CCU market options in the Rotterdam Harbour Industrial Complex

CE Delft

Committed to the Environment

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Committed to the Environment

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Preface

The Rotterdam Harbour Industrial Complex faces a serious challenge in the transition to meet the Paris Treaty goals. The industrial processes and activities in the area must be almost completely decarbonized. This requires new technologies to achieve this goal.

CO_2 capture is able to avoid significant amounts of CO_2 from larger point sources. An alternative of storage is utilisation of the captured CO_2 for use in materials, chemicals and fuels. In Germany several CCU projects already have led to a first demonstration plant for use in polyurethanes.

The Rotterdam Harbour Industrial Complex has an optimal position to catch up and obtain a top position on industrial application of CCU process. This by the combination of CO_2 and hydrogen infrastructure, nearby wind parks in combination with CO_2 point sources and various prospective industrial clients.

Plant One Rotterdam is currently realising an infrastructure which demonstrates realistic capture of CO_2 for use in various CCU pilot processes. These pilot processes should successively deliver the starting points for demonstration and full scale realisation of the processes and contribute to the required reduction of CO_2 emissions in Rotterdam Harbour Industrial Complex.

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Summary

The Paris treaty gives a strong impetus for the reduction of greenhouse emissions. The target of less than 2°C temperature rise and preferably 1.5°C leads to a CO_2 emission reduction target of 80-95% compared to 1990, an enormous challenge for all CO_2 emitting sectors and industries.
Like many other industrial areas, for the Rotterdam Harbour Industrial Complex (HIC) this requires a wide transition towards low- and zero-carbon technologies. It is very likely that industrial areas which are best equipped to handle this challenge have better chances to survive this transition process and remain in a healthy and profitable condition.

The technologies and processes which enable this deep decarbonisation are ranging from widely available to still under research, and from short-mid-term to long term. Many short-mid-term measures are applicable and compatible with existing industrial operations. On the mid to long term biobased materials and renewable energy sources will be used in new processes.

The capture of CO_2 is one of the options for reducing CO_2 emissions from existing processes on the short to mid term. This captured CO_2 can be stored or buffered in empty oil or gas fields or aquifers, which is called Carbon Capture and Storage, or CCS. However, in the current situation this would have to be done at a cost without sufficient income to mitigate these costs. The current low ETS price does not cover the cost for the storage option of CCS by far.

The reuse of the captured CO_2 with Carbon Capture and Utilisation, CCU, is an alternative, which under certain conditions could provide income to cover the cost. The higher the added value of the product and the lower the energy cost to achieve this, the better this is for the business case.

Our assessment of various CCU options shows that there are two classes of business cases, a categorisation based on the chemical reaction:

1. **Early business cases**
   Reactions do not require large energy input and/or result in high added value products.
   Examples: mineralisation to filler in concrete, polyols for polyurethanes, high value products from algae.
   These applications are usually limited in scale, with a CO_2 capture potential to several MT/year.
2. **Longer term business cases**
   Reactions require external energy input like hydrogen or power.
   This business case will only become positive when further in the value chain customers allow significant mark-up for low carbon products and when the cost of renewable electricity has sharply declined.
   These applications include bulk chemicals and fuels and have an enormous potential.

Contrary to CCS, in the business case of CCU the ETS-price of CO_2 plays a secondary role, because of the financial added value which is not present in CCS. In CCU the added value is usually 100's to 1,000's €/ton CO_2, much larger than the current ETS-price of 5-7 €/ton. The ETS-price is for CCU more a 'cherry on the pie' and only at substantial high levels of several 100's €/ton CO_2 will it play a decisive and dominant role in CCU bulk products.

The impact of CCU on emission reduction varies, however, and can be much less than in the case of CCS, depending on the type of CCU.
Some store CO_2 in a long cyclic or eternal way like in mineral filler materials, leading to comparable CO_2 mitigation as CCS. In other types, the CO_2 is emitted on the short term, typically resulting in (much) less CO_2 reduction. This complexity asks for an objective approach to determine the real impact of a CCU route. A Life Cycle Assessment, or LCA, is a widely accepted methodology to objectively determine the CO_2 mitigation value of the CCU route of choice.

The current EU ETS system only accepts CCS as a transfer, not yet as a carbon abatement technique, but negotiations are underway and CCU is expected to be added in the future ETS-regulations. This is supported by the 2015 Energy Strategy (EC, 2015) that stated the EU seeks 'A forward-looking approach to carbon capture and storage (CCS) and carbon capture and use (CCU) for the power and industrial sectors.

Developing CCU in Rotterdam HIC requires three major types of stakeholders: CO_2 sources, CO_2 and CCU-supporting infrastructures and the utilisation processes connected to it. The HIC has a unique position, as it already houses all of these three; see Table 1 for major contributors.

Table 1 **Major contributors**

Large CO_2 sources	CO_2- and CCU-infrastructure	Utilisation reaction
Alco	Linde-OCAP CO_2-line	Greenhouses
Shell	Air Liquide hydrogen	
Uniper	Wind power landing	
Engie	Electrolysis (chlorine and planned hydrogen)	
AVR		

Conclusions

Depending on market conditions, CCU has the potential for the storage or reuse of limited (hundreds of ktons) up to very large amounts of CO_2 (tens of million tons). Specialty production with **algae, mineralisation and polyols for polyurethane are early candidates** to achieve positive business cases on the short to mid-term due to their limited energy consumption and high added value products. They can act as a stepping stone for larger projects in the future.

There are also ample large volume CCU opportunities for the longer term.
In this, **methanol is a strategically important candidate**, while being an platform chemical for oil free production of olefins (MTO process) and gasoline (MTG process) as well as for admixture in fuels. However, today the business case for CCU methanol is still far from profitable without a support scheme.

Next steps to be taken in the HIC area comprise the identification of high value creating CCU opportunities and promoting symbiosis between industrial parties. New supply chains are to be set up, enabling this industrial symbiosis required for CCU. This includes the delivery of captured CO_2, heat integration for the capture, use of currently available residual materials, creation of products with added value in other sectors, etc. Setting up of these new CCU supply chains requires the organisation of joint projects with strategic partners. These joint activities are initiated by desk studies on the specific CCU opportunities, technical and economic feasibility studies, realisation of pilot plants for execution of pilot tests, which provide confirmation of the positive CCU business case.

Active support from Rotterdam HIC stakeholders will help initiate CCU realisation by supporting pilot tests and offering low cost captured CO_2 by economy of scale. This will improve the competitiveness for new CCU plants in this area and attracts new business for reduced carbon CCU chemicals to the Rotterdam HIC creating additional profitability and employment in the region. We furthermore conclude that CCU is a technology which offers a flexible system of absorption of residual CO_2 of both current fossil as well as new low carbon processes preventing or reducing CO_2 emission. It is able to grow and shrink with the degree of carbon free processes in the years to come and provides a potent instrument to help comply with the Paris COP21 treaty, if the developments focus on the CCU routes with high CO_2 reduction potential.

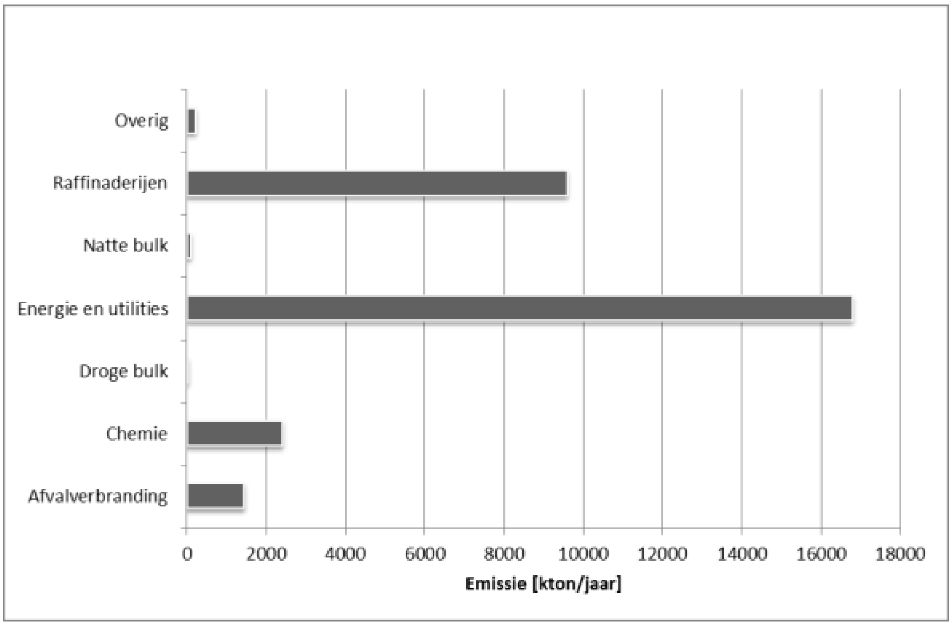
1 Introduction, motivation for CCU projects in the Rotterdam Harbour Industrial Complex

1.1 Current greenhouse gas emission level in the Rotterdam area

Current total CO_2 emissions in Rotterdam HIC amounted to a total of 30.5 Mt in 2015, an increase of 5 Mt compared with the 2007 emission level.

Emissions are mostly associated with coal fired and natural gas fired power generation and production of H_2 for refining and vegetable oil processing (16.8 Mt/year) and refining of crude mineral oil and natural gas condensate (9.6 Mt/year). Approximately 12 Mt/year of the emissions associated with power generation are emitted by coal fired power stations.

Figure 1 **CO_2 emission per sector in the Rotterdam HIC area (2015)**



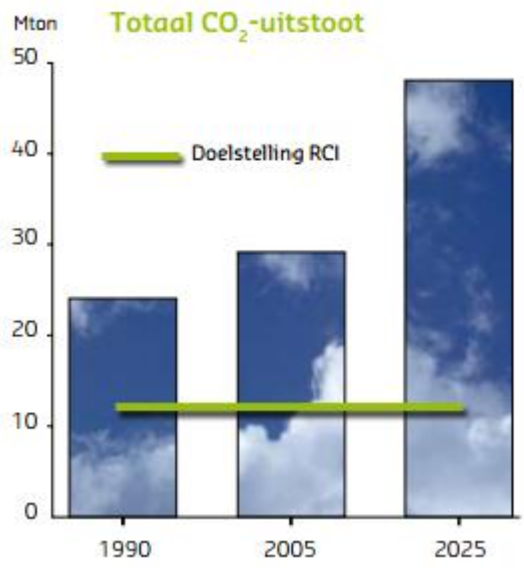
Source: DCMR, 2016: inventarisatie-en-vergelijking-jaaremissies-Rijnmond-2007-2015.

Greenhouse gas emissions associated with chemical industry (2.4 Mt) and waste incineration (1.4 Mt) are modest by comparison.

1.2 Desired and required reduction levels for greenhouse gas emissions

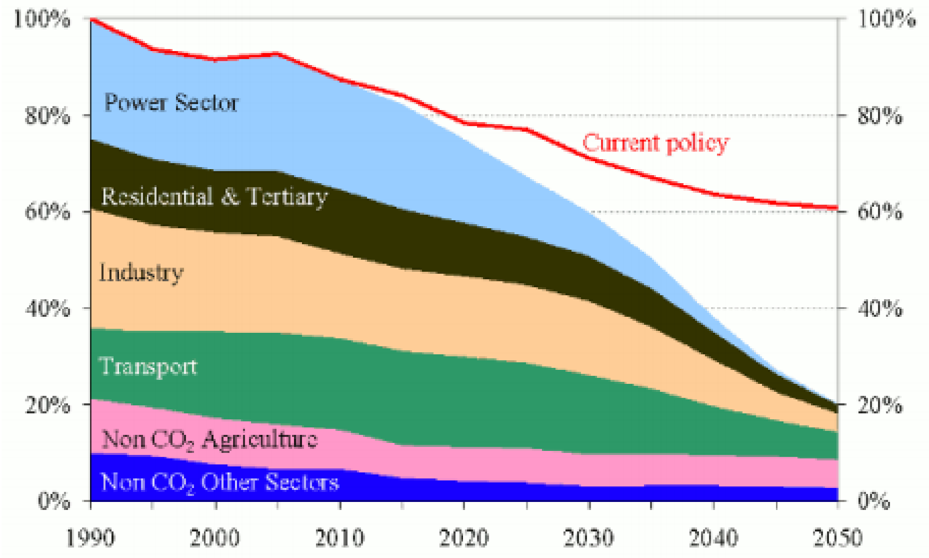
According to the original goals of the Rotterdam Climate Initiative, greenhouse gas emissions are to be reduced with 50% in 2025, compared with the 1990 emission level.

Figure 2 **Rotterdam Climate initiative goal for 2025**



For 2050 an even more demanding reduction rate of 80-95% compared with the 1990 emission level will have to be realized if global increase in average temperature is to be limited to 1.5-2.0°C.

Figure 3 **Possible 80% cut in greenhouse gas emissions in the EU (100% =1990)**



Source: EC, DG Climate Action, 2017.

Most of the required reduction could be realized by substitution of fossil fuels and associated products (power, heat, H_2) by energy carriers from renewable sources (wind, photovoltaic). Next to that, use of mineral oil based fuels will have to be reduced drastically, as the use of such fuels represents diffuse greenhouse gas emissions. For maritime transport for example, the range of the required reduction is -63 to -98%, according to a study for the EU Policy Department A for the Committee on Environment, Public Health and Food Safety (ENVI) (Öko-Institut, 2015). This will also result in a reduction of greenhouse gas emissions related to refining.

1.3 Potential requirement for CCU

Nevertheless, the reduction in greenhouse gas emissions that can be realized by conversion from fossil fuels to renewable energy may not be enough for meeting required reduction percentages and additional measures may be necessary.

CCU, next to CCS, may be one of the additional options required for realizing the required reduction in greenhouse gas emissions. CCU may also be good business as demonstrated by existing examples of commercial CO_2 utilization, e.g.:
- use in horticulture to accelerate plant growth;
- addition to soda;
- use as a raw material for high-purity $CaCO_3$ - limestone - for example for use in paper (white colour of paper);
- use of supercritical CO_2 as a solvent;
- use as extinguishing agent in fire extinguishers, automatic extinguishing systems in buildings and installations where water use would cause unwanted damage.

However potential for use of CO_2 in these applications in the Rotterdam area is limited and what potential there is, has already been utilized.
Potential for another option, enhanced oil recovery in oil fields in the North Sea, is uncertain as demonstrated by e.g. studies by Shell, BP, Norway and UK (IEAGHG, 2015). EOR also requires a significant investment in infrastructure and a lengthy process before the infrastructure has been realized.

Therefore, commissioned by Deltalinqs and Uniper, CE Delft conducted a limited search for additional opportunities for CO_2 utilization in industrial production processes in the Rotterdam area.

1.4 Aim of this project

This project is aims to identify possible buyers of CO_2 from Uniper and other companies in the Harbour Industrial Complex region (HIC) and at assessing the potential market opportunities for CCU in the region.
The project is a second step in implementation of CCU in the region and is intended as a stepping stone for a demonstration project for CCU at Plant One testing facilities or at the site of capture. The piloting of the specific route should in its turn prepare the way for a commercial scale implementation.

Obviously, CCU processes that already have been implemented commercially or have been demonstrated at a commercial scale are also relevant for the objective of the project and the long term goals of Uniper and other (potential) CO_2 suppliers.

1.5 Reading guide

Next chapter describes the execution of the project. The first section describes and underpins which aspects are considered for the evaluation of the different processes. Next, a summary of the evaluation results is given. The last paragraph of next chapter contains conclusions and recommendations. Background information about specific processes can be found in the appendices.

2 CCU options

2.1 The ideal CCU project for Rotterdam HIC

In view of the goal of initiating demonstration projects at Plant One and successively implementing commercially available technology in the Rotterdam HIC region, first an overview of existing and emerging pathways for use of CO_2 as a raw material and the current state of technical development of these technologies was made.

Based on the current state of technical development a selection of processes was made, that have been developed sufficiently for a demonstration project at Plant One or could be implemented commercially directly.
Technologies still in the phase of component prototype development or earlier stages of technical development will not allow for a demonstration project at the scale of the CATO pilot plant with its capture capacity of 250 kg/hr.

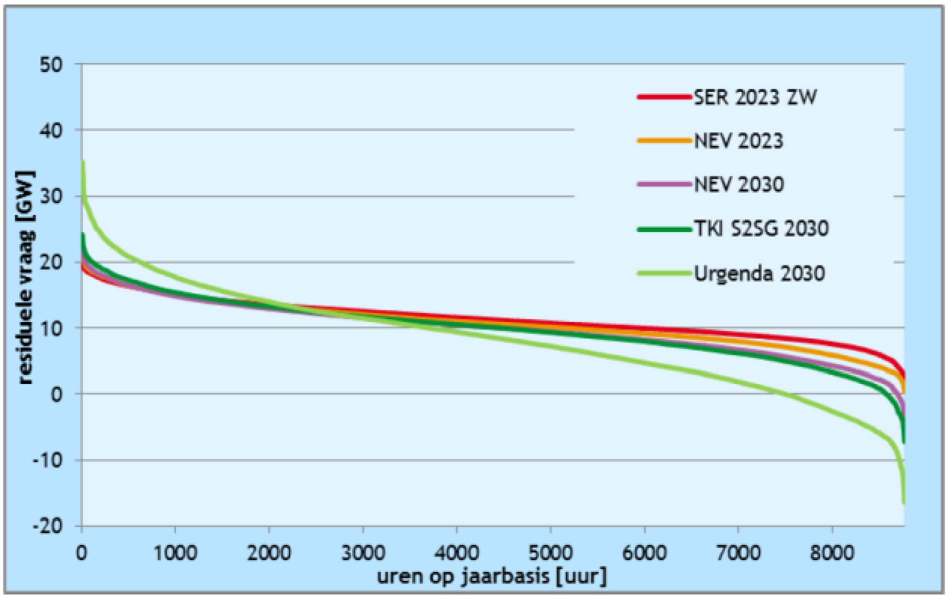
In view of the intended demonstration projects followed by commercial roll out, next an assessment was made of the specification requirements for the CO_2 feedstock imposed by the different technologies. These requirements will determine whether CO_2 rich gas flows from different industrial sources could be applied as feedstock or which gas treatment processes are required to bring the CO_2 feedstock on specification.
As illustrated by $CaCO_3$ production from purified flue gases, not all CCU processes require food grade CO_2 (>99.9% purity) as currently distributed along the OCAP pipeline. The ability for accepting relatively diluted and polluted CO_2- ich flue gas flows will be beneficial for the business case, as requires less investments and operational costs are related to conditioning the CO_2.

In view of commercial implementation an assessment was made of:
- which raw materials currently used by existing industries in the Rotterdam HIC region could be produced based on CO_2;
- which products and by-products from existing industries in the Rotterdam HIC region could be processed by reaction with CO_2 into new products with added economic value.

Next to this an assessment in broad was conducted of various other aspects:
- Can the technology be economically viable and what CO_2 market price and energy prices are required for competitiveness?
- Can the technology be utilized as a peak shaver technology, taking advantage of future temporary surplus of renewable power?
- Can a significant amount of CO_2 be sequestered?
- For what period of time is the processed CO_2 sequestered and what is approximately the net greenhouse gas saving that can be realized?
- How much energy and additives are required per unit of processed CO_2?
- Does the process have significant benefits in terms of product quality and/or environmental impacts and risks?

An economic viable process will allow for implementation without significant public financial and process-oriented support. Having high ramp rates and a low partial load level may improve competitiveness in the future, when high capacities of renewable power generation may result in frequent surpluses of power on the electricity grid. The future scenario's containing these surpluses are shown in Figure 4.

Figure 4 **Demand and supply on the power grid**



Source: (CE Delft, 2016a).

On the right side the supply exceeds the demand during a part of the year, generating a surplus.

If CCU is seen as a measure for reduction of greenhouse gas emissions in the Rijnmond region, it is only relevant if at least several hundreds of kilotonnes/ annum of CO_2 can be sequestered, given current emission levels and required reduction of greenhouse gas emissions up to 2050.

The question of the length of time during which the processed CO_2 is sequestered and the net reduction in greenhouse gas emissions refer to the alternative of perpetual geologic storage of CO_2 in case of CCS. Perpetual geological storage of CO_2 can be considered a guaranteed way for CO_2 emission reduction.
If, for example, CO_2 is captured from flue gases of coal and biomass fired power plants in the context of reduction of greenhouse gas emissions, CCU should – from a societal perspective - result in a similar net reduction to be as beneficial for combating climate change.
A limited consumption of energy and additives per unit of processed CO_2 in general helps minimizing greenhouse gas emissions related to CO_2 processing and/or leaves more renewable energy for substitution of fossil fuels based energy.

On the other hand, significant reduction in environmental impacts and risks or significant improvements in product quality may be a good reason to implement CCU nonetheless.

The different assessments have in general been broad and based on literature and various discussions with companies and stakeholders in Rotterdam HIC.

2.2 Current technological development status of technologies

2.2.1 Technologically (more) advanced routes

For the CO_2 utilization routes identified in previous project current technological development status was estimated, based on publicly available literature. During this assessment, several additional conversion routes were identified and several routes could be defined more precisely.

Of the identified technologies, following have been demonstrated on a semi-commercial scale or have been implemented commercially:

1. Thermochemical and microbiological production of methane by way of CO_2 hydrogenation.
2. Thermochemical production of methanol by way of CO_2 hydrogenation.
3. Production of linear polypropylene or polyethylene carbonates by carbonation of propylene or ethylene epoxides.
4. Production of dimethyl carbonate (DMC) by carbonation of ethylene oxide into cyclic ethylene carbonate and subsequent transesterification of the produced with methanol.
5. Further processing of DMC into aromatic carbonates (Asahi Kasei process).
6. Production of polyether carbonate polyols by copolymerization of CO_2 with a starter molecule (mono-, di- and poly-ols; alkoxylated oligomers of glycols) and an alkylene oxide/epoxide.
7. Production of ethanol (and several other oxo-chemicals) by fermentation of CO/CO_2 containing gases.
8. Carbonation of minerals, ashes and slags.

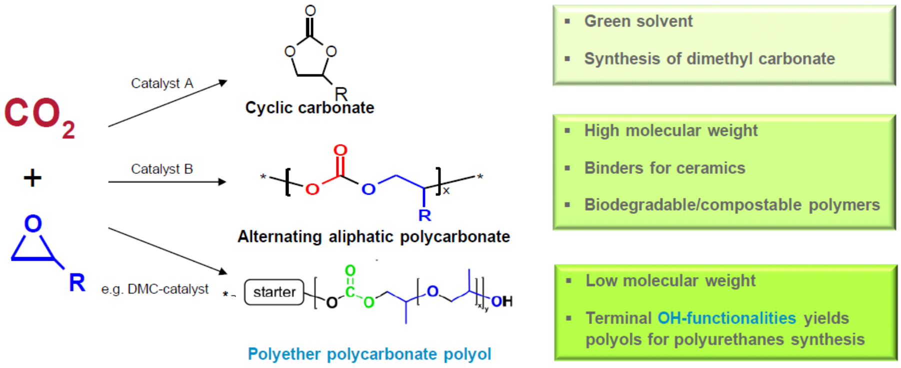
Previous study	**This study**	**TRL**		**Selected for next analysis**
Methanol	Thermochemical production (ICR)	7	Semi commercial scale demo plant operational (Iceland)	X
Carbamates		2	No sufficiently selective catalyst	
Poly-urethane	Polyols via carbonation of epoxides and oligomeric alcohols (Bayer and Novomer)	6-7	Two semi-commercial scale demo plants operational	X
Linear and cyclic organic polycarbonates	Linear polycarbonates from expoxide carbonation (Novomer)	7	Semi commercial scale demo plant operational (Novomer)	X
Aromatic polycarbonates	By way of epoxide carbonation (Asahi Kasei)	9	5 commercial plants operational	X
	By way of alcohol carbonation (Asahi Kasei)	6	Pilot plant has been financed	X
	Shell process with CO_2, ethylene or propylene and phenol	6	Pilot plant has been financed	X
Mineralisation and utilization in cement and concrete	Solidia	9		X
	Carbstone	9		X
	Green Minerals	4	Capture with asbestos conversion option	X
	Carbon8 Aggregates	9		X
Carbon monoxide/syngas		2	No sufficiently selective catalyst, problems with carbon deposition	
Ureum (and melamine)		9	Market saturated	
Organic acids (e.g. formic acid, acetic acid)	Photanol technology	3-4	Only very small pilot plants for testing	
Koppelingen naar ethanol en hogere alcoholen/aldehyden	Ethanol from gas fermentation (Lanzatech)	6-8	Demonstrated on pilot scale, first-of-a-kind commercial scale installation under construction (Arcelor Mittal Ghent)	X
Electrochemical production routes	Liquid Light Corp, Evonik Coval (formic acid)	2-4 2-3	No pilot plant build yet, Laboratory Component Testing No pilot plant build yet, Laboratory Component Testing	
Methane production	Thermochemical production Etogas	6-7	Semi commercial scale demo plant operational (Werle)	
	Microbiological production MicrobEnergy	6-7	Semi commercial scale demo plant operational (Allendorf)	X

Hydrogenation of CO_2 into methane is being developed inter alia as peak shaving technology for conversion of surplus renewable power into storable energy. Methane can be stored in the existing natural gas infrastructure. Technology developers include Etogas and MicrobEnergy GmbH, a subsidiary of the Viessmann Group. But other initiators are also mentioned in various sources.

Hydrogenation of CO_2 into methanol can also be utilized for this purpose, but with a higher minimum load (35%). Methanol is presented as a platform chemical that allows access to the markets for transportation fuels and olefins. Methanol production technology is supplied by Carbon Recycling International, in cooperation with Mitsubishi Hitachi Power Systems Europe GmbH.

Carbonation of epoxides (route 3-6) can be utilized as a stepping stone for several production routes, the products being determined by the applied catalysts. See Figure 5.

Figure 5 **Carbonation of epoxides routes**

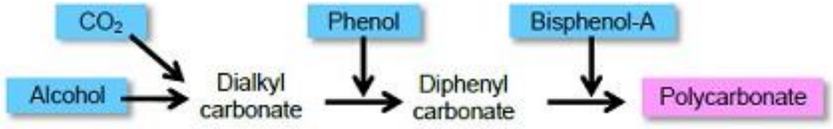


After the successful DREAM CCU development in Germany, it was logical that Bayer company Covestro started with the realisation of a plant for CCU polyols for low carbon polyurethane with financial support to reduce the cost of CO_2 capture. Similarly, this could be interesting CCU route to pursue in Rotterdam HIC for Covestro competitors already producing polyols and polyurethane.

If in a similar way, the Technology developers include Novomer (partly sold to Saudi Aramco), Bayer MaterialScience and also Akzo (for DMC production). The production of DMC and subsequent utilization of DMC into aromatic carbonates is a commercially available technology supplied by Asahi Kasei, which has been used in five production plants in Asia, Russia and Saudi Arabia.

Asahi Kasei Chemicals (Tokyo) has also announced plans to construct a 1,000 tonnes/year validation plant at its Mizushima Works (Kurashiki Japan) for its newly developed process, based on carbonation of alcohols (Plastics Today, 2015).

Figure 6 **Carbonation of alcohol route**



Shell Global Solutions is developing another production route, based on a multi-stage reaction involving carbon dioxide, phenol and either propylene oxide or ethylene oxide (Chemical Processing, 2009), (Shell, 2011).
The process produces DPC, together with mono-propylene glycol (MPG) or mono-ethylene glycol (MEG). A 500-tonne per year demonstration unit to be realized in Singapore has been announced in 2011.
For ethanol production by gas fermentation Lanzatech seems to be a leader in this technology. A demonstration plant is currently under construction at ArcelorMittal in Ghent. Lanzatech claims it can also produce other oxo-chemicals, including various isomers of butanol and butanediol and including aceton and lactic acid, using different strains of bacteria. Practical experiences for these alternative products are limited. 2,3-butanediol (2,3-BDO) production by gas fermentation has been demonstrated.

Solidia Technologies and Carbstone Innovation NV (a cooperation between Recmix Belgium BVBA and VITO NV) provide technology for carbonation of mineral matter:

Solidia Technologies has developed an alternative wollastonite ($CaSiO_3$)-based cement. That binds in a reaction with CO_2 instead of water like regular Portland cement does.

Green Minerals has developed a process for accelerated CO_2 reaction using the mineral olivine. As an option, using this process also asbestos and cement bonded asbestos react with CO_2, resulting in non-dangerous carbonate mineral, but this is slower than using olivine. Currently, Green Minerals aims to develop an accelerated process version for asbestos as well.

Carbstone Innovation focuses primarily on slags from metals production. Similar technology for utilization of ashes is indicated to be also under development. Slags from a steel plant offer a logical route to reduce CO_2 emissions for energy intensive steel plants.
Please refer to the appendix for a more detailed description.

U.K. start-up Carbon8 Aggregates has commercialized (c&en chemical and engineering news, 2015) a method of making building aggregates using waste CO_2.
Carbon8 combines CO_2 with waste residues, including ash from municipal incinerators and energy plants. Under tightly controlled reaction conditions, the CO_2 is rapidly absorbed by the residues in the presence of water to form calcium carbonate.

The calcium carbonate is then mixed with fillers and binders to produce pellets in a drum pelletizer where more CO_2 is added to carbonate the binder. Most of these pellets end up in blocks used in building and construction.
In addition to generating sales from its final product, Carbon8 is able to charge suppliers of its waste residues up to $ 190 per metric ton, which is less than they would have to pay to put their material in landfills.
Carbon8 currently treats 25,000 metric tons of residues and consumes 2,000 metric tons of CO_2 per year at a facility in Brandon, England. The CO_2 is purified from the waste stream of a sugar beet factory 20 miles from the Carbon8 plant. CO_2 represents 25% of Carbon8's costs. High-purity CO_2 is required because the CO_2 can otherwise not be liquefied.
The firm is about to commission a new plant near Bristol, England, that will treat 40,000 metric tons of residues and consume 4,000 metric tons of CO_2. Carbon8 is planning three more sites in the UK in the next two years.

2.2.2 Low TRL technological routes

Several routes mentioned in previous study prove to have a TRL < 5:

- direct production of formic acid from CO_2 (and H_2);
- reduction of CO_2 into CO;
- carbamate and isocyanates for polyurethane synthesis (MDI);
- microbiological production of lactic acid, acetic acid, butanol, flavours and fragrances, terpenes and polyols;
- electrochemical reactions (Evonik, Liquid Light).

Direct formic acid production is still in an infancy phase. A recent Dutch TKI subsidy was given to a consortium for developing direct electrochemical CO_2 to formic acid conversion technology up to the level of demonstrating components and realizing a pilot scale continuous operational plant.

CO_2 reduction with H_2 to CO can currently only be realized at high temperatures but the available catalysts are not yet selective enough to allow for industrial commercialisation. There are also problems with carbon depositions on the catalyst surface.

About production of carbamates, one of the used sources of information states: although long-chain carboxylic acids and carbamates are amenable to a similar synthetic route as amendable for acrylic acid and although these products find use in different industrial sectors with some large existing markets (e.g., a 10 Mt/a market for long-chain carboxylic acids) only very few demonstration-level developments have been reported.

Microbiological production of lactic acid, acetic acid, butanol, flavours and fragrances, terpenes and polyols as e.g. under development by Photanol has only been demonstrated in very small scale pilot plants.

For electrochemical reactions a significant amount of patents has been applied for and have been assigned for, but to our knowledge there has been no pilot plant tests yet.

All these synthesis routes are on the other hand in theory all very interesting because of the market potential of the products in terms of market size and value, the limited amount of energy needed in manufacture and the often significant improvements in environmental risks and impacts.
These potential benefits may lead to the decision to initiate a demonstration project with one or several of these technologies, regardless of the current level of technological development (TRL).

2.2.3 Other processes

Production of urea (and melamine) is currently the most commonly utilized process for conversion of CO_2 into chemical products, but the urea market seems saturated. Next to that, it seems more logical to produce urea from the CO_2 produced during the synthesis of NH_3, but additional CO_2 works as a booster for this process.

Acrylic acid production by reaction of CO_2 and ethylene has been pursued by BASF. In 2014 BASF was very positive about developments, but since then no new statements have been made.

2.3 CO_2 specifications

Based on the consulted literature and websites following overview of the specifications of the CO_2 feedstock utilized in the different selected CCU processes could be produced. If no solid information was available in literature it was left blank.

Table 2 Specifications of CO_2 for different CCU-processes

	Pressure	Dried?	Sulphur sensitive?	Flex option?	Used in practice
Thermochemical production (ICR)	100 bar	Yes	Yes	Yes	High-purity, desulphurized (< ppmv S) CO_2 from geothermal non condensable gases
Polyols via carbonation of epoxides and oligomeric alcohols (Bayer and Novomer)		Yes		Probably	CO_2 from coal fired power station (>99.8 vol%, Bayer) or ethanol plant (>99.9 vol%, Novomer)
Linear polycarbonates from expoxide carbonation (Novomer)		Yes			High-purity CO_2 from ethanol plant (> 99.9 vol%)
PC by way of epoxide carbonation (Asahi Kasei)	Limited (10 – 15 bar)	Yes			High-purity CO_2 from ethylene oxide production, captured with hot aqueous K_2CO_3 solution or physical absorbents
PC by way of alcohol carbonation (Asahi Kasei)					
Shell process with CO_2, ethylene or propylene and phenol					
Solidia	Ambient (Solidia Technologies, 2013)			No power consumption in CO_2 application	High-purity CO_2 (> 99.9 vol%), lower purity may be acceptable

	Pressure	Dried?	Sulphur sensitive?	Flex option?	Used in practice
Carbstone	20 bar (Quaghebeur , et al., 2010)			Batch	High-purity CO_2 (> 99.9 vol%), down to 20 vol% acceptable (Quaghebeur, et al., 2015)
Carbon8 Aggregates (Carbon8, 2017)	Liquid CO_2 and atmospheric gas	Yes			High-purity CO_2 from ethanol plant (> 99.9 vol%)
Ethanol from gas fermentation (Lanzatech)	Slightly increased	No	No		Raw off gases
Thermochemical methane production Etogas	7 bar (Werle)	No	Yes	Yes	High-purity CO_2 captured from biogas with amine scrubber
Microbiological methane production MicrobEnergy	Slightly increased	No		Yes	Desulphurised biogas

Information availability is limited, especially for carbonates and polyols production routes. Some information was derived from student reports or thesis.

More general, following aspects may be taken into consideration.

In general highly concentrated CO_2 flows will need to be dried to avoid corrosion in pipelines and other components.

Catalysts utilized in thermochemical conversion reactions tend to be sensitive to poisoning with sulphur. Hence, sulphur will probably need to be limited to a very low level, as illustrated by the CRI CO_2-to-methanol process.
In case of post combustion capture or biogas conditioning, most sulphur containing components will be removed anyway, but it is uncertain whether residual concentrations will be sufficiently low. Concentrations mentioned by Berghout amount to <10 ppmv SO_x and <10 ppmv NO_x for CO_2 from post combustion capture.

Requirements with regard to e.g. content of O_2, NO_x, CO, N_2 and Ar are not discussed in the considered literature sources.

3 Economic viability and CO_2 market prices

In general the business case of CCU routes is determined by several factors:
- capital expenditures (CAPEX);
- operational (OPEX);
- cost of capital mitigated for investment risk;
- income streams during the lifetime of the investment.

Many methods exist but there are three methods which are widely used:
1. Simple payback time.
2. Return on Investment (ROI).
3. Net Present Value (NPV).

The net present value is most accurate, while it takes the time effect of when investments and when cash flows occur into account. The Net Present Value is calculated as:

Figure 7 **Net Present Value calculation**

Net Present Value (NPV)

$$\text{NPV} = \sum_{t=1}^{T} \frac{\text{Cash Flow}_t}{(1+i)^t} - \text{Initial Cash Investment}$$

t = Cash Flow Period
i = Interest Rate Assumption

Source: (MY SMP, 2017).

The cash flow in a year comprises income minus total cost.

It is clear that many different business cases can be generated based on specifics of a project, the economies scale and the risk and capital requirements of the investing company.

For the scope of this project we zoom in on the cash flow and compare the order of magnitude of the CO_2 cost per ton of the input with the income stream from the product per ton at the output.

The CO_2 cost for the feed start with the capture at the source where it depends on the concentration of CO_2 in the (flue) gas. The additional CO_2 cost depends on the required purity and pressure.

These are controlled by the process and the fact if a CO_2 grid is used or not. In time the CO_2 price will drop and depend on the reached scale on the long term. Based on private communications, the following first order price estimations for the long term were assumed for large > 1 MT scale applications:

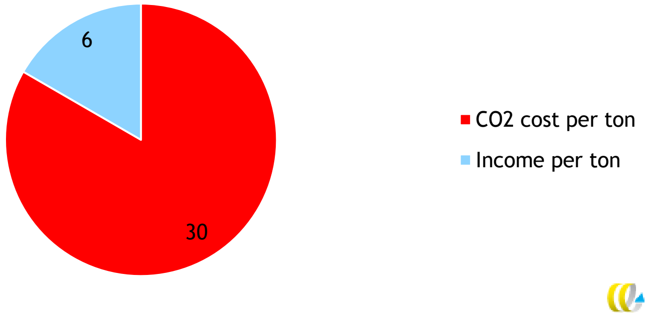
Table 3 **Estimated future bulk cost for supply of CO_2**

CO_2 cost type	Long term estimated CO_2 acceptance cost in €/ton
CO_2 for CCS, supercritical	30
CO_2 via grid, dried and purified	25
CO_2 from untreated flue gas	10

Now, to evaluate its contribution these CO_2 costs can be compared to the CCU income streams per ton. Of course the amount of CO_2 absorbed per ton of product can deviate per individual CCU-case and is not included here.

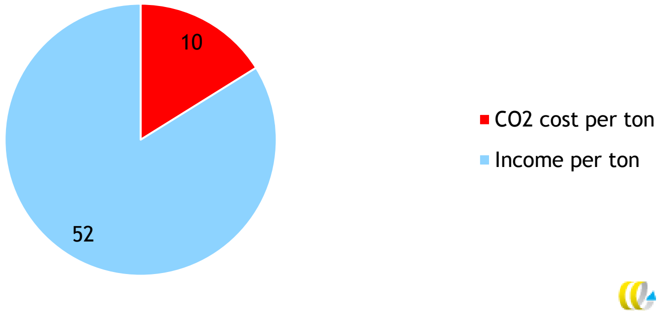
The following graphs indicate the contribution of the CO_2 cost per ton to the income of the product per ton in order to provide a first-order comparison. CAPEX and other OPEX are not included here:

Figure 8 **CO_2-cost contribution in CCS**



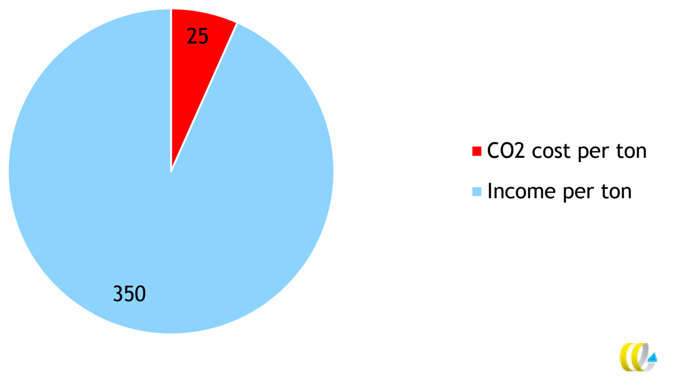
In the case of CCS there is cost for capture, purification and transport of super critical CO_2 and a small income from ETS (now € 6 per ton) resulting in the absence of a positive business case. In time the ETS-price may increase.

Figure 9 **CO_2-cost contribution in mineralisation**



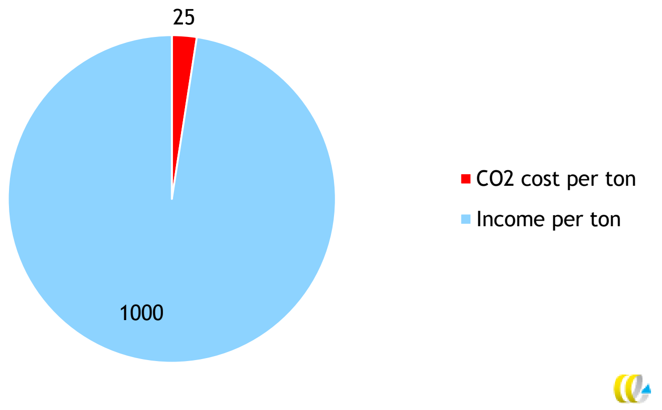
For CCU by mineralisation there is income from increased value of the cement product. And the CO_2 stream can be applied non-purified, saving cost.

Figure 10 **CO_2 cost contribution for methanol**



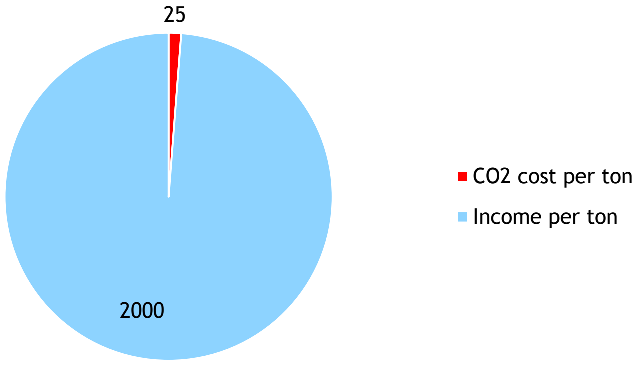
Methanol is a bulk product so currently it has a moderate market value. In comparison the cost of purified CO_2 is low. Other cost are more dominant here, like the cost of hydrogen.

Figure 11 **CO_2 cost contribution for formic acid**



Formic acid has a higher market value compared to the cost for the CO_2 (again other cost will be dominant like hydrogen and/or power costs).

Figure 12 CO_2 cost contribution for high value products



For CCU products with a higher added value like specialty chemicals and value polymers the cost of CO_2 is least relevant.

Conclusion: the cost of CO_2 does not seem to be a major factor in CCU.
The fact that the up-scaled CCU polyol project of Covestro is started with a subsidised CO_2 price of supposedly € 20/ton, indicates that there is already a business case at this price for these polyols which are used in polyurethane production. Furthermore customers like Ford openly advocate the use of CCU based polyurethane and may pay a premium.

4 CCU in the EU ETS

4.1 Present situation: CCU is excluded from use in the EU ETS

The MRV-guidelines from the EC currently do not (yet) recognize CCU as a carbon abatement technique. Only provisions have been made for CCS under article 49 ('Transport of carbon') of the MRV Guidelines (EC, 2012). These guidelines put two conditions to carbon flows to be eligible for recognized carbon transfers under the EU ETS:

1. The transfer should be a transfer to another EU ETS installation.
2. The transfer of pure CO_2 should only occur for the purposes of storage in a geological storage site pursuant to the Union's greenhouse gas emission allowance trading scheme, which is at present the only form of permanent storage of CO_2 accepted under the Union's greenhouse gas emission trading scheme.

Article 49 states explicitly that "For any other transfer of CO_2 out of the installation, no subtraction of CO_2 from the installation's emissions shall be allowed". This rules out the possibility of CCU under the present guidelines.

This is also exemplified by the use of ammonia in the EU ETS. In the fertilizer industry, natural gas is used to make ammonia from which ureum and nitrogen fertilizer is being made. In principle, CO_2 is being captured in the fertilizer and ureum, but this capture is short-lived and the CO_2 is released when the fertilizer is applied. The EU ETS Directive includes since 2013 also the emissions of CO_2 in downstream products, as well as the emissions due to the production of consumed steam.

However, the MRV-regulations also make clear that such may change in the future due to future innovations. The question whether CCU would qualify for such an innovation is at present not clear.

4.2 Present situation: treatment of cross-boundary flows

4.2.1 Introduction

The question if CCU is excluded because of its novelty, or that the regulators have aligned the CCU-treatment with other treatment of cross-sectoral flows, is to be answered here. We will thereby discuss the existing provisions for cross-sectoral flows of:

- cross-sectoral transfers of pure carbon for CCS;
- cross-sectoral transfers of waste gasses;
- cross-sectoral transfers of heat flows;
- treatment of biomass.

By doing this we will provide insight in the arguments why CCU may not have been included in the present-day EU ETS and the toolkit through which a future inclusion could be modelled.

4.2.2 Cross-sectoral flows of carbon

Cross-sectoral flows of carbon imply the transfer of pure carbon emissions from one sector to the other. Under the EU ETS a provision is made for cross-sectoral transfers of carbon emissions stored in a CCS-unit.
If the carbon is captured and transferred to another EU ETS installation with the explicit purpose of storing this carbon in a geological storage facility, the CO_2 emissions can be subtracted from the installation that captured the emissions. Under the MRV Guidelines, the captured emissions must be established using the same sources of information as the reporting requirements of emissions released to the air.

The EU ETS guidelines allow the transfer to a CO_2 transport network, as long as the purpose of this network is long-term geological storage.

4.2.3 Cross-sectoral flows of waste gasses

Waste gasses form another cross-sectoral transfer of flows in the EU ETS. The treatment of waste gasses is laid down in the Benchmarking Regulation (EC/278/2011). The interpretation of this law is exemplified in the so-called Guidance Document #8.

The Guidance Document #8 defines waste gasses as: gases which emerge from incomplete combustion or other chemical reaction in an EU ETS installation and which comply with all of the following criteria:

- waste gases are not emitted without further combustion due to a significant content of incompletely oxidised carbon;
- the calorific value of waste gases is high enough for the waste gas to burn without auxiliary fuel input, or to contribute significantly to the total energy input when mixed with fuels of higher calorific value;
- the waste gas is produced as by-product of a production process.

Waste gas issues are typically arising in the iron and steel industry where high-carbon blast furnace gas is used for electricity production. This is a cross-sectoral flow of gases and became relevant when electricity production fell under an auctioning regime while the iron and steel industry receives free allowances (up to the benchmark). Also in the chemical industry and refineries, waste gas issues may emerge.

The EU ETS regulation prescribes the routine how allocation of allowances occurs in these situations. There are two conditions that must be met:

1. These waste gasses are being used to produce electricity and/or heat.
2. These waste gasses have a carbon content higher than 97% of natural gas. Only emissions which are additional to the emissions that would occur if natural gas was used are taken into account.[1]

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[1] In calculating the additional emissions the ‘technically usable energy content’ should be considered. Compared to other fuels, most waste gases have a higher emission intensity and can therefore be used less efficient compared to other fuels. A correction therefore needs to be applied for the difference in efficiencies between the use of waste gas and the use of a reference fuel.

The EU ETS regulations assign additional ETS credits (compared to natural gas) to either the producer or consumer of these waste gasses:

- Emission allowances are being allocated to the producer of the waste gas, in case the waste gas is produced within the boundaries of a product benchmark. This is the case in the iron and steel industry.
  The idea is that the iron and steel industry will pass through (part) of the freely obtained allowances to the electricity producers to compensate for the higher carbon content.
- In case the waste gas occurs outside the boundaries of a product benchmark, the allowances are allocated to the consumer of the waste gas. Processes that do not fall under a product benchmark are subject to a heat benchmark. Waste gases in this area can occur in the chemical industry.

The EU ETS regulation has stated that “the ETS should set incentives for the efficient energy recovery from waste gases” and has thus made provisions to do this. Waste gas recovery is being stimulated by the fact that electricity production falls under an auctioning regime, while the additional carbon content of waste gases in the iron and steel industry are being compensated with free allowances.

4.2.4 Cross-sectoral transfers of heat flows

A similar mechanism occurs if heat flows are trespassing sectors in the EU ETS. In these cases, different allocation rules may emerge. In order to guarantee a level playing field, the ETS Directive has set rules to compensate for cross-sectoral heat flow issues. These are explained in more detail in Guidance Document #6 on the harmonized free allocation methodology for the EU ETS post 2012 Cross-Boundary Heat Flows Final.

Heat is eligible for free allocation up to the benchmark if two conditions are being met:

- the producing or consuming installation is covered by the EU ETS;
- the heat is not produced by electric boilers.

The following four situations may now occur.

1. Heat flow within one ETS installation. In this case the installation may choose whether he applies the product benchmark (e.g. paper) for the consumption of this heat, or the heat benchmark for the consumption of heat.
2. Heat flows between two ETS installations. As a general rule, free allocation up to the benchmark is given to the consumer of the heat who has to count this heat as a fuel input in its product benchmark.
3. Heat flows from an ETS installation to a non-ETS installation (or entity). In this case, the free allowances are given to the heat producer. However, non-ETS units are supposed to be non-carbon leakage. Therefore, the carbon leakage factor does not apply unless the heat exporter provides satisfactory evidence that it exports heat to a unit that is exposed to a significant risk of carbon leakage. It could, for example, be the case that the consumer is a non-ETS industry that falls under a NACE-4 classification that qualifies for free allowances under the EU ETS.
4. Heat flows from a non-ETS entity towards an ETS installation.
   The consumption of heat produced outside the EU ETS is not eligible for free allocation (since the producers do not fall under the EU ETS).

4.2.5 Treatment of biomass

Biomass currently is included in the EU ETS as a carbon abatement measure. The treatment of biomass is explained in the MRR Guidance Document #3. The EU ETS includes the same definition of biomass as in the Renewable Energy Directive (RED), as "'Biomass' means the biodegradable fraction of products, waste and residues from biological origin from agriculture (including vegetal and animal substances), forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste; it includes bioliquids and biofuels."

The EU ETS applies a zero-rating of emissions from biomass. In the MRR Guidance document, it states that this implies that within the EU ETS bioliquids and biofuels are only included if the sustainability criteria from the RED are being applied. For biomass and biogases no such criteria can be formulated and hence they are always counted with zero emissions.

The caloric value of the biomass can be important in order to determine the total emissions of an installation that partly uses biomass. In this case, the guidance document describes specifically which methods can be used to determine the relative carbon content of the biomass used. These can be used in the monitoring and reporting from the installations.

4.3 Future potential of inclusion of CCU in the EU ETS

4.3.1 General

Currently, it is expected that CCU will be included in the new ETS system similar to the position of CCS. Details of the conditions for such inclusions are not yet known and under discussion. The current EU ETS system only accepts CCS as a transfer, not yet as a carbon abatement technique, but negotiations are underway and CCU is expected to be added in the future ETS regulations. This is supported by the 2015 Energy Strategy (EC, 2015) that stated the EU seeks 'A forward-looking approach to carbon capture and storage (CCS) and carbon capture and use (CCU) for the power and industrial sectors, which will be critical to reaching the 2050 climate objectives in a cost-effective way. This will require an enabling policy framework, including a reform of the Emissions Trading System and the new Innovation Fund, to increase business and investor clarity, which is needed to further develop this technology'.

4.3.2 Outlook to level playing field of CCU with biomass

In the future more research needs to be devoted to the extent that reductions in carbon emissions through CCU can be included in the EU ETS. On the one hand there is a need for an accurate account of the CO_2 reductions that can be achieved through CCU taking into account the time that carbon is withdrawn from the atmosphere. On the other hand a level playing field with the input of biomass in the EU ETS is desirable. The extent to which this level playing field could be guaranteed falls outside the scope of the present study and should be addressed in further study. Such a study could include a comparison of the CO_2 emissions from biomass earlier in the cycle and the extent to which these emissions are already regulated by EU regulation and not. This could then be compared with the net reduction achieved through CCU.

4.3.3 Inclusion in the NER400 innovation fund

New installations that are covered by the scope of the ETS Directive, and installations that increase capacity, are eligible for additional free allocation from the New Entrants' Reserve (NER) in Phase 3 of the EU Emission Trading System.

5 Conclusions

In the Rotterdam HIC there are ample CO_2 point sources with concentrations ranging from almost pure to flue gas. To mitigate these emissions post combustion carbon capture can play a significant role on the short to mid-term, while it can be added in retrofit to current industrial processes.

CCS requires high-purity super critical CO_2, so with current ETS-prices the cost exceeds the ETS-price for CO_2. The reuse of CO_2 to products in CCU offers an alternative with a higher added value. Now ETS-prices become secondary, but in most cases energy and hydrogen prices need to drop and decarbonized require a premium for their products in order to obtain positive business cases. The current trend is that the cost of renewable power will indeed drop at a high rate. This also opens up possibilities for flex use when prices are low due to surpluses.

Some CCU-processes do not require high amounts of energy in the form of hydrogen or power and this brings positive business cases nearby. This is the case for mineralisation of CO_2 in fillers for concrete and paper and cement. And polyols for polyurethanes, which remain in an oxygen rich state.

Thus, for Rotterdam HIC the following CCU processes either appear to reach a positive business case on the short to mid-term or are of strategic value for Rotterdam HIC and are attractive for realisation of a pilot or demonstration:

Table 4 Attractive CCU projects for Rotterdam HIC

CCU process	Company type	Expected annual CO_2 uptake	CO_2 uptake
Algae	Algae cultivator for specialty products	Limited, depends on market for algae product	Short term
Polyols	Polyurethane base material manufacturer	120 kton	Mid term
Di-isocyanates	Polyurethane base material manufacturer	400 kton	Mid term
Mineralisation	Mineralisation developing companies (silicate, asbestos, metal slag based)	300 kton	Long term/eternal
Methanol	Petrochemical companies (admix, DME and MTG) Chemical companies, polymers and resins (MTO, formaldehyde)	40 Mton	Short term

For uptake of CCU in ETS there is a need for an accurate account of the CO_2 reductions that can be achieved through CCU taking into account the time that carbon is withdrawn from the atmosphere. A level playing field with the input of biomass in the EU ETS is desirable and should be addressed in further study.

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Annex A CCU technology factsheets

A.1 Microbiological methane synthesis

Microbiological methane synthesis from CO_2 and H_2 is a technology being developed by Krajete GmbH and by MicrobEnergy GmbH, a subsidiary of the Viessmann Group.

Together with Audi, the Viessmann Group has realized a pilot plant at Allendorf with a production capacity of 55 Nm^3 SNG/hr in 2016, utilizing CO_2 from a sewage sludge digestion plant (DENA, [2015]).
Methane or SNG is produced by reaction of CO_2 with H_2. The required H_2 is produced with a PEM electrolysis cell.
The process consumes H_2 in a kg ÷ kg ratio to CO_2 of 8 ÷ 44. H_2 utilization rate seems to be 98-99% and the produced SNG seems to contain only a few percent H_2.

Figure 13 **Pilot plant at Allendorf**

Possibilities for flexible operations

The technology is aimed at utilization of surplus renewable electricity from wind power and photovoltaic power and hence – if proven – allows for flex production.

Technical readiness level

The Allendorf is a first of a kind pilot installation, aimed at gaining experiences with the process and its dynamics, especially possibilities of following fluctuations on the power grid and associated fluctuations in H_2 production. On the other hand, the different have already been developed and tested, also in combination. Based on this, TRL is estimated at 6.

CO_2 purity specifications

The microorganisms also have a high tolerance for the impurities that are typically found in the types of gases that are used as feed gas for methanation. Such impurities include the sulphur and ammonia that come from the CO_2 source (i.e. biogas) and the oxygen that comes from the electrolysis process.

Economic aspects

This relies on the type of products to be selected. Specialty products with high added value are usually more profitable.

Drivers and bottlenecks, possibilities for integration in the Rotterdam petrochemical industry

This process is mainly aimed at storage of surplus renewable power as methane/SNG in the existing natural gas transportation and distribution pipeline system. There is no obvious relation with the petrochemical industry in the Port of Rotterdam.

A.2 Steelanol, production of ethanol and from CO_2 and CO

Description

In this process developed by Lanzatech from New Zealand H_2 and CO/CO_2 containing raw blast furnace gas is fed to a 'once-through' fermentation reactor in which H_2 and CO/CO_2 are converted by the microorganisms - acetogens, as present at subsea hydrothermal vents (black smokers) -into ethanol or other organic oxo-chemicals (e.g. 2,3 butanediol).

The product is isolated from the fluid in the fermentation reactor – in case of ethanol by way of distillation. Waste water from distillation can be cleaned with conventional technologies. Gas utilization efficiency is stated to exceed 90%, a presentation about the Ghent initiative mentions an energy efficiency of 70%.

Required additional raw materials

For ethanol production, H_2 is required in kg ÷ kg ratio of 88 ÷ 12.

Possibilities for flexible operations

No information can be found indicating possibilities for flex operations.

Technical readiness level

The process has been demonstrated with pilot plants with a production capacity of several hundreds of tonnes per year. The technology has been proven at TRL 5.

A commercial scale demonstration unit with production capacity of up to 30 ktonnes/a is being constructed at ArcelorMittal's integrated steel mill in Ghent, Flanders. If this project succeeds, the TRL is estimated as being 7 or 8 and further implementation at other ArcelorMittal sites will begin immediately.

In theory a wide variety of other chemicals can be produced with the acetogens bacteria, including various isomers of butanol and butanediol and including aceton and lactic acid. Practical experiences for these alternative products seem limited.

CO_2 purity specifications

As far as can be deducted from publicly available sources, there are no or specification requirements for the composition of and levels of pollutants in the CO_2 containing gas.
At ArcelorMittal Ghent filtered and scrubbed blast furnace gas and other product gases from coke and steel making are redirected to the fermentor. In a 2015 presentation following statement is given, indicating pollutants present in the gases:

> *Additional technology advantages include a local* SO_x*/*NO_x *reduction, total removal of BTEX and decreased dust emissions from the steelmaking source.*

In other words, the process also acts as gas cleaning equipment.

Economic aspects

According to data referring to an initiative in Taiwan, a 100 ktonnes/a production plant requires a M€45 investment (LanzaTech, 2014). In contrast, the Steelanol website mentions a M€ 87 investment required for the 47 ktonnes/a project in Ghent (Phases 1 & 2) (Steelanol, 2017).

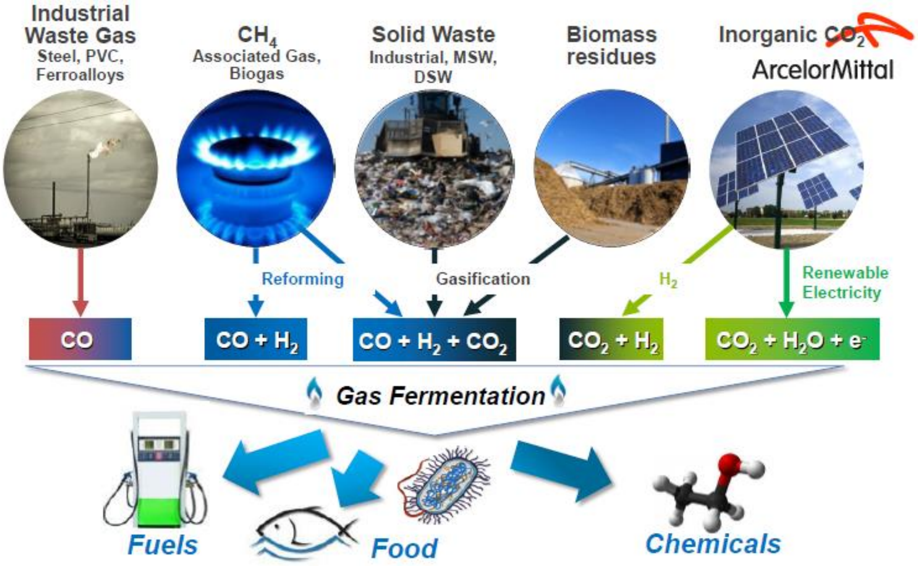
Drivers and bottlenecks, possibilities for integration in the Rotterdam petrochemical industry

Lanzatech's ambition seems to be focused primarily at production of transportation fuels, either ethanol or alternatives for Jet A. On the website production of butadiene from 2,3 butanediol is also mentioned.

As far as can be deducted, these products provide no drop in chemical product for existing petrochemical plants, as there seem to be no industrial consumers in the port area that utilize these chemicals as a raw material.

As an alternative approach, produced ethanol could be dehydrated with commercially available catalytic processes and the produced ethylene could be utilized as a raw material for e.g. Lyondell.

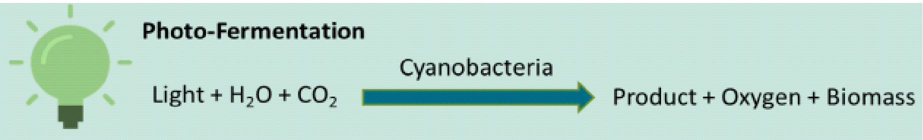
Figure 14 H_2 and CO/CO_2 to ethanol process routes



A.3 Microbiological process

Description

In Photanol’s microbiological process CO_2 is converted by cyano bacteria into organic alcohols and acids in a reaction with water, with oxygen and biomass as a by-product.

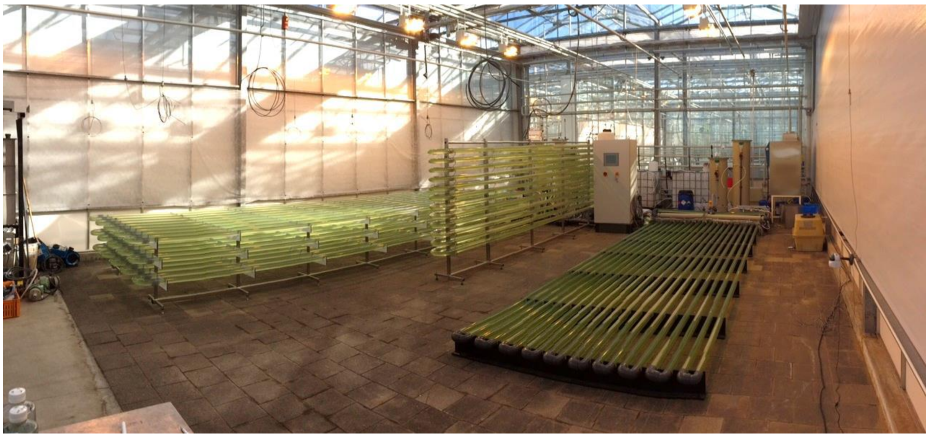


Current efforts in development are focussing on lactic acid. In cooperation with AkzoNobel several other strains of bacteria are being developed. These strains will produce acetic acid, butanol and a ‘compound X’ (market size > $ 1 billion/a) (RVO, 2013). In addition development of strains for production of flavours and fragrances are being developed (Hamacher, 2014). Other substances that could be produced include terpenes and polyols.

Technical development level

Photanol has several operational pilot plants with reactor volumes of 0,2-1,0 m^3.

Figure 15 **Closed tubular pilot reactors**



Intended next step is realisation of a 173 m^3 pilot-unit with a surface area of 0.5 ha. This installation would be able to produce approximately 20 tonnes of lactic acid annually, with an additional 8 tonnes/a of biomass as a by-product. Production capacity would be comparable with approximately 0.02% of that of a commercial scale installation. Based on this percentage, current TRL level has been estimated as 4. See also the outlook of the TRL in Figure 16.

Figure 16 TRL outlook of Photanol process

CO_2 purity specifications

No information is currently available.

Economic aspects

No information is currently available.

Drivers and bottlenecks, possibilities for integration in the Rotterdam petrochemical industry

Could in theory produce drop in raw materials for existing production processes in the Port of Rotterdam petrochemical industry, e.g. polyols. Could also produce raw materials for new industries, in particular lactic acid.

A bottleneck is the Energy intensity of light irradiation in The Netherlands. Light for the cyanobacteria might be supplied with LED lighting, but this will give increased investments and increased operational costs. It seems more logical to implement this technology in tropical regions or desert regions, where light intensity is far higher and for free.

A.4 Thermochemical methanol production

In this route CO_2 is hydrogenated with separately produced hydrogen. The process yields methanol and water, but also yields CO as a by-product by way of a side reaction - the reverse water-gas-shift reaction.

$CO_2 + 3H_2 \rightarrow CH3OH + H_2O$
$CO_2 + H_2 \rightarrow CO + H_2O$

Other hydrogenated products, such as higher alcohols and hydrocarbons, are also produced (in small amounts) in this process.

The CO_2 hydrogenation reaction is often carried out at 5.0-10.0 MPa and 473-523 K. Since CO_2 is not very reactive, considerably high reaction temperatures are necessary for acceptable CO_2 conversion rates. The heat of the exothermic CO_2 hydrogenation reaction is partially used to heat feed streams.

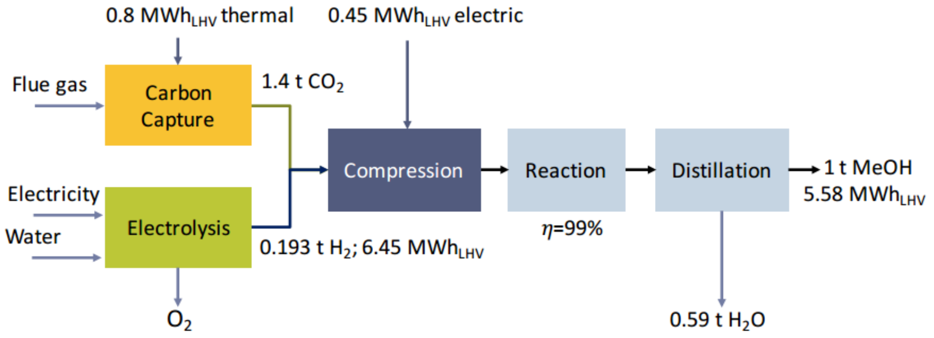
The produced methanol is separated from water in a distillation column, which is operated at ambient pressure. Unreacted H_2 and CO_2 together with formed CO are partly recycled in order to push selectivity towards methanol formation.
Gaseous purge streams can be combusted in a furnace or gas turbine for e.g. steam production which can be sold as by-product or used in an upstream carbon capture unit.

The reverse water-gas shift reaction is undesirable as the associated hydrogen consumption results in decreased yield for methanol. However, currently, a catalyst which is sufficiently selective from an industrialist point of view is not yet available. The large amount of water produced by both reactions has certain inhibitory effect on the catalyst, leading to its deactivation eventually.

Required additional raw materials

The ratios of weight between raw materials and desired products are illustrated in Figure 17.

Figure 17 **Weight ratios of raw materials and desired products**



Possibilities for flexible operations

According to system evaluations found in publicly available sources, the process can operate at 50-100% capacity and has a very high ramp rate, allowing for following load levels on the grid.

Technical readiness level

A demonstration installation with a 4,000 tonnes/a production capacity of 'Vulcanol' has been realized by Carbon Recycling International and has been operational since 2012. CRI aims at a commercial scale of 35–40 ktonnes/a. Based on this information TRL level is estimated at 7-8. A second technology provider is Japanese company Mitsui Chemicals Inc., but this technology seems less evolved.

CO_2 purity specifications

According to one publicly available source, in case of methanol production, the sulphur content of the CO_2 feedstock is limited to 0.1 ppmv.

Economic aspects

The CRI industrial plant realized in 2011 (1.3 ktonnes/a MeOH) required an investment of $ 8 million.

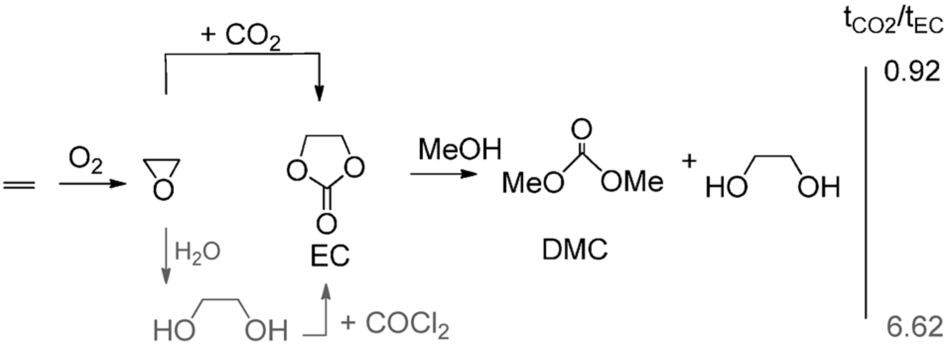
Figure 18 Thermochemical methanol plant

A.5 Thermochemical production of cyclic carbonates from CO_2 and epoxide

Description

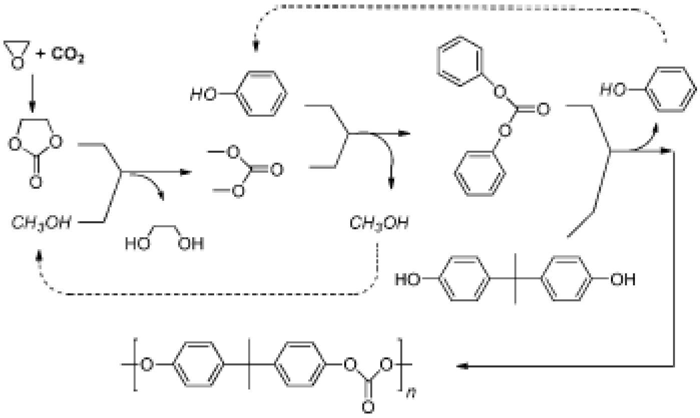
Carbonates are becoming industrially viable alternatives to toxic phosgene $COCl_2$.

For example, carbonation of the ethylene oxide as opposed to phosgenation of ethylene glycol for ethylene carbonate (EC) synthesis is both a less toxic route and reduces CO_2 emissions seven-fold (0.92 t per ton vs. 6.62 t per ton). The resulting EC is a marketable product by itself, used as organic solvent in pharmaceutical and cosmetic preparations and as electrolyte in lithium-ion batteries. The transesterification of the resulting cyclic carbonate with methanol to dimethyl carbonate (DMC) is a relevant route to produce DMC and dry ethylene glycol. Current DMC production is about 0.5 Mt/year.



The Japanese firm Asahi Kasei has taken the process further and has developed a production process for polycarbonates. In this process, a glycol (e.g., a monoethylene glycol if the starting epoxide is ethylene oxide) and bisphenol-A (BPA) polycarbonate are produced in high yields from three starting materials (the epoxide, bisphenol-A, and CO_2), the intermediary phenol being recycled Asahi Kasei's process is still unable to make polycarbonate chains that are long enough for applications such as water bottles. But it is cost-competitive with the standard method.

The Asahi Kasei process avoids consumption of large amounts of water and CH_2Cl_2, the production of large quantities of waste and contamination of final product with Cl-containing impurities.



Possibilities for flexible operations

No information can be found indicating possibilities for flex operations.

Technical readiness level

The technology has been implemented commercially, with plants being operated by

- Chimei Asai plant in Taiwan (150 kt since 2007);
- Cheil Industries and Honam Petrochemical in Yeosu, Korea (two plants:of 65 kt/a each);
- Kazan Orgsintez, Russia (65 kt/a);
- Saudi Kayan Petrochemical Co, in Jubail, Saudi Arabia (260 kt/a).

Drivers and bottlenecks, possibilities for integration in the Rotterdam petrochemical industry

As stated in the first subparagraph, this technology offers several environmental, cost and performance benefits compared with conventional polycarbonate production. Partially driven by this new environmentally friendly process, the total market for polycarbonates has grown to 3 Mt/year. The route to polycarbonates could also increase the share of this specialty turned-commodity polymer in the engineering plastics market, with an expected market growth of 35%. The low cost of CO_2 as starting material and the avoidance of toxic phosgene partly explains the successful industrialization.

A.6 CO_2 into linear polycarbonates technologies

Description

The company Novomer has developed a catalyst for production of polypropylene and polyethylene carbonates from epoxides and CO_2. The chemicals and materials contain up to 50% carbondioxide.

The technology has been demonstrated at a demonstration plant in Houston, with a production of 3,000–4,000 tonnes of polyols per year (Lim, 2015), using CO_2 from an ethanol fermentation plant. Polypropylene carbonate Novomer Binder has been utilized commercially by Jowat AG polyurethane hot melt adhesive applications (Novomer, 2014). Early November 2016 Saudi Aramco has acquired the Converge® product line and associated operations and technologies for further commercialisation Saudi Aramco is planning for full-scale production facilities in Saudi Arabia to support the manufacture of specialty and intermediate chemical products to supply a wide variety of industries when requiring a binder that decomposes rapidly and cleanly. Beside potential cost reductions, these coating resins are said to perform well environmentally and technically.

A.7 Polyols

Ford expects to be the first automaker to use foams and plastics containing captured CO_2 in seating and hood applications. The new materials are expected to be in Ford vehicles by 2018.

Converge® polyols are designed to replace conventional petroleum-based polyether, polyester, and polycarbonate polyols. They are based on the o-polymerization of carbon dioxide (CO_2) and epoxides and the resulting products contain more than 40% by weight CO_2. The use of waste CO_2 as a significant raw material yields a product with an extremely low carbon footprint. In addition, since waste CO_2 is significantly lower in cost than conventional petroleum-based raw materials, Converge® polyol manufacturing costs are favourable compared to conventional polyols when produced at full commercial scale. In terms of performance, Novomer's Converge® polyols have a unique polycarbonate backbone which increases the strength and durability of polyurethane products. Incorporating these new polyols into existing formulations yields foams with higher tensile and tear strength, and increased load bearing capacity; adhesives and coatings with improved adhesion, cohesive strength, and weather ability; and elastomers with greater tensile and flexural strength.

A.8 Thermochemical production of methane

This route is based on the complete hydrogenation of CO_2 to methane is the Sabatier reaction:

$CO_2 + 4H_2 \leftarrow\rightarrow CH4 + H_2O$

In terms of hydrogen consumption, and hence overall energetics, CO_2 reduction to methanol rather than to methane might appear favourable given the better ratio by energy value of the product relative to the starting H_2.

A pilot plant has been realized by Etogas in Werle, Germany.

A similar, but significantly smaller pilot has been realized in Rozenburg by Stedin (Stedin, 2014).

A.9 Mineralisation by production of Green Mineral™ ($MgCO_3$)

Description

CO_2 can be captured by reaction with mineral material to $MgCO_3$. This reaction can be accelerated by fine milling of olivine material and apply pressure and temperature while contacting it with the CO_2. The resulting carbonate is called Green Mineral™. The production process for Green Mineral™ is under development at Green Minerals, previously Innovation Concepts.

During production of Green Mineral™ CO_2 379 kg CO_2 is captured per ton mineral CO_2, including CO_2 from the energy consumption during the production process (Green Mineral, 2016). The production process results in residual heat, which can replace heat consumption in another process.
Based on the assumptions below, this results in a net CO_2 footprint of 0,30 to 0,37 ton CO_2/ton mineral CO_2.

- Per ton captured CO_2 2,6 GJ of heat is released, which is recovered at 75% efficiency for use elsewhere. In the CO_2 footprint, the heat recovery is assumed to replace heat from a gas fired burner[2].
- For mining and shipping of olivine from Norway to the production location and for milling of olivine to the proper particle size, the calculated CO_2 emission per ton mineral CO_2 amounts to 33 to 39 kg (Green Mineral, 2016).
- For capture, purification and concentration of CO_2 required for use in the carbonation an additional CO_2 emission of 53 to de 226 kg per ton of concentrated CO_2.

Level of technical development

Pilot scale testing has delivered a proof of concept of the production of the mineral CO_2, thus TRL 4 was reached. Further upscaling and optimisation of the product use are in a preparation phase (Knops, 2017):

- a collaboration with Heidelberg Cement by order of the German government on the use in concrete as CO_2 capture agent will start 1-4-2017, with a duration of three years;
- the development program on the application in the paper industry as a replacement of precipitated calcium carbonate (PCC) is yet to start;

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[2] Gas fired heat is fossil heat with the lowest CO_2 footprint, so herewith the effect of replacement of fossil powered heat has been calculated most conservatively.

– the material was demonstrated for use in 3D-printers in combination with PLA to replace conventional fossil polymers by the Centre of Expertise Chemelot Innovation and Learning Labs (Chill), more info on chillabs.com.

Footprint

This is limited: the unit is planned to be built underground, while this is an economic and safe way to realise high pressures. In this way a site area of 200 m^2 including office and staff parking will suffice.

CO_2 purity requirements

The process is based on wet mineralisation. This limits the requirements to the concentrating the flue gas to only 60% CO_2 instead of almost 100%.
The presence of NO_x and SO_x is allowed and no problem.

Economic aspects

The cost estimate for Green Minerals™ production amounts to 46-59 €/ton Green Mineral which relates to 121 to 156 €/ton captured CO_2. Thus a positive business case should be based on the replacement value of the material replacing another material with a similar market price. And/or a significantly higher ETS CO_2 price. After completion of the development phase the CO_2 capture potential using this route amounts to 300-450 kton CO_2 per annum.

A.10 Mineralisation during the production of Carbstone™ (concrete alternative material)

Description

Carbstone™ is a material that resembles concrete which is formed by carbonation of mineral oxides in steel slags (mainly calcium oxides and magnesium oxides). Duet to the fact that the carbonation reaction determines the rate of solidification, the product can be put under mechanical load soon after being applied.

This means that twofold CO_2 emission reduction is obtained:
1. It reduces the production of Portland clinker cement which produces a lot of CO_2 per ton cement produced due to decarbonation of marl).
2. The formation of Carbstone™ occurs by the carbonation reaction of the metal oxides, which are present in the steel slag. This means that CO_2 is captured from air by reaction with the metal oxides to metal carbonates, like calcium carbonate and magnesium carbonate.

Residual streams containing calcium currently in use by Carbstone™ comprise steel slags. In The Netherlands steel slags (‘LD-slakken’) of Tata Steel are made available in IJmuiden. These steel slags are currently in use in road and water works.

When used for the production of Carbstone™ these steel slags are first ground, sieved and valuable minerals are removed. Successively the ground and cleaned slag is mixed with water and pressed in the desired shape. For the specific composition of these slags about 2 tons of slag per m^3 Carbstone™ is required (Vito, 2016). The produced shape is carbonated in an oven at a temperature between 80 C and 140°C. In this process up to 300 kg CO_2 per m^3 Carbstone™ concrete is captured (Vito, 2014).

Level of technical development

The concrete produced can be applied in non-structural concrete products like tiles, construction bricks and non-supporting interior walls in housing and utility construction sector. This application is probably at TRL level 8, which is supported by the announcement of the Dutch company Ruwbouwgroep from Harderwijk end of 2016 that they started commercial production for application in non-supporting walls in the housing and utility construction sector (Cobouw, 2016). For admission in other applications as concrete longer trajectories of admission are required. The issue of how much chloride from steel slags remains bound to the salts in the concrete during recycling is subject to further study. This is also the case for the possible accumulation of chloride in the material chain.

Footprint

Similar to the footprint of regular production of non-supporting concrete products.

CO_2 purity requirements

Currently, industrial food grade CO_2 quality is used but according to research organisation VITO this is not a requirement and CO_2 concentrated flue gas would also be applicable.

Economic aspects

While the current demand for the specific types of steel slags is low and thus their market prices, this process competes well with other methods of production.

A.11 Mineralisation by Solidia alternative cement application

Description

Solidia™ cement is an alternative binder for concrete, which solidifies by a reaction with CO_2. Thus, application of Solidia™ cement captures CO_2.
The concrete formed, does no longer require regular cement. Because the solidification process is determined by the carbonation reaction, a similar strength as in regular concrete products is now already reached within 24 hours instead of 28 days (Solidia, 2013). This under the condition that carbonation takes place at temperatures between 40°C and 60˚C.
Lower temperatures result in longer times of solidification.

Solidia Technologies has developed an alternative cement based on Wollastonite ($CaSiO_3$), a calcium silicate. The Solidia™ cement can be produced in the same factories as the current Portland cement. The Solidia™ cement results in concrete using the same ingredients as in Portland cement, only difference is in the curing reaction being a carbonation reaction with CO_2. This reaction is as follows:

$$CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2$$

During the carbonation CO_2 is captured in the concrete. Using this process up to 300 kg of CO_2 can be captured per ton of Solidia™ cement (International Cement Review, 2015). This means that this technology leads in two ways to CO_2 emission reduction:

1. It reduces the production of Portland clinker cement which is related to a high degree of CO_2 emissions per ton of cement produced (due to decarbonation of the marl).

2. During formation of concrete by the reaction of Solidia™-cement with atmospheric CO_2 which is captures by carbonation.

Research funded by the US Environmental Protection Agency has shown that fly ashes can replace 20% of Solidia cement in concrete and in steel slags up to 40% of the Solidia™ cement in concrete (EPA, 2013). Thus, there is no reason why Solidia™ cement could not 1-on-1 replace Portland clinker in blast furnace slag based cement.

Solidia also successful tested concrete mortar based on Solidia cement, by contacting the mortar under a tent containing CO_2. Corrosion tests were executed at the University of Florida. Reinforcement materials of steel, stainless steel, coated steel and galvanised steel were tested in Solidia cement-based concrete under different conditions. Conventional steel did show more corrosion in some tests, but the protected steel samples all showed similar corrosion behaviour in the concrete as reinforcements in Portland clinker cement based concrete (Ramirez, 2015).

However, due to the safety regulations in place, concrete materials based on Solidia production process can in The Netherlands before 2020 only be applied in non-structural concrete products like tiles and construction bricks. Admission in other concrete material applications takes longer time.

Level of technical development

Solidia cement is currently produced on industrial scale producing clinker production campaigns both in the US as in Europe. In the US production took place near the Lafarge-Holcim plant in Whitehall, PA. Here more than 5,000 tons of Solidia cement was produced in 7 days time. In Europe, more than 6,000 tons of Solidia cement was produced at the Lafarge-Holcim plant in Pecs, in Hungary, also in a period of 7 days. Thus, the production of this cement is proven in a full scale commercial production process (TRL 9).

In the US a commercial manufacturer produces 10% of concrete production capacity (40 ton per day) based on Solidia cement, which is produced in the test run at Lafarge-Holcim plant in Whitehall. This means that the cement is applied on commercial scale in the US (TRL 9). Solidia is expected to also start in 2016 with commercial implementation in concrete in Europa. For this, the Solidia cement produced in the production run in Pecs will be used for that purpose.

Footprint

Similar to the footprint of conventional non-constructive concrete products.

CO_2 purity requirements

Currently industrial food grade CO_2 is applied, but according to Nick de Cristofaro, technical director of Solidia, this is not strictly required and a lesser quality CO_2 would also be acceptable.

Economic aspects

The production of Solidia cement is less costly than the production of conventional cement. So, no reason exists not to use Solidia cement in The Netherlands for non-construction concrete products. This is market with a turnover of 2.856 million m^3 concrete in 2010. If this amount of concrete would have been produced based on Solidia cement instead of conventional Portland cement 276-304 kilotons of CO_2 emissions would have been prevented (CE Delft, 2016b).

A.12 CCU technologies with a low TRL

The technologies with TRL < 5 include:

- direct production of formic acid from CO_2 (and H_2);
- reduction of CO_2 into CO;
- acrylic acid production;
- carbamate and isocyanates for polyurethane synthesis.

Formic acid production is still in the infancy phase. A recent Dutch TKI subsidy was granted to a consortium for developing direct electrochemical CO_2 conversion into formic acid up to the level of demonstrating components and realizing a pilot scale continuous operational plant.

CO_2 reduction with H_2 to CO can currently only be realised at high temperatures but the available catalysts are not yet selective enough to allow this conversion to be efficiently.

Annex B Definition

B.1 Definition of TRL

TRL 1 Basic Principles Observed
TRL 2 Application Formulated
TRL 3 Analytical, ‘Proof of Concept’
TRL 4 Laboratory Component Testing
TRL 5 Component Prototype Development
TRL 6 Component Prototype Demonstration (0,1-5% of full scale)
TRL 7 Pilot Plant (>5% commercial scale)
TRL 8 Sub-Scale Commercial Demonstration Plant (>25% commercial scale)
TRL 9 Full-Scale Commercial Deployment

Figure 19 Definitions of TRL levels

	Technology Readiness Level Definition
TRL 1	**Basic Research:** Initial scientific research has been conducted. Principles are qualitatively postulated and observed. Focus is on new discovery rather than applications.
TRL 2	**Applied Research:** Initial practical applications are identified. Potential of material or process to solve a problem, satisfy a need, or find application is confirmed.
TRL 3	**Critical Function or Proof of Concept Established:** Applied research advances and early stage development begins. Studies and laboratory measurements validate analytical predictions of separate elements of the technology.
TRL 4	**Lab Testing/Validation of Alpha Prototype Component/Process:** Design, development and lab testing of components/processes. Results provide evidence that performance targets may be attainable based on projected or modeled systems.
TRL 5	**Laboratory Testing of Integrated/Semi-Integrated System:** System Component and/or process validation is achieved in a relevant environment.
TRL 6	**Prototype System Verified:** System/process prototype demonstration in an operational environment (beta prototype system level).
TRL 7	**Integrated Pilot System Demonstrated:** System/process prototype demonstration in an operational environment (integrated pilot system level).
TRL 8	**System Incorporated in Commercial Design:** Actual system/process completed and qualified through test and demonstration (pre-commercial demonstration).
TRL 9	**System Proven and Ready for Full Commercial Deployment:** Actual system proven through successful operations in operating environment, and ready for full commercial deployment.