evolved over billions of years in harsh environments. The specific strain used by Electrochaea's methanation system has been selectively evolved to exhibit properties ideal for applications in industrial environments. Those properties include [56]:

- Low energy metabolic pathway from carbon dioxide to methane
- Very high carbon mass conversion efficiency
- High tolerance to contamination (oxygen, hydrogen sulfide, particulates)
- Moderate operating temperatures (60-65°C)
- High selectivity in product gas (100% methane, no intermediate products)
- Low catalyst operating costs enabled by self-maintenance and self-replication
- Very high responsiveness (ability to cycle on/off within seconds)

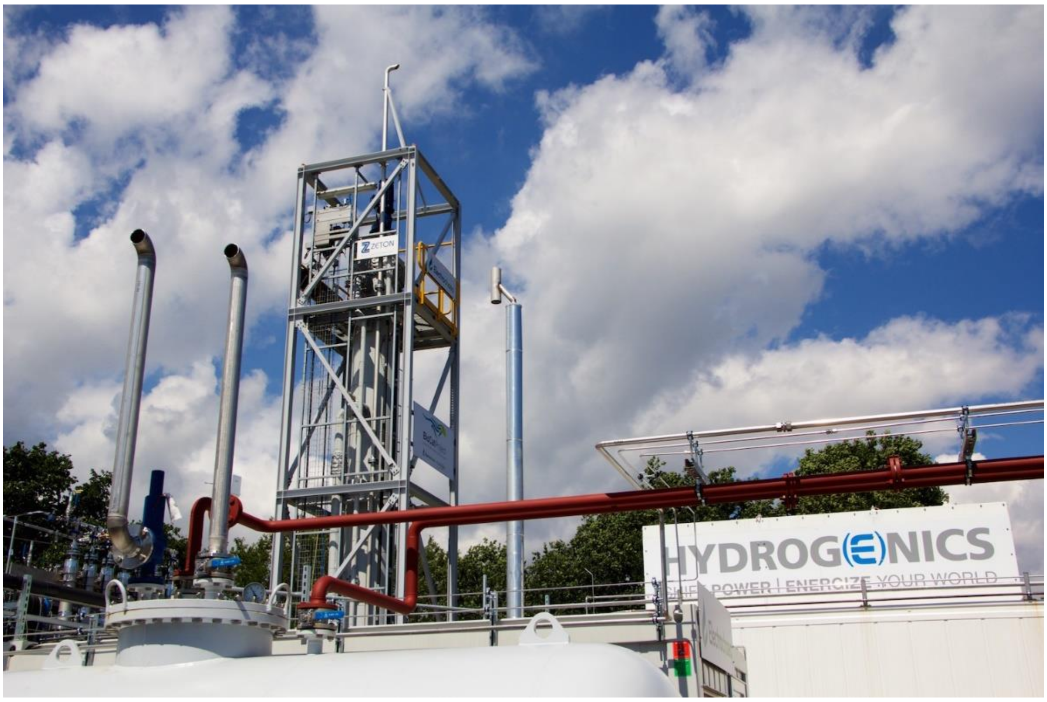


Figure 4-13: Biocat PtG demonstration plant. Source: [56]

4.4.3 Methane market and CO_2 uptake potential

Global natural gas production in 2015 was 3538.6 billion standard cubic meters. The methane content of natural gas varies according to the production well, but typically it varies from 70% to 90% in volume. This is equivalent to an yearly production of 1.1 to 1.5 Gt CH_4.
If all the methane was to be produced by CO_2 hydrogenation, the consumption of CO_2 would be around 3 to 4 Gt per year. Likewise, if 1.05 Gt of CO_2 produced in the cement industry were to be converted to methane, the obtained volume would be 25% to 34% of the global methane production.

4.4.4 Methane: merits and challenges

Merits
Methane is a drop-in fuel that face no challenges regarding infrastructure or public acceptance.

Challenges
Literature argues that the larger consumption of H_2, lower energy per volume and more difficult storage with respect to oxygenated products (methanol, DME), do not indicate this route as suitable for the conversion of carbon dioxide to fuels using H_2 [33].
However, some initiatives on the power-to-gas route suggest using H_2 itself as energy storage. Methane has several advantages over hydrogen, e.g., higher volumetric energy content and safety insurance. Meanwhile, there is no limit for synthetic natural gas admittance into the gas grid. The CO_2 hydrogenation to methane requires an expensive finely designed Ru-based catalyst, and for this reason it has been defended that large scale industrial application of this route has may be unfeasible [55].
As every fuel, methane has short term sequestration period, indicative sink factor: 0-10% [10].

4.5 Ethanol

4.5.1 State-of-the art ethanol production

Ethanol is commonly produced by fermentation of sugars present in biomass feedstocks. The bioconversion of glucose (from corn starch or sugar-cane) by yeasts is a mature technology, leading to so-called first-generation bioethanol. This is inherently a CO_2-utilization route, since the biomass feedstocks consume CO_2 in photosynthesis. Nevertheless, ethanol production actually leads to an emission of ca. 500 kg CO_2 per m^3 of ethanol from sugar-cane, and 1300 kg CO_2 per m^3 of ethanol from corn [57].

Moreover, bioethanol may compete with the food sector either by using food commodities as the energy source (e.g. corn), or by cultivating bioenergy crops on soil that would otherwise be used for food production [58]. Thus, the development of a second-generation bioethanol, produced from lignocellulosic biomass is of great interest. Feedstocks from lignocellulosic materials include agricultural and forestry residues.

Production of fuel ethanol from the mixture of sugars present in lignocellulosic biomass, however, remains challenging with many opportunities for improvement. More robust microorganisms are needed with higher rates of conversion and yield to allow process simplification through consolidating process steps. This development would reduce both capital and operating costs, which remain high by comparison with those of corn.

The commercial production of second-generation bioethanol is in its beginning, with “first-of-a-kind” plants in operation in the USA, China, Canada, the EU and Brazil. The world installed capacity is was ca. 1.4 million liters in 2015 [59].

4.5.2 Technologies for ethanol production from CO_2

4.5.2.1 Ethanol from CO_2 catalytic hydrogenation: TRL 3-5

Ethanol synthesis from CO_2 can be achieved based on rWGS followed by CO hydrogenation. Despite extensive research on catalyst development [60], there are no commercially viable catalysts for the production of higher alcohols (C2-C4) from CO hydrogenation (using syngas). However, the presence of CO_2 can greatly change the product yield [61].

A pilot plant in Güssing, Austria, produces a mixture of methanol (45%), ethanol (14%), propanol (14%) and water (27%) from biosyngas (synthesis gas produced by steam gasification of biomass) containing 27% CO_2, 53% H_2, 14% CO and 6% CH_4 on a dry basis [62].

A recent study show that CO_2 hydrogenation leads to methanol, whereas CO hydrogenation leads to hydrocarbons and higher alcohols [63].

4.5.2.2 Ethanol production via CO_2-based DME (catalytic hydrogenation): TRL 3

Alternatively, ethanol can be produced via DME. The process occurs in two steps: DME carbonylation to methyl acetate in the presence of H-Mordenite (H-MOR) zeolite, followed by methyl acetate hydrogenation over the Cu/ZnO catalyst [34]. This DME-based ethanol production can be adapted to a CO_2 utilization route if DME is produced from CO_2 (either directly or via methanol). Both process steps have TRL 3.

4.5.2.3 *Bio-based ethanol (biohydrogenation): TRL 3*

Early efforts in direct incorporation of CO_2 to produce bioalcohols have focused mainly on ethanol production in *Rhodobacter* and *Synechococcus* [64]. This is done by coupling the metabolism of CO_2 to the synthesis of ethanol, two remarkably successful metabolic strategies in nature, using recombinant DNA technology. This leads to a chimeric bacterium that can metabolize CO_2 to ethanol. There are two different pathways in which this can be done. In the light-dependent pathway, hydrogen and CO_2 are used as feed, whereas in the light-independent pathway, hydrogen, oxygen and CO_2 are required. Although the results confirm the formation of ethanol, the lab experiments conditions were performed under a huge excess of hydrogen, 98.5 mol% H_2 and 1.5% mol CO_2 [65].

Other TRL3 attempts to produce ethanol from CO_2 include electroreduction over Cu/TiO2 catalyst [66] and negative ion plasma induced reduction of CO_2 by steam [67].

4.5.3 Ethanol market and CO_2 uptake potential

The present market for ethanol is quickly expanding as the car fleet adapts to the new fuel. The world consumption of ethanol is currently around 110 billion liters per year. All petrol sold in the EU typically contains up to 5% ethanol (E5). E10 can be used in about 90% of all petrol-driven cars used in Europe and in 99,7% of the petrol vehicles produced since 2010. E10 is currently available Finland, France and Germany – where it reaches 63%, 32% and 17% of petrol sales, respectively. Elsewhere E10 is being used in the USA, Australia and New Zealand. Ethanol can also be used in higher concentrations. E85 is widely available in Sweden, France, Germany, and more sporadically in Hungary, Austria, the Netherlands and Spain. E85 requires dedicated ‘flex fuel vehicles’ (FFVs), which are able to run on E85, petrol, or any mixture of the two. Brazil was the first country to introduce FFVs, in 2003, and today they account for more than 90% of new car sales in that country. Unfortunately, Europe is lagging behind and must significantly improve its infrastructure to enable the increased uptake of ethanol.[68]

Producing 110 billion liters of ethanol per year (86,8 Mton/year) from CO_2 would consume 166 Mton CO_2/year. That is the equivalent of the CO_2 produced in 195 reference cement plants, or 15.8% of the total CCUS target in the cement industry.

4.5.4 Ethanol: merits and challenges

Merits
Ethanol is preferable to methanol as product of CO_2 hydrogenation in terms of safer handling and transport, and better compatibility to gasoline [33].

Challenges
An economic evaluation of CO_2-based ethanol production [34] can be seen in Figure 4-14, showing that the DME route is a better option than the rWGS route. Nevertheless, the conventional ethanol production from either sugar cane or corn starch is two to three times less costly than the CO_2-based ethanol. The relatively high production cost of CO_2-based ethanol is a result of high feedstock (hydrogen) cost.
In the same study, the ethanol price in the work of is reported to be in the range of 0.64 to 0.71 EUR/l [34]. Over the last 10 years, ethanol prices have covered the range from 0.29 to 1.23 EUR/l.

This project has received funding from the European Union's Horizon2020 Research and Innovation Programme under Grant Agreement No 641185. This work was supported by the Swiss State Secretariat for Education, Research and Innovation (SERI) under contract number 15.0160

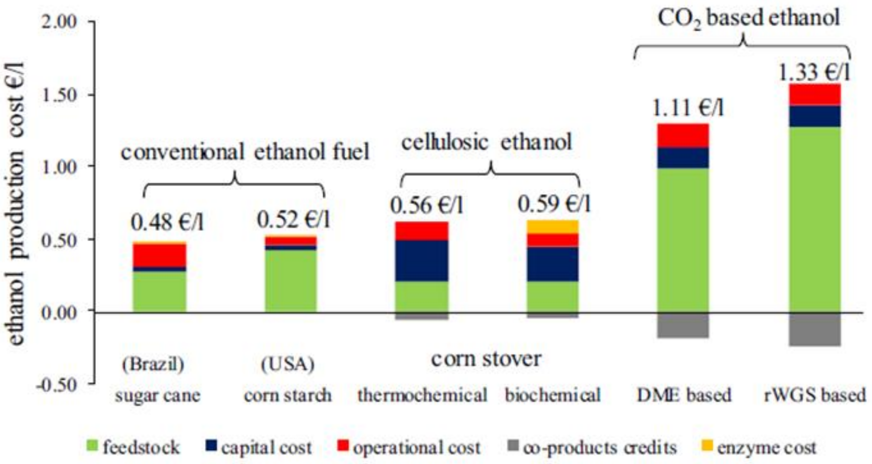


Figure 4-14: Ethanol production cost. Source: [34]

As every fuel, ethanol has short term sequestration period, indicative sink factor: 0-10% [10].

4.6 Biodiesel

4.6.1 State-of-the art technology for biodiesel production

Biodiesel is produced from triglycerides, which are oils in which three fatty acid molecules are esterified with a molecule of glycerol. Fatty oil sources commercially used in biodiesel production include soybeans, canola oil, animal fat, palm oil, corn oil and waste cooking oil. Triglycerides react with methanol in a reaction known as transesterification or alcoholysis to produce biodiesel (methyl esters of fatty acids). Transesterification requires 3 moles of alcohol for each mole of triglyceride to produce 3 moles of methyl esters and 1 mole of glycerol as a biproduct. In industrial processes a large excess of methanol ensures that the reaction is driven in towards biodiesel [69].

4.6.2 Technology for biodiesel production via CO$_2$

4.6.2.1 Biodiesel production from microalgae: TRL 5

Microalgae have a high oil content (up to 80 wt% depending on the species). Lipids, in the form of triacylglycerides (TAGs), typically provide a storage function in the cell that enables algae to endure adverse environmental conditions. About 80% of the microalgae oil content can currently be converted to biodiesel. The biodiesel production from extracted microalgae oil follows the same technology path as the commercial state-of-the-art process, but using oil produced by microalgae as a resource. [70]
As compared to energy crops, microalgae are easier to cultivate and have much higher growth rates and productivity. Different microalgae species can be adapted to live in a variety of environmental conditions, thus it is theoretically possible match the local environmental conditions to the optimal microalgae growth conditions.
Chlorella sp., *Chlorococcum sp.* and *Neochlorosis oleabundans* are found to be potential biodiesel feed stocks. [71]

This project has received funding from the European Union's Horizon2020 Research and Innovation Programme under Grant Agreement No 641185. This work was supported by the Swiss State Secretariat for Education, Research and Innovation (SERI) under contract number 15.0160

4.6.3 Biodiesel market and CO_2 uptake potential

The growth of the global production of biodiesel between 2000 and 2010 is given in Figure 4-15 in million tonnes. Most of the world capacity is installed in the EU [72]. If 20 million tonnes of biodiesel are produced via microalgae cultivation, the CO_2 uptake is approximately 25-50 million tonnes. This number is highly dependent on the lipids content in the microalgae.

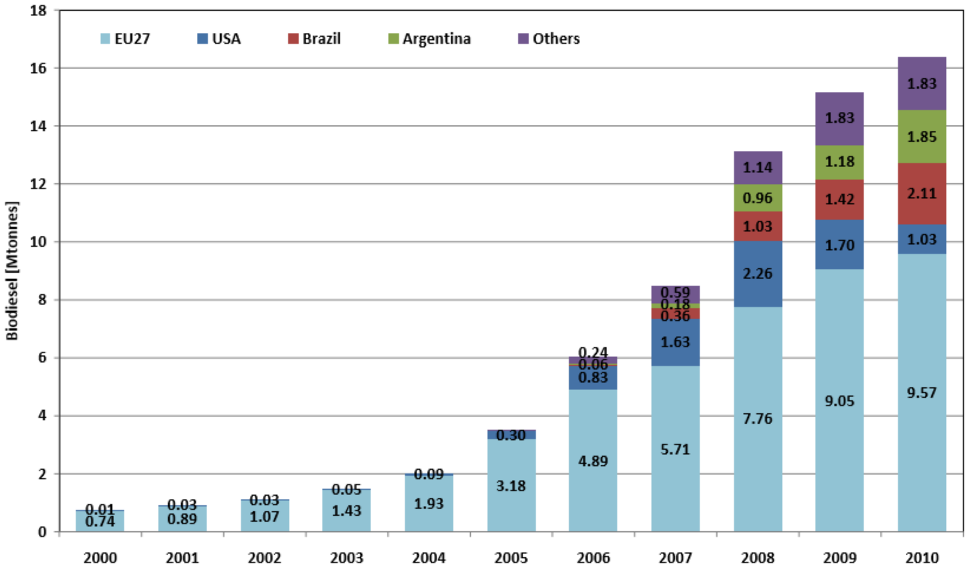


Figure 4-15: World biodiesel production between 2000-2010 in million tonnes. Source: [72]

4.6.4 Biodiesel: merits and challenges

Merits:
As compared to other biodiesel sources (higher plants), microalgae have higher productivity.

Challenges:
The TRL is low. As every fuel, biodiesel has short term sequestration period, indicative sink factor: 0-10% [10].

5 POLYMERS

Typically, polymer synthesis uses intermediates and monomers/oligomers derived from fossil based feedstock such as ethylene or propylene. As discussed in item 4.3 of this report, these light olefins can be obtained by hydrogenation of CO_2.

CO_2 can be used in combination with traditional feedstocks to form certain polymers. These polymers can be either intermediates or finished products.

Co-polymerisation of CO_2 with epoxides (which are obtained from partial oxidation of light olefin) has been already shown in 1969 using a heterogeneous catalyst derived from diethyl zinc and water [73]. Figure 5-1 shows the reaction schemes of CO_2 with epoxides. As indicated, the type of product formed depends on the catalyst used and the competing reaction schemes.

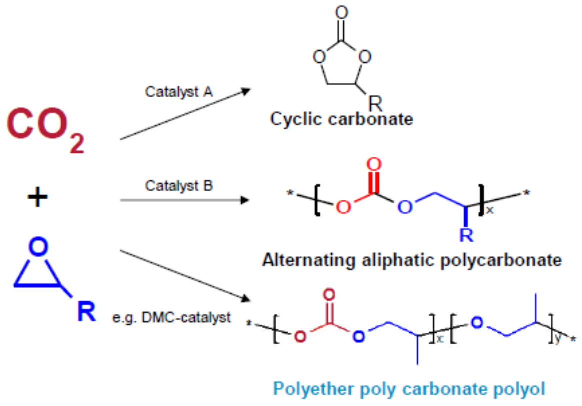


Figure 5-1: Reactions of CO_2 with epoxides. [74]

Aliphatic polycarbonates are high molecular weight polymers with diverse applications. Polyether poly carbonate polyol are low molecular weight polymers and can be used for polymer synthesis due to their terminal –OH functionalities.

The two main class of polymeric finished products that are being synthesized using CO_2 are polycarbonates (PC) and polyurethanes. Polycarbonates are the most widely used engineering plastics and are used in applications such as compact discs, specialty opticals, cars and buildings. Polyurethane foams are used as coatings, specialty materials, thermoacoustic insulators, packaging and in several other applications [75].

Cyclic carbonates are addressed in item 6.1.

5.1 Poly(propylene carbonate), PPC

Poly(bisphenol-A carbonate), BPA-PC, is the most widely produced and used polycarbonate, due to its high impact strength, heat resistance and being highly transparent. It was first introduced by Bayer AG in 1958. [76]. Currently, the industrially important polycarbonates are synthesized from bisphenol A and diphenyl carbonate, which are highly toxic. Most of the BPA-PC is currently produced by the phosgene process as shown in Figure 5-2 [77], [78].

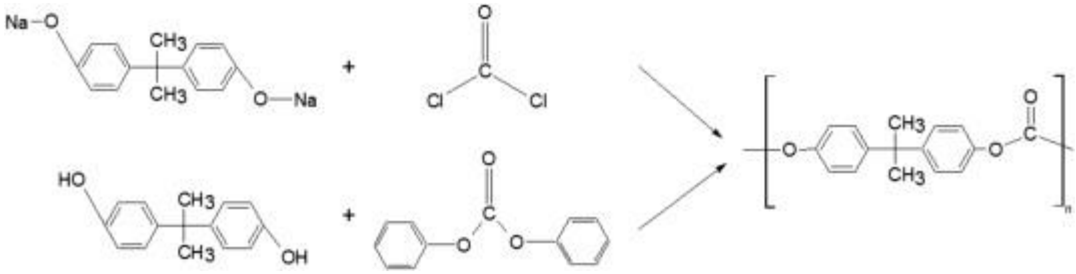


Figure 5-2: Industrial routes for the production of Poly(bisphenol-A carbonate) (BA-PC) [77]

There is an inherent driver to use alternatives to phosgene due to its severe toxicity. CO_2 based routes have, therefore, being explored either by direct use of CO_2 or CO_2 derived feedstocks.

Poly(propylene carbonate) (PPC) is an alternating copolymer of propylene oxide and CO_2. It is an emerging low-cost and eco-friendly polymer material. PPC has high molecular weight and high carbonate contents, exhibiting good biodegradability. It has wide application in packaging materials, or even gas barrier films [79]. The commercialization of PPC is currently being initiated in several countries, especially in China.

An alternative route to polycarbonate that utilizes CO_2 instead of phosgene is utilized by Samsung Cheil Industries. The reaction scheme is showed in Figure 5-3. The polycarbonate resin is commercialized under the brand INFINO.

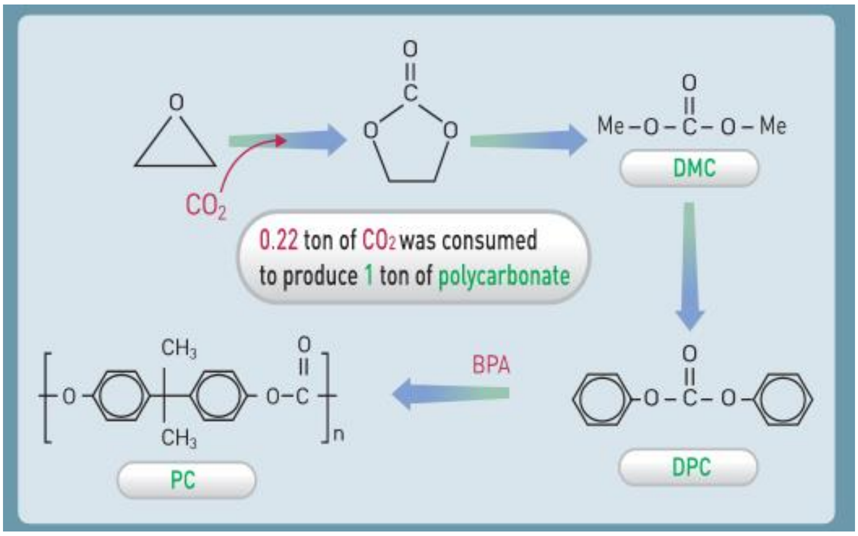


Figure 5-3 Production of polycarbonate via CO_2 utilization. Source: [80]

5.1.1 State-of-the art technology for PPC production

The state-of the-art technology for PPC production is based on CO_2 utilization. See next item for description.

5.1.2 Technology for PPC production utilizing CO_2: TRL9

The synthesis of PPC from PO and CO_2 has already been commercialized [81]. Novomer has commercialized the production of PPC polyols for use in polyurethane hot melt adhesive applications in 2014, under the name of Converge®. In November 2016, Aramco Services Company and Saudi Aramco Technologies have acquired the Converge® patent portfolio. Empower materials commercialize PPC under the brand QPAC®40 [82].

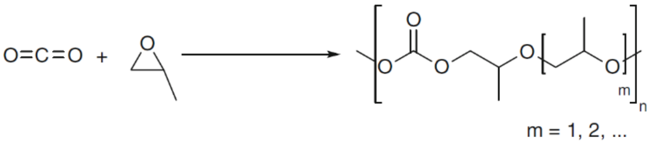


Figure 5-4: PPC production from CO_2 and propylene oxide

Nantong Huasheng Company in China is developing biodegradable plastics based on PPC, brand mark PCO2. This plastic is fully biodegradable and has received the Biodegradable Products Institute (BPI) certification after passing requirements specified in the ASTM D6400 standard for plastics intended for composting [79].
Typical conditions for the co-polimerization of PO and CO_2 to PPC are 17-19bar, 75ºC using a double metal catalyst (DMC) [83].

5.1.3 PPC market and CO_2 uptake potential

On average, the polycarbonates contain 20 wt% CO_2, [84], but PPC polyols can contain up to 50 wt% CO_2. Converge® is an emerging material in the landscape of thermoplastic polymers and may compete for the market of other polymers. The Japanese AsahiKasei informs in its website to "have sold polycarbonate resins made from CO_2" [85].
The global plastic production was ca. 300 million tonnes in 2013. It is estimated that 41% of plastics are used in packaging, and that almost half of that volume is used to package food products. The oxygen permeability of PPC is below 20 $cm^3/m^2/day/atm$, much better than those of other biodegradable polymers, such as poly(butylene succinate) (PBS), PLA, and Ecoflex. The oxygen barrier feature may be a unique factor for promoting the utilization of PPC in food packaging [79]. If PPC would achieve a 1% market share, the CO_2 uptake potential would be 6Mt CO_2/year.
In 2015, China's total PPC production installed capacity was 63000 ton/year, and the ex-works price was ca. USD4000/ton. [86]

5.1.4 PPC merits and challenges

Merits
PPC has a high (up to 50 wt%) CO_2 content, and is biodegradable
From a thermodynamic perspective, PPC is more favorable than most CCU products. See Figure 1-1.

Challenges
PPC must compete with other well-established plastics for a market share. Because of its poor processability and mechanical performance, PPC has a narrow range of applications when compared with other degradable plastics such as polylactic acid (PLA) and polybutylene

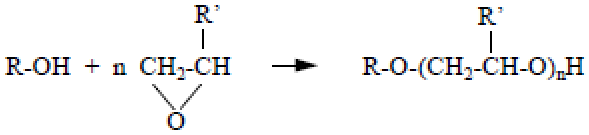
succinate (PBS) [86]. As a disposable and biodegradable plastic, PPC has short term sequestration period, indicative sink factor: 0-10% [10].

5.2 Polyols

Polyols are typically used as co-monomers in the production of polyurethanes. Polyurethanes were first produced by Otto Bayer and his co-workers in 1937 [87], and are synthesized from di-isocyanates and co-monomers, such as di- and polyols. Typically, the polyols used are polyether polyols (> 75%), which are petroleum-based [88].

5.2.1 State-of-the art technology for polyols production

The production of polyols involves an alkoxylation reaction between an alcohol and an epoxide, as shown in Figure 5-5. Divalent glycols such as ethylene glycol and propylene glycol or multivalent alcohols such as of glycerol and sucrose can be used. This determines the degree of crosslinking. Generally, the epoxides used are either propylene or ethylene oxides. [79]



$$R\text{-}OH + n\ \underbrace{CH_2\text{-}\overset{R'}{\overset{|}{C}}H}_{O} \longrightarrow R\text{-}O\text{-}(CH_2\text{-}\overset{R'}{\overset{|}{C}}H\text{-}O)_nH$$

Figure 5-5: Reaction scheme in the production of polyether polyols.

5.2.2 Technology for polyols production utilizing CO_2: TRL 9

Low-molecular weight CO_2/PO based polyols can be produced as per the scheme shown in Figure 5-7. These CO_2-based polyols can replace the petroleum-based polyols in the polyurethanes industry. For instance, Figure 5-7 shows the reaction scheme to produce polyurethane using CO_2-derived poly(carbonate-ether) polyols in combination with isocyanates [89] [79].

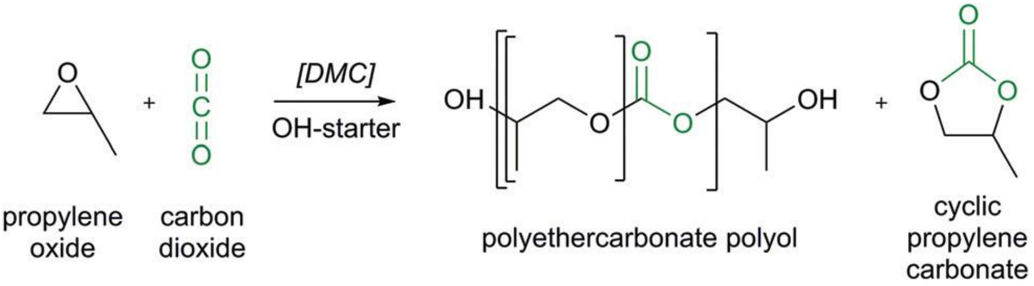


Figure 5-6: Production poly(carbonate-ether) polyol from propylene oxide and CO_2 [90].

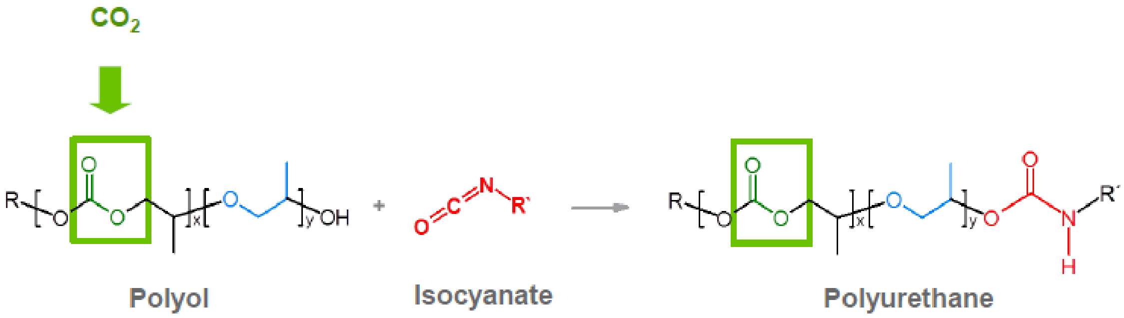


Figure 5-7: Production of polyurethane using CO_2 derived poly(carbonate-ether) polyol and isocyanate[74] .

Commercial CO_2-based polyol: Cardyon™
Covestro has developed a CO_2-based process that leads to 20 wt% CO_2 content in the polyol intermediate. The polyol, cardyon™, and has been used in the fabrication of flexible polyurethane foam for mattresses. Belgian manufacturer Recticel launched the first products on the market end of 2016 (information available at: https://www.co2-dreams.covestro.com/)

5.2.3 Polyols market and CO_2 uptake potential

Polyethercarbonate polyols can substitute conventional polyether polyols of which the global production was 8 Mt/y in 2012 [90], and 10 Mt/y in 2015 [79]. Assuming an average CO_2 content of 20 wt%, the production of CO_2-based polyols could theoretically utilize up to 2 Mt/y of CO_2 as feedstock [90].
Because of the petroleum-based propylene oxide in the formulation, the CO_2-derived polyol is not a net greenhouse gas (GHG) sink. However, substituting the petroleum-based for CO_2-based polyols reduces GHG emissions by 11-19% (assuming 20wt% CO_2) and saves fossil resources by 12-16 %. [90] .

5.2.4 Polyols: merits and challenges

Merits
Polyurethane foams prepared from CO_2-based polyols display similar properties as that of petroleum-based polyether polyols, indicating that the current industrial standard can be achieved by the CO_2-based product [79]. From a thermodynamic perspective, polyols are more favorable than most CCU products. See Figure 1-1.

Challenges
The polyols market is limited. It still relies on fossil fuel derived epoxide, limiting its overall net CO_2 reduction. If the final products are disposable plastics, polyols have short term sequestration period, indicative sink factor: 0-10% [10]. Depending on the final product, however, polyurethane can have a lifetime above 10 years (e.g., when used in composite wood), leading to a medium-term sink factor (10-40%).

6 CHEMICALS

6.1 Cyclic carbonates

6.1.1 State-of-the art technology for cyclic carbonates production

As already indicated in Figure 5-1, the reaction schemes of CO_2 with epoxides will follow different routes depending on the catalyst used and conditions used. Commercial production of cyclic carbonates relies on the use of quaternary ammonium or phosphonium salts as catalysts, at temperatures above 100ºC and pressures above 20 bar. This process was first commercialized by Huntsman in the 1950's and is highly exothermic.[91].
Under the commercial reaction conditions, cyclic carbonate synthesis is a net producer rather than consumer of CO_2. However, research is currently focusing on alternative routes for producing cyclic carbonates with focus on CO_2 utilization.

6.1.2 Technology for cyclic carbonates production via CO_2: TRL 3

The research on the production of cyclic carbonates from CO_2 focuses on fundamental reaction aspects, such as development of catalysts and optimization of solvent matrix. As an example, the CyclicCO2R project (2012-2016) focused on the development of a continuous process to produce cyclic carbonates from CO_2 and renewable feedstocks. The main scientific activities were catalyst development, process development, and process scale up [92].

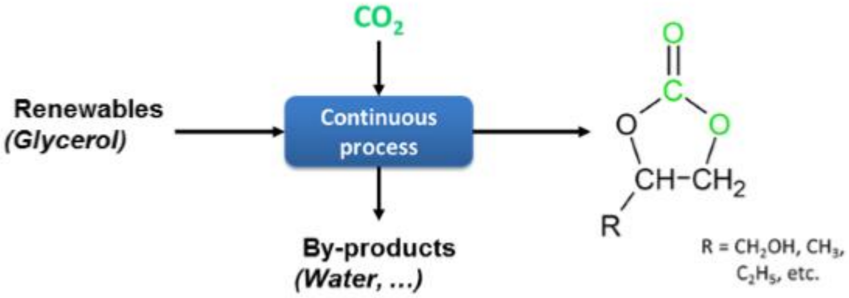


Figure 6-1: Cyclic carbonates production from renewable feedstock and CO_2. Source: [92]

Two routes were investigated in CyclicCO2R. In the direct route glycerol, and related diols, were reacted with CO_2 using an innovative catalyst to glycerol carbonate. Glycerol is a green renewable feedstock that is readily available as a byproduct from biodiesel production. Challenges were in the equilibrium limitation, side reactions, by-product (water) removal and process conditions. In the indirect route an allyl alcohol is formed first, then epoxidized to glycidol, and then a step of cycloaddition of CO_2 leads to glycerol carbonate. It was shown that other cyclic carbonates could also be produced by the developed catalyst and process [92].

6.1.3 Cyclic carbonates market and CO_2 uptake potential

Three commercially relevant products are: ethylene carbonate, propylene carbonate and glycerol carbonate. Cyclic carbonates have numerous commercial applications, either as chemical intermediates (e.g. for dimethyl carbonate and ethylene glycol) and as solvents. A particularly important and rapidly growing application is their use as electrolytes in lithium ion batteries. Cyclic carbonates are niche products, with a total market size of around 100 ktonnes per year by 2012 [91]. Assuming an average CO_2 content of 40 wt% (average between ethylene- and propylene carbonates), then about 40 ktonnes/year of CO2 can be used as feedstock in cyclic carbonates production. This is equivalent to 5% of the emission from a BAT cement plant. Bulk prices for ethylene and propylene carbonates are between 1000 and 2000 EUR/ton [93].

6.1.4 Cyclic carbonates: merits and challenges

Merits
From a thermodynamic perspective, cyclic carbonates are more favorable than most CCU products. See Figure 1-1. Cyclic carbonates are high value products

Challenges
Cyclic carbonates are niche products, offering limited CO_2 utilization potential. It still relies on fossil fuel derived epoxide, limiting its overall net CO_2 reduction. However, the direct route offers significant CO2 reduction potential. Cyclic carbonates have short term sequestration period, indicative sink factor: 0-10% [10].

6.2 Formic Acid

Formic acid was first extracted in 1671 by the English naturalist John Ray by distilling a large number of crushed red ants. Formic acid (HCOOH) synthesis is an alternative possibility to convert CO_2 to liquid products that may be used as both fuels and chemicals. Formic acid interest in relation to CO_2 conversion derives from the fact that liquid product of CO_2 hydrogenation requires the lower consumption of H_2 (1:1). Given this, a formic acid-based economy has been proposed [94].

6.2.1 State-of-the art technology for formic acid production

About 90% of the formic acid is produced via the methyl formate hydrolysis route, developed industrially in the 1980's. This process involves carbonylation of methanol and subsequent hydrolysis of the methyl formate produced. The methanol resulting from this process is returned to the first stage. [95]

6.2.2 Technology for formic acid production via CO_2

The VoltaChem program is promoting the "Power-2-Formic Acid" technology. The direct conversion of CO_2 to formic acid (FA) is presented as an alternative to a renewable energy carrier. Within power-2-FA, two technological routes are being developed: CO_2 hydrogenation (TRL 5) and CO_2 electrolysis (TRL 3).

6.2.2.1 CO_2 hydrogenation: TRL5

The thermocatalytic conversion of hydrogen and carbon dioxide has been shown to produce 85wt% FA dissolved in methanol (solvent). CO_2 and hydrogen react at around 90ºC and 100 bar in the presence of two catalysts (ruthenium- and phosphino-based catalysts), using aqueous MeOH as solvent [96].

6.2.2.2 CO_2 electrolysis: TRL3

In the electrolysis route, the hydrolysis reaction (hydrogen production) is combined to the CO_2 hydrogenation. This route has lower TRL level.

6.2.3 Formic acid market and CO_2 uptake potential

Formic acid (FA) is used by the textile, pharmaceutical and food industries. The main consumption of FA is for animal feed (it is used as a preservative and antibacterial agent). In 2013, this application corresponded to 34% of the FA global demand, while the leather and tanning industry responded for about 32% of the global demand. The world production for FA in 2013 was 620 kt in 2012 and is projected to achieve 760 kt in 2019 [96].
Formic acid is commercialized as 85, 90, 95, 98 and 99wt% aqueous solution, with 85wt% being the most common concentration. The price of FA 85% grade in Europe varied between 510 and 600 EUR/tonne in 2014. Formic acid is a high valued product, with a concentrated, small and mature market, with low risk of substitution [96]. The fuel-grade formic acid is called hydrozine: it consists of 99% formic acid, supplemented by additives [97].
The forecasts of CO_2 uptake potential by year 2030 vary considerably, from 450 kt [3] to 4–21 $MtCO_2$/yr, assuming optimistic penetration pathways for hydrogen [98]. Team FAST (Formic Acid Sustainable Transportation) has built a prototype car running on hydrozine, and is currently working to build the world's first hydrazine-fueled bus – an important milestone in the roadmap for employing FA as an energy carrier [97].

6.2.4 Formic acid: merits and challenges

Merits

From all the fuel options, FA is the most thermodynamically favorable. The conversion of FA to CO_2 only requires one H_2 molecule.

Challenges

Formic acid is a toxic chemical (the US OSHA Permissible Exposure Level of formic acid vapour in the work environment is 5 ppm) and some animal experiments have demonstrated it to be a mutagen. Therefore, some authors argue that it would be unlikely that FA may be proposed on a large scale as a suitable chemical to be produced from carbon dioxide [33]. Formic acid has short term sequestration period, indicative sink factor: 0-10% [10].

6.3 Isopropanol

6.3.1 State-of-the art technology for isopropanol production

There are two main commercial routes to isopropanol (IPA). The older method is based on the indirect hydration of refinery-grade propylene using sulphuric acid to form isopropyl sulphate which is then hydrolysed with steam to form sulphuric acid and IPA. The crude IPA is distilled to the desired purity. A more modern route is the direct hydration of chemical grade (90-99%) propylene [99].

6.3.2 Technology for isopropanol production via CO_2

6.3.2.1 Biological production of isopropanol: TRL3

Isopropanol can be biologically produced by genetically engineered *Escherichia coli*. Laboratory tests shows it is possible to produce 81.6 mM isopropanol with a yield of 43.5% (mol/mol) in the production phase [100]. IPA was also produced by Cyanobacteria *Synechococcus elongates* PCC 7942 in the concentration of 26.5 mg/L [70].

6.3.3 Isopropanol market and CO_2 uptake potential

The main use for isopropanol (IPA) is in solvents with outlets in cosmetics and personal care products, de-icers, paints and resins, pharmaceuticals, food, inks and adhesives. It is also used as a cleaning and drying agent in the manufacture of electronic parts and metals, and as an aerosol solvent in medical and veterinary products. IPA is also an intermediate chemical in the manufacture of ketones such as methyl isobutyl ketone (MIBK), isopropylamines and isopropyl esters. The global IPA market is relatively small, around 2 Mt/year, but the IPA price is high, around 1200 to 1700 EUR/tonne [101].

6.3.4 Isopropanol: merits and challenges

Merits
The price of IPA is high.

Challenges
The available production paths require genetically modified organisms, which leads to a public acceptance issue. IPA has short term sequestration period, indicative sink factor: 0-10% [10].

7 CO_2

CO_2 can be commercialized in many different purity grades, for different end-uses. In this chapter, different commercial CO_2 products are discussed. The grade of CO_2 product depends both on the CO_2 purity and on the nature and amount of the impurities present in the gas. Apart from the end-use, the CO_2 purity is also defined by process constraints, which are connected to the conditions under which CO_2 transported. CO_2 may transported by ships, (rail)road or pipelines. Typical conditions for each one of these operations is given in Table 7-1.

Table 7-1: CO_2 state depending on transport mode. Adapted from [102]

Property	Ship (tank)	Road (tank)	Pipelines	Injection for CCS
State	Liquid	Liquid	Supercritical	Supercritical
Density, kg/m3	1163	1078	838	702
Pressure, bar	6,5	20	73-150	100
Temeprature, ºC	-52	-30	20	35

7.1 Impurities

The moisture content is important for all CO_2 production processes and applications, since the solubility of water in liquid or vapor CO_2 is limited. For example, at -20°C, water solubility in CO_2 in the liquid phase is only 20,8 ppmw. Above this level, water molecules precipitate out of solution in its solid form (ice). The ice crystals can block valves, filters and other equipment. Above 0ºC, water will be in its liquid state and can react with CO_2 to form carbonic acid, which is corrosive to metals. The presence of water in the CO_2 vapor phase can also lead to operational problems: if the water concentration is relatively high, CO_2 and water in vapor phase can react to form a CO_2 gas hydrate; a large molecule that exists above 0°C, that can create problems in control equipment and filters. Figure 7-1 shows the water solubility in vapor and liquid CO_2. If high purity CO_2 is to be transported as a liquefied product at -25ºC and 20 bar, than a safe limit for the water content is 200 ppmw. However, if the CO_2 is to be used as refrigerant, a much stricter moisture content has to be reached (<10ppmw). [103].

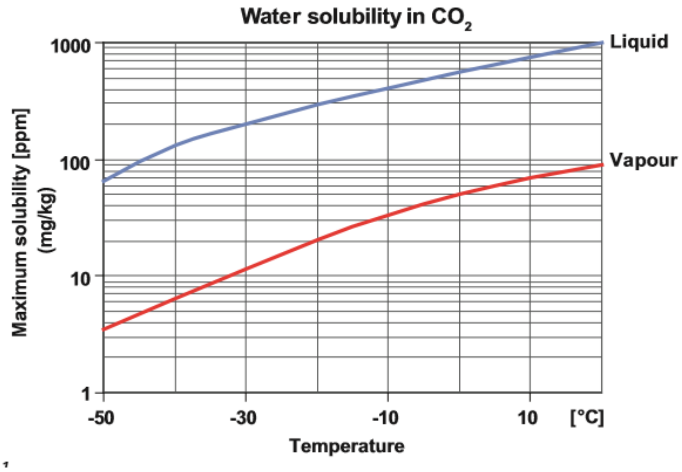


Figure 7-1: Water solubility in CO_2. Source: [103]

The presence of volatile impurities in CO_2 is of extreme importance for the CO_2 liquefaction process, because the pressure required for liquefying CO_2 mixtures is higher than that required for liquefying pure CO_2. As can be seen in Figure 7-2, at -50ºC and 1MPa, pure CO_2 is in the liquid state, whereas a mixture of 99% CO_2 and 1% N_2 exists both as vapor and liquid.

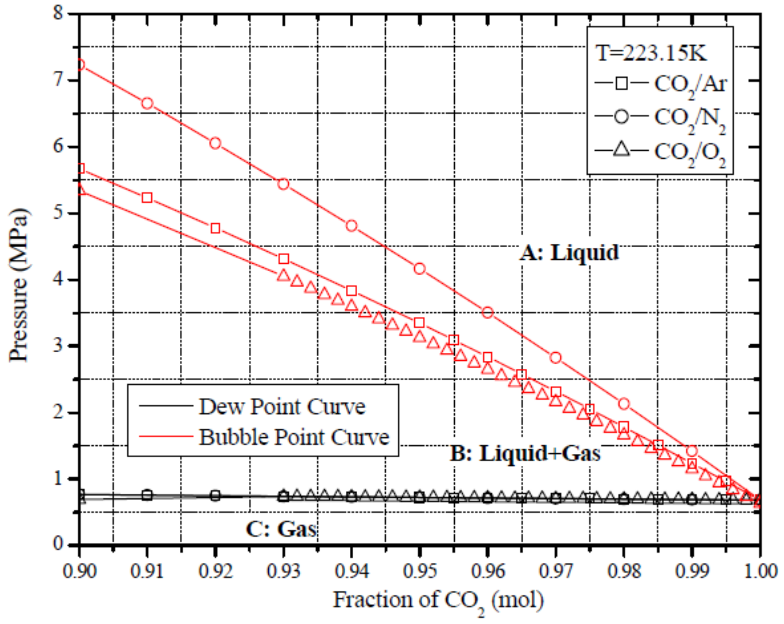


Figure 7-2: Phase envelope of CO_2 mixtures. Source: [104]

7.2 CO_2 grades

7.2.1 Food- and beverage-grade CO_2

The European Industrial Gases Association (EIGA) has published standards for the composition of food- and beverage-grade carbon dioxide. These are given in Table 7-2 [105]. These standards are in very good agreement with those proposed by the International Society of Beverage Technologists [106]. The ISBT informs the reasons behind each concentration limit, and this information is included in Table 7-2.

Table 7-2: EIGA/ISBT standards for the composition of food- and beverage-grade CO_2

Component	Concentration	Rationale
CO_2	99,9% min.	Process
Moisture	20 ppmw max.	
Ammonia	2,5 ppmv max	
Oxygen	30 ppmv max	
Carbon Monoxide	10 ppmv max	
NO and NO_2	2,5 ppmv max. each	Regulatory
Phosphine	0,3 ppmv max	
Benzene	0,02 ppmv max	
Methanol	10 ppmv max	
Hydrogen Cyanide	0,5 ppmv max	
Oil and grease	5 ppmw max	Sensory
Total volatile HCs	50 ppmv max. of which 20 ppmv max non-methane HCs	
Acetaldehyde	0,2 ppmv max	
Particulates	10 ppmw max	
Total Sulphur	0,1 ppmv max	

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Concentration limitations that are based on process conditions will most likely apply to any CO_2 product grade. Regulatory (law inforced) limits, on the other hand, may be specific to the use of CO_2 in the food and beverage industry. Sensory limitations indicate that, over the specified concentration, the impurities may affect the taste, odor or visual aspect of the beverage or food product.

Interestingly, Praxair has a different definition of food- and beverage-grade CO_2. In fact, the company's website differentiates the CO_2 beverage grade (purity 99,9%) from the food grade (purity 99,8%). In general, it seems that the CO_2 purity grades are not well defined so the EIGA standards can only be used as guidance.

7.2.1.1 State of the art production of food-grade CO_2

CO_2 purification and liquefaction plants are typically capable of handling CO_2 feed composition from 95% up, at atmospheric pressure. Therefore, typical liquefaction plants can handle CO_2 from post-combustion capture systems. A conventional CO_2 purification plant consists of the following units:

- Water scrubber: normally the first separation step, in which the water soluble impurities are removed;
- Compressor: screw compressors are used to pressurize the CO_2 to about 22 bar;
- Dehumidifier: a knock-out drum to remove condensed water;
- Dehydrator: an adsorption tower design to achieve the required water dew point;
- Adsorption in carbon beds: to remove sulfur and hydrocarbons;
- Cryogenic distillation: this unit consists of a condenser, a stripper column and reboiler. Non-condensables (N_2, Ar, etc.) are vented to the atmosphere;
- Storage tank: CO_2 is stored as a liquid.
- Refrigeration unit: ammonia is typically used as refrigerant.

Typical large plants for CO_2 purification and liquefaction plants have capacity to produce 10 t/h of food grade CO_2. This capacity is a function of the market, as scaling-up to higher throughputs wouldn't represent a challenge for any of the above-mentioned operations. Adapting the plant to operating on CO_2 from an oxy-fuel cement plant (80 mol% CO_2) is possible, but the process would demand a higher energy in the distillation unit/refrigeration unit.

7.2.1.2 Food-grade CO_2 market

Food and beverage industries consume about 17 $MtCO_2$/y, equivalent to the CO_2 emission of 20 reference cement plants, or 1,6% of the CCUS target for the cement industry. The price of food-grade CO_2 is highly dependent on the location, but for Europe it can be around 80-150 €/ton [107].

7.2.1.3 Food-grade CO_2 merits and challenges

Merits

No conversion reaction is needed, therefore the process has low energy requirement and low cost

Challenges

The market of food-grade CO_2 is limited, and the purity required is very high. Short term sequestration period, indicative sink factor: 0-10% [10]. Only has an abatement effect if replacing fossil-based CO_2.

7.2.2 Greenhouse-grade CO_2

Atmospheric CO_2 levels of 600-1000 ppmw are often used in order to accelerate the plants growth inside of greenhouses. In The Netherlands, during the summer, natural gas is combusted on a large scale to provide CO_2 to greenhouses, leading to net emissions of about 7 $MtCO_2$/year. As an alternative, using high purity CO_2 obtained as a by-product in many industries to the greenhouses provides a better control of the CO_2 level in the greenhouse atmosphere and avoids the need to combust natural gas [107].

7.2.2.1 Greenhouse CO_2 market

OCAP is a pipeline network currently suppling about 500 ktons of CO_2 per year to approximately 500 greenhouse companies in the western part of the Netherlands via a transport pipeline and an extensive distribution network. The entire Dutch greenhouse sector consumed about 3,7 $MtCO_2$/year in 2008. The CO_2 demand was estimated to grow by additional 1,2 Mt by 2020 [107].

The CO_2 used in the greenhouses is a by-product of the production of hydrogen at Shell in the Botlek area, and of the production of bio-ethanol by fermentation at Abengoa in Europoort Rotterdam. The CO_2 collected in fermenters already has a high purity. The CO_2 production plant supplied by Linde purifies it further to >99%. The plant capacity is 42 t/h CO_2 [107].

CO_2 delivered via the OCAP pipeline to growers has a market cost of between €50-80 per ton CO_2, also dependent on distance and capacity [107].

7.2.2.2 Impurities in greenhouse grade CO_2

The CO_2 concentration and the impurities in the OCAP pipeline gas are presented in Table 7-3. The composition after a dilution factor of 100 times and the limit composition are also indicated. The limitation in the impurity concentration may be due to its negative effect on human health or because of inhibition of plant growth.

Table 7-3: Impurities in OCAP CO_2

Component	OCAP gas	Diluted 100x	Limit
CO_2	99% min.	10000 ppmv	5000 ppmv (human health)
Moisture	40 ppmv	-	-
THC	1200 ppmv	12 ppmv	-
Aromatics	0,1 ppmv	0,001 ppmv	1 ppmv (human health)
CO	1,1 ppmv	0,011 ppmv	25 ppmv (human health)
NO and NO_2	2,5 ppmv. each	0,025 ppmv each	0,04 ppmv (crop growth)
VOCs	1,2 ppmv	0,012 ppmv	40 ppmv (human health)
Total S	5 ppmv	0,05 ppmv	1,6 ppmv (human health)
Ethene	1 ppmv	0,01 ppmv	0,01 ppmv (crop growth)
HCN	20 ppmv	0,2 ppmv	0,9 ppmv

7.2.2.3 Greenhous grade CO_2 merits and challenges

Merits

No conversion reaction is needed, therefore the process has low energy requirement and low cost. Despite the short term sequestration period (indicative sink factor 0-10% [10]), the use directly displaces that of fossil-based CO_2.

Challenges

The market of greenhouse grade CO_2 is limited, and the purity required is very high.

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7.2.3 Refrigerant-grade CO_2 (R744)

Although CO_2 was widely used as refrigerant in the early 20th century, its use disappeared from around 1940 with the advent of the fluorocarbon chemicals. Recently, increasing focus on environmental issues of fluorocarbon chemicals created a strong interest in systems using natural refrigerants in general, and CO_2 in particular due to its nonflammability and non-toxicity (Nekså, 2004). R744 is the ASHRAE code given to refrigerant-grade CO_2.

A comprehensive overview of the natural refrigerants markets in Europe is given by (shecco, 2014). This report shows that the use of R744 both in refrigeration and heating systems is rapidly increasing. For instance, the number of supermarkets in Europe using transcritical CO_2 refrigeration technology increased from 1330 in 2011 to 2885 in 2013. Moreover, a German car manufacturer plans to have some series equipped with CO_2 air conditioning system already in 2016. This scenario creates a market opportunity for industries which produce CO_2 as a by-product and vent it to the atmosphere. Nevertheless, this is a much smaller market than those of the food and beverage or greenhouse farming industries. If all the vehicles worldwide start using R744 in their air conditioning systems, the total CO_2 consumption capacity is estimated to be around 80kt/y.

Although all the major gas suppliers sell CO_2, it is not necessarily available at a quality at which it can be used as refrigerant. There is no standard universal specification for refrigerant grade CO_2, as it varies according to the location and application. The Linde Group sells R744 with typical specifications of purity >99.99% and water content <10ppmw. This purity is higher than that required for food- and beverage-grade CO_2. R-744 is normally supplied at cylinders containing 5 to 40 kg of liquid CO_2, at pressure varying from 50 to 60 bar (depending on ambient temperature) (Linde).

7.3 Other CO_2 purity grades

Other typical purity grades of CO_2 are given in Table 7-4. Carbon dioxide is also commercialized in mixtures with nitrogen, helium, air and hydrogen, among many other gases.

Table 7-4: Other typical CO_2 grades

Grade	Minimum Purity	Impurity restrictions (ppmv)
Standard	99.5%	H_2O <120
Medical	99.5%	H_2S < 10; NH_3 < 25; CO < 10; NO < 1; NO_2 < 1; SO_2 < 5; H_2O <10
Welding or Industrial	99.8%	H_2O < 32
Bone Dry	99.9%	
Instrument (Coleman)	99.99%	O_2 < 15; H_2O < 10; THC < 4
Research	99.998%	O_2 < 2; H_2O < 3; N_2 < 10; THC < 4; CO < 0.5

CO_2 for geological storage is discussed in chapter 12.

This project has received funding from the European Union's Horizon2020 Research and Innovation Programme under Grant Agreement No 641185. This work was supported by the Swiss State Secretariat for Education, Research and Innovation (SERI) under contract number 15.0160

8 PART B

Catalytic hydrogenation, electrochemical conversion and CO_2 mineralization processes are discussed in this part of the report.

9 CATALYTIC HYDROGENATION

9.1 Background

As shown in this report, the hydrogenation of CO_2 can lead to the production of different fuels and chemicals. However, if CO_2 hydrogenation is the chosen route of CO_2 utilization, the availability of hydrogen poses a technological challenge, as sustainable hydrogen production is an energy intensive and therefore expensive step. Due to the high energy demand of the hydrogenation technologies, life cycle assessments are required to understand the CO_2 utilization implications. From a CO_2 abatement perspective, the utilization of fossil-fuel based energy to produce hydrogen in order to convert CO_2 into energy-rich compounds is a total ‘‘non-sense’’: in fact, in this route more CO_2 would be emitted than converted [2].

The work of [32] can be cited as an example of this point: the authors simulated the production of methanol from CO_2 via catalytic hydrogenation and determined the CO_2 abatement potential of the technology considering different sources of electricity. The authors conclude that using electricity from wind leads to an abatement of 1.43 kg of CO_2-eq per kg of methanol produced. If electricity is produced by solar photovoltaic (PV) panels, the abatement is 1.14 kg of CO_2-eq per kg of methanol. However, in case electricity is produced from a fossil fuel, the process leads to emissions of ca. 6 kg (natural gas) and 10 kg (coal) of CO_2-eq per kg of methanol produced. It should be noticed that the fossil-fuel-based production of methanol leads to emissions of 0.79 kg of CO_2-eq per kg of methanol.

In a review analysing the opportunities and prospects in the chemical recycling of CO_2 to fuels, [33] remark that the requisites for a technology to be feasible are (i) minimize as much as possible the consumption of hydrogen (or hydrogen sources), (ii) produce fuels that can be easily stored and transported, and (iii) use renewable energy sources.

CO_2 reduction reactions with H_2 to molecules that can serve as fuels are established in the literature, and some technologies are close to commercialization (PtG, CO_2 to methanol). Heterogeneous catalysis is a pivotal technology in such a context for reactions such as direct conversion of CO_2 to methanol, to CO (reverse water gas shift reaction) or to methane (Sabatier reaction). The access to CO and methanol can serve as an entry point to produce drop-in fuels using mature technologies, such as: Gas-to-Liquid technology (via Fischer-Tropsch catalysis), methanol-to-olefin conversion, and methanol dehydration to DME [1].

9.2 State-of-the art hydrogen production

CO_2 hydrogenation technologies are hydrogen-intensive, requiring H_2/CO_2 ratios that may be as high as 4:1. The availability and cost of hydrogen are therefore crucial for the technology feasibility.

Hydrogen can be produced from fossil fuels (steam reforming, oil-based and from coal gasification) or from water. In water electrolysis, water is split into O_2 and H_2 by means of electrical power. The current global hydrogen production is 7,2 EJ per year, with 96% being produced from fossil fuels. The two main hydrogen consumers are the oil refineries and ammonia manufacture [108]. Currently, water electrolysis is considered as the best option for sustainable and clean hydrogen production in large scale [38].

9.2.1 Water electrolysis

There are three main electrolysis options, namely: alkaline electrolysis, polymer electrolyte membranes and high-temperature electrolysis. Alkaline electrolysis using KOH is the best available technology, since it is mature up to large scale H_2 production. Moreover, it has been tested successfully for discontinuous operation, and its load can be altered easily by adapting the current density. Therefore, KOH electrolysis is considered as the state-of-art technology for generation of large volumes of sustainable hydrogen. A conceptual process diagram of the KOH electrolysis is given in Figure 9-1. The diagram includes an optional O_2 liquefaction unit [38].

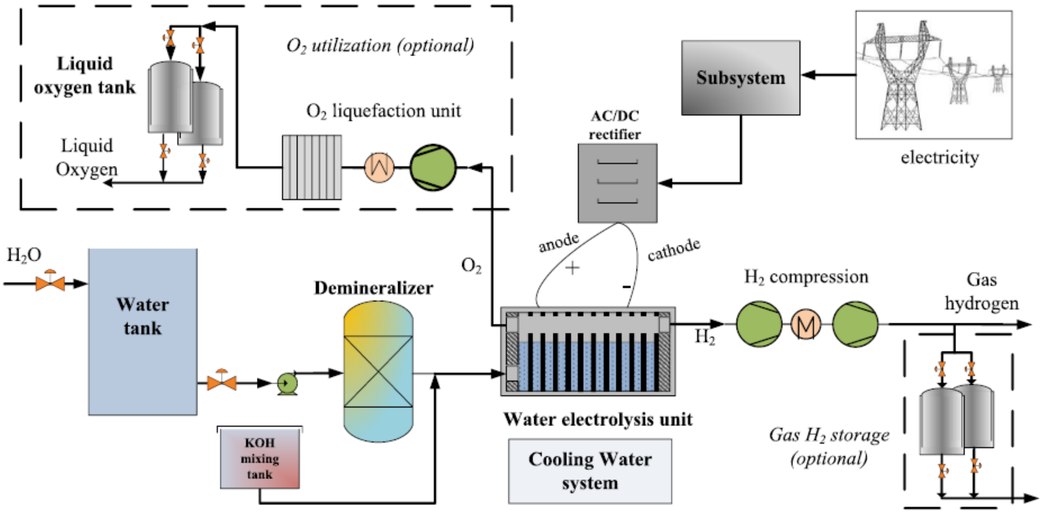


Figure 9-1: Conceptual process diagram of the KOH electrolysis of water. Source: [38]

The concept of generating hydrogen via water electrolysis using sustainable energy sources (power-to-hydrogen or power-to-gas) is developing quickly. In Germany, at least 13 pilot plants and pre-commercialization projects are active. One example is the Energiepark Mainz, where wind energy is used to generate electricity. Three SILYZER 200 electrolysers equipped with innovative proton exchange membrane (PEM), developed by Siemens, are used to produce up to 112 kg/h (1250 Nm^3/h) of hydrogen. A possible application for hydrogen produced at the site is feeding it into the natural gas grid. Within the research project, it will also be tested whether the hydrogen can be used to fuel the steam turbine of a nearby power plant (Kraftwerke Main-Wiesbaden AG at Ingelheimer Aue).

Other sources of hydrogen include waste gases from many industries, in which hydrogen is present at low purity. Examples include the coke-oven gas produced in steel mills, containing about 50 to 70% hydrogen by volume, or the water-saturated hydrogen produced in the chlroalkali industry. Surpluses of hydrogen are typically burned to generate heat or energy, which may be a non-optimal usage of this gas.

This scenario creates opportunities for valorizing the industrial waste gases by recovering high purity hydrogen in gas treatment units, or for designing processes in which the waste gas containing hydrogen can be used directly, with no need for pre-treatment. An example of a direct application of a hydrogen-containing waste gas is given in the following section.

9.2.2 CO_2-free fossil-based hydrogen

In a recent review [108], different technologies for combining hydrogen production and CO_2 capture where evaluated. A scheme of the most mature route for hydrogen production from fossil sources with CO_2 capture is shown in Figure 9-2. In this scheme, the CO_2 capture and H_2 purification units must be designed to deliver the required purity of both products.

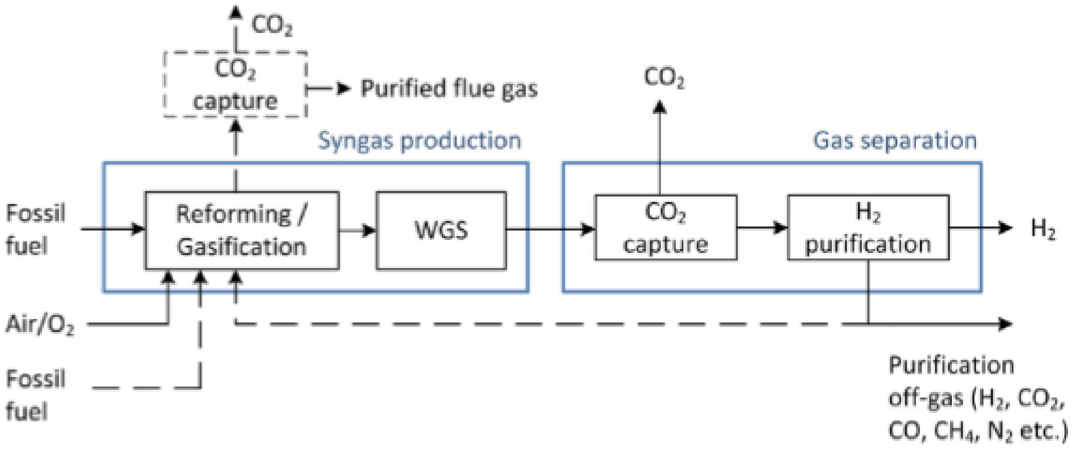


Figure 9-2: Most mature route for hydrogen production from fossil sources with CO_2 capture. Source: [108]

Statoil, Gasunie and Vattenfall have announced a project in which CO_2-free fossil-based hydrogen will be produced at large scale. The project involves modifying one of the three power trains in Vattenfall's gas power plant Magnum (in Eemshaven, The Netherlands) so that it can run on hydrogen instead of natural gas. Each train has a capacity of 440 MW. The natural gas, will be produced in Norway, and fed to a hydrogen production unit (reforming + WGS). The CO_2 will be captured injected for geological storage by Statoil. Gasunie will define the optimal hydrogen transportation (and possible storage) option [109].

9.3 Future potential

Cost breakdown in various Power-to-Fuel concepts confirm that the electricity and therefore the hydrogen cost is the most critical component in the fuel cost [38]. TNO internal evaluations, based on Dutch industrial price consumption bands and 2016 prices indicates that the cost of production of H_2 via reforming of coal or methane is around 1,3 €/kg (at large scale). Adding CO_2 capture to SMR-based hydrogen brings the cost up to 2,21 €/kg. The cost of renewable hydrogen has been reported as 2,5 €/kg for solar PV ([2], [110]) and TNO's internal evaluations indicate a cost of about 3 €/kg for electrolysers.
The rise in renewable energy generation, through e.g. wind and solar, has increased the interest in hydrogen production via water electrolysis. The electricity supply fluctuations and the linked electricity price fluctuations associated with renewable energy generation could result in a viable business case for large-scale industrial electrochemical hydrogen production.

10 ELECTROCHEMICAL CONVERSIONS

10.1 Background

Electrochemical conversion is a method in which electrical energy is used to drive chemical reduction or oxidation reactions. Between two electrodes, the cathode and anode, in a solution containing reactants, the electrolyte, a voltage is applied to lower the activation energy for a chemical conversion. As a result electrons are exchanged between the electrodes and the reactants giving an electrical current that determines the rate of the conversion reaction. This is analogous to temperature (voltage) and heat (current) in common thermally driven chemical reactions. The advantage of electrochemical conversion reactions is that they can be done at room temperature and atmospheric pressure. Electrochemical conversion does require a reaction medium, which is typically water.
The chloralkali process (Figure 10-1) is the most well-known industrial scale electrochemical conversion process. Chlorine gas, sodium hydroxide (caustic soda), and hydrogen gas as by-product, are produced from brine (sodium chloride) solutions in tens of millions tons a year [111]. When a voltage is applied to the sodium chloride solution the chloride ions are oxidized to chlorine gas and water is reduced to hydrogen gas leaving a sodium hydroxide solution.

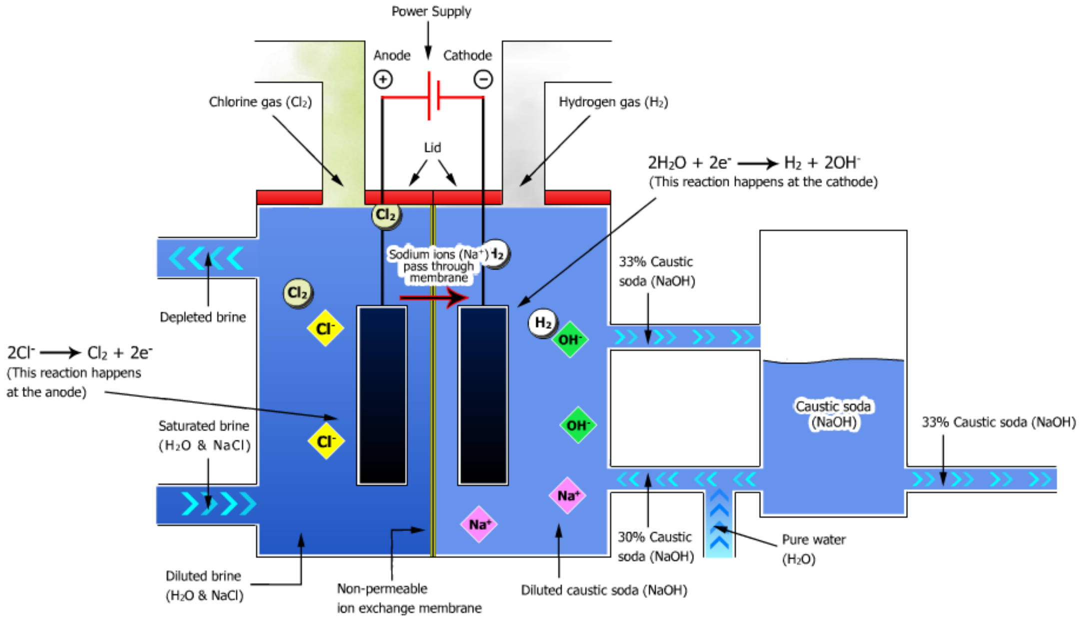


Figure 10-1: Schematic picture of the membrane chloralkali process. Source: [112]

Apart from the chloralkali process, the winning and electrorefining of some metals (aluminium, copper, zinc) and the electrohydrodimerization of acrylonitrile to adiponitrile are commercial large-scale electrochemical production processes[113]. Other electrochemical conversion processes are only done on small or semi-industrial scale, despite extensive R&D effort and the technical feasibility of many of these processes. Consumables and energy costs limit the economic viability of most of these processes, however. For example, the chloralkali industry in Europe spends 28% of its turnover on energy costs as around 3 MWh of electricity is needed to produce 1 ton of chlorine.

These limitations also holds for electrochemical conversion of CO_2 to chemicals and fuels, which has been known and studied for over 100 years.

10.2 State of the art

The role of CO_2 in climate change has increased R&D activities in electrochemical conversion of CO_2 in the last 25 years. Thermodynamically, electrochemical reduction reactions of CO_2 are well feasible at room temperature in water. Figure 10-2 shows the main electrochemical CO_2 reduction reactions yielding commercial relevant chemicals, namely: carbon monoxide, formate ($HCOO^-$), methane, ethylene, methanol and ethanol. The reactions are shown in the following equations, that evidence the degree of hydrogenation needed for each product:

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$$
$$CO_2 + H^+ + 2e^- \rightarrow HCOO^-$$
$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$$
$$2CO_2 + 12H^+ + 12e^- \rightarrow C_2H_4 + 4H_2O$$
$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$$
$$2CO_2 + 12H^+ + 12e^- \rightarrow CH_3CH_2OH + 3H_2O$$

Slightly alkaline aqueous hydrogen carbonate solutions saturated with CO_2 are typically used as electrolyte solution for these reactions. Oxalic acid ($H_2C_2O_4$) is a main product when non-aqueous solutions are used, and higher hydrocarbons have been observed.

Despite the well-established technical feasibility, the electrochemical conversion of CO_2 to commodity or fine chemicals is still in an research and development phase. A lot of research is focused on elucidating the complex mechanisms behind the CO_2 reduction reactions.

As shown in Figure 10-2 the conversion of CO_2 to chemicals involves a highly complex sequence of interrelated reaction steps. The electrochemical conversion of CO_2 is an electrocatalytic process, because the formation of reaction intermediate adsorbed on the cathode plays an decisive role. As a consequence the formation of a specific chemical is largely determined by the type of catalyst used. Both heterogeneous catalyst, i.e. metallic cathodes, and homogeneous catalyst, i.e. dissolved metal-ion complexes, have been extensively investigated. The main objective of current research is to develop a catalyst that combines a high activity for CO_2 reduction with a high selectivity for a particular chemical.

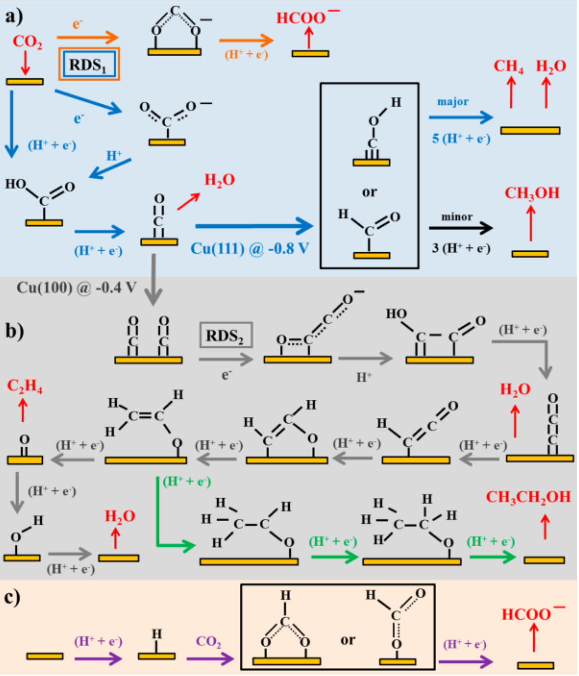


Figure 10-2: Possible reaction pathways for the electrochemical CO_2 reduction. Source: [114]

A high potential is required for CO_2 reduction reactions to take place. This increases the energy demand of the process. The low activity of the catalysts also results in the reduction of water to hydrogen gas a side reaction. This reduces the selectivity (or faradaic efficiency) of the process. The energy and faradaic efficiency for formic acid, syngas and C1-C2 (ethylene, methanol and ethanol) are shown in Figure 10-3.

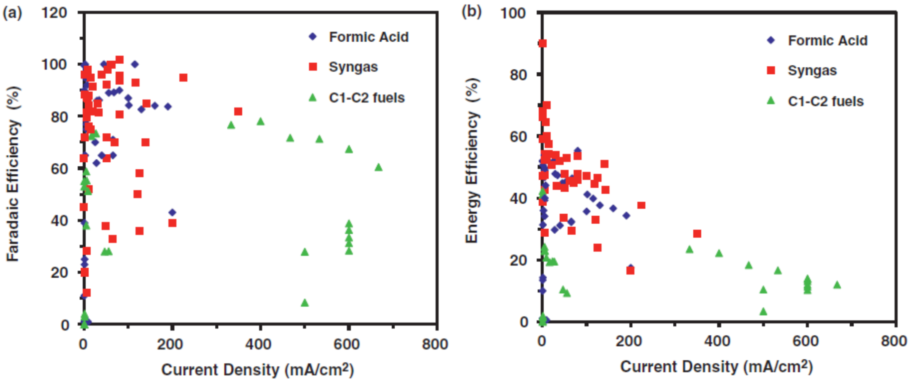


Figure 10-3: Reported faradaic efficiency (left) and energy efficiency (right) for electrochemical conversion of CO_2. Source: [115]

Significant steps for the industrial development of electrochemical CO_2 reduction have been reported recently. Avantium is investing in the electrochemical synthesis of oxalic acid, glycolic acid, ethylene glycol and other chemicals (the Volta Project, see Figure 10-4). The German "Power-to-X" project focuses on the conversion to carbon monoxide and synthesis gas, and the European development program EnCO2re includes projects in electrochemistry and catalysis [116].

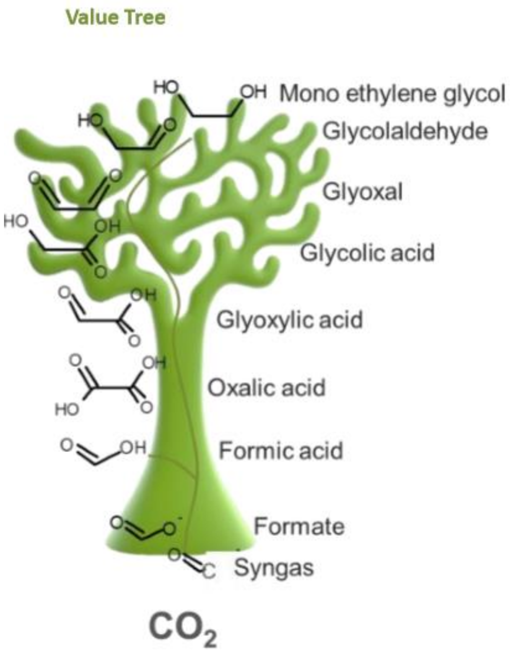


Figure 10-4: Avantium's value tree for the Volta project. Source: [117]

10.3 Future potential

The future potential of electrochemical conversion will depend on both economic and technical factors. Consumable and energy costs are typically limiting commercial viability of electrochemical conversion process. A comparison between the estimated energy cost and the market price of the products is given in Figure 10-5. It is clear that the potential of electrochemical production of the products that require a lower degree of hydrogenation (less energy) such as formic acid and CO is higher.

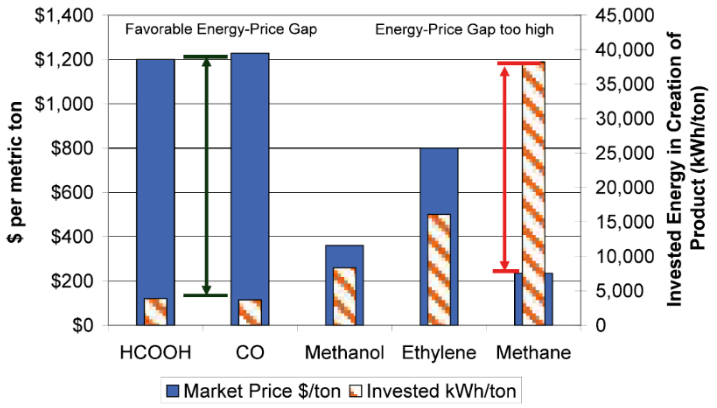


Figure 10-5: Gap between price and required energy costs (2011 data). Source: [118]

Based on the current state-of-the-art of the following four technological challenges need to be tackled to come to commercial viable electrochemical CO_2 conversion [118], as seen in Figure 10-6:

1. Current density higher than 1 kA/m^2;

2. Faradaic efficiency higher than 50%;
3. Power consumption lower than 500 kWh/kmol;
4. The electrocatalyst lifetime should be longer than 4000 h.

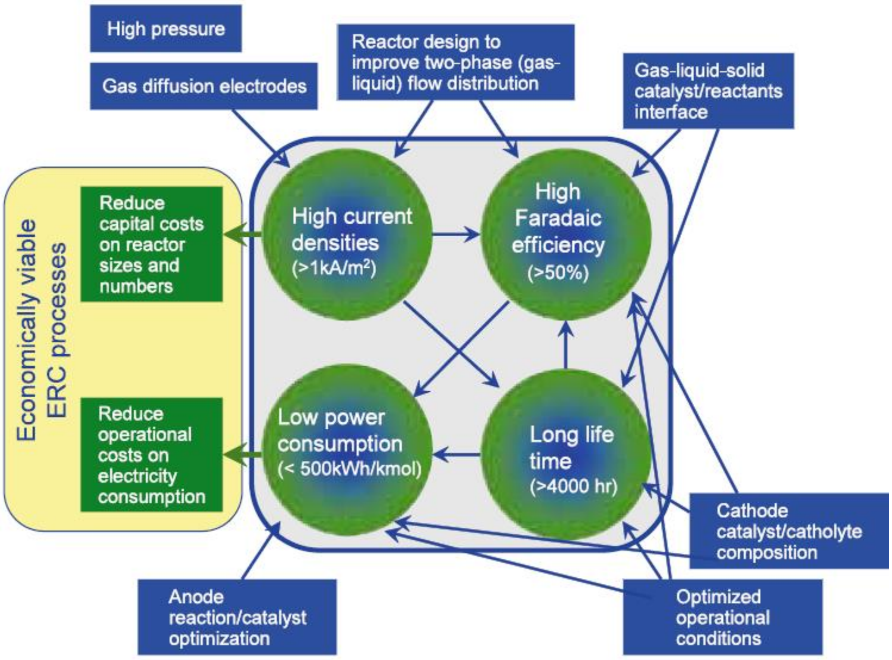
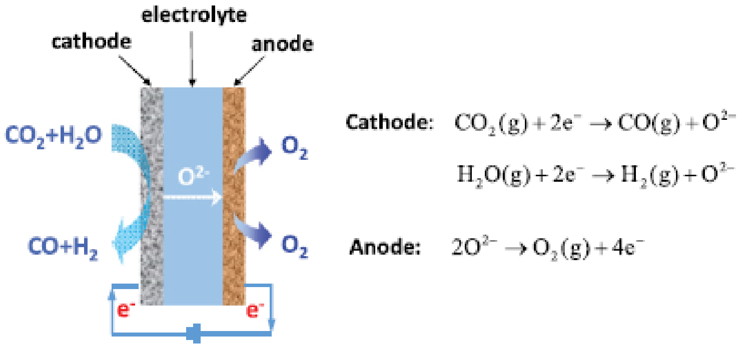


Figure 10-6: Key parameters in electrochemical reduction of CO_2. *Source:* [118]

10.3.1 Co-electrolysis of CO_2/H_2O-TRL level 3

Co-electrolysis is a future electrochemical method for producing hydrocarbons, that is intensively investigated at the moment in scientific research. In a co-electrolysis cell, CO_2 and H_2O are simultaneous reduced and converted to syngas CO/H_2. The cell is composed of a cathode where reduction takes place, an oxygen ion conducting electrolyte and an anode where O_2 is formed from the oxygen anions (see Figure 10-7). Here the gas reactions are carried out at a high temperature (>600°C) and the liquid reactions are carried out at a low temperature (<100°C) [119].



$$CO_2(g) + 2e^- \rightarrow CO(g) + O^{2-}$$

$$H_2O(g) + 2e^- \rightarrow H_2(g) + O^{2-}$$

$$2O^{2-} \rightarrow O_2(g) + 4e^-$$

Figure 10-7: Co-electrolysis cell from Zhang et al. [119] *At the cathode* CO_2 *and* H_2O *are reduced to syngas and at the anode the oxygen anion from the electrolyte is converted to* O_2.

By adding a Fischer-Tropsch catalyst to the cathode, commercial relevant chemical products such as methane can be formed (see Figure 10-8 Figure 10-8 shows a tubular reactor where co-electrolysis and Fischer-Tropsch synthesis are carried out along a temperature gradient [120]. This example yielded a methane flow of 0,84 mL/min and a CO_2 conversion of 64%.

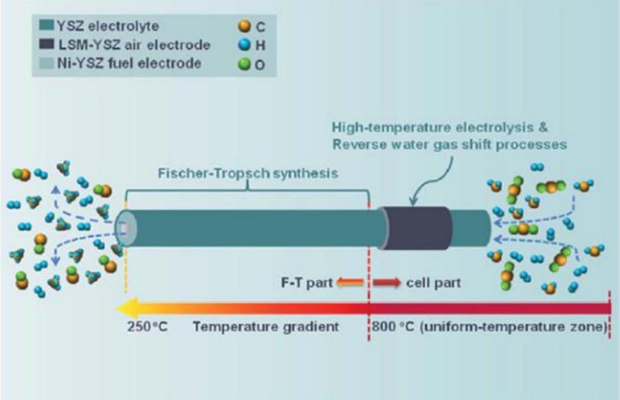


Figure 10-8: Combined co-electrolysis of H_2O/CO_2 to produce syngas and Fischer Tropsch synthesis to convert syngas to methane [120].

An advantage of the co-electrolysis electrochemical cell is the possible integration with renewable energy. Electrical energy from renewable energy sources such as solar or wind power, can be converted to synthetic hydrocarbon fuels in the solid oxide electrochemical cell.

The efficiency of the co-electrolysis process can be best compared to high temperature electrolysis of water to H_2. Although the introduction of CO_2 complicates the reactions, the efficiency of the process is not significantly affected compared to pure water electrolysis [121].

Although co-electrolysis of CO_2/H_2O has the potential to produce interesting hydrocarbon fuels and nicely integrates with renewable energy sources, more research and development for highly active cathode materials, understanding of the mechanism of CO_2 electrolysis and industrial implementation is necessary before commercialization.

10.4 Advantages and disadvantages

10.4.1 Advantages

In comparison to other CO_2 utilization methods electrochemical conversion has the following advantages in CO_2 abatement:

- Electrochemical conversion of CO_2 is performed under mild conditions, at room temperature and ambient pressure in an aqueous solution;
- Electrochemical processes can cope with fluctuation in energy supply making them compatible with fluctuating renewable energy supply sources, like solar and wind power. In particular solar peak power at mid-day could be used for industrial electrochemical CO_2 conversion. In addition the production volumes could be matched to electricity price fluctuations associated with the electricity supply fluctuations to reduce energy costs of the process.

- Electrochemical conversion is a scalable technology with a proven industrial record, e.g. in the chloralkali process. Although some engineering specific for CO_2 conversion is needed, a lot of technology, materials and equipment for large industrial-scale electrochemical production is already available.
- Electrochemical reactors are modular allowing a gradual increase in production volume from pilot to full industrial scale production. In addition the factory footprint of electrochemical reactors is low due to their compactness.

10.4.2 Disadvantages

Currently the electrochemical CO_2 conversion has the following advantages:

- The electrochemical conversion of CO_2 does still require a significant improvement on all aspects relevant for commercial viability (see Figure 10-6);
- As electrochemical conversion requires electrical energy it can only result in CO_2 abatement if it runs on a renewable energy supply. Figure 10-9 shows that for the most efficient electrochemical conversion process reported (formic acid formation at 90% faradaic efficiency), around 4 MWh of energy is needed to convert one ton of CO_2. Hence, CO_2 abatement is only realized if less than 0.25 ton CO_2 is generated per MWh of electrical energy used in the conversion process. CO_2 emissions of fossil fuel-based electricity generation is around 0.5 ton CO_2 per MWh.
- Of the electrochemical CO_2 conversion products only ethylene, ethanol and methanol are commodity chemicals with production volumes in the Mtons/year range. Hence, only these products have the potential for significant CO_2 abatement. Unfortunately, these products have the lowest faradaic efficiency (selectivity).

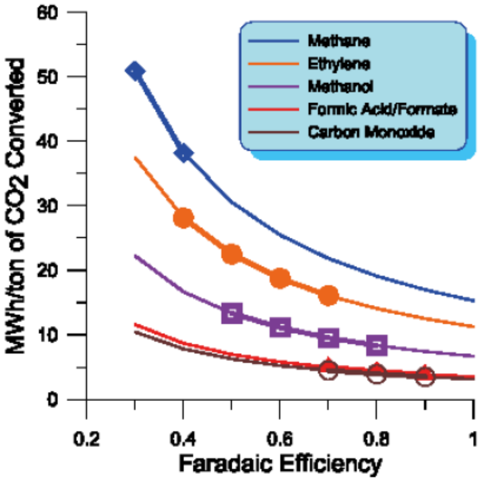


Figure 10-9: Energy requirement to convert CO_2 to various chemicals: dependence on the faradeic efficiency of the electrochemical process. Source: [118]

11 CO_2 MINERALIZATION

11.1 Background

CO_2 mineralization or mineral carbonation provides an alternative to the underground storage of carbon dioxide by converting gaseous CO_2 into a thermodynamically more stable state, namely solid inorganic carbonates. The natural analogue of this CO_2 sequestration process is called silicate weathering where calcium (Ca) and magnesium (Mg) bearing rocks (the source materials) react with atmospheric carbon dioxide to form carbonate rocks at geological time scales[122]. In order to speed up the kinetics of this process, ex situ CO_2 mineralization was proposed where a Ca or Mg source mineral is reacted with a higher concentration of CO_2 in a reactor [123]–[125]. The rate-limiting step for these processes is often the dissolution of source materials to release Ca^{2+} and Mg^{2+} ions. This makes the choice of the source material for CO_2 mineralization a critical one. The products of the process, namely the carbonates, could have potential market value thereby making the CO_2 mineralization process economically viable.

11.1.1 Natural source minerals

Carbon dioxide can form stable solid carbonate products with a wide range of metals. The most ideal and abundant candidates for CO_2 mineralization are the alkaline earth metals, Mg and Ca whose carbonates have a very low solubility in water [122], [126]. Other divalent metals like Fe, Ni, Pb, etc. can also form stable carbonates. However, they are too valuable a resource to be used for the purpose of large-scale CO_2 mitigation. Alkali metals like Na and K form solid carbonates and bicarbonates that have a very high solubility in water. Therefore, they are not good candidates for long-term CO_2 storage. Natural minerals, typically calcium and magnesium silicates, have been reacted with carbon dioxide in an industrial setting to form solid carbonates. The transformation of these silicates into carbonates is thermodynamically favorable, and is exothermic. Typical transformation of silicates into carbonates can be written as:

$$\text{Olivine: } \mathrm{Mg_2SiO_4 + 2CO_2} \leftrightarrow \mathrm{2MgCO_3 + SiO_2} + 178\ \mathrm{kJ}$$
$$\text{Serpentine: } \mathrm{Mg_3Si_2O_5(OH)_4 + 3CO_2} \leftrightarrow \mathrm{3MgCO_3 + 2SiO_2 + 2H_2O} + 192\ \mathrm{kJ}$$
$$\text{Wollastonite: } \mathrm{CaSiO_3 + CO_2} \leftrightarrow \mathrm{CaCO_3 + SiO_2} + 90\ \mathrm{kJ}$$

Since only Ca^{2+} and Mg^{2+} ions in a source mineral can store CO_2, minerals with high mass ratios of Ca (or CaO) and Mg (or MgO) are desirable as source minerals. This allows for the handling of a lower mass of source mineral to sequester a given amount of CO2. Each mineral, therefore, can be assigned its Ca and Mg oxide content and a theoretical carbonation potential, R_{CO2}, which is defined as [127]:

$$R_{\mathrm{CO2}} = \frac{\text{weight of source material needed}}{\text{weight of CO}_2\text{ sequestered}}$$

A higher Ca and Mg oxide content and a lower R_{CO2} are desirable characteristics of a source mineral. The mafic and the ultramafic rocks are rich in their MgO and CaO content and have a low content of silica, sodium, and potassium. Table 11-1 presents a list of some natural minerals and shows their respective oxide content and R_{CO2}. The calculated R_{CO2} assumes that the source mineral is pure and that all of the cation (Mg or Ca) can be extracted to sequester CO_2.

The molar abundances of Ca and Mg silicates on the earth's crust are estimated to be similar. However, most of the calcium oxide occur as Feldspar that has a CaO content of about 10 wt% [122]. The lower content of CaO implies that a much larger amount of source mineral needs to be mined, processed, and handled to sequester CO_2. The estimate of global reserves of CaO rich wollastonite is only between 90 and 270 Mt [128], [129]. MgO content in magnesium silicate rocks, on the other hand, is much higher. This renders magnesium silicates like serpentine and olivine as attractive source materials for CO_2 mineralization. Global estimates for accessible olivine and serpentine reserves are estimated to significantly exceed the total Mg requirement to neutralize the CO_2 from all worldwide coal resources (which is estimated at 10,000 Gt) [125].

Table 11-1 Natural source materials for CO_2 mineralization

Name	Formula	Mol. wt. [g/mol]	Oxide content [wt. %]	R_{CO2} [g/gCO_2]
Magnesium oxide/Periclase	MgO	40.30	100	0.92
Calcium oxide	CaO	56.08	100	1.27
Slaked lime	$Ca(OH)_2$	74.09	75.7	1.68
Brucite	$Mg(OH)_2$	58.32	69.1	1.33
Olivine/Forsterite	Mg_2SiO_4	140.69	57.3	1.60
Wollastonite	$CaSiO_3$	116.16	48.3	2.64
Serpentine	$Mg_3Si_2O_5(OH)_4$	277.11	43.6	2.10
Enstatite	$MgSiO_3$	100.39	40.1	2.28
Talc	$Mg_3Si_4O_{10}(OH)_2$	379.27	31.9	2.87
Plagioclase/Feldspar	$Na_{0.5}Ca_{0.}5Si_3AlO8$	277.41	10.4	12.30

11.1.2 Industrial wastes

Besides natural mineral resources, several industrial wastes or low value products are rich in CaO or MgO that can be carbonated. These include mine tailings, cement kiln dust (CKD), fly ash from combustion of fossil fuels or biomass, construction and demolition wastes, waste concrete, and wastes from steel production. Estimates of exact chemical composition and therefore, the carbonation potential, R_{CO2}, is hard to estimate due to large variations across the different sources of these waste resources. Industrial wastes have the advantage of the source material being readily available, and in most cases, the carbonation of these wastes neutralizes their alkalinity allowing for a safer disposal. Although industrial wastes appear to be attractive feedstock for the mineral carbonation process, their availability is very small in comparison to natural mineral resources.

With regard to the cement industry, an estimated 0.20 tons of CKD is generated for every ton of clinker or cement produced [130], [131]. Many manufacturing facilities recycle the CKD back into the cement kiln as raw feed. The degree to which CKD is recycled is determined by its composition and varies from one production plant to another [130].

11.2 State of the art

A number of process routes for carbonation of natural minerals have been proposed in literature and they primarily involve a combination of mineral pre-treatment and a sequestration process. The mineral pre-treatment typically involves some or all of these following steps:

- Particle size reduction – In order to achieve faster reaction rates, minerals need to be crushed and ground to small particle sizes that offer a larger reactive surface area.

- Magnetic separation – Oxidation of Fe_3O_4 to form Fe_2O_3 has been found to slow down the carbonation process [132]. Removal of the Fe_3O_4 particles by magnetic separation can avoid this limitation.
- Thermal activation by dehydroxylation – Serpentine contains about 13 wt. % of chemically bound water. Dehydroxylation of serpentine by heating it to 600°C – 650°C has been found to be effective in enhancing its reaction rate significantly. The dehydroxylation transforms serpentine into the more reactive olivine, as well as creates pores in the particles that enhance the reactive surface area [133]–[135].

A number of mineral carbonation reviews exist in literature, some of which are rather recent, e.g.[136], [137]. In this section we do not intend to re-discuss every process idea that has been covered in recent reviews. Instead, the following sections will highlight some of the well-known processes, together with newly reported process designs that have not been covered in above reviews.

11.2.1 Direct gas-solid carbonation – TRL3

A direct gas-solid carbonation route would be an ideal process operation for storing CO_2 as solid carbonates by means of a gas-solid chemical reaction. The carbonation process of metal oxides results in a net increase in the volume of the solid products formed. The kinetics of direct gas-solid carbonation process, however, suffers greatly from diffusion limitations arising from the carbonate product and silica matrix layers. These limitations can be tackled by reducing the particle sizes, fluidization of the bed and continuous mechanical abrasion of the diffusion layer. Zevenhoven et al. [138] demonstrated that silicate minerals like powdered serpentine, did not undergo carbonation under the dry gas-solid route. On the other hand, direct gas-solid carbonation at high temperatures (>400°C) and moderate CO_2 pressures (>10 bar) of pure metal oxides and hydroxides, like $Mg(OH)_2$, has been shown to be effective with conversion extents ranging from 50% - 100% in less than 30 min [139], [140]. The presence of moisture in the gas was found to further enhance the extent of carbonation. A recent experimental study demonstrates the possibility of using milder temperatures (~150°C) and high humidity conditions for the carbonation process [141]. $Mg(OH)_2$, in all these studies, is extracted from serpentine rocks using additives like ammonium salts [141], [142] and strong acids [140]. The recovery of these additives is often an energy intensive process, and plays a significant role in the choice of additives. Heat treated serpentine has been recently shown to have up to 50% conversion extent in a fluidized bed operating with moist CO_2 at 1 bar pressure and 90°C [143]. Heat activation is an energy intensive process, but it provides a very reactive silicate material which does not need additives for Mg-extraction. The direct gas-solid carbonation of CKD at room temperature and pressures resulted in up to 70% conversion [130]. CKD would be the most ideal source material for those cement industries which do not have a better use for CKD.

11.2.2 Single step aqueous processes – TRL3

The presence of water has in general been shown to enhance the reaction rates for carbonation of all source materials. However, the faster reaction rates comes with an energy penalty associated to the heat-up of aqueous solutions to sustain the reaction temperature. A single step aqueous process is one where Mg or Ca ions are extracted from the silicate matrix and are precipitated as carbonates in the same reactor.

Pioneering work on single step aqueous process was first performed at the National Energy Technology Laboratory (NETL) [127]. Based on experimental data from a wide range of operating conditions for olivine, wollastonite, and heat activated serpentine, suitable conditions were identified to be between 100°C and 200°C, and CO2 pressures exceeding 100 bar. They also performed a case study to estimate the cost of mineral pre-treatment to capture 100% of the emissions from a 1 GW power plant. They eventually concluded that only olivine and wollastonite, the two minerals that are not very abundant, have the potential to sequester CO_2. Further studies from other research groups have used the data from NETL as benchmark values, and have demonstrated improved efficiency with serpentine (a very abundant mineral) in multi-step aqueous processes. Recently, Li and Hitch [144] investigated the effect of mechanical activation on olivine (forsterite) –rich mine tailing minerals and obtained results that exhibit similar energy penalty as NETL [127].

11.2.3 Multi-step aqueous processes

Although a single step processes may have a lower capital and operating costs, the overall efficiency of the process is limited. This is because the optimal operating conditions for each of the different steps involved in CO_2 mineralization, namely CO_2 dissolution in the aqueous solution, silicate dissolution to release Mg/Ca, and the precipitation of carbonates, are different. For example, while the dissolution of CO_2 in aqueous solution is preferable at low temperatures, the precipitation of carbonates is faster and favorable at high temperatures. This has led to subsequent research in the direction of multi-step aqueous processes that offer a higher degree of freedom with regard to the operating conditions. In multi-step processes, Mg^{2+} or Ca^{2+} cations are first extracted from the silicate mineral and are then carbonated in a different reactor. Such a process can provide a carbonate product stream of high purity. Some processes use additives in order to extract the cations and/or precipitate the carbonates. In such scenarios, there is a need for an additional step involving the recovery of additives.

11.2.3.1 The Nottingham University (NU) process – TRL3

The Nottingham University (NU) process uses natural serpentine to sequester CO2 as magnesium carbonates [145]. Figure 1 shows the scheme of the proposed flowsheet where ammonium bisulphate is used to extract magnesium from serpentine at temperatures under 100°C in an aqueous medium. The kinetics of extraction of Mg under these operating conditions were measured in an independent study [146]. A CO_2 capture step using aqueous chilled ammonia is integrated into this process, and the resulting ammonium bicarbonate solution is reacted with the aqueous solution from serpentine dissolution step to precipitate magnesium carbonate at 90°C through a pH swing operation. In order to recover ammonium bisulphate and ammonia to be reused in the process, an energy intensive step of evaporating large amounts of water, followed by a regeneration step is necessary [136].

Improvements are currently being made in order to reduce the energy demand for this regeneration step. A recent communication demonstrated the ability to recover ammonium sulphate by using methanol as an anti-solvent to crystallize out ammonium sulphate, followed by a distillation process to separate methanol and water [147]. The energy demand for the mineralization process was estimated to have been reduced by 34%, by switching to an extraction step in order to recover ammonium bisulphate. In another move to make the entire process economically more attractive, the ability to sequester CO_2, NOx, and SOx simultaneously was also investigated[148]. However, the presence of NOx and SOx decreased the carbonation efficiency, and the first attempts at removing of NOx and SOx were not ideal (25% NOx removal and 41% SOx removal). Nevertheless, these results can be seen as promising first results, and the ability of a CO_2 mineralization process to simultaneously sequester NOx and SOx will make the process more attractive.

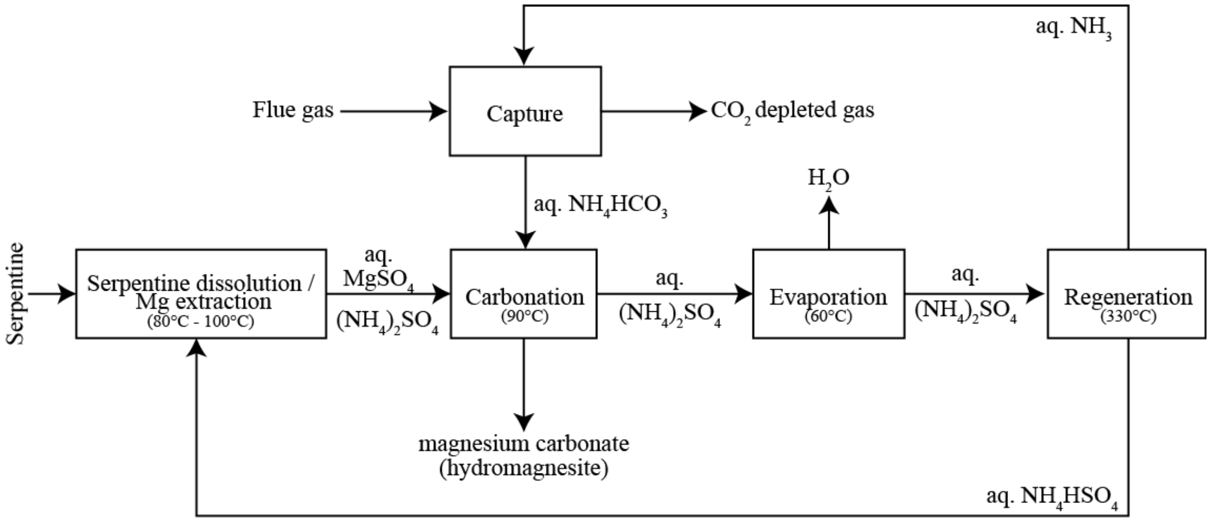


Figure 11-1 Flowsheet scheme of the Nottingham University process [145]

11.2.3.2 The Åbo Akademi (AA) process – TRL3

The Åbo Akademi (AA) process is an alternative process to the NU process that uses natural serpentine found in Finland to sequester CO_2 as magnesium carbonates [139]. Figure 11-2 shows a scheme of this proposed process, where ammonium sulphate is used to extract magnesium from serpentine at high temperatures (T > 400°C). This extraction is a gas-solid reaction and the product solids are dissolved in an aqueous solution. $Mg(OH)_2$ is then precipitated from the aqueous solution using ammonia through a pH swing process. The solid hydroxide particles are then carbonated in a fluidised bed reactor at 500°C and 20 bar pressure to form $MgCO_3$. In order to regenerate ammonium sulphate, the aqueous solution from the dissolution step is evaporated to remove water. The advantage of this process is that it is a dry serpentine reaction process; therefore it does not require the aqueous solutions to be heated to the high temperatures of 400°C in the extraction step. Nevertheless the regeneration process is energy intensive, and continuous efforts have been made in order to reduce the energy requirements of the process. In a recent communication, the authors have investigated a wet carbonation route (see Figure 11-3) where the fluidised bed reactor is replaced with an aqueous precipitation reactor operating at T < 100°C [149], and have employed a membrane separation step to recover ammonium sulphate [142], instead of evaporating water. The advantage of the wet carbonation route is that the precipitation of carbonates operate at atmospheric pressure conditions, therefore requiring no compression of the flue gas.

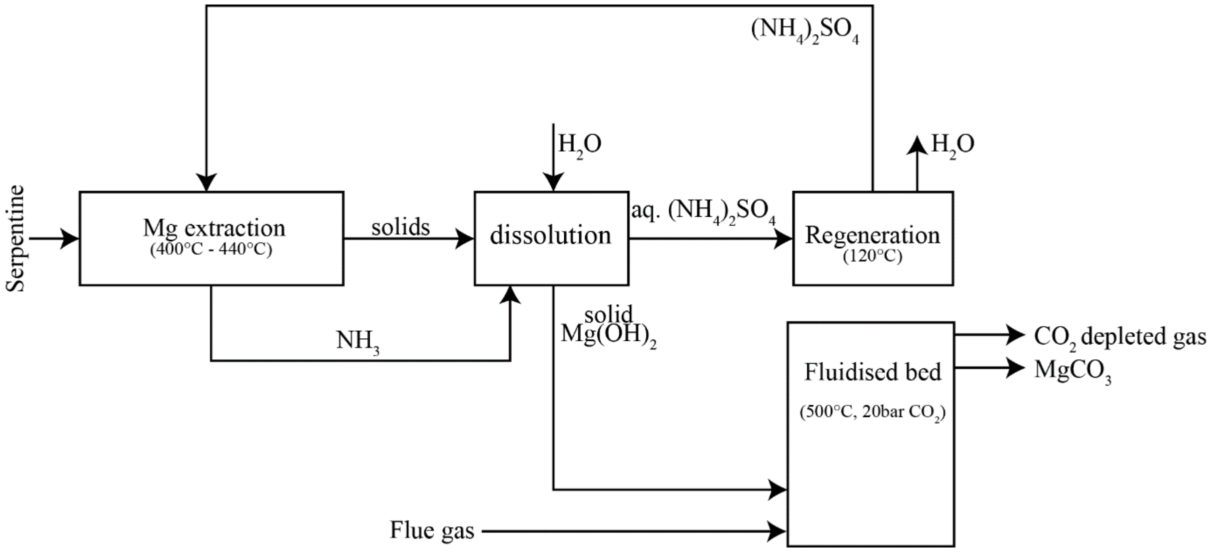


Figure 11-2 Flowsheet scheme of the dry carbonation route of the AA process [139]

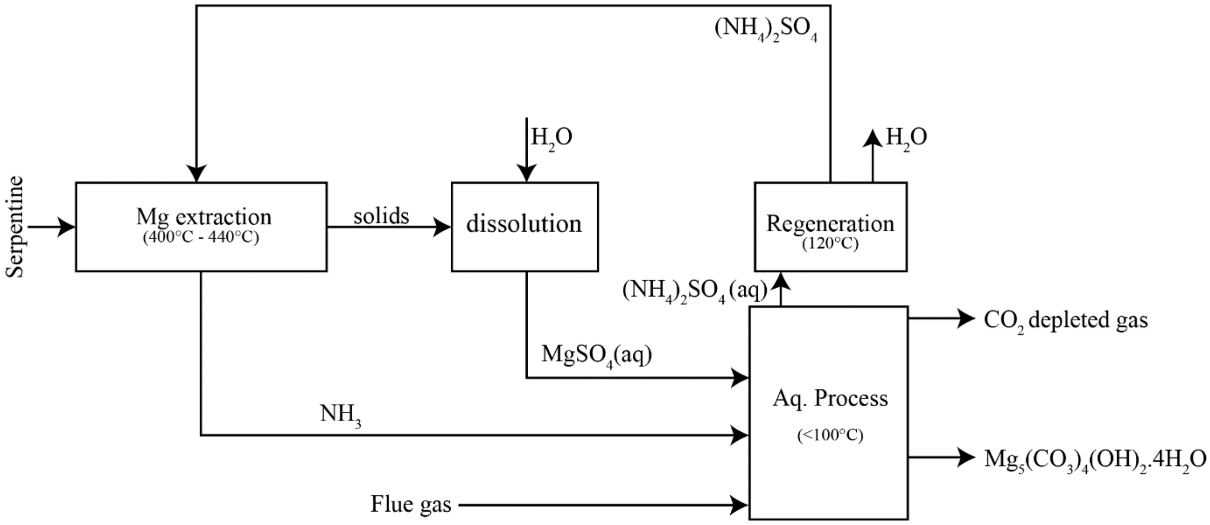


Figure 11-3 Flowsheet scheme of wet carbonation route of AA process [149]

11.2.4 Processes involving heat activated/treated serpentine (HTS) – TRL3 to 5

Natural serpentine particles when heated to a high temperature (> 600°C) undergoes dehydroxylation, which results in destruction of crystal lattice, formation of olivine grains, and the generation of pores that result in an increased reactive surface area for dissolution (e.g. [30]). Batch/single step carbonation of HTS was first studied at NETL[127]. An optimal activation temperature of 630°C for 2 hours was reported to yield 83% conversion at 185°C and CO_2 pressure of 112 atm. However, the authors considered heat activation to be extremely energy intensive due to their calculated results of 326kWh/t serp. – which assumed electrical heating and no heat integration in the heat activation step.

This calculated energy demand was challenged in several subsequent publications, where efforts were made to achieve an optimal heat activation strategy (see [150], [151] and references therein). Partial dehydroxylation of serpentine was found to be desirable, and the extent of dehydroxylation depended on the source of serpentine. In particular, Balucan et al. demonstrated that optimal heat activation required only 80% dehydroxylation of serpentine from the Great Serpentine Belt in Australia[150]. This when combined with a strategy of using natural gas for heat activation (to minimize secondary emissions) together with 80% sensible heat recovery resulted in an energy demand for thermal activation of about 158 kWh/t serp. Their calculation estimate that only 7% of the HTS will be needed to sequester the secondary emissions resulting from thermal activation (in comparison, the NETL study suggested that secondary emissions would be too high that no net CO_2 can be captured from a thermally activated process). Several process designs have been tested using HTS. Sanna et al. [152] performed studies to measure the dissolution rates of magnesium from HTS using ammonium bisulphate for its use in the NU process. Mazzotti and co-workers [134], [135], [153], [154] performed a detailed investigation into the dissolution kinetics of HTS particles under flue gas conditions at moderate temperatures (<120°C). In parallel, Blais and co-workers investigated the dissolution kinetics at room temperature [155]–[158]. Farhang et al. studied the effect of particle sizes and slurry density on the dissolution kinetics of HTS [159]. Brent[151] has designed a process that carbonates HTS at high temperatures (up to 175°C) and CO_2 pressures (50 – 160bar). An Australian based company, Mineral Carbonation International, has built a pilot plant to demonstrate the feasibility of the above process [160].

11.2.4.1 The Shell Process – TRL5

Shell has developed a mineral carbonation process using HTS that operates at lower temperatures and CO_2 pressures [161]. The advantage of the proposed process is that it uses no additives, and therefore needs no additive recovery step. Heat activation was performed in a fluidised bed reactor at temperatures between 600°C and 700°C[162]. Technical feasibility of the proposed process was investigated through a continuous pilot plant [161]. However, no experimental data have been published from this study. A simple conceptual flowsheet of their proposed process was published and is as shown in Figure 11-4. It consists of three steps: 1) HTS is dissolved under flue gas atmosphere with concurrent grinding and CO_2 sorption, 2) HTS is further dissolved under flue gas atmosphere without grinding, and 3) magnesium carbonate are precipitated at high temperatures.

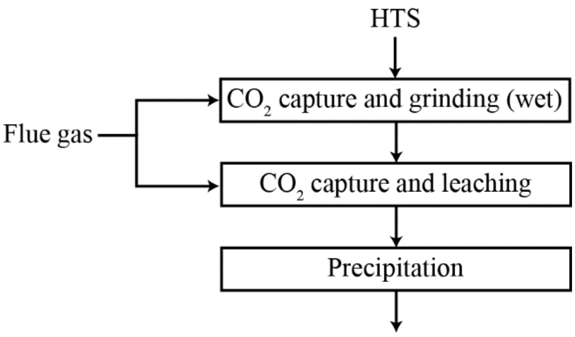


Figure 11-4 Conceptual flowsheet of the 'Shell process'.

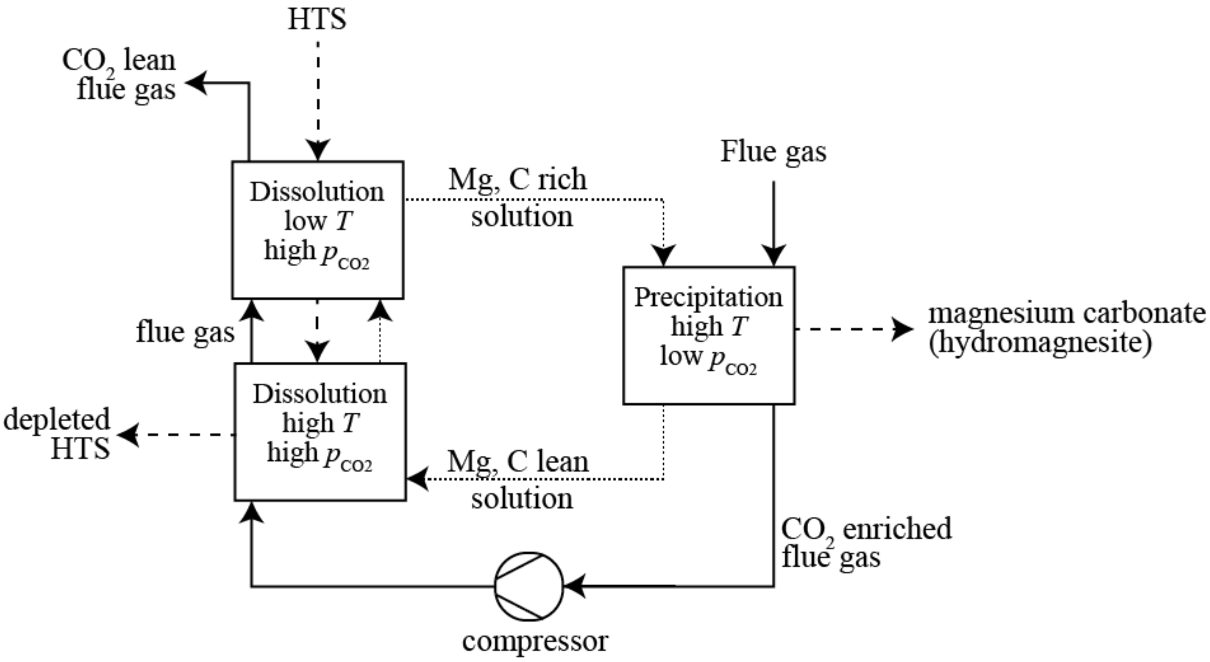


Figure 11-5 Flowsheet scheme of ETH Zurich process using HTS[163]. *The gas (solid lines), liquid (dotted lines), and solid (dashed lines) streams are indicated.*

11.2.4.2 ETH Zurich process – TRL3

Investigation into this 'Shell process' was continued at ETH Zürich where the dissolution kinetics of HTS was investigated at moderate temperatures (30°C – 120°C) and low CO_2 pressures (< 2 bar) [134], [135], [153], [154]. The HTS material was supplied by Shell, and was prepared at 610°C to produce a 75% dehydroxylated sample. The motivation to study the magnesium extraction rates at lower temperatures and very low CO_2 pressures was to avoid cost related to CO_2 capture and minimize the cost associated with gas compression. However, operation at such lean conditions does not result in very high conversions. Lab-scale investigations of single-step and double-step aqueous processes were investigated, and conversion values of up to 50% were obtained at CO_2 pressures < 1 bar [163]. However it should be noted that the data for the net CO_2 captured and energy requirements were not provided in that study. Figure 11-5 shows a scheme of their proposed multi-step process, involving two dissolution steps and one precipitation step. Although the exact operating temperatures and pressures of the different steps were not indicated in their study, the entire process was envisaged to operate at under 90°C and low pressures [163]. A significant advantage of this process is its relative simplicity and the absence of additives for promoting the process and steps for their recovery; the energy intensive step instead lies in the production of HTS. In parallel, Bhardwaj et al. [143] used the same HTS material from Shell and obtained a 50% conversion and 40% CO_2 capture efficiency in a fluidized bed reactor operating at 90°C and with moist CO_2 at a pressure of 1 bar.

11.2.4.3 Université du Québec (UQ) process

Researchers from the Université du Québec have performed a detailed investigation on the performance of a process similar to the idea of 'Shell process' [164]. Figure 11-6 shows a simplified scheme of their proposed process. It consists of six parallel dissolution steps where magnesium is sequentially leached from HTS under flue gas atmosphere. An intermediate milling step of partially leached serpentine is included in order to improve the leaching performance. The six dissolution reactors operate at room temperature and 10 barg pressure, while the precipitation reactor operates at 40°C. Technical and economical evaluations were performed for the direct flue-gas carbonation of HTS (mine tailings) from a cement plant flue gas source.

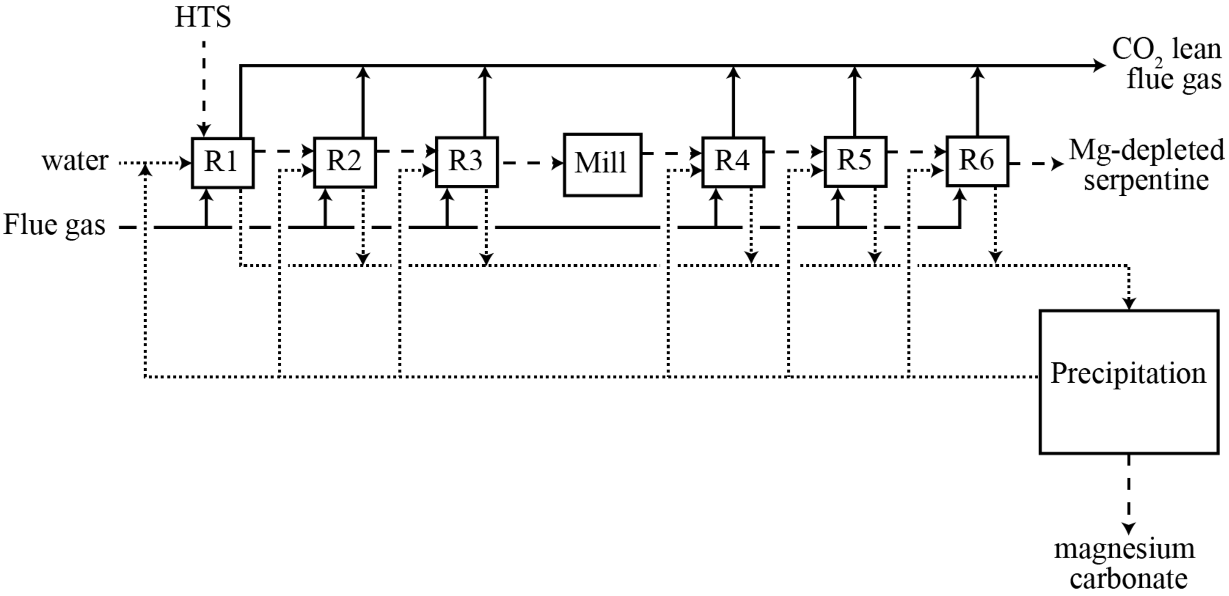


Figure 11-6 Flowsheet scheme of Université du Québec process [164]. *The gas (solid lines), liquid (dotted lines), and solid (dashed lines) streams are indicated.*

11.3 Future Potential

Compared to most other process operations, CO_2 mineralization is relatively new and has a small research community. The engineering challenge is definitely not trivial, and the misinformation about the exorbitant costs of the process, or its non-feasibility continues to keep this research community small [165], and the progress, perhaps slow. There is a large potential for further improvements in the process designs reported in literature. In particular, the ‘low hanging fruit’ for industries are the carbonation of alkaline industrial residues and mine tailings – whose resource availability is not abundant, but offers very fast reaction kinetics [136]. In many of these industrial residues, their carbonation also neutralizes their alkalinity and allows for the safe disposal of the wastes. With regards to cement industries, the use of CKD as a source material to store CO_2 would be an ideal opportunity.

With regard to mineral resources like serpentine, further attempts to improve and understand its heat activation is necessary. HTS has the advantage of running a mineral carbonation process at lean carbonation conditions without the use of additives. However, an experimental and simulated demonstration of the complete process has not yet been made, and investigations in this direction may lead to viable process. Mineral carbonation also offers two solid products, namely residual silica (or silicate) and Mg/Ca carbonate, whose potential as a feedstock in other industrial processes can be evaluated. This will bring a product value for the products of CO_2 mineralization, thereby making it economically competitive to other sequestration options.

11.4 Advantages and disadvantages

The biggest advantage of CO_2 mineralization is that the CO_2 storage is highly verifiable and unquestionably permanent [122]. Figure 11-7 shows the energy states of carbon in its different form, namely as a fuel carbon, as CO_2, and as a solid carbonate. The figure reveals that the transformation of CO_2 to carbonates is exothermic and thermodynamically spontaneous. The carbon stored as a carbonate is stable and will not release the carbon as CO_2 unless it is dissolved in harsh acidic environments. This makes the monitoring process for the carbonates practically cost-free [122]. The carbonate product, the residual silica/silicate mineral, and the precious rare earth metals that are leached from silicate rocks can have industrial value and make the entire process economically attractive.

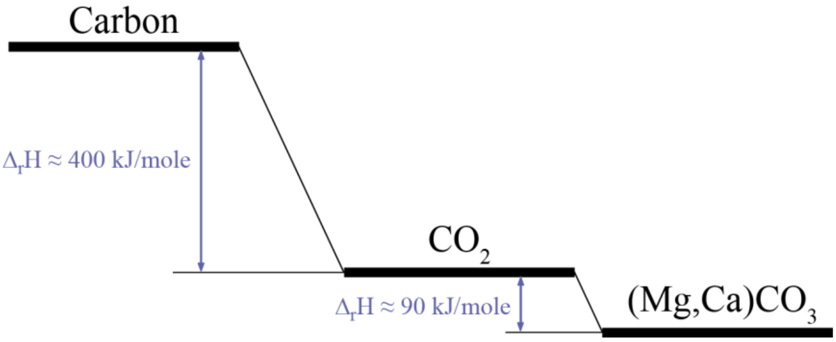


Figure 11-7 Enthalpy of reaction for the combustion of carbon to CO2 and of a typical carbonation reaction of the silicate mineral (olivine), expressed per mole of carbon.

However, the assurance of a safe storage of CO_2 comes with a cost, having both an economic and environmental impact. Mineralization is often viewed with skepticism due to its higher costs in comparison to short-term operational costs for geological storage. The absolute safety associated to storing CO_2 as carbonates unfortunately cannot be monetized. Large scale mining of serpentine and other silicate rocks can have significant impact on the local environment, and efforts need to be made to reduce the secondary impact on the environment [122]. Processes involving industrial wastes like cement kiln dust as source material can be quite cheap. However the lack of their abundance and possible competing usages limits their potential to sequester large quantities of CO_2. Recent advances in the understanding of the reaction kinetics of the cation extraction from large source silicate minerals will potentially reduce the costs associated with large scale CO_2 mineralization processes.

11.5 Potential in connection with the cement industry

CO_2 mineralization processes that use a Ca-based source feedstock offer the possibility to form calcium carbonate products. The calcium carbonate products may be landfilled (as a CO_2 storage option), or may be utilized in cement industry (as a replacement for limestone [166]) or other industries which need precipitated calcium carbonates (e.g. paper industry, etc.). However, a detailed techno-economic evaluation of such process with Ca-based feedstock and applied to a cement plant, to the best of our knowledge, is yet to be made.

Given its larger abundance, many studies have performed LCA and techno-economic evaluations of processes using serpentine feedstock [127], [164], [165], [167], [168]. In particular, researchers have estimated the energy requirements for fixing CO_2 from the flue gas of a cement plant as magnesium carbonates for the AA process (see item 11.2.3.2) and the UQ process (see item 11.2.4.3). It is to be noted that currently both processes do not need a separate CO_2 capture step.

Zevenhoven and co-workers compared the exergy demand of their dry and wet AA processes to fix unit mass of CO_2 from the flue gas of a cement kiln (23% CO_2) [149], [169]. They estimated a thermal exergy demand of 2.6 MJ/kg CO_2fixed and 15.4 MJ/kg CO_2fixed for their dry and wet AA process, respectively, assuming identical carbonation potentials, R_{CO2} of 2.9 kgRock/kgCO_2. However, the dry AA process requires an additional electrical power of 0.89 MJ/kgCO_2fixed due to the compression of the flue gas. Life cycle analysis on the two processes were also performed in order to estimate secondary (and equivalent) CO_2 emissions for a scenario where serpentine is mined, transported, and carbonated in Finland [169]. It was shown that the wet AA process, with a life cycle CO_2 emission reduction of 74%, outperforms the dry AA process (life cycle CO_2 emission reduction of 44%).

Pasquier et al. [164] performed a technical and economic evaluation for the UQ process applied to carbonate mine tailings using the flue gas from a cement plant (18% CO_2). They assumed a lower serpentine carbonation efficiency (of 50%) resulting in a higher R_{CO2} of 4.3 kgRock/kgCO2. They calculated thermal and power demands of 6.9 MJ/kgCO_2fixed and 1.1 MJ/kgCO_2fixed, respectively, for the UQ process. Additionally, they compared the effect of choice of the energy source on the cost and CO_2 reduction potential. Hydroelectric power and thermal energy from biomass were found to be the optimal energy sources, however, the authors acknowledge the unmonetizable challenges with regard to the use of biomass on a large scale. The operating cost for the combination of hydroelectric power, biomass thermal energy, and trains for transportation was found to be \$144/tCO_2 avoided. Assuming an optimistic market price for magnesium carbonate of about \$275/t, they claim that the UQ process would make economic sense.

12 PART C: GEOLOGICAL SEQUESTRATION

12.1 Background

CO_2 storage can be implemented mainly through oceanic and underground geological sequestration (besides mineral carbonation, covered in chapter 11). The oceanic sequestration process presents inadequate safe storage life span, high operational and transportation costs and a number of environmental issues such as ocean acidification. Therefore, based on economic factors, the availability of sites and the storage lifetime, geo-sequestration has been identified as the most feasible solution to the problem [170], [171]. Geological storage of CO_2 can take place in various geological formations, as depicted in Figure 12-1.

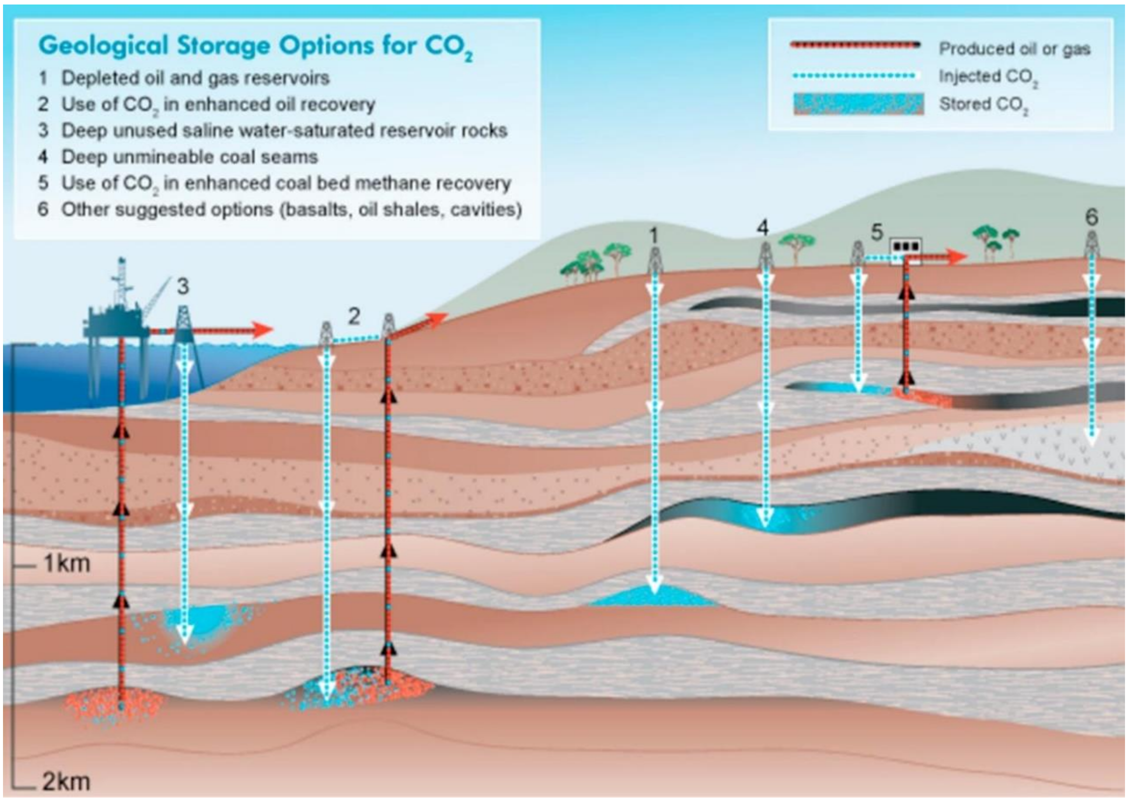


Figure 12-1 Geological Storage Options for CO_2. Source: [171]

In this report, saline aquifers and depleted oil and gas reservoirs are discussed.

12.1.1 Saline aquifers

Saline aquifers are highly mineralized and therefore not suitable to supply potable water These aquifers have a high storage capacity of about 30 $kgCO_2/m^3$, resulting in a global potential for sequestrating up to 10,000 gigatons of CO_2. Saline aquifers normally have high rock porosity and permeability, which facilitates the injection and storage of CO_2 by displacing the brine or gas in the pore structure. Therefore, from a technical perspective, saline aquifers are considered as the most suitable sinks to store CO_2. [170]. However, from an economic aspect, saline aquifers are a less desirable option due to the absence of necessary infrastructure, such as injection wells, surface equipment and pipelines, and the capital cost associated with developing such infrastructure [171].

The most preferable aquifers for CO_2 sequestration are located 800–3000 m below the earth's surface, where geological parameters such as temperature, pressure, salinity and density increase with increasing depth. CO_2 reaches its supercritical state at 31,8ºC and 7,38 MPa [170]. The density of CO_2 in saline reservoirs is expected to be around 0.6–0.7 g/cm^3, which is lower than the density of saline formation water, thus causing CO_2 to rise towards the caprock due to buoyancy force. To assure long-term CO_2 storage, the host basin must be considerably large and a caprock with good sealing capacity must be present above the CO_2 storage formation, through which no CO_2 migration occurs [171].

Once injected, CO_2 must be trapped safely in the aquifer for a geologically significant time-period. The trapping process plays a major role in this aspect, and are influenced by the physical properties (temperature, pressure and density of CO_2), and the chemical composition of both aquifer water and formation rock [170]. The four main trapping mechanisms are represented in Figure 12-2.

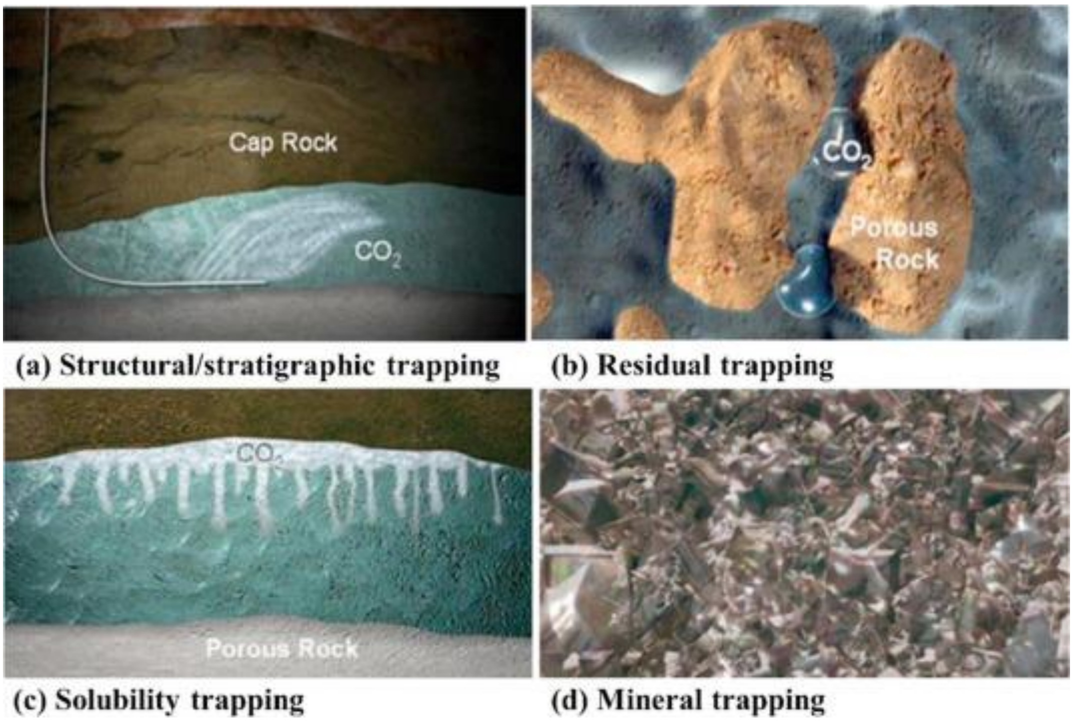


Figure 12-2: The four main CO2 trapping mechanisms. Source: [171]

i. <u>Structural/stratigraphic trapping</u> (Figure 12-2a): CO_2 can rise up to the top of geological structures. This is the most dominant trapping mechanism, and therefore it is key that an impermeable top seal (caprock) is in place, below which CO_2 is safely stored as a high-density free phase that is unable to enter the pore space of the caprock, except through slow diffusion or through faults [171]
ii. <u>Residual trapping</u> (Figure 12-2b): CO_2 initially displaces the fluid as it progresses through the porous rock. If water drainage occurs during CO_2 injection, the displaced fluid returns

and traps the remaining CO_2 in "pockets" within pore spaces. This phenomenon does not happen within structural and stratigraphic traps [171]

iii. Solubility trapping (Figure 12-2c): CO_2 dissolves in brine, reducing the volume of the dense CO_2 phase. CO_2 dissolution leads to a CO_2-rich brine solution of increased density, which can induce mixing in the brine due to gravitation instability, pushing CO_2-lean brine upwards and accelerating the transfer of injected CO_2 to CO_2-lean brine [171]

iv. Mineral trapping (Figure 12-2d): CO_2 is involved in geochemical reactions with saline water and minerals in host rock leading to the precipitation of carbonate phases that effectively lock up the CO_2 in immobile secondary phases for geological timescales, as described in chapter 11 [171]

12.1.1.1 *CO_2 storage in saline aquifers – TRL9*

The Sleipner CO_2 injection project was the world's first industrial offshore CO_2 Capture and Storage (CCS) project with more than 16 Mt CO_2 injected since 1996. The CO_2 is injected into the saline, highly porous Utsira aquifer, in Norway. Remote geophysical monitoring has convincingly demonstrated that the CO_2 stays safely in the storage unit [172].
These and other CO_2 storage projects in saline aquifers are summarized in Table 12-1. A typical scale of these early commercial storage projects is 1 Mt of CO_2 stored per year (Sleipner, Snøhvit, Boundary Dam, Decatur).

Table 12-1: Overview of projects on CO_2 storage in saline aquifers. Adapted from: [171]

Name	Location	Status	Other important information
Ketzin	Brandenburg, Germany	2008–2009	First European onshore CO_2 storage project
Sleipner	Offshore, Norway	since 1996	World's first commercial-scale CO_2 injection project
Snøhvit	Offshore, Norway	since 2007	
Boundary Dam	Saskatchewan, Canada	since 2014	World's first commercial-scale fully integrated CCS project with CO_2 capture from a coal-fired power plant. Storage in oil field (EOR Weyburn) and saline aquifer (Aquistore).
Frio Brine Pilot Project	Texas, USA	2004–2006	First demonstration on CO_2 storage in saline aquifer in the United States
Citronelle	Alabama, USA	since 2011	
Decatur	Illinois, USA	since 2011	Storage of biogenic CO_2 from ethanol production
Ordos	Ordos, Inner Mongolia, China	since 2010 at pilot scale, from 2020 full scale	
Gorgon	Western Australia	full capacity (3.4 – 4.0 Mt/year) in 2018	

12.1.2 Depleted oil and gas reservoirs

CO_2 storage in depleted oil and gas reservoirs is considered as one of the most effective storage options. These reservoirs are safe options for CO_2 storage, given the fact that effective caprocks are in place (otherwise the hydrocarbons would not have stayed trapped in the formation). [171] Since these depleted reservoirs have been extensively studied before and during the hydrocarbon exploration stage, the storage capacity is known. From an economical perspective, depleted oil and gas reservoirs are preferable because surface and underground infrastructure are in place and can be utilized for the storage process. Moreover, if enhanced oil recovery (EOR) is connected to the CO_2 injection, than a business case may exist. [171]

The injection of gases such as (CO_2, nitrogen and natural gas) for EOR technique is well-known and has been employed within the oil and gas industry. CO_2 is considered as the most suitable option, since it can reduce the oil viscosity, and also is cheaper compared to liquefied natural gas. [171]

12.1.2.1 *CO_2 storage in depleted oil and gas reservoirs– TRL9*

A summary of projects on CO_2 storage in depleted oil and gas reservoirs is given in Table 12-2.

Table 12-2: Overview of projects on CO_2 storage depleted oil and gas reservoirs. Adapted from: [171]

Name	Location	Status	Other important information
In Salah	Tamanrasset, Algeria	2004–2011	
Weyburn-Midale	Saskatchewan, Canada	since 2000	World's largest CCS project
Alberta Carbon Trunk Line	Alberta, Canada	from 2018	Will be the world's largest CCS project when in operation
Otway Basin	Victoria, Australia	since 2008	The largest geosequestration onshore project in Australia
Cranfield	Mississippi, USA	since 2009	Commercial-scale project. More than 3 Mt of CO_2 injected and monitored since the start of the project.
Northern Reef Trend	Michigan, USA	since 2013	
Port Arthur	Texas, USA	since 2013	
Zama	Alberta, Canada	since 2006	

12.1.3 Mineralization

A summary of projects on CO_2 storage via mineralization is given in Table 12-3.

Table 12-3: Overview of projects on CO_2 mineralization. Sources: [136], [173]*:*

Name	Location	Status	Resource	Other important information
CarbFix	Iceland	Since 2012,	Basalts (*in situ* carbonation)	CO_2 (and H_2S) from the Hellisheiði geothermal power plant was injected at depths of 500-800m into basaltic formations
Big Sky CSP	Washington, USA	Since 2017	Basalts (*in situ* carbonation)	1,000 tons of CO_2 to be injected into a deep basalt formation near Wallula, Washington.

12.2 CO_2 purity for geological sequestration

Saline aquifers and EOR projects have different requirements when it comes to CO_2 purity, and the admissible level of the different impurities. Examples of these are given in Table 12-4.

Table 12-4: CO_2 quality for geological storage. Adapted from: [174][7]

	Weyburn pipeline	Gullfaks	US pipelines	DYNAMIS	DOE/NETL	CEMCAP
Application	EOR	EOR	EOR	EOR and aquifer	EOR and aquifer	EOR and aquifer
CO_2 purity (vol%)	96	99.5	>95	>95.5	>95	>95

This project has received funding from the European Union's Horizon2020 Research and Innovation Programme under Grant Agreement No 641185. This work was supported by the Swiss State Secretariat for Education, Research and Innovation (SERI) under contract number 15.0160

CO	0,1 vol%	<10ppm		<2000ppm	35ppm	<35ppm$_v$
Total non-condensables (N_2 + Ar + CH_4 + O_2)				<4%	<1% (EOR) <4% (aquifer)	<4%
H_2O	< 20ppm	Saturated at -5ºC	0,4805g/Nm3	500 ppm	500ppm	<300 ppm$_w$
O_2	<50ppm	<10ppm	<10ppm	100-1000 ppm (EOR)	<100 ppm	<4%

The acceptable impurities and their concentration are determined based on a combination of transport, storage, and economics-related parameters. Major impurities (oxygen, nitrogen, argon, methane) shift the boundaries in the CO_2 phase diagram, implying higher operating pressures are needed to obtain a dense phase. Moreover, non-condensable impurities lead to a reduction in the CO_2 storage capacity. Corrosive impurities (such as NO_2, SO_2, H_2S, Cl) impact the transport and injection facilities. Oxygen can trigger microbial activity in the reservoir and therefore the O_2 concentration is specified at a low level, in special for EOR applications. [171] The purity requirements reported in the CEMCAP framework [7] represent typical specifications for pipeline transport of CO_2 and are based on an extensive literature review.

12.3 Geological sequestration costs

The CO_2 storage costs consist of six components, which include all of the phases in the lifetime of the CO_2 storage project: 1) Pre-Financial Investment Decision, 2) Platform, 3) Injection wells, 4) Operating, 5) Monitoring, Measurement and Verification and 6) Close-down [175].
The cost for CO_2 storage in depleted oil and gas fields in case legacy wells are available is estimated at 7,4 euros/ton CO_2. If the wells are not available, then the cost rises to 9,9 euros/ton CO_2. Higher cost (13 euros/ton CO_2) is expected in case of EOR operation, but the associated revenues due to oil recovery could lead to a positive business case. Onshore saline aquifers have the lowest expected CO_2 storage cost, at 5,8 euros/ton [175].

12.4 Potential in connection to the cement industry

As discussed throughout this document, the quantity of CO_2 avoided by CCU is limited by factors such as the product(s) demand, and/or the renewable hydrogen availability. The market limitations are especially stringent for high value products, such as polymers. Therefore, in order to achieve the intended decarbonisation through carbon capture, CO_2 geological sequestration has to be complementary to CCU processes.

13 CASE STUDIES FOR THE CEMENT INDUSTRY

The authors of this report (TNO, ETHZ, VDZ and SINTEF ER) have selected different case studies for applying CCUS technologies to the cement industry. For that, the BAT cement plant as defined within the CEMCAP project was used as a reference (see item 1.1.1 of this report). The detailed description of the cement plant is given elsewhere [176], [177]. The CO_2 emissions of the cement plant originate mainly from the use of raw materials, but also significantly from fuel combustion, as represented in Figure 13-1. The CCUS case studies are presented in this chapter.

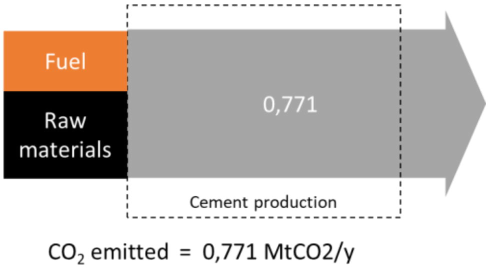


Figure 13-1: CO_2 emissions from the CEMCAP reference cement plant

Initially, three sequestration scenarios are evaluated. The first and second sequestration cases (CCS1 and CCS2) are based on geological sequestration by injection of purified CO_2 streams into storage sites, whereas the third sequestration scenario (CCS3) describes the use of serpentine for the mineralization of CO_2.

Then, in order to evaluate the economic and environmental impacts of including CO_2 utilization in the CCUS chains, five scenarios utilization where evaluated, regarding the production of ethanol (U1), polyols (U2), food-grade CO_2 (U3), the combined production of ethanol, polyols and food-grade CO_2 (U4), and finally the utilization of CO_2 for EOR.

The results for the CC(U)S full chains are reported in terms of total CO_2 avoided, and the cost of CO_2 avoided. The economic and emission factors considered in the calculations are given in Table 13-1.

Table 13-1: Economic and emission factors

Factor	Value
Equipment lifetime	25 years
Interest rate	8%
Electricity cost	30 €/MWh
Steam cost (from natural gas)	9,1 €/GJ
Cooling water cost	0,035 €/m^3
Ethanol price	633 €/ton
Polyol price	1400 €/ton
Food-grade CO_2 price	80 €/ton
Oil price	39,5 €/bbl
CO_2 emissions:	
Electricity	170 kgCO_2-eq/MWh
Steam	56,1 kgCO_2-eq/GJ
Transportation by train	0,015 kgCO_2-eq/km/ton

13.1 Introduction to CCS chains

CCS1 evaluates CO_2 capture from a cement plant assumed to be located in Belgium, while an offshore storage on the Dutch continental shelf is considered for the storage. In this case, after capture, the CO_2 is conditioned and transported by a stand-alone pipeline to a hub in the Rotterdam area. From this hub, the CO_2 is assumed to be transported in a shared offshore pipeline to a saline aquifer. A shared transport and storage infrastructure with an annual flow of 13.1 $MtCO_2$/y as in the EU project COCATE [178] is considered. This case is meant to be representative of both CCS from an inland cement plant and implementation of CCS once a strategy for joint CCS transport and storage infrastructure has been established.

CCS2 evaluates CO_2 capture from a cement plant assumed to be located in coastal Germany, while the CO_2 storage is assumed to take place on the Norwegian continental shelf. After capture, the CO_2 is transported by ship, on a stand-alone basis, to a harbour [179] located on the Norwegian coast, followed by a shared offshore pipeline to a saline aquifer. In this case, the shared transport and storage infrastructure is assumed to be three times the CO_2 emissions of the stand-alone cement plant. This case is meant to be representative of early CCS deployment from coastal plants, especially in countries in which onshore CO_2 transport meets a strong public opposition.

CCS3 is based on the work of Pasquier et al. [164]. This case is defined for a cement plant situated 200 km away from a mining site. The mining tailings are transported to the cement plant by train, where they are used to sequestrate CO_2 directly from the cement plant flue gas. The product, $MgCO_3$, is transported back to the mining site for disposal. A valuable by-product, the magnetic fraction of the mining tailings, is recovered and generates revenue. This case is intended to evaluate the benefits and challenges of CO_2 mineralization as an alternative to geological sequestration.

13.2 Introduction to CCUS chains

In the first utilization scenario, U1, a fraction of the captured CO_2 is utilized to produce ethanol via catalytic hydrogenation. The required hydrogen is produced via hydrolysis using wind-generated electricity. For this end, an electrolyser is required. The flowrate of CO_2 that is utilized (23,8 kton/year or 2,8% of the CO_2 emitted) is limited by the electrolyser design. In U1 it is considered that the ethanol produced from the cement plant purified CO_2 stream displaces ethanol from sugarcane.

In the second utilization scenario, U2, a fraction of the captured CO_2 is utilized to produce polyols. The CO_2 partially replaces propylene oxide as a raw material. The flowrate of CO_2 that is utilized (57,5 kton/year or 6,8% of the CO_2 emitted) is limited by the polyol plant capacity, which reflects the size of the polyols market.

In the third utilization scenario, U3, a fraction of the captured CO_2 is further purified in order to reach food-grade. The food-grade CO_2 is conditioned so that it can be transported by the already existing truck fleet. The flowrate of CO_2 that is utilized (50 kton/year or 5,9% of the CO_2 emitted) is limited by the market.

As the CO_2 utilization routes evaluated in this project require high purity CO_2 as a feedstock, they could not be integrated in CCS3 (mineralization directly from the flue gas). Moreover, CCS1 represents a better scenario in terms of CO_2 transportation, and will lead to lower costs than CCS2. Therefore, the integration of the utilization routes is considered for CCS1 only. Table 13-2 gives an overview of the investigated scenarios.

Table 13-2: Overview of investigated scenarios

Scenario	Sequestration	Utilization
CCS1	CCS1 - Dutch continental shelf	None
CCS1 + U1		U1 – Ethanol
CCS1 + U2		U2 – Polyols
CCS1 + U3		U3 – Food-grade CO_2
CCS2	Norwegian continental shelf	None
CCS3	CO_2 mineralization to $MgCO_3$	None

13.3 CCS1 and CCS2: Geological sequestration of CO_2

Table 13-3 presents a more detailed description of the two first CCS chains. For CCS1 and CCS2, the technical, cost, and climate impact performances of the CO_2 capture unit is extracted from [179], while the iCCS CO_2 value chain tool developed by SINTEF Energy Research [175], [180] is used to assess the performances of the CO_2 conditioning, transport and storage parts of the chain. More detailed description on the modelling of the CO_2 conditioning, transport and storage in the iCCS tool can be found in previously published studies [175], [179], [181], [182].

Table 13-3: Characteristics of CCS1 and CCS2

Section	**Parameter**	**CCS from Belgium cement plant**	**CCS from a coastal German cement plant**
Cement plant	Cement plant location	Inland Belgium	Coastal Germany
	Cement plant capacity [Mt_{cement}/y]	1.36	
	CO_2 emissions without CO_2 capture [$MtCO_2$/y]	0.771	
	Exhaust flue gas average flow [kg/h]	353 150	
	Exhaust flue gas average CO_2 content [%]	19.8	
CO_2 capture and conditioning	Type of capture technologies	MEA-based capture	
	CO_2 capture ratio [%]	90%	
	CO_2 captured [$MtCO_2$/y]	0.694	
	Conditioning specification after capture	Pipeline	Shipping
	Pressure after conditioning [bar]	150	7
	Temperature after conditioning [ºC]	40	-53
First CO_2 transport step	Transport scenario	Stand-alone onshore pipeline to a Dutch hub	Stand-alone ship transport to a Norwegian harbour
	CO_2 transported [$MtCO_2$/y]	0.694	
	Transport distance [km]	120	750
	Required pressure after reconditioning [bar]	200	
Second CO_2 transport step	Transport scenario	Shared offshore pipeline to storage	
	CO_2 transported [$MtCO_2$/y]	13.1	2.08
	Transport distance [km]	150	65
	Minimum delivery pressure at storage [bar]	60	
CO_2 Storage	Storage type	Saline Aquifer	
	CO_2 stored [$MtCO_2$/y]	13.1	2.08
	Well injectivity [$MtCO_2$/y/well]	0.8	
	Storage location	Dutch continental shelf	Norwegian continental shelf

For both CCS1 and CCS2, the CO_2 capture rate is 90%, or 0,694 $MtCO_2$/y. However, due to emissions related to energy usage in the capture, conditioning and shipping processes, the amount of CO_2 avoided is lower than that, and different for each chain. The quantity of CO_2 avoided is determined by the difference between the quantity of CO_2 captured and the emissions associated to each one of the processes of the chain, as summarized in Figure 13-2 and Figure 13-3. The costs and emissions associated with conditioning and shipping in CCS2 result in substantially higher cost of CO_2 avoidance as compared to CCS1.

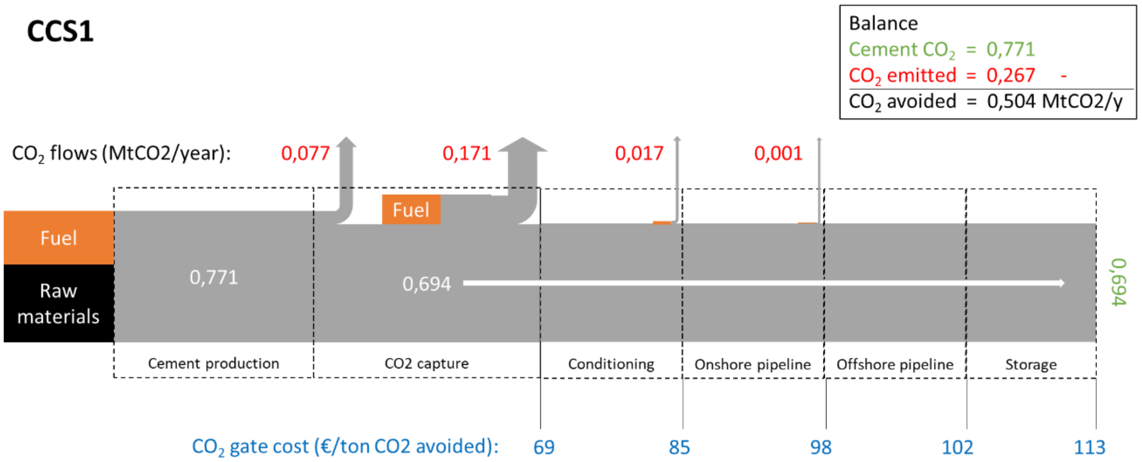


Figure 13-2: Summarized results of CCS1

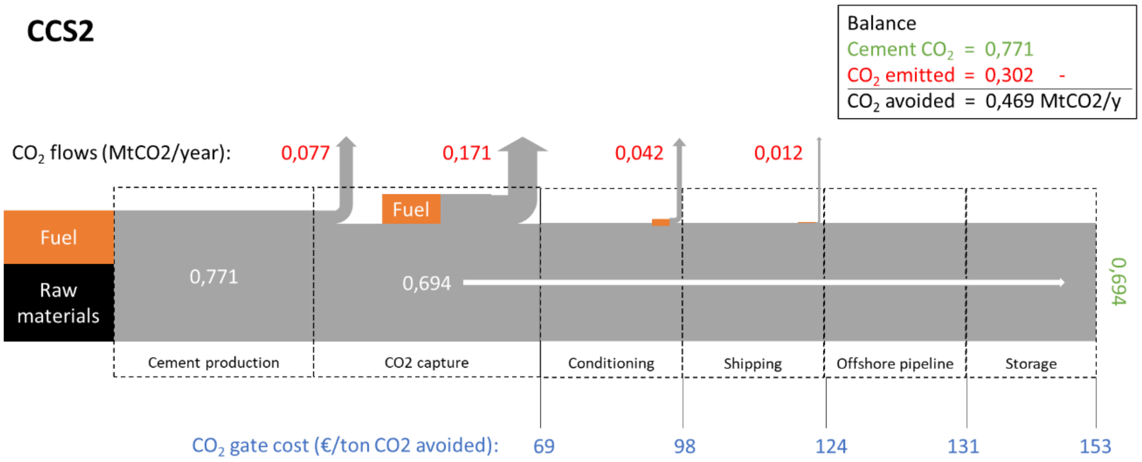


Figure 13-3: Summarized results of CCS2

In CCS1 0,504 MtCO_2/y are avoided, or 65% of the CO_2 emitted by the cement plant.. In CCS2, due to higher emissions in the long distance shipping, 0,469 MtCO_2/y are avoided, or 61% of the CO_2 emitted by the cement plant. The total cost of CO_2 avoided is 114 €/ton in CCS1 and 153 €/ton in CCS2.

13.4 CCS3: Mineralization to $MgCO_3$

13.4.1 Previous work

As reported in item 11.5, Pasquier et al. [164] performed a technical and economic evaluation of CO_2 mineralization applied to carbonate mine tailings using the flue gas from a cement plant (18% CO_2). This process is investigated in the present report as it can be directly applied to flue gases, without the need of a CO_2 capture step.

Pasquier et al. [164] show that the process costs are quite dependent on the electricity and heat sources, as well as on the transportation mode used for bringing the tailings from the mining site to the cement plant, situated 200 km away. The best-case scenario is achieved when the plant uses hydroelectric power, heat is provided from biomass combustion, and the transport is done by train, leading to a cost of 123 €/ton CO_2 (using a conversion factor of 0,86 €/USD). The cost associated to rock transportation represents about 30% of the total cost. In this mineralization process, 62 wt% of the CO_2 present in the flue gas is captured. For each kg of CO_2 captured, 2,26 kg of $MgCO_3$ are produced. The break-even price of $MgCO_3$ is 46 €/ton, and the production is 570 kton/year. The $MgCO_3$ market price considered by [164] is 237 €/ton, which is much above the break-even price. That, together with the additional revenues from the process, namely the recovery of a magnetic fraction by-product (10,3 €/ton of CO_2) and the carbon taxes (9,5 €/ton CO_2), lead to a profit of 431 €/ton CO_2. The costs are informed in tonnes of CO_2 converted.

13.4.2 Application to CEMCAP reference cement plant

The heat and mass balances developed in this work are derived making the same assumption of Pasquier et al. [164]. However, the economic model is rather different. Pasquier et al. [164] assume an optimistic market price for $MgCO_3$: as discussed in item 3.2, magnesite ($MgCO_3$) has limited market and, more importantly, that market is directed to the production of magnesia (MgO). When the oxide is produced, the captured CO_2 is directly re-emitted. Thus, for effective and durable sequestration, $MgCO_3$ cannot be utilized for its current applications. Since $MgCO_3$ is being discussed in the current section with the target of sequestrating CO_2, the produced $MgCO_3$ is considered as waste and its value is set to zero. The product is disposed of in the mining site, and the cost of transportation of $MgCO_3$ as well as the associated CO_2 emissions are included. The revenues from the recovered magnetic fraction are included in the calculations, but no carbon taxes are considered.

In order to treat the flue gas of the reference cement plant as defined in the CEMCAP project, the process described in [164] has to be scaled-up by a factor of 2.17. Considering that the process efficiencies are kept the same at this somewhat larger scale, the operational costs and revenues, in specific basis (i.e., per tonne of CO_2 captured) remain the same.
On the other hand, the specific CAPEX is expected to decrease. Using a power-law with exponent 0.6, the CAPEX is estimated as 69 €/ton CO_2 avoided. Heat is the main cost component, contributing with 138 €/ton CO_2 avoided. The results are summarized in Figure 13-4

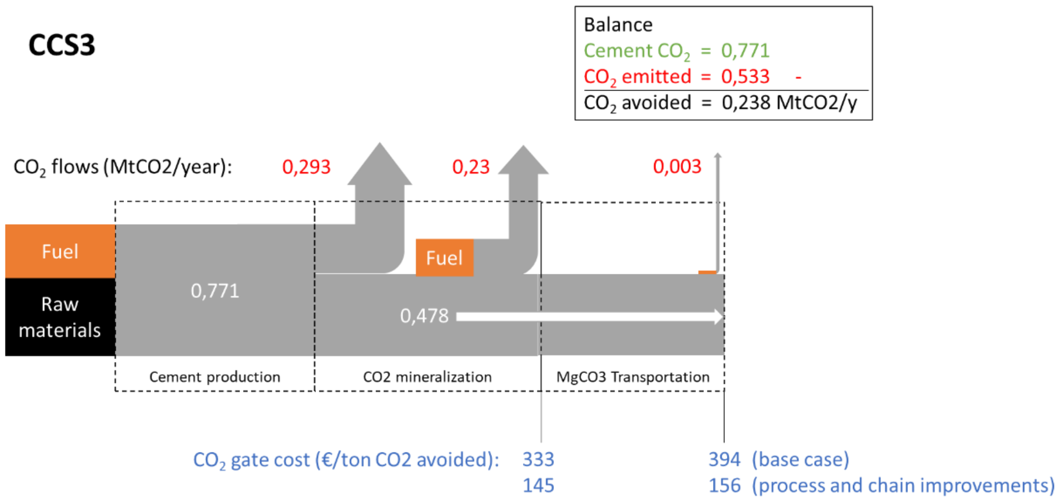


Figure 13-4: Summarized results of CCS3

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The mineralization technology requires considerable development, piloting and demonstration, as well as scale-up. Further process developments and an optimized chain can bring the costs significantly down.

An alternative scenario in which the conversion is increased form 62% to 90%, and the distance between the cement plant and the mining site is decreased from 200km to 50km lowers the CCS3 cost down to 156 €/ton of CO_2 captured – close to the cost of CCS2.

13.5 CCS1+U1: CO_2 hydrogenation to ethanol + CO_2 storage

13.5.1 Previous work

Ethanol production via CO_2-based DME is described in [31]. The authors provide an economic evaluation showing that this route leads to ethanol costs close to the market price. Moreover, most of the cost is due to the feedstock cost – in this case, hydrogen.

As presented at the 9th Trondheim Conference on CO_2 Capture, Transport and Storage (TCCS9) held in June 2017, the total amount of electricity required to generate hydrogen in order to convert 90% of the CO_2 emitted from the CEMCAP cement plant into ethanol is above 900 MW (even when considering 100% efficient systems). In this scenario, it is not reasonable to assume that the plant could run on excess electricity, as having 900 MW excess available is extremely unlikely. In other words, a dedicated power plant (renewable) would be needed. Accounting for the cost of electricity production leads to extremely high costs, and in face of the actual ethanol market price, this would be an unprofitable scenario [183].

13.5.2 Application to CEMCAP reference cement plant

As an alternative approach to that described in [183], in the present evaluation we consider that about 50 MW of excess renewable electricity are available. This value represents 0,07% of the predicted 70 GW of installed wind generation capacity in the North Sea by 2030 [184].
The 50 MW can be used to produce 3244 tonnes of hydrogen per year (considering an efficiency of 61,6% and an availability of 40,5%), at a cost of 1,04 €/kg. This cost is obtained considering that the excess electricity is available for free.

Via the utilization of 23,8 ktonnes CO_2 per year, or 3,1% of the emissions of the CEMCAP plant, 12,5 ktonnes of ethanol can be produced per year. The cost of producing ethanol via DME, estimated based on [31], is 656 €/ton of ethanol, only slightly above the market value of 633 €/ton. Hydrogen, even at a relatively low cost, represents 41% of this total.

The calorific value of ethanol is 29,7 GJ/ton. In terms of energy, the ethanol production cost is 22 €/GJ. In the cement plant, coal is used as fuel, and has the price of 3 €/GJ. Therefore, substituting coal by ethanol would lead to a weaker business case. From that perspective, the produced ethanol should be sold on the market.

Green ethanol can be produced from fermentation of biomass. Currently, the most cost- and CO_2-effective process is the production from sugarcane. While sugarcane growth fixates CO_2 from the atmosphere, the various steps in the production of green ethanol emit CO_2, and the net result is the emission of 3,3 tonCO_2/ton green ethanol. In case of ethanol production from wheat, the efficiency is lower, and the emissions are 3 times higher. Ethanol from CO_2 from industrial

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sources is referred to as blue ethanol, to differentiate it from green ethanol. In the current case, 12,5 kt of blue ethanol are produced per year, thus replacing the same flow of green ethanol. This replacement leads to the avoidance of 41 and 123 kt of CO_2 per year, using sugarcane and wheat as raw material, respectively.

While the process of producing blue ethanol is not profitable, it contributes to increasing the total CO_2 avoidance of the CCS1+U1 chain to 0,518 $MtCO_2$/y (67% of the cement plant emissions) in the sugarcane case and 0,6 $MtCO_2$/y in the wheat case, as compared to 0,504 $MtCO_2$/y of CCS1. In this way, the cost per tonne of CO_2 avoided drops from 114€ (CCS1) to 111€ (sugarcane) or 96€ (wheat). The cost difference for sugarcane is only marginal, but in the case of wheat, it becomes more relevant. This exemplifies the complexity involved in the CO_2 avoidance cost analysis: it must take into consideration not only the product that is formed, but also the market in which it is placed.

The results of CCS1+U1 are summarized in Figure 13-5 for the sugarcane case.

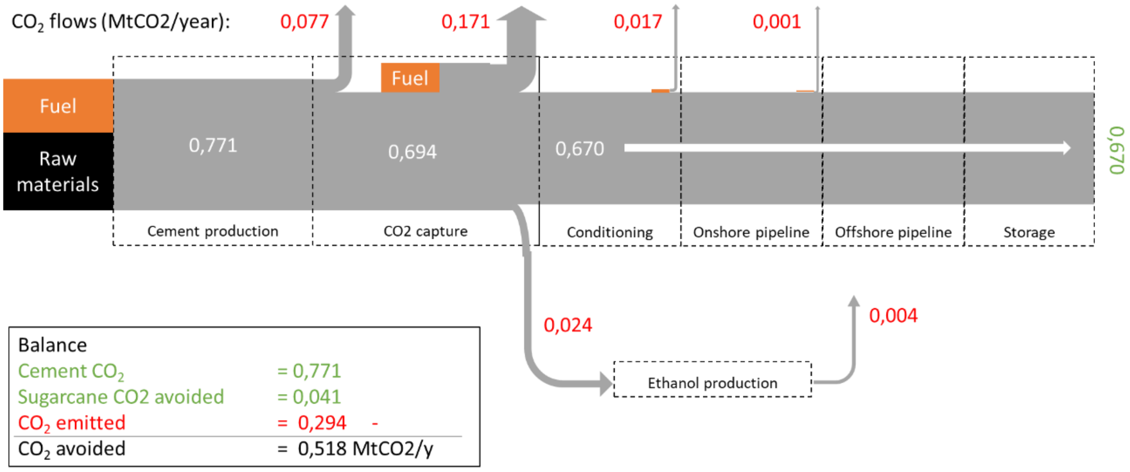


Figure 13-5: Results of CCS1+U1

13.6 CCS1+U2: CO_2 polymerization to polyols + CO_2 storage

13.6.1 Previous work

A polyol plant using CO_2 as a feedstock is described in [185], and is used in this work as a reference case. In the literature scenario, the polyol plant is connected to a refinery, which produces propylene oxide (PO), the main feedstock to the polyol process. In the proposed design, a side-stream of the PO is used to produce 250 kt polyols per year. The typical size of polyols plants is around 100 kt per year, meaning that the chosen scale is relevant. It should be noted that, as described in item 5.2, the polyols market is around 10 million tons per year.

13.6.2 Application to CEMCAP reference cement plant

In the current project, the throughput is set at 288 kt polyols per year. The plant consumes 57,5 kt CO_2, which is equivalent to 7,5% of the emissions of the CEMCAP reference plant. Therefore, 82,5% of the CO_2 emitted needs to be stored (capture rate of 90%).

Since the heat and mass balances are described in detail in [185], adapting the reference case to a cement plant was straight forward. The polyol plant CAPEX is estimated to be 21 M€ [185]. The price of polyols estimated by [185] is 1700 €/ton, whereas the price of PO is set as 1400 €/t. In the present work, a more conservative approach is used, and the prices of both polyol and PO are set as 1400 €/t (zero spread).

The business case of blue polyol production lies in the fact that the CO_2 content in the material is replacing PO. As given in Figure 13-2, the gate cost of CO_2 after capture is 69 €/t, much lower than that of PO. Therefore, the production costs are greatly reduced.

The production of PO is CO_2 intensive: 4,5 tCO_2-eq are emitted per ton of PO. Therefore, even with the substitution of PO by CO_2, the polyol production process is still a net CO_2 emitter if the CO_2 content in polyol is 20wt%, as possible by the currently developed technology. This fact only changes when at least 50% of the PO is substituted by CO_2. Nevertheless, the production of blue polyol avoids the emission of 0,91 tCO_2-eq are emitted per ton of PO as compared to the conventional route.

Figure 13-6 shows the results of CCS1+U2. The CCUS chain avoids 0,708 $MtCO_2$ per year, and produces 288 kt of polyols. Due to the high value of polyols, the full chain is profitable. Even when setting the spread between the polyol and the PO prices to zero, the profit is of 43 €/ton of polyol produced, or 18 €/ton CO_2 avoided.

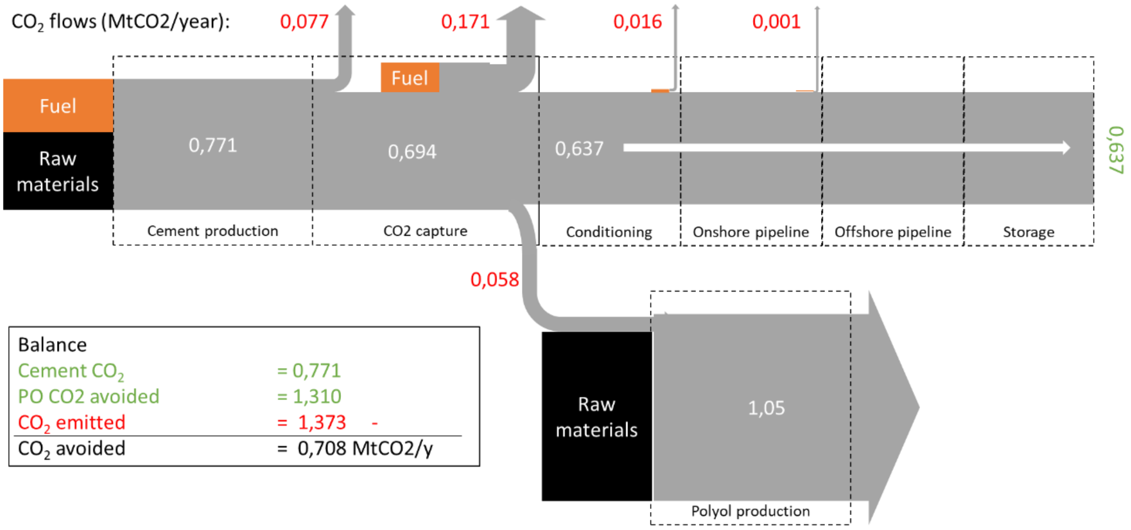


Figure 13-6: results of CCS1+U2

13.7 CCS1+U3: food-grade CO_2 + CO_2 storage

The production and specification of food-grade CO_2 was discussed in item 7.2.1. The food and beverage industries consume about 17 $MtCO_2$/y [107]. In The Netherlands, the greenhouse CO_2 market is also relevant, and an annual growth of 100 $ktCO_2$ per year is expected up to 2020 in connection to the OCAP pipeline network.

13.7.1 Application to CEMCAP reference cement plant

The conceptual design of a plant for purifying CO_2 to food-grade quality and liquefying it are developed. The plant was simulated and the equipment cost were determined using ASPEN plus v.8.8. The flow diagram is shown in Figure 13-7. The plant capacity is set as 50 ktCO_2 per year or about 6,5% of the emitted CO_2. It is considered that the plant will serve end-users which are currently producing their own CO_2 locally. As discussed, burning natural gas to generate CO_2 is still a common practice in the horticulture industry in The Netherlands. The blue CO_2 directly replaces fossil-derived CO_2.

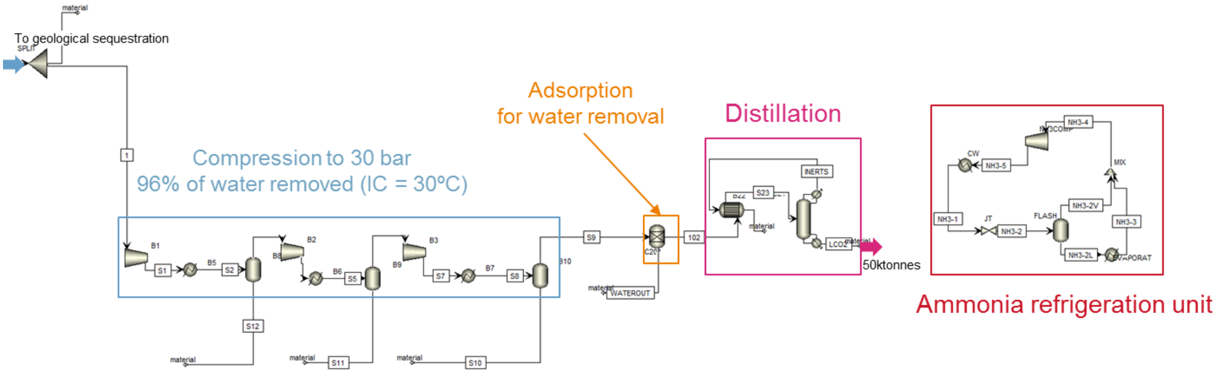
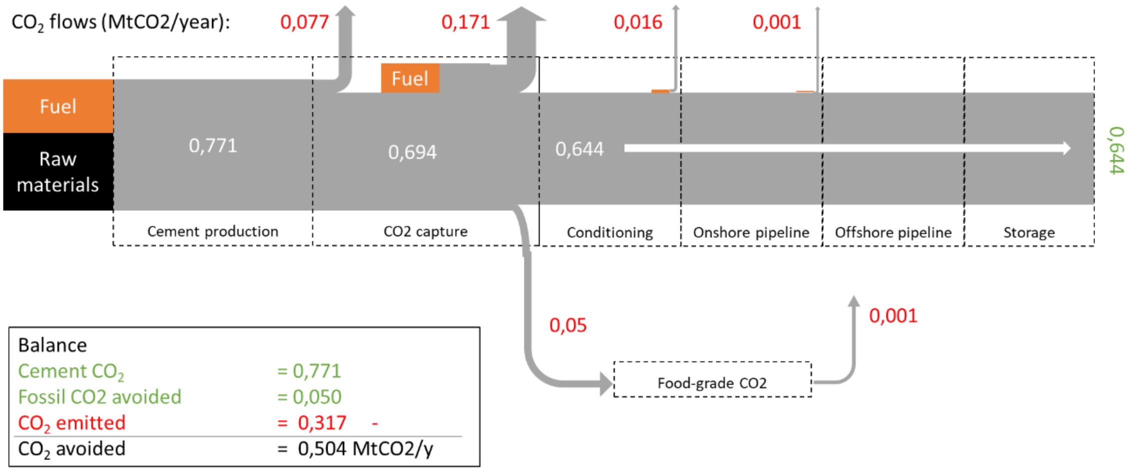


Figure 13-7: Simulation of the CO_2 purification and liquefaction plant in ASPEN Plus



Balance
Cement CO_2 = 0,771
Fossil CO2 avoided = 0,050
CO_2 emitted = 0,317 -
CO_2 avoided = 0,504 MtCO2/y

Figure 13-8: Results of CCS1+U3

The results of CCUS3 are summarized in Figure 13-8. Because the direct avoidance of fossil CO_2 cancels out the emissions of food-grade CO_2, the total CO_2 avoidance of CCUS3 are the same as that of CCS1: 0,504 MtCO_2/year or 65% of the cement plant emissions. Given the revenue generated by the sales of food-grade CO_2 at 80 €/ton, the avoidance cost drops 5%, from 114 to 108 €/ton.

It should be noticed that is the price of food-grade CO_2 is equal to 25€/ton, the avoidance cost of CCS1 and CCS1+U3 are the same. Moreover, if green CO_2 is available (e.g. from fermentation), the CCUS option actually leads to a higher cost than CCS1: 120 €/ton CO_2 avoided, even when the $_{CO2}$ market price is 80 €/ton.

14 CONCLUSIONS

This report evaluates post-capture CO_2 management options for the cement industry. A number of possible CCU products are evaluated according to:

1) the energy demand;
2) the technology readiness level (TRL);
3) the market size.

These three metrics are not absolute. While the energy demand is a function of the carbon oxidation state in the product molecule (low oxidation state indicates high energy demand), other factors such as the reaction conditions (pressure, temperature), the conversion per pass and selectivity also influence this metric. In Table 14-1, the average carbon oxidation state is used as an energy demand indicative. It indicates that the fuels (methanol, DME, methane, IPA and biodiesel) require a high amount of energy, as opposed to carbamates (inorganics and organics). From this perspective, formic acid would be a preferable fuel.

The marker size indicated in Table 14-1 is based on the current market for the selected products. However, some of these products have a potential for a substantial market increase in the future. In particular, methanol, formic acid and DME could be largely employed as fuels, displacing fossil-based fuels by CO_2-based fuels.

Table 14-1: Overview of different metrics for CCU products

Product	Price (€/ton)	Market (Mt/year)	CO_2 uptake (Mt/year)	CEMCAP cement plants	TRL	Oxidation state
$CaCO_3$ (GCC)	50	75	33	39	7	4
$CaCO_3$ (PCC)	400	14	6,16	7	7	4
Aggregates	20	53200	3600	4235	9	4
Carbonated concrete	25	16500	1650	1941	9	4
Methanol	250	80	110	129	9	-2
DME	350	8	7,65	9	9	-2
Methane	330	1100	3025	3559	9	-4
Ethanol	630	86,8	166	195	5	-2
Isopropanol	1500	2	4,33	5	3	-2,33
Biodiesel	860	20	30	35	5	-3,29
PPC	3400	6	3	4	9	3
Polyols	1500	10	2	2	9	3
Cyclic carbonates	2000	0,1	0,04	0,05	4	4
Formic acid	600	0,7	0,67	0,8	5	2
CO_2 (food-grade)	115	17	17	20	9	4
CO_2 (greenhouses, NL)	65	5	5	6	9	4

The technology readiness level metric indicated in Table 14-1 refers to the most advanced CO_2-based production route for each product. Therefore, DME has TRL 9 because it can be indirectly produced via methanol dehydration using CO_2-based methanol.
Based on the market, the CO_2 uptake potential (CUP) for each product is determined. The CO_2 abatement potential (CAP) is a combination of the CUP and the energy demand, amongst other factors. Therefore, while methane and aggregates have comparable CUP, it is expected that the aggregates CAP is significantly higher, due to the high energy demand in the methane production route. Table 14-1 shows the number of CEMCAP cement plants from which the CO_2 emissions could be theoretically utilized to make each product, given the determined CUP. Table 14-1 also shows the price of each product. The high price of polymers and cyclic carbonates in combination with the relatively low energy demand leads to attractive cases, but the low markets limit the CUP.

In order to help the visualization of the data presented in Table 14-1, each one of the metrics is associated to an icon. Furthermore, levels are defined for each metric, and associated to a color code (bad, intermediate and good), as shown in Table 14-2. These icons and colors are used in Table 14-3 to give a visual summary of the results for each CCU product. The shaded lines indicate the products that were further investigated in the case studies for the CEMCAP reference plant.

Table 14-2: Definition of metric levels

Metric	**Icon**	**Bad**	**Intermediate**	**Good**
		🟥	🟧	🟩
Product Market	📈	Below 10 Mt/year	10-100 Mt/year	Above 100 Mt/year
Energy demand	🧪	Carbon oxidation state above 2	Carbon oxidation state between 0 and 2	Carbon oxidation state below 0
Technology Maturity	🧓	TRL < 5	5 ≤ TRL ≤ 7	TRL >7
Product price	💵	Below 200 €/ton	200-500 €/ton	Above 500 €/ton

Table 14-3: Visual summary of the results for CCU products

Product	Market	Energy demand	Maturity	Price
$CaCO_3$ (GCC)	🟧	🟩	🟩	🟥
$CaCO_3$ (PCC)	🟧	🟩	🟩	🟧
Aggregates	🟩	🟩	🟩	🟥
Carbonated concrete	🟩	🟩	🟩	🟥
Methanol	🟧	🟥	🟩	🟧
DME	🟥	🟥	🟩	🟧
Methane	🟩	🟥	🟩	🟧
Ethanol	🟧	🟥	🟧	🟩
Isopropanol	🟥	🟥	🟥	🟩
Biodiesel from microalgae	🟧	🟥	🟧	🟩
PPC	🟥	🟩	🟩	🟩
Polyols	🟧	🟩	🟩	🟩
Cyclic carbonates	🟥	🟩	🟥	🟩
Formic acid	🟥	🟧	🟧	🟩
CO_2 (food-grade)	🟧	🟩	🟩	🟥
CO_2 (greenhouses, NL)	🟥	🟩	🟩	🟥

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In order to evaluate the feasibility of the CCU technologies described in this report in connection to the cement industry, and to understand the interaction between CCU and storage, illustrative scenarios are evaluated in this report.

Three geological sequestration cases were evaluated: mineralization to $MgCO_3$ and injection in two distinct deep saline aquifers. For the mineralization scenario, the cost of CO_2 sequestration is around 400 €/ton. For the saline aquifer cases, the estimated cost was 114 €/ton CO_2 (CCS1) and 153 €/ton CO_2 (CCS2), depending on the chain configuration. In CCS1, the CO_2 is captured from a cement plant in Belgium and stored in the Dutch continental shelf. In CCS2, the CO_2 is captured from a cement plant in Germany and stored in the Norwegian continental shelf.

From a cost perspective, the mineralization process as proposed is not an effective solution for CCS. However, it should be emphasized that the chain configuration has a major impact on the calculated costs. The availability of low cost heat, combined with a short distance between the cement plant and the mining source could lead to business cases competitive to those of geological sequestration. The optimal CCS solution for each cement plant will be location-dependent.

In terms of maturity and scale, CO_2 storage is to be considered commercially mature on the required scale and above, whereas the mineralization option requires considerable development, piloting and demonstration, as well as scale-up.

It is important to note that the existing large-scale CO_2 storage projects, such as e.g., Quest (64 km pipeline, saline aquifer storage), Boundary Dam (2 and 66 km pipeline for saline aquifer storage and EOR, respectively), Uthmaniyah (85 km pipeline for EOR), are more in line with the proposed CCS1 scenario. Nonetheless, CCS2 reflects the current proposal of the development of a storage solution on the Norwegian continental shelf with potential to receive CO_2 from multiple Norwegian and European industrial sources [187].

When combining CO_2 utilization and geological storage (CCUS), three different scenarios were evaluated – U1: making a fuel (ethanol); U2: a polymer feedstock (polyols), and U3: food-grade CO_2.

For the ethanol case, the high electricity demand for the hydrogenation route limits the production throughput. Considering that 50 MW of excess renewable electricity would be available for free, hydrogen can be generated at low cost. With this, 23,8 ktCO_2 can be utilized to produce 12,45 kt ethanol per year. This CO_2 amount is equivalent to 3,1% of the emissions of the CEMCAP cement plant. The capture rate is kept at 90%, and therefore 87% of the generated CO_2 must be stored.

In the CCS1+U1 scenario, when blue ethanol replaces green ethanol from sugarcane, the combined CCUS cost is 110 €/ton of CO_2 – as opposed to 114 €/ton CO_2 for the base CCS1 scenario. Therefore, adding the utilization to the chain leads to a marginal cost decrease. However, if the product displaced is more CO_2 intensive, the relative cost of CO_2 avoidance drops. Considering wheat-based ethanol, the CCS1+U1 cost drops to 96 €/ton CO_2 avoided.

It should be emphasized the results of U1 are highly sensitive to the hydrogen (electricity) price. Also, the possibility of a premium for blue ethanol could make the CCUS1 route more attractive.

The questions related to the future price and availability of electricity discussed in the blue ethanol production scenario are relevant for any fuels generated by hydrogenation (e.g. methanol, DME, hydrocarbons), and more critical for products which demand a high degree of hydrogenation, such as methane.

For the polyol case, the high value of the end product leads to a positive business case. It is estimated that a profit of 12,5 million euros/year can be obtained by producing 250kt of polyols. For this, 57,5 kt of CO_2 are utilized, which is equivalent to 7,5% of the emissions of the CEMCAP reference plant, while 82,5% of the CO_2 emitted is stored (total capture rate of 90%). The profit is equivalent to 18 €/ton CO_2 avoided or 43 €/ton polyol produced.

For the food-grade CO_2 case, the revenue obtained by selling CO_2 at 80€/ton lowers the avoidance cost of the CCUS3 chain and compared to CCS1. However, the food-grade CO_2 market is small, and is a “low hanging fruit” in The Netherlands. Therefore, the plant capacity is limited to 50 kt of CO_2/year. In this scenario, the combined CCUS3 cost is 107 €/ton of CO_2 – as opposed to 114 €/ton CO_2 for the base CCS1 scenario.

The framework of the CCS+U1 (blue ethanol) study is in general more favorable than that of CCS1 and CCS2. The design of the hydrogen production unit assumes renewable electricity to be available free of charge and at 40,5% availability. Because that would require a dynamic model of a future energy grid to be available, which is beyond the scope of this report, the question of intermittence of excess electricity is not taken into consideration in detail, and the impact of that intermittence to the ethanol production process (designed as a continuous system) is neglected. Moreover, any CO_2 emissions in the electricity generation process are disregarded (i.e. gray emissions for electricity generation and grid).

Revenues or spared costs due to CO_2 emission certificates are not considered. If emission certificates had been considered, they would have led to a cost reduction for the stakeholders involved in the storage case, i.e. the cement plant operator and the storage reservoir operator. In the present report, a simplified approach was used to determine the CO_2 avoidance potential of each route evaluated. In a future study, detailed LCA should be conducted, in order to re-evaluate the CO_2 abatement taking into consideration the sink factor of each product in its respective destination market. The CCS scenarios lead to CO_2 sequestration with a sink factor of 100%. Although for the CCUS cases the sink factor of the CO_2-based product is low, the fraction of the CO_2 that is utilized is expected to be lower than 10% (due to market or hydrogen availability constraints) – therefore the CCUS chains as proposed in this work have high CO_2 sink factors.

As a general conclusion, it is clear that for full scale cement plants, CO_2 utilization should be considered in combination with storage. Integrating the production of high added-values products, such as polyols, in the CCUS chain may lead to positive business cases. However, the number of cement plants that could benefit from this option will be strongly limited by the products’ market. Moreover, this might be a special case, since only polymers and cyclic carbonates were identified as having the combination of high-value, favorable chemistry.

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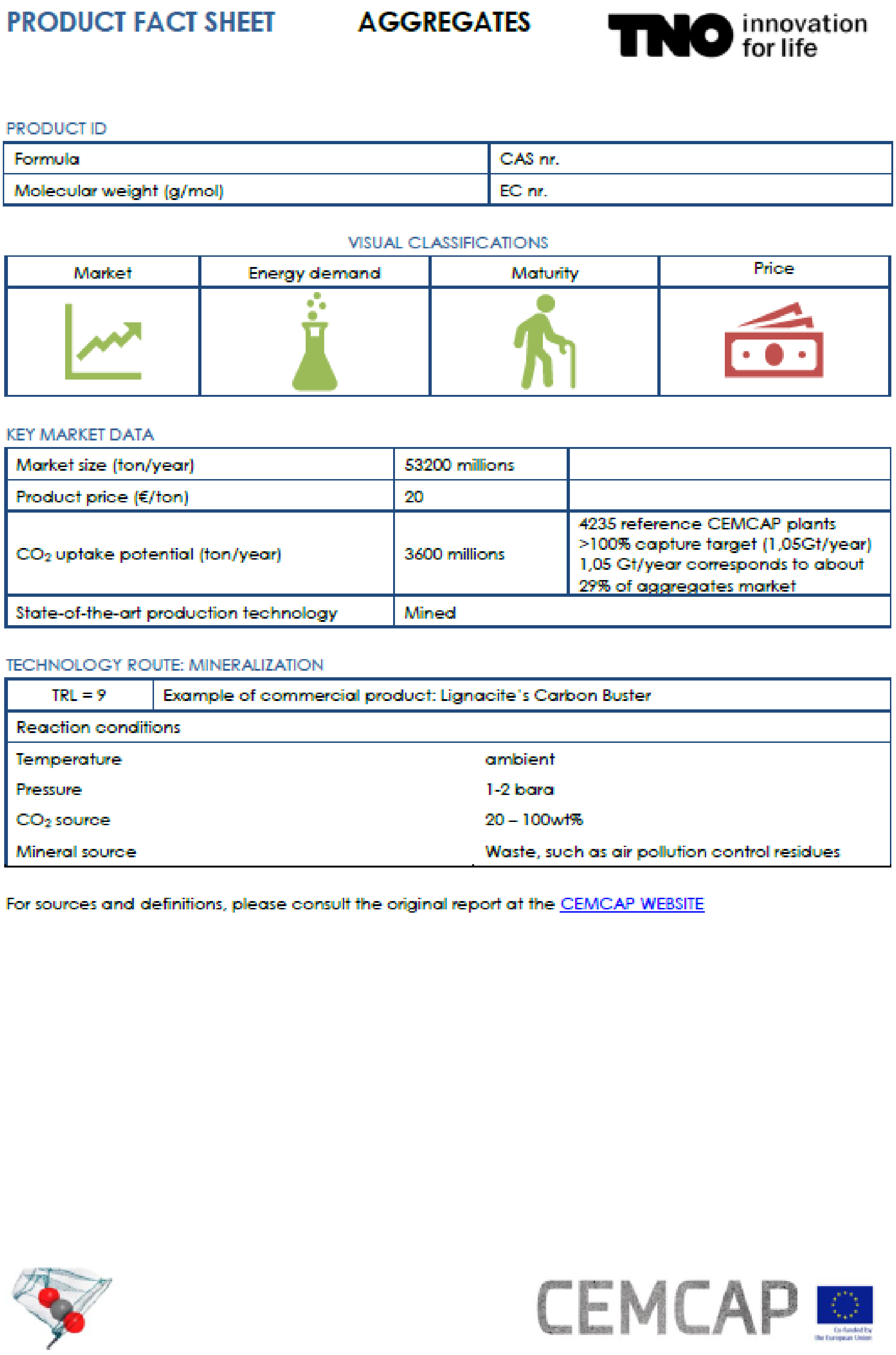
APPENDIX

A CO2 UTILIZATION PRODUCTS FACT SHEETS

A.2 Aggregates



PRODUCT FACT SHEET **AGGREGATES** TNO innovation for life

PRODUCT ID

Formula	CAS nr.
Molecular weight (g/mol)	EC nr.

VISUAL CLASSIFICATIONS

Market	Energy demand	Maturity	Price

KEY MARKET DATA

Market size (ton/year)	53200 millions	
Product price (€/ton)	20	
CO_2 uptake potential (ton/year)	3600 millions	4235 reference CEMCAP plants >100% capture target (1,05Gt/year) 1,05 Gt/year corresponds to about 29% of aggregates market
State-of-the-art production technology	Mined	

TECHNOLOGY ROUTE: MINERALIZATION

TRL = 9	Example of commercial product: Lignacite´s Carbon Buster
Reaction conditions	
Temperature	ambient
Pressure	1-2 bara
CO_2 source	20 – 100wt%
Mineral source	Waste, such as air pollution control residues

For sources and definitions, please consult the original report at the CEMCAP WEBSITE

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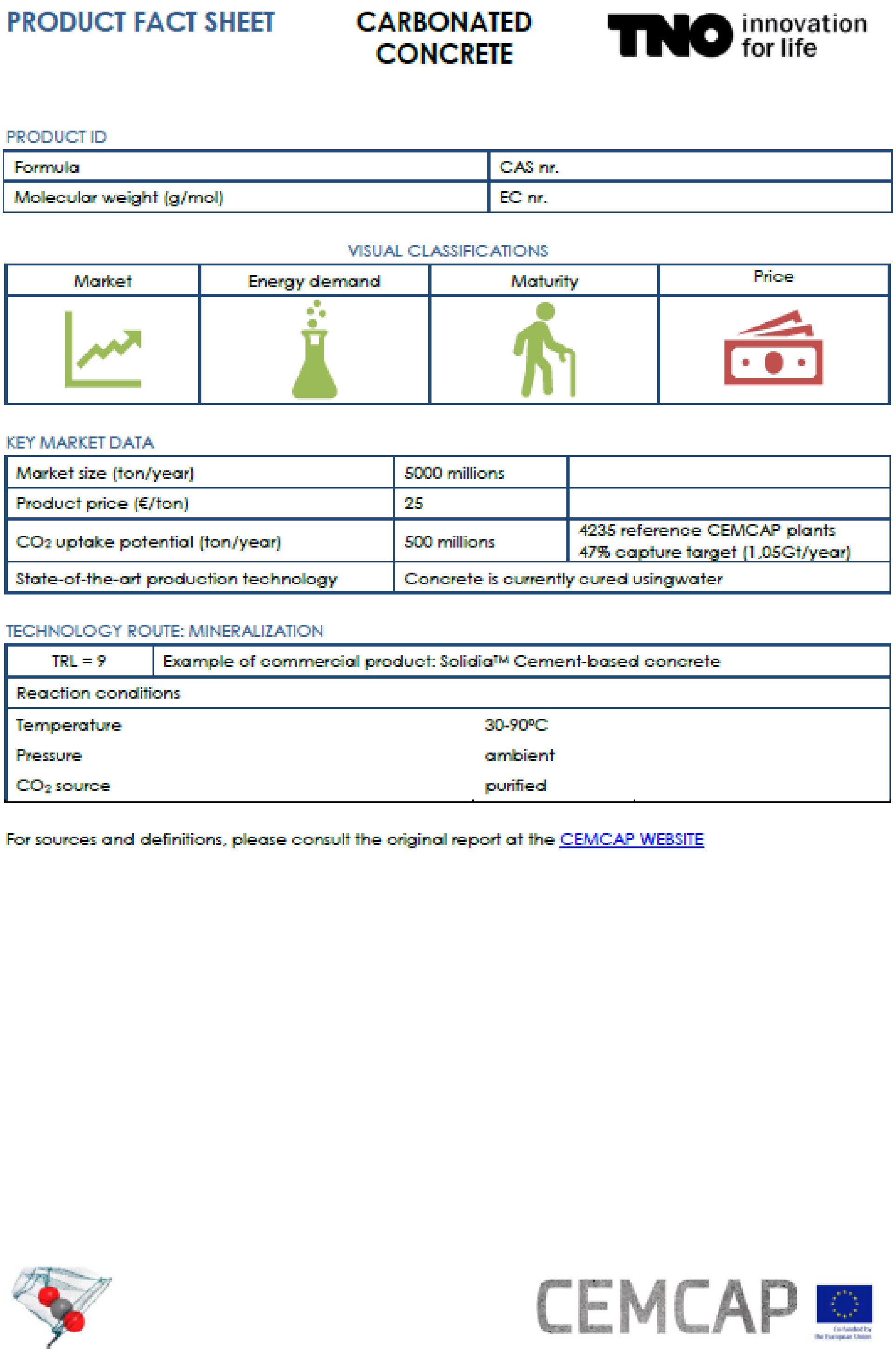
A.4 Carbonated concrete



PRODUCT FACT SHEET

CARBONATED CONCRETE

TNO innovation for life

PRODUCT ID

Formula	CAS nr.
Molecular weight (g/mol)	EC nr.

VISUAL CLASSIFICATIONS

Market	Energy demand	Maturity	Price

KEY MARKET DATA

Market size (ton/year)	5000 millions	
Product price (€/ton)	25	
CO_2 uptake potential (ton/year)	500 millions	4235 reference CEMCAP plants 47% capture target (1,05Gt/year)
State-of-the-art production technology	Concrete is currently cured usingwater	

TECHNOLOGY ROUTE: MINERALIZATION

TRL = 9	Example of commercial product: Solidia™ Cement-based concrete
Reaction conditions	
Temperature	30-90ºC
Pressure	ambient
CO_2 source	purified

For sources and definitions, please consult the original report at the CEMCAP WEBSITE

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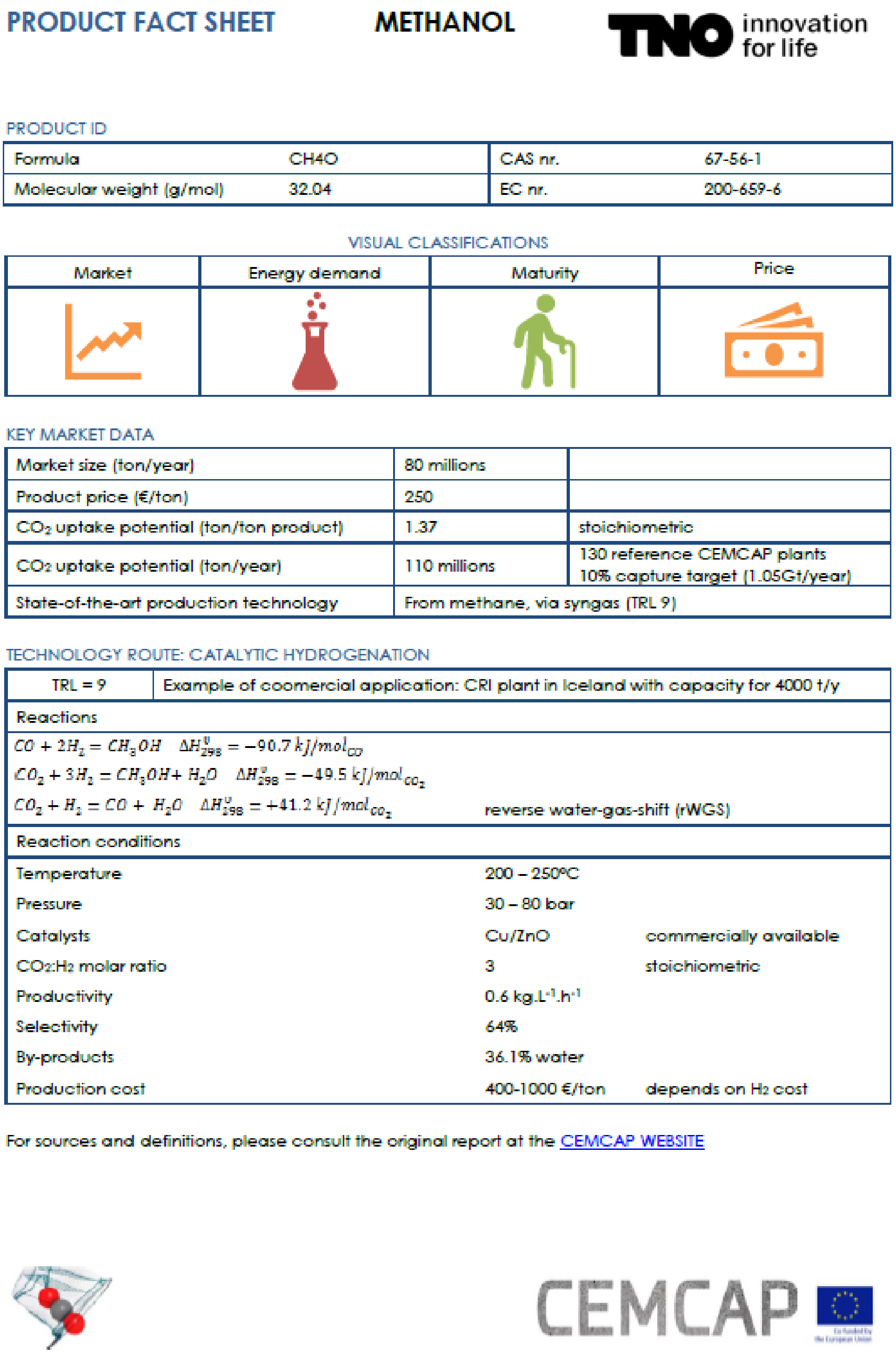
A.6 Methanol



PRODUCT FACT SHEET **METHANOL**

TNO innovation for life

PRODUCT ID

Formula	CH4O	CAS nr.	67-56-1
Molecular weight (g/mol)	32.04	EC nr.	200-659-6

VISUAL CLASSIFICATIONS

Market	Energy demand	Maturity	Price
📈	⚗	🧓	💵

KEY MARKET DATA

Market size (ton/year)	80 millions	
Product price (€/ton)	250	
CO_2 uptake potential (ton/ton product)	1.37	stoichiometric
CO_2 uptake potential (ton/year)	110 millions	130 reference CEMCAP plants 10% capture target (1.05Gt/year)
State-of-the-art production technology	From methane, via syngas (TRL 9)	

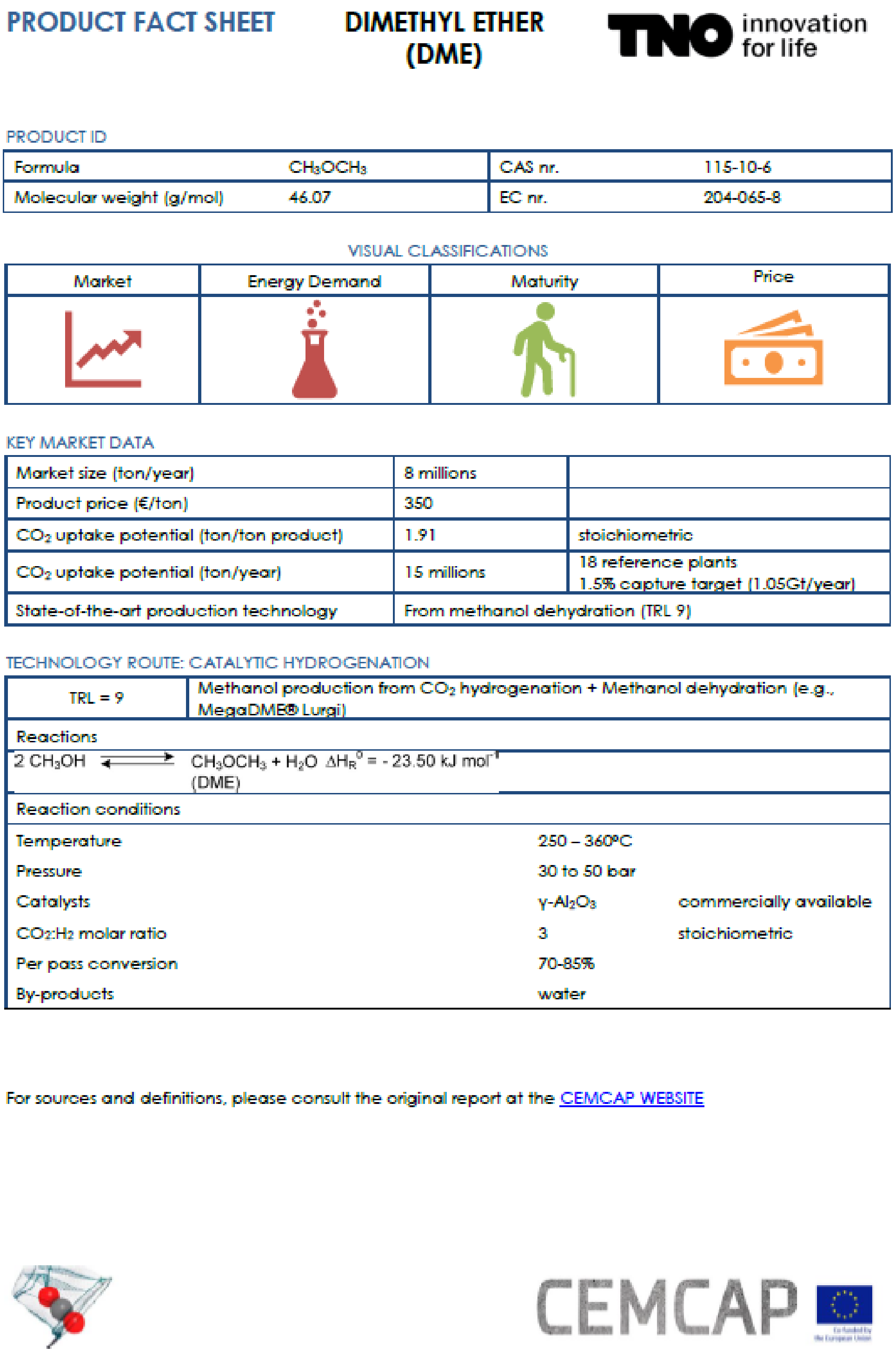
TECHNOLOGY ROUTE: CATALYTIC HYDROGENATION

TRL = 9	Example of coomercial application: CRI plant in Iceland with capacity for 4000 t/y	
Reactions		
$CO + 2H_2 = CH_3OH \quad \Delta H^0_{298} = -90.7\ kJ/mol_{CO}$		
$CO_2 + 3H_2 = CH_3OH + H_2O \quad \Delta H^0_{298} = -49.5\ kJ/mol_{CO_2}$		
$CO_2 + H_2 = CO + H_2O \quad \Delta H^0_{298} = +41.2\ kJ/mol_{CO_2}$	reverse water-gas-shift (rWGS)	
Reaction conditions		
Temperature	200 – 250ºC	
Pressure	30 – 80 bar	
Catalysts	Cu/ZnO	commercially available
CO_2:H_2 molar ratio	3	stoichiometric
Productivity	0.6 kg.L^{-1}.h^{-1}	
Selectivity	64%	
By-products	36.1% water	
Production cost	400-1000 €/ton	depends on H_2 cost

For sources and definitions, please consult the original report at the CEMCAP WEBSITE

CEMCAP

A.8 Dimethyl Ether



PRODUCT FACT SHEET

DIMETHYL ETHER
(DME)

TNO innovation for life

PRODUCT ID

Formula	CH_3OCH_3	CAS nr.	115-10-6
Molecular weight (g/mol)	46.07	EC nr.	204-065-8

VISUAL CLASSIFICATIONS

Market	Energy Demand	Maturity	Price
📈	⚗	🧓	💵

KEY MARKET DATA

Market size (ton/year)	8 millions	
Product price (€/ton)	350	
CO_2 uptake potential (ton/ton product)	1.91	stoichiometric
CO_2 uptake potential (ton/year)	15 millions	18 reference plants 1.5% capture target (1.05Gt/year)
State-of-the-art production technology	From methanol dehydration (TRL 9)	

TECHNOLOGY ROUTE: CATALYTIC HYDROGENATION

TRL = 9	Methanol production from CO_2 hydrogenation + Methanol dehydration (e.g., MegaDME® Lurgi)

Reactions

$$2\ CH_3OH \rightleftarrows \underset{\text{(DME)}}{CH_3OCH_3} + H_2O \quad \Delta H_R^0 = -23.50\ kJ\ mol^{-1}$$

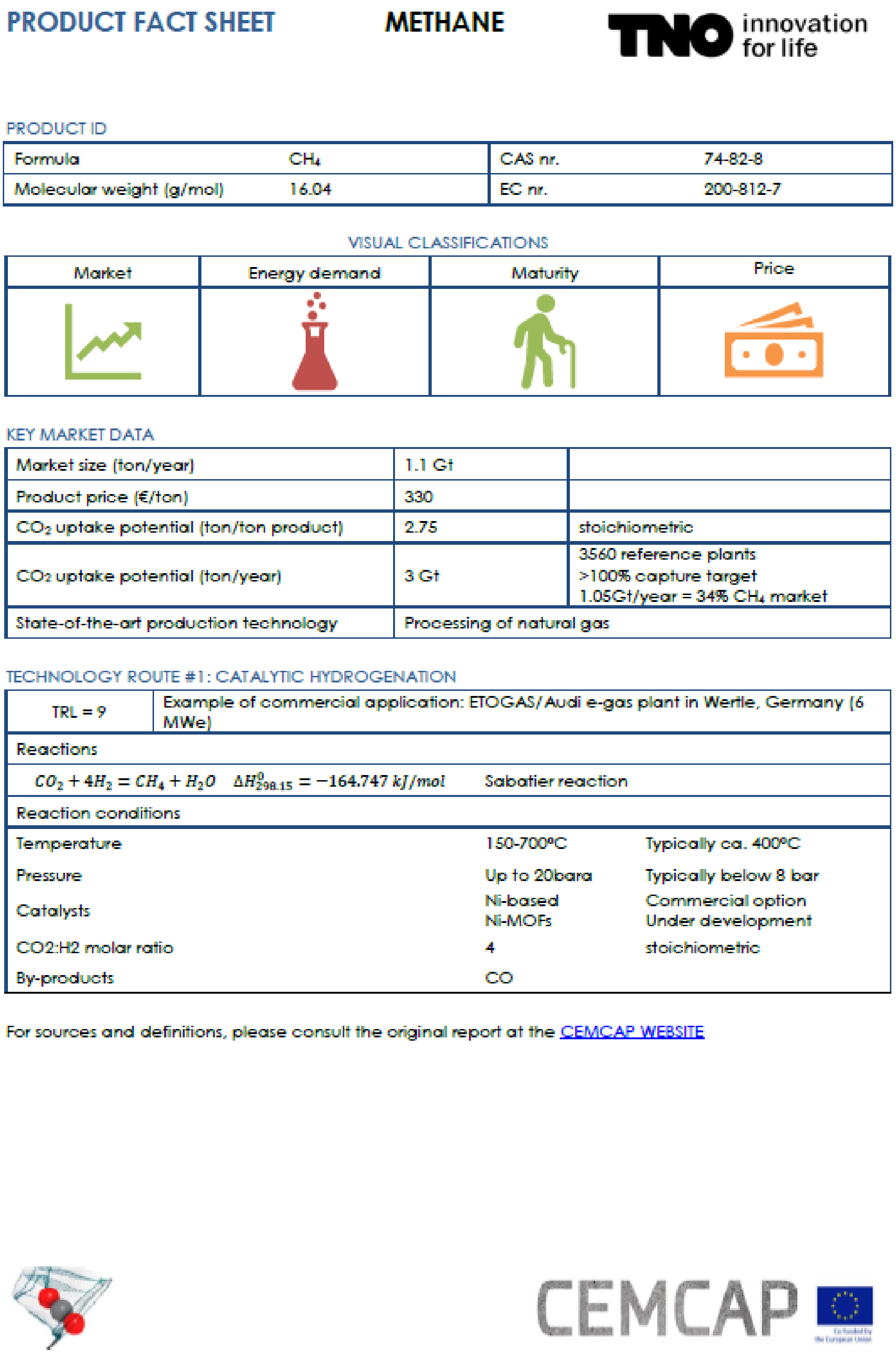
Reaction conditions

Temperature	250 – 360ºC	
Pressure	30 to 50 bar	
Catalysts	γ-Al_2O_3	commercially available
CO_2:H_2 molar ratio	3	stoichiometric
Per pass conversion	70-85%	
By-products	water	

For sources and definitions, please consult the original report at the CEMCAP WEBSITE

CEMCAP Co-funded by the European Union

A.10 Methane



PRODUCT FACT SHEET **METHANE**

TNO innovation for life

PRODUCT ID

Formula	CH_4	CAS nr.	74-82-8
Molecular weight (g/mol)	16.04	EC nr.	200-812-7

VISUAL CLASSIFICATIONS

Market	Energy demand	Maturity	Price

KEY MARKET DATA

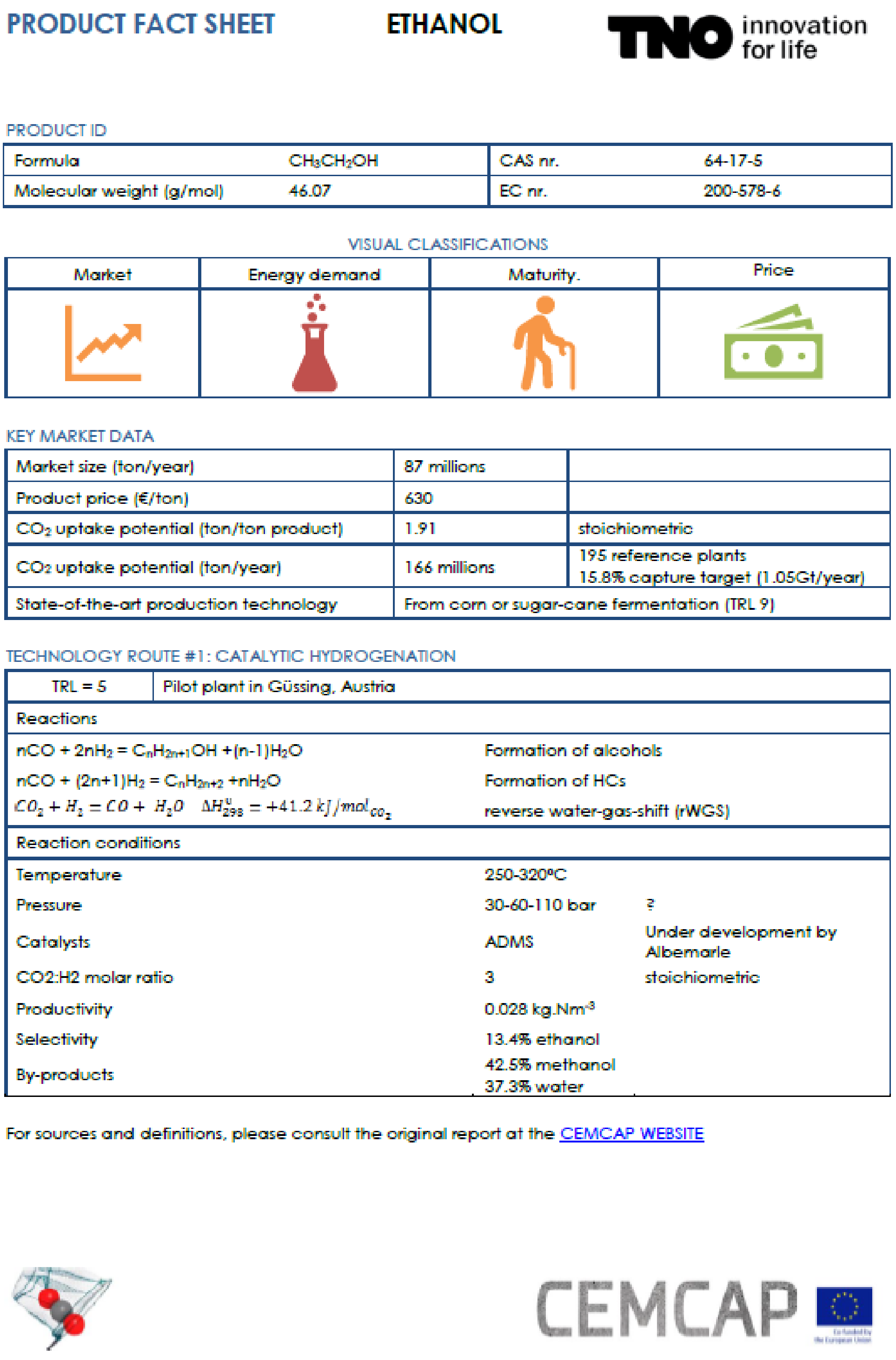
Market size (ton/year)	1.1 Gt	
Product price (€/ton)	330	
CO_2 uptake potential (ton/ton product)	2.75	stoichiometric
CO_2 uptake potential (ton/year)	3 Gt	3560 reference plants >100% capture target 1.05Gt/year = 34% CH_4 market
State-of-the-art production technology	Processing of natural gas	

TECHNOLOGY ROUTE #1: CATALYTIC HYDROGENATION

TRL = 9	Example of commercial application: ETOGAS/Audi e-gas plant in Werlte, Germany (6 MWe)	
Reactions		
$CO_2 + 4H_2 = CH_4 + H_2O \quad \Delta H^0_{298.15} = -164.747\ kJ/mol$	Sabatier reaction	
Reaction conditions		
Temperature	150-700°C	Typically ca. 400°C
Pressure	Up to 20bara	Typically below 8 bar
Catalysts	Ni-based Ni-MOFs	Commercial option Under development
CO2:H2 molar ratio	4	stoichiometric
By-products	CO	

For sources and definitions, please consult the original report at the CEMCAP WEBSITE

A.12 Ethanol



PRODUCT FACT SHEET **ETHANOL**

TNO innovation for life

PRODUCT ID

Formula	CH_3CH_2OH	CAS nr.	64-17-5
Molecular weight (g/mol)	46.07	EC nr.	200-578-6

VISUAL CLASSIFICATIONS

Market	Energy demand	Maturity.	Price

KEY MARKET DATA

Market size (ton/year)	87 millions	
Product price (€/ton)	630	
CO_2 uptake potential (ton/ton product)	1.91	stoichiometric
CO_2 uptake potential (ton/year)	166 millions	195 reference plants 15.8% capture target (1.05Gt/year)
State-of-the-art production technology	From corn or sugar-cane fermentation (TRL 9)	

TECHNOLOGY ROUTE #1: CATALYTIC HYDROGENATION

TRL = 5	Pilot plant in Güssing, Austria	
Reactions		
$nCO + 2nH_2 = C_nH_{2n+1}OH + (n-1)H_2O$	Formation of alcohols	
$nCO + (2n+1)H_2 = C_nH_{2n+2} + nH_2O$	Formation of HCs	
$CO_2 + H_2 = CO + H_2O \quad \Delta H^0_{298} = +41.2\ kJ/mol_{CO_2}$	reverse water-gas-shift (rWGS)	
Reaction conditions		
Temperature	250-320°C	
Pressure	30-60-110 bar	?
Catalysts	ADMS	Under development by Albemarle
CO2:H2 molar ratio	3	stoichiometric
Productivity	0.028 $kg.Nm^{-3}$	
Selectivity	13.4% ethanol	
By-products	42.5% methanol 37.3% water	

For sources and definitions, please consult the original report at the CEMCAP WEBSITE

CEMCAP Co-funded by the European Union

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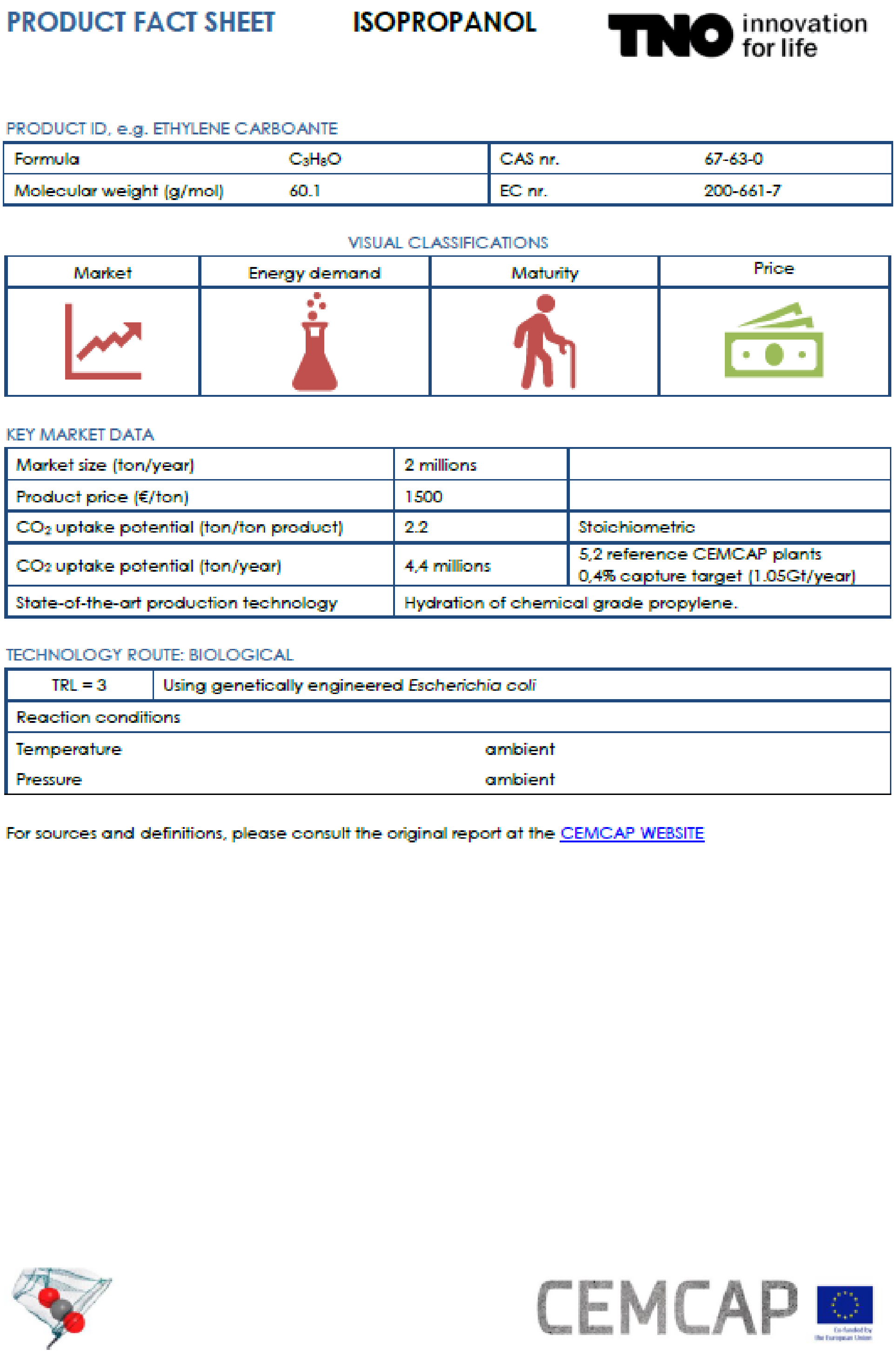
A.14 Isopropanol



PRODUCT FACT SHEET **ISOPROPANOL**

PRODUCT ID, e.g. ETHYLENE CARBOANTE

Formula	C_3H_8O	CAS nr.	67-63-0
Molecular weight (g/mol)	60.1	EC nr.	200-661-7

VISUAL CLASSIFICATIONS

Market	Energy demand	Maturity	Price
📈	🧪	🧓	💵

KEY MARKET DATA

Market size (ton/year)	2 millions	
Product price (€/ton)	1500	
CO_2 uptake potential (ton/ton product)	2.2	Stoichiometric
CO_2 uptake potential (ton/year)	4,4 millions	5,2 reference CEMCAP plants 0,4% capture target (1.05Gt/year)
State-of-the-art production technology	Hydration of chemical grade propylene.	

TECHNOLOGY ROUTE: BIOLOGICAL

TRL = 3	Using genetically engineered *Escherichia coli*
Reaction conditions	
Temperature	ambient
Pressure	ambient

For sources and definitions, please consult the original report at the CEMCAP WEBSITE

A.15 Poly(Prolylene) Carbonate

PRODUCT FACT SHEET

POLY(PROPYLNE CARBONATE), PPC

TNO innovation for life

PRODUCT ID

Formula	$[CH(CH_3)CH_2OCO_2]_n$	CAS nr.	25511-85-7
Molecular weight (g/mol)	100 000 to 600 000	EC nr.	

VISUAL CLASSIFICATIONS

Market	Energy demand	Maturity.	Price
📈	🧪	🧓	💵

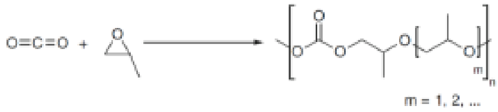
KEY MARKET DATA

Market size (ton/year)	6 millions	Estimate (1% share of plastics market)
Product price (€/ton)	3400	
CO_2 uptake potential (ton/ton product)	0,5	
CO_2 uptake potential (ton/year)	3 millions	3,5 reference plants 0,3% capture target (1.05Gt/year)
State-of-the-art production technology	From CO2 utilization, see description below	

TECHNOLOGY ROUTE: POLYMERIZATION

TRL = 9	Example of commercial product: Converge® from Aramco Services Company and Saudi Aramco Technologies

Reactions



Reaction conditions

Temperature	75	°C
Pressure	Ca. 20	Bar
Catalysts	Double metal cyanide (DMC)	
Reaction time	3	Hours
Selectivity	> 94%	

For sources and definitions, please consult the original report at the CEMCAP WEBSITE

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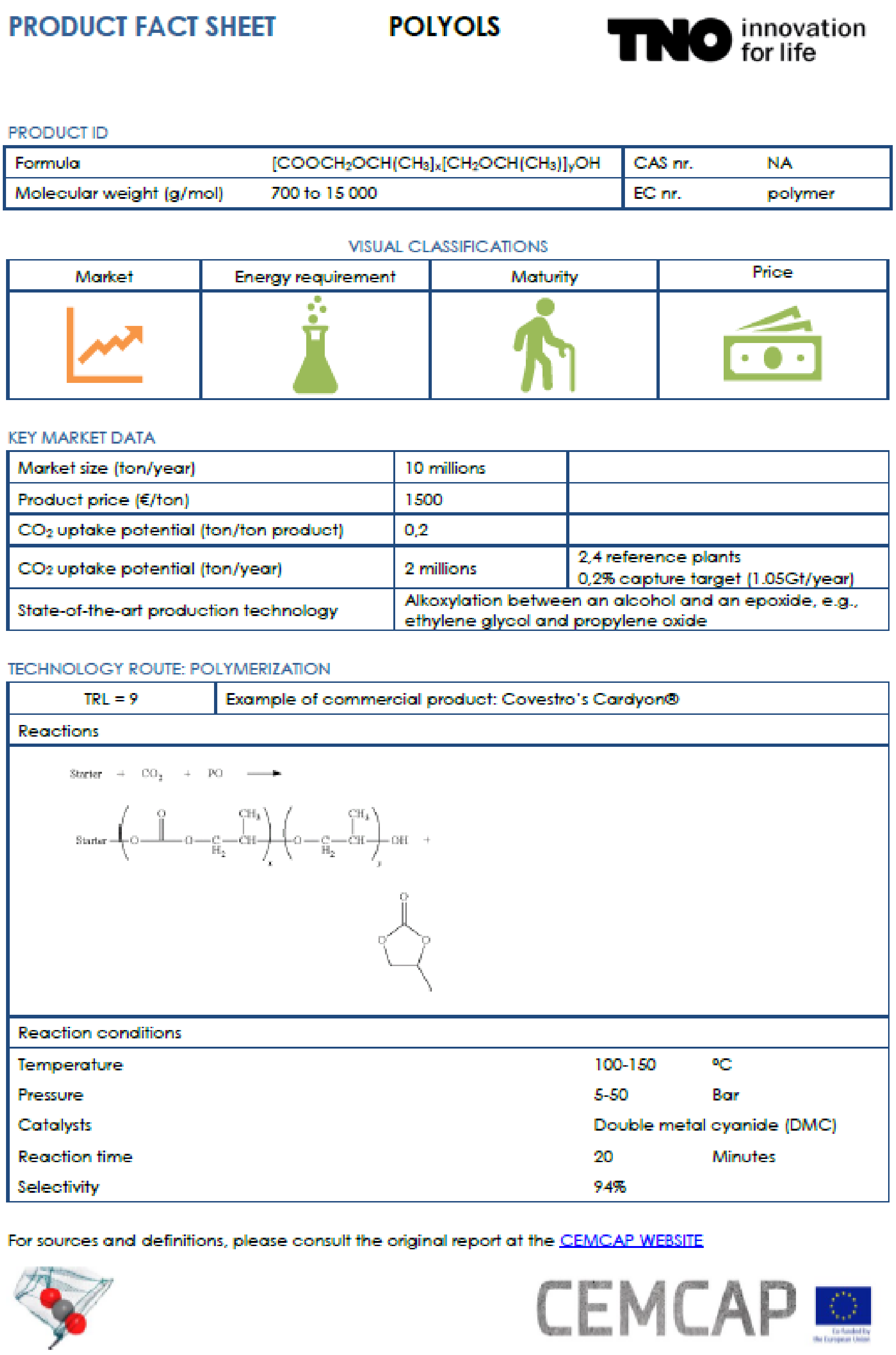
A.17 Polyols



PRODUCT FACT SHEET **POLYOLS** TNO innovation for life

PRODUCT ID

Formula	$[COOCH_2OCH(CH_3]_x[CH_2OCH(CH_3)]_yOH$	CAS nr.	NA
Molecular weight (g/mol)	700 to 15 000	EC nr.	polymer

VISUAL CLASSIFICATIONS

Market	Energy requirement	Maturity	Price

KEY MARKET DATA

Market size (ton/year)	10 millions	
Product price (€/ton)	1500	
CO_2 uptake potential (ton/ton product)	0,2	
CO_2 uptake potential (ton/year)	2 millions	2,4 reference plants 0,2% capture target (1.05Gt/year)
State-of-the-art production technology	Alkoxylation between an alcohol and an epoxide, e.g., ethylene glycol and propylene oxide	

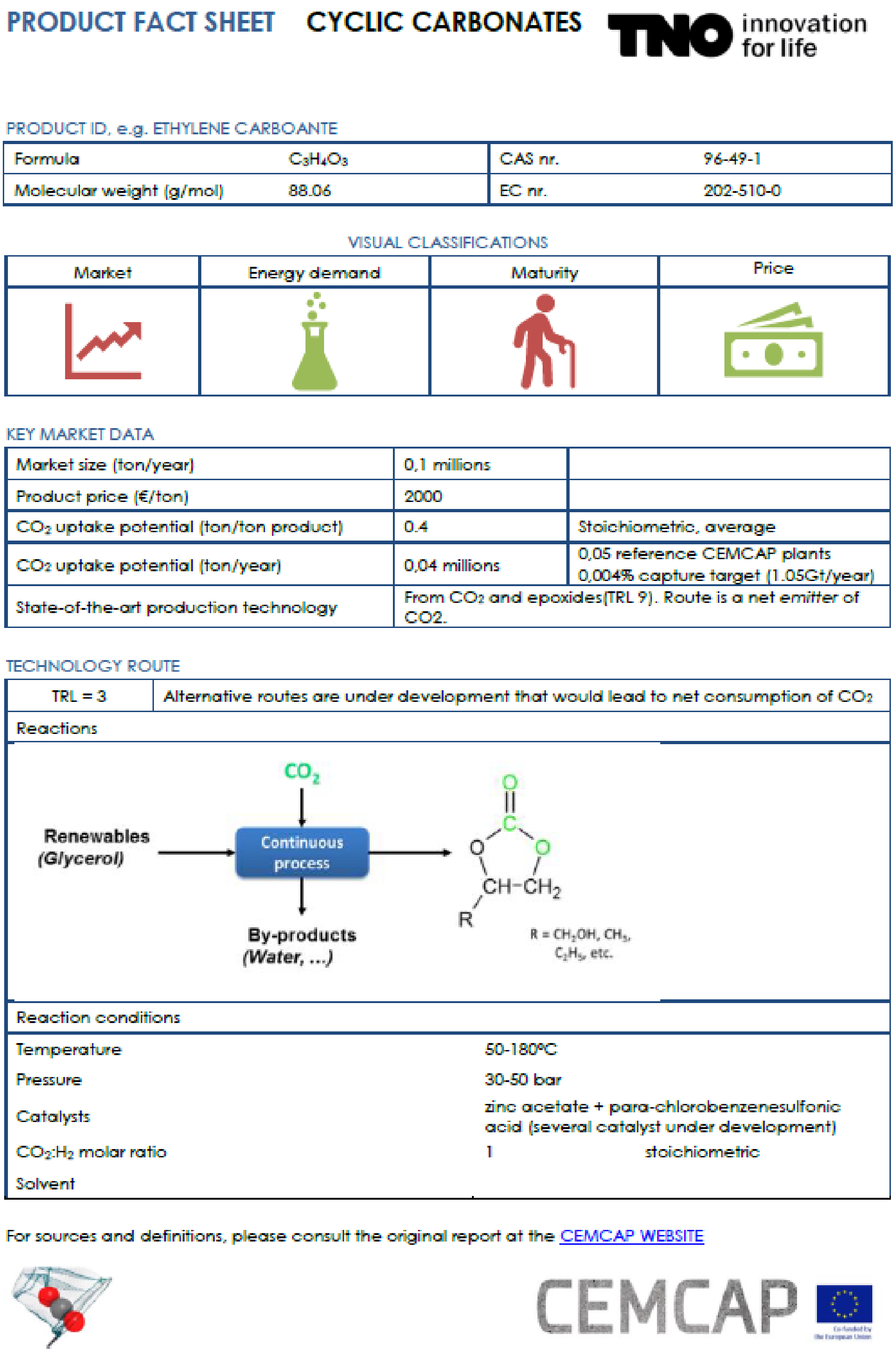
TECHNOLOGY ROUTE: POLYMERIZATION

TRL = 9	Example of commercial product: Covestro's Cardyon®
Reactions	

Reaction conditions		
Temperature	100-150	°C
Pressure	5-50	Bar
Catalysts	Double metal cyanide (DMC)	
Reaction time	20	Minutes
Selectivity	94%	

For sources and definitions, please consult the original report at the CEMCAP WEBSITE

A.19 Cyclic Carbonates



PRODUCT FACT SHEET CYCLIC CARBONATES TNO innovation for life

PRODUCT ID, e.g. ETHYLENE CARBOANTE

Formula	$C_3H_4O_3$	CAS nr.	96-49-1
Molecular weight (g/mol)	88.06	EC nr.	202-510-0

VISUAL CLASSIFICATIONS

Market	Energy demand	Maturity	Price

KEY MARKET DATA

Market size (ton/year)	0,1 millions	
Product price (€/ton)	2000	
CO_2 uptake potential (ton/ton product)	0.4	Stoichiometric, average
CO_2 uptake potential (ton/year)	0,04 millions	0,05 reference CEMCAP plants 0,004% capture target (1.05Gt/year)
State-of-the-art production technology	From CO_2 and epoxides(TRL 9). Route is a net emitter of CO2.	

TECHNOLOGY ROUTE

TRL = 3	Alternative routes are under development that would lead to net consumption of CO_2

Reactions

Reaction conditions

Temperature	50-180°C	
Pressure	30-50 bar	
Catalysts	zinc acetate + para-chlorobenzenesulfonic acid (several catalyst under development)	
CO_2:H_2 molar ratio	1	stoichiometric
Solvent		

For sources and definitions, please consult the original report at the CEMCAP WEBSITE

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A.21 Formic Acid

PRODUCT FACT SHEET **FORMIC ACID**

innovation
for life

PRODUCT ID

Formula	HCOOH	CAS nr.	64-18-6
Molecular weight (g/mol)	46.03	EC nr.	200-579-1

VISUAL CLASSIFICATIONS

Market	Energy demand	Maturity	Price
📈	⚗	🧓	💵

KEY MARKET DATA

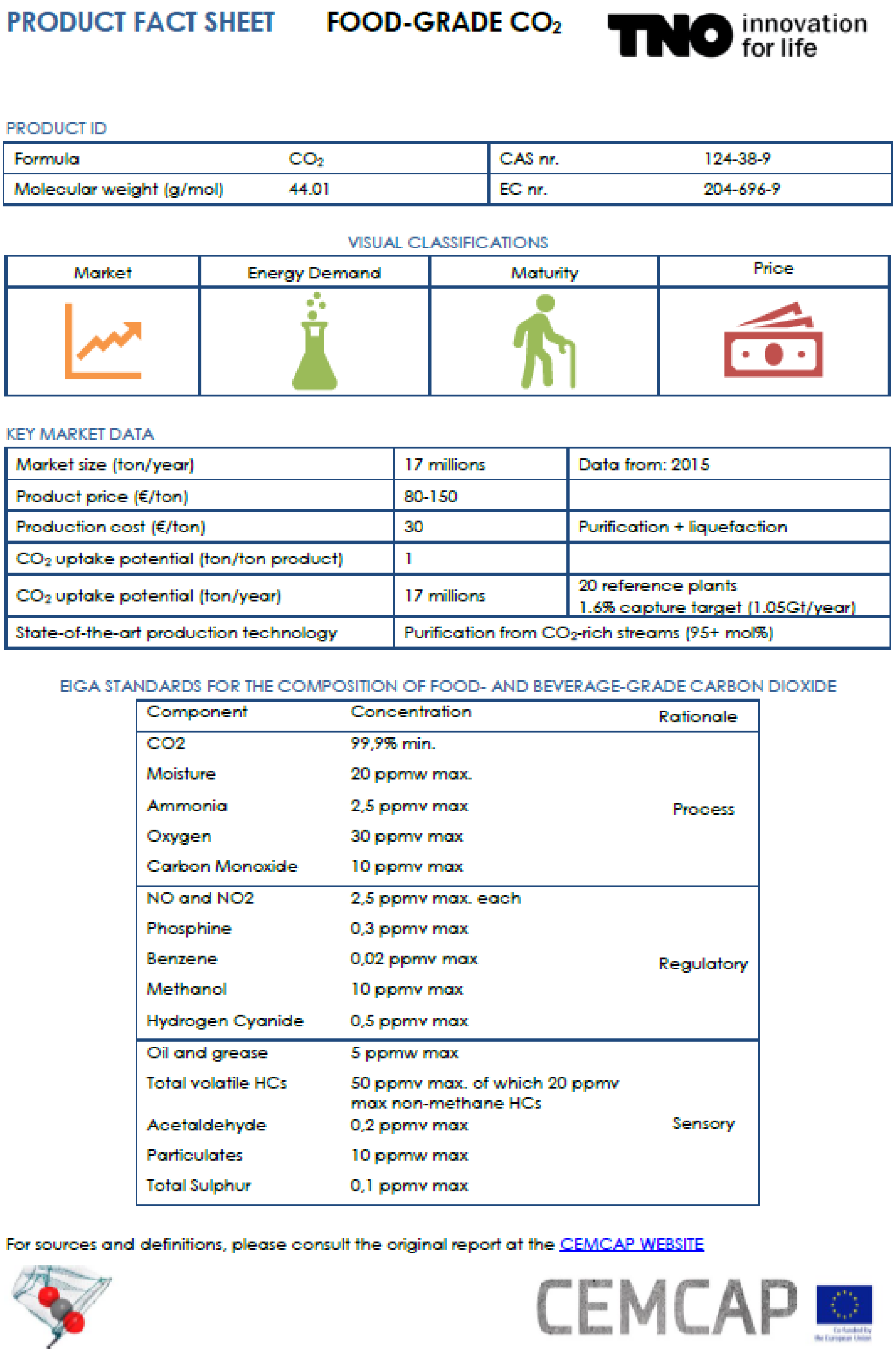
Market size (ton/year)	0,7 millions	
Product price (€/ton)	600	
CO_2 uptake potential (ton/ton product)	0.96	stoichiometric
CO_2 uptake potential (ton/year)	0,67 millions	0,8 reference CEMCAP plants 0,1% capture target (1.05Gt/year)
State-of-the-art production technology	Carbonylation of methanol and subsequent hydrolysis of the methyl formate produced (TRL 9)	

TECHNOLOGY ROUTE: CATALYTIC HYDROGENATION

TRL = 5	Pilot plant in Güssing, Austria	
Reactions		
$nCO + 2nH_2 = C_nH_{2n+1}OH + (n-1)H_2O$	Formation of alcohols	
$nCO + (2n+1)H_2 = C_nH_{2n+2} + nH_2O$	Formation of HCs	
$CO_2 + H_2 = CO + H_2O \quad \Delta H^0_{298} = +41.2\ kJ/mol_{CO_2}$	reverse water-gas-shift (rWGS)	
Reaction conditions		
Temperature	90ºC	
Pressure	100 bar	
Catalysts	ruthenium- and phosphino-based catalysts	
CO_2:H_2 molar ratio	1	stoichiometric
Solvent	Aqueous methanol	

For sources and definitions, please consult the original report at the CEMCAP WEBSITE

A.23 Food-grade CO_2



PRODUCT FACT SHEET FOOD-GRADE CO_2

TNO innovation for life

PRODUCT ID

Formula	CO_2	CAS nr.	124-38-9
Molecular weight (g/mol)	44.01	EC nr.	204-696-9

VISUAL CLASSIFICATIONS

Market	Energy Demand	Maturity	Price

KEY MARKET DATA

Market size (ton/year)	17 millions	Data from: 2015
Product price (€/ton)	80-150	
Production cost (€/ton)	30	Purification + liquefaction
CO_2 uptake potential (ton/ton product)	1	
CO_2 uptake potential (ton/year)	17 millions	20 reference plants 1.6% capture target (1.05Gt/year)
State-of-the-art production technology	Purification from CO_2-rich streams (95+ mol%)	

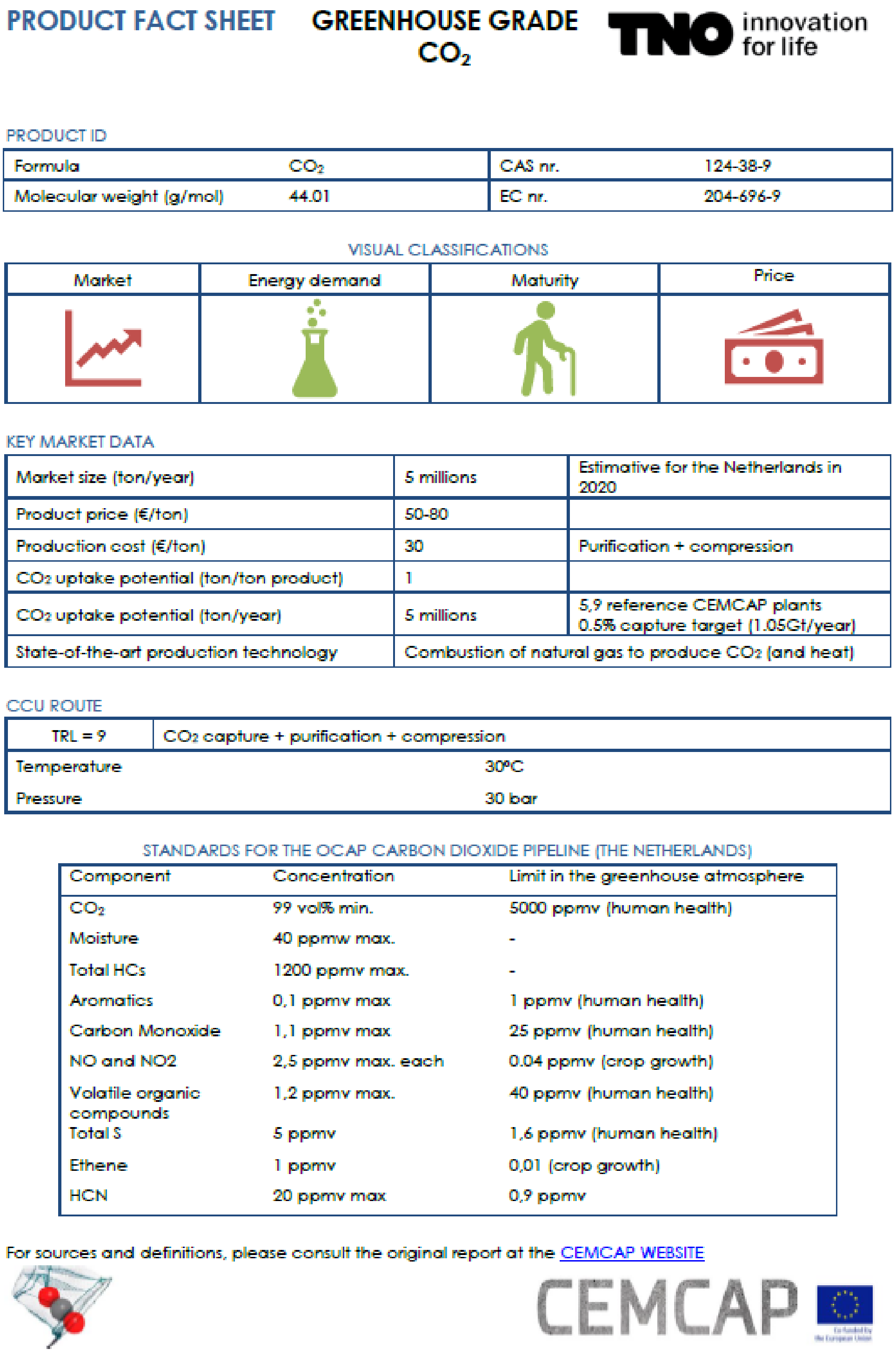
EIGA STANDARDS FOR THE COMPOSITION OF FOOD- AND BEVERAGE-GRADE CARBON DIOXIDE

Component	Concentration	Rationale
CO2	99.9% min.	Process
Moisture	20 ppmw max.	
Ammonia	2,5 ppmv max	
Oxygen	30 ppmv max	
Carbon Monoxide	10 ppmv max	
NO and NO2	2,5 ppmv max. each	Regulatory
Phosphine	0,3 ppmv max	
Benzene	0,02 ppmv max	
Methanol	10 ppmv max	
Hydrogen Cyanide	0,5 ppmv max	
Oil and grease	5 ppmw max	Sensory
Total volatile HCs	50 ppmv max. of which 20 ppmv max non-methane HCs	
Acetaldehyde	0,2 ppmv max	
Particulates	10 ppmw max	
Total Sulphur	0,1 ppmv max	

For sources and definitions, please consult the original report at the CEMCAP WEBSITE

CEMCAP

A.24 Greenhouse-grade CO_2



PRODUCT FACT SHEET **GREENHOUSE GRADE CO_2** TNO innovation for life

PRODUCT ID

Formula	CO_2	CAS nr.	124-38-9
Molecular weight (g/mol)	44.01	EC nr.	204-696-9

VISUAL CLASSIFICATIONS

Market	Energy demand	Maturity	Price

KEY MARKET DATA

Market size (ton/year)	5 millions	Estimative for the Netherlands in 2020
Product price (€/ton)	50-80	
Production cost (€/ton)	30	Purification + compression
CO_2 uptake potential (ton/ton product)	1	
CO_2 uptake potential (ton/year)	5 millions	5,9 reference CEMCAP plants 0.5% capture target (1.05Gt/year)
State-of-the-art production technology	Combustion of natural gas to produce CO_2 (and heat)	

CCU ROUTE

TRL = 9	CO_2 capture + purification + compression
Temperature	30°C
Pressure	30 bar

STANDARDS FOR THE OCAP CARBON DIOXIDE PIPELINE (THE NETHERLANDS)

Component	Concentration	Limit in the greenhouse atmosphere
CO_2	99 vol% min.	5000 ppmv (human health)
Moisture	40 ppmw max.	-
Total HCs	1200 ppmv max.	-
Aromatics	0,1 ppmv max	1 ppmv (human health)
Carbon Monoxide	1,1 ppmv max	25 ppmv (human health)
NO and NO2	2,5 ppmv max. each	0.04 ppmv (crop growth)
Volatile organic compounds	1,2 ppmv max.	40 ppmv (human health)
Total S	5 ppmv	1,6 ppmv (human health)
Ethene	1 ppmv	0,01 (crop growth)
HCN	20 ppmv max	0,9 ppmv

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