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Carbon Capture and Utilisation Workshop

Background and proceedings

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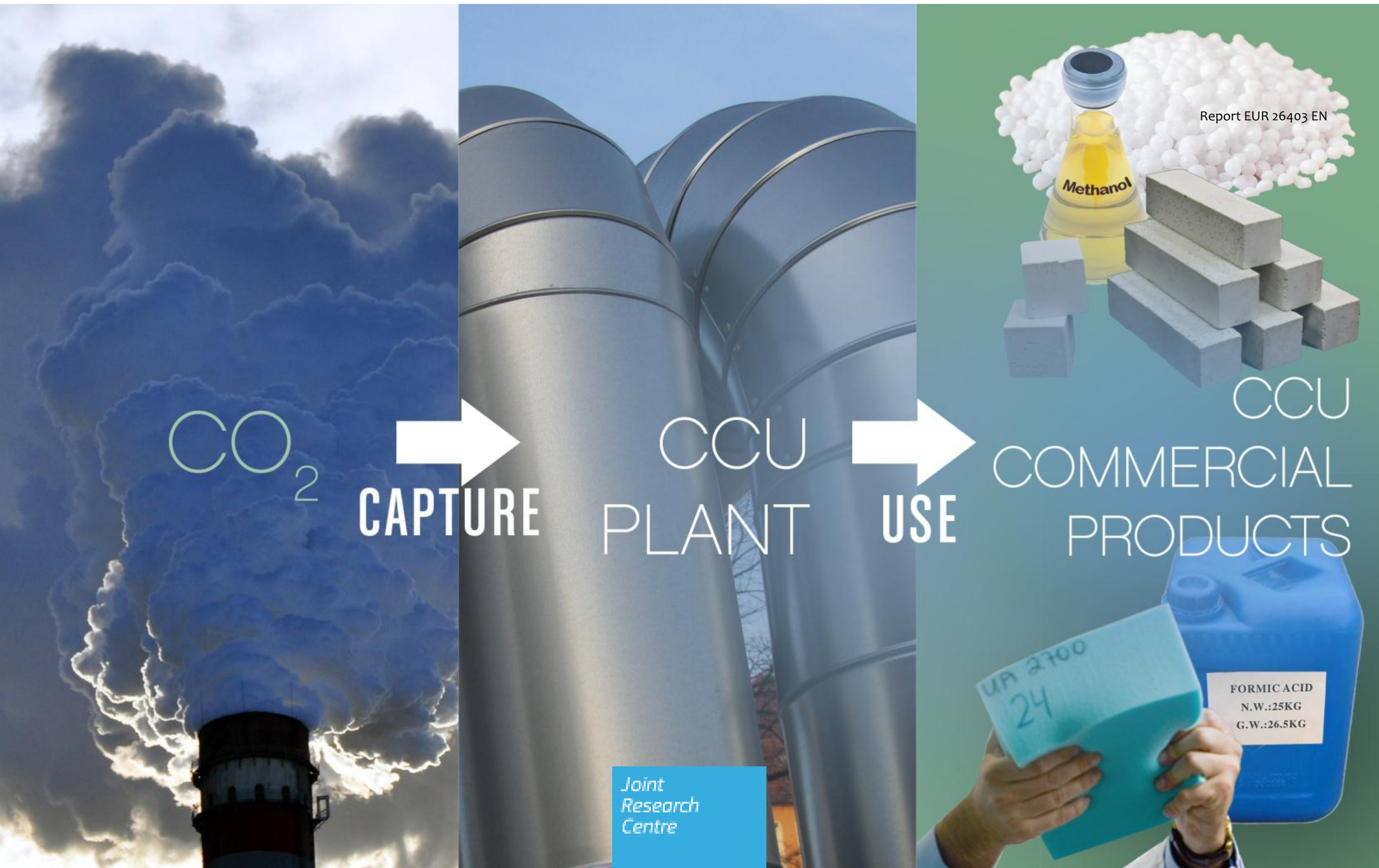

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Outline

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DISCLAIMER

Part II of this report (i.e. the proceedings of the workshop) does not represent the views of the European Commission, but only those of the authors of these presentations.

Introduction

The European Union announced in July 2009 the objective to reduce the greenhouse gas emissions (GHG) by at least 80% below the 1990 levels by 2050. In October 2009 the European Council set the European economy on the path to reach this decarbonisation objective. The European energy policy has a pivotal role for achieving this goal ("An energy policy for Europe" [COM(2007) 1]). To this end, the EU is pursuing the development and deployment of a portfolio of low carbon energy technologies which can decarbonise the European economy: renewable energy systems (RES), energy efficiency and carbon capture and storage (CCS). The CCS is of particular importance since fossil fuels will remain a key fuel for the European economy in the short to medium term. The EU Roadmap 2050, based on a large number of different decarbonisation scenarios, provided effective cost-efficient pathways of reducing GHG emissions for different economic sectors depending on their technological and economic potential. Among these sectors, the power sector has the biggest potential for cutting emissions whereas the CCS could play a decisive role. In 2008 the European Union adopted the European Strategic Energy Technology Plan (SET-Plan), which aims at the accelerated development and deployment of the low carbon energy technologies. Other measures that can catalyse the development and deployment of CCS include the Directive 2009/31/EC (CCS Directive) and EU Emissions Trading System (EU-ETS). In this context, more efficient energy use or fostering novel energy sources with partial transformation of EU energy system from fossil fuels to renewable sources is considered of high priority. However, simply mitigating CO2 emission is not enough and therefore active measures such as storing the CO2 in geological formation (CCS) or CO2 utilisation (CCU) can play a major role to the future sustainable energy supply or the production of a wide range of carbon derived products.

The utilisation of CO2 as working fluid or as feedstock in chemical processes and in biotechnological applications has the potential to be a very efficient pathway for reducing the CO2 emissions when merged with the development of innovative and potentially feasible technologies that are less energy intensive and are associated with reduced materials consumption and the capacity of temporary or permanent storage of CO2 (other than geological storage).

The forthcoming EU Framework Programme for Research and Innovation (Horizon 2020) supports the development of technologies for the large-scale re-use of captured CO2 in order to achieve reduction of GHG and foster innovation. Hence, there is the need for detailed information about the CO2 utilisation options that have the potential to yield a significant, net reduction of CO2 emissions in volumes sufficient to make a meaningful contribution to EU climate objectives. The assessment of the impact that different CO2 utilisation options on the European energy system as well as the development of a sustainable market for their products is however needed, taking into account energy balance, cost-effectiveness, CO2 budget and hydrogen availability (where applicable).

The Joint Research Centre of the European Commission (Institute for Energy and Transport) and the Directorate General for Climate Action co-hosted a workshop on CO2 re-use technologies in Brussels on the 7th June 2013. The aim of the workshop was to present how the most promising pathways for CO2 re-use are related to climate and energy technology policies, facilitate a dialogue between stakeholders (industry, academia and policy makers) and address the challenges for a possible large scale roll-out of CO2 re-use technologies. A number of six presentations from experts focused on the state-of-the art of the technology, the needs of the sector for large scale deployment and the impact of the CO2 re-use products on the market. In particular, the workshop focused on three promising pathways, i.e. methanol production, mineralisation and polymer production.

I. Overview of CCU technologies

I.1. Literature overview

The Directorate Generale Joint Research Centre (DG JRC) of the European Commission performed in the first half of the 2013 a literature overview of the most important scientific papers, reports and other publications that investigate existing and emerging Carbon Capture and Utilisation (CCU) technologies. In addition, the DG JRC also reviewed the technology readiness levels of the CO2 utilisations options. As a result, the five most promising European CCU technologies were shortlisted and three of them were chosen to be the focus of the CO2 re-use workshop.

The Global CCS Institute and Parsons&Brinckerhoff published an extensive report on the industrial use of captured CO2 (GCCSI and PB, 2011). The report assessed the CO2 utilisation technologies, presenting the economic and commercial key findings, while making a number of recommendations about their development and deployment. The key conclusions of this report are summarised as follows: a) CO2 utilisation uptake potential could represent only few percent of the anthropogenic emissions (low abatement) but has the near term potential to produce revenues coupled with favourable CCS projects; b) most of the emerging re-use technologies were (i.e. 2011) in the research and development phase, years from commercial deployment but they may provide feasible complementary support to CO2 geological storage or other abatement methods (e.g. CO2 mineralisation, CO2-to-fuel); c) CO2 utilisation can play a major role in large scale CCS projects in developing economies, releasing some of the pressure on the energy costs and abatement; carbonate mineralisation, CO2 concrete curing, formic acid production, polymer production, urea yield boosting and renewable methanol could fill in the gaps once they passed the R&D phase; d) the CO2 market price which was €10-14/tonne (i.e. 2011) and currently traded at €4.5/ton (i.e. December 2013) gives indicative expectations about the future market value and the revenues generated; CCS in power, steel and cement plants are not going to be driven by the low projected CO2 price, and alternative specific funding is necessary; but, natural gas processing and fertilizer production are going to benefit; e) CO2 utilisation could play the role of facilitator of CCS demonstration projects in the absence of a strong carbon price; however, it becomes less important as and when the cost of emitting carbon rises due to enforced (by mitigation targets) widespread-commercial deployment of CCS.

The CO2 utilisation technologies family has the potential to reduce CO2 emissions by at least 3.7 gigatonnes per year (Gt/y), which is equal to about 10% of the world's current annual emissions (DNV, 2011). Another feature of CCU is that it can result in value-added products that create jobs and economic benefits, and help offset the cost of implementing CCS technologies.

Figure 1 shows the main CO2 utilisation options as classified by US D0E. After switching from CCS to CCUS (adding the Utilisation to the "green economy") adopting the same terminology like the US DoE, the Carbon Sequestration Leadership Forum (CSLF) has created a special CO2 Utilisation Options Task Force. In their Phase 1 Report (2012) the technologies are classified into three main categories: resource recovery (e.g. Enhanced Oil and Gas Recovery, Enhanced Coal-Bed Methane Recovery), non-consumptive uses (see below), and consumptive uses (see below). In order to have a meaningful impact and become a feasible solution the CO2 use process should use large quantities of CO2 or result in a large net-benefit (preferably both).

Further, the non-consumptive CO2-use applications are considered by CSLF to have an indirect-CO2 reduction benefit in the form of production of fresh water or valuable minerals, higher efficiency, or the displacement of fossil fuels. Seven non-consumptive uses are included in the CSLF report: desalination, beneficiation, slurry transport, heat transfer fluid, freight pipelines, solvent extraction, and the conversion of CO2 to fuels and chemicals. Of these, 'closed-loop' re-use applications where CO2 is used to produce minerals, or higher process efficiency may have limited potential demand for CO2. Income from the sale of fresh water may offset some of the cost of CO2 capture. The use of CO2 as supercritical working fluid is a commercial-scale process. The rest of the non-consumptive, 'closed-loop' re-use applications are relatively less-technologically mature, and require research and development.

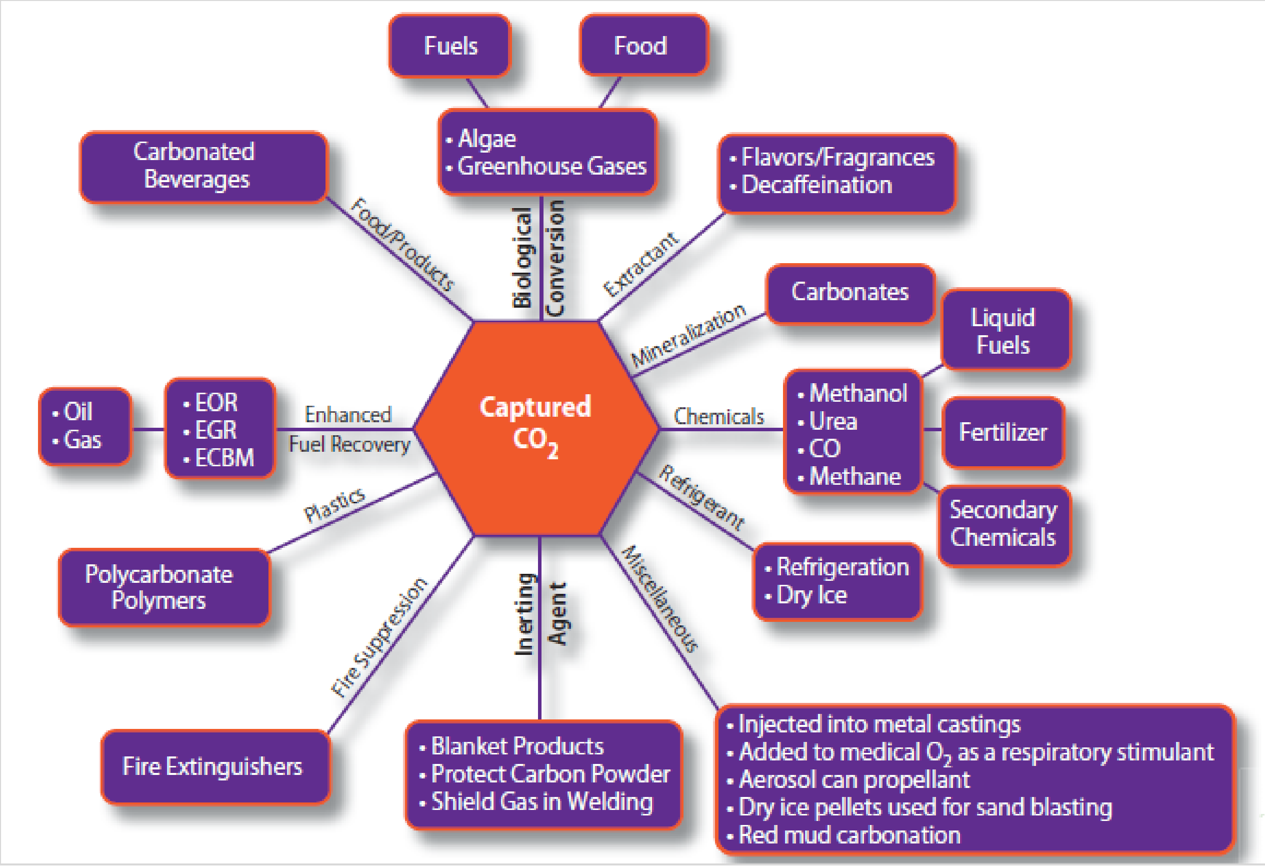

Figure 1. US DoE classification of CO2 utilisation options. Source: US DoE (2013), Carbon Storage: CO2 Utilization Focus Area.

The CSLF report (2012) cites that the CO2 consumptive utilisation options may have the potential to use or mitigate large quantities (billions of tonnes per year globally) of CO2. Within these options the CO2 is converted into products with a long-life such as: CO2 to sodium or calcium/magnesium carbonates/bicarbonates. However, CSLF foresees that larger scale demonstration pilots are needed to evaluate the feasibility of the cited technologies. In addition to mineral carbonates, other by-products from consumptive-use processes include chlorine, hydrogen, soil amendments, fertilizers, and building materials. The production of urea and certain other chemicals from CO2 is already deployed on a commercial-scale. In contrast, the conversion of CO2 to fuels still requires large-scale demonstrations, and the integration of multiple proven steps; similarly the conversion of CO2 to high-value chemicals also requires pilot-scale testing and development.

The Low Carbon Futures (LCU) report (Styring et al., 2011) evaluates the contribution that CCS can make to carbon dioxide abatement in the United Kingdom and worldwide. However, in parallel to CCS, the report puts forward also the possibility of capture and utilisation of CO2 (CCU) as an important contributor to a green economy. It suggests the possibilities for funding CO2 utilisation technology development such as building material production, fuels or in the chemical industry. Although considered only a partial solution to the CO2 emissions reduction, under some conditions using CO2 for CCU rather than storing it underground can add value as well as offsetting some of the CCS costs.

The LCU report quotes that Europe (in particular Germany), the USA and Australia are well advanced in the research and development of CCU technologies. Substantial investment has been made in those countries by extending CCS technology to incorporate utilisation in addition to storage. Furthermore, the Danish government has released a statement that it will aim to go to a zero fossil fuel energy economy by 2050 where the CCU could play a significant role in achieving that aim.

The LCU report considers the CO2 chemical conversion to chemical feedstocks and fuels very favourably; not treating anymore CO2 as waste but regarding it as a chemical feedstock for the synthesis of other chemicals, which will release the pressure on petrochemical industry and reduce CO2 emissions. The correlation of this family of technologies with renewable energy sources (wind or solar energy) and the necessary development of new catalysts is considered beneficial for the overall energy and emissions final balance. This process can build on current post-combustion CCS technologies to give value-added products that can in theory offset the costs of plant investment or even make the process profitable.

Another identified CO2 Utilisation option (Styring et al., 2011) is the accelerated mineralisation through carbonisation of rocks (Mineral carbonation); it involves the reaction of minerals (mostly calcium or magnesium silicates) with CO2 whereas the final output is inert carbonates, which is an excellent construction materials silicates. The CO2 is permanently stored with simultaneous heat generation hence there is no no necessary external energy inputs as the energy state of magnesium and calcium carbonates is lower than CO2. There is however a bottleneck, the slow reaction rate of carbonation in order to create a viable mineral carbonation process on an industrial scale. To enhance reaction rates, heat, pressure, chemical processing and mechanical treatment (grinding) of the mineral could be applied, but these treatments are expensive (60-100/t CO2 stored), cost energy and raise environmental impacts. The potential, globally and in the UK, is considered very large, but the technology is in the R&D phase.

The Ecofys and Carbon Counts in their forthcoming report summary (2013) provide a classification of the diverse range of CCU applications. Their taxonomical approach used the sectors in which the CCU technologies could apply as the base of their classification; the applications were differentiated in a functional rather than technical grouping. The results of their classification are presented below (also in Table 1):

- CO2 to fuels – within this group, technologies which can provide a means for new types of energy vectors are covered. They partly consist of commercially established technologies linked to more novel use (e.g. renewable methanol), and more embryonic forms of energy carrier development (e.g. biofuels from algae).
- Enhanced commodity production – this group of technologies involve using CO2 to boost production of certain goods, typically where CO2 is already used but could be modified (e.g. urea yield boosting). It also includes the use of CO2 as a substitute in existing technologies (e.g. for steam in power cycles). These technologies generally involve applying new methods to techniques which are in commercial practice today, but could be modified to use CO2.
- Enhanced hydrocarbon production – this group of technologies involve the use of CO2 as a working fluid to increase recovery of hydrocarbons from the subsurface (e.g. CO2-Enhenaced Oil Recovery). They range in maturity from commercially viable under certain conditions through to pilot phase;
- CO2 mineralisation – this group of technologies relies on the accelerated chemical weathering of certain minerals using CO2. It can be used in a range of applications, typically involving construction materials (e.g. concrete curing) or in niche circumstances such as for mine tailing stabilisation;

- Chemicals production – CO2 can be used in the synthesis of a range of intermediates for use in chemical and pharmaceuticals production, including carbamates, carboxylation, insertion reactions, inorganic complexes and polymer production. Conversion methods require the use of catalysts, heat and/or pressure to break the stable CO2 structure, and include photocatalysis or electrochemical reduction. One of the most promising technologies is the use of CO2 to make various polymers such as polycarbonate.

CCU category	CCU technology	Research	Demonstration	Economically feasible under certain conditions	Mature market
CO_2 to fuels	Hydrogen (renewable methanol)		Main	Some	
	Hydrogen (formic acid)	Main	Some		
	Algae (to biofuels)	Main	Main		
	Photocatalytic processes	Main			
	Nanomaterial catalysts	Main			
Enhanced commodity production	Power cycles (using $scCO_2$)	Main			
	Enhanced production (urea; methanol)				Main
Enhanced hydrocarbon recovery	Miscible/immiscible floods (CO_2-EOR)			Some	Main
	Miscible/immiscible floods (CO_2-EGR)		Main		
	Sorption-based displacement (ECBM)		Main		
CO_2 mineralisation	Cement production	Some	Main		
	CO_2 concrete curing		Some	Main	
	Bauxite residue carbonation (red mud)			Main	
	Carbonate mineralisation (other)	Main	Main		
Chemicals production	Sodium carbonate				Main
	Polymers	Main	Some		
	Other chemicals (e.g. acetic acid)	Main			
	Algae (for chemicals)		Main	Some	

Legend
Main activities
Some activities

Table 1. Ecofys and Carbon Counts forthcoming reporton CCU technologies classification and maturity. Source: Ecofys and Carbon Counts summary (2013).

Additionally to the classification, the Ecofys the forthcoming report conducted also a technology readiness assessment of the CCU categories. The results are presented in Table 1. Within this table "Research" means that while the basic science is understood, the technology is conceptually feasible and some testing at the laboratory or bench scale has been carried out, it has not yet been demonstrated in a pilot plant. "Demonstration" means that the technology has been, or is being, built and operated at the scale of a pilot plant, but that further development is required before the technology is ready for use in a commercial/full scale system. "Economically feasible under certain conditions" means that the technology is well understood and is applied in selected commercial applications, although it has not been proven in all conditions. "Mature market" means that the technology is in commercial operation with multiple replications, or could be easily modified to accommodate new applications involving non-captive CO2.

The research and industrial sectors from France also foresee the high potential to re-use CO2, considering it as a raw material, as a source of carbon. CO2 recovery in order to produce chemical compounds is then similar to recycling and would involve an environmental benefit and an economic opportunity at the same time. Therefore, the French Agency for

Energy and Environment (ADEME) and French public authorities (MEEDDM, MSR, etc.) commissioned ALCIMED to provide a report that would allow them to understand the different pathways of CO_2 recycling and to identify the main development opportunities of such technologies in France. This report (Ademe, 2010) contains a cross-sectional analysis of the literature and consultations with industrial and institutional experts that lead to the identification of 12 pathways of carbon dioxide recycling, which have been divided into three segments: the use of CO_2 without processing, chemical processing and biological processing. The technological, economic and environmental factors have been evaluated for each pathway, and key stakeholders and related projects have been complemented. A first analysis has been then conducted in order to compare the different pathways to each other. In addition, ALCIMED and the members of the steering committee of this study have had a first discussion on the position of France in regard to carbon dioxide recycling.

Sumarising, Table 2 shows the CO_2 utilisation options short listed by the previous technology potential evaluation studies.

No.	Ecofys	GCCSI and Parsons&Brinckerhoff	Ademe
1	Renewable Methanol Production	CO2 Enhanced Oil Recovery	Enhanced Hydrocarbon Recovery
2	Formic Acid Production	CO2 as a feedstock for urea yield boosting	Industrial Utilisation
3	Algae Cultivation	Enhanced geothermal systems (including CO2 working fluid)	Synthesis of organic matter
4	CO2 Concrete Curing	CO2 as a feedstock in polymer processing	Mineral Carbonisation
5	Carbonate Mineralisation (including Cement&Others)	Mineralisation (including carbonate mineralisation/concrete curing/ bauxite residue carbonation)	Hydrogenation
6	Polymer Processing	Liquid fuels (including renewable methanol / formic acid)	Dry Reforming
7		CO2 enhanced coal bed methane (ECBM) recovery	Electrolyse
8			Photoelectrocatalysis
9			Termochemistry
10			Microalgae (free air or cultivation)
11			Microalgae Photobioreactors
12			Biocatalysis

Table 2. Short listed CO_2 utilisation options by previous assessments: Ecofys and Carbon Counts, GCCSI and PB and Ademe.

I.2. Technology Readiness Levels of CCU technologies

Technology Readiness Levels (TRLs) is a systematic metric/measurement system that assesses the maturity of a particular technology and the consistent comparison of maturity between different types of technology. The TRL approach has been used initially for NASA's space technology planning for many years, and since, to a plethora of technology families. The simplicity but also the versatility of this method has facilitated the migration of this method to various domains.

The TRL levels are the primary mechanism to position the technology activity in the innovation process (innovation chain). The nine scales of technology readiness are shown in Figure 2. Conformably to this TRL scale the "commercial valley of death" is about getting prototype products from the laboratory (TRL 4) to the final stage of design (TRL 9). The pilot activities are located between levels TRL5-8, where the product prototype is scaled up to demonstration in an operational environment (Figure 2).

	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.

Figure 2. DG RTD's Technology Readiness Levels scale (DG Research and Innovation, 2013)

Adopting a suitable set of definitions, GCCSI uses TRL to assess the pathways of capture technologies and indicate their development level (GCSSI, 2012).The TRL scale measures in this case the development of technology from its basic concept (TRL 1) to being available at "commercial" scale (TRL 9). Each step in-between represents the increase in the level of maturity of the technology. In particular, the GCCSI assessment is placing the technology at TRL 9 when reaching the physical scale of deployment or its maximum technical maturity. The commercial deployment stage which would enable the access to the existing markets may not be yet met although the technology is situated at TRL 9. The TRLs from 5 to 9 in the GCCSI report (2012) focus on the development and demonstration activities.

The TRLs is an effective assessment tool to diagnose the technological or commercial maturity of technologies and therefore could apply to CCS and potentially to CCU technologies. Table 3 presents an overview of the most promising CCU technological pathways as identified by various international reports and respectively the DG JRC short listed technologies (top three selected for the CO2 reuse workshop). Briefly, the table specifies the CO2 uptake potential and the DG JRC in-house TRLs assessment for each of the CCU technologies. Table 4 presents the status of the most promising technology options as selected by DG JRC depending on a set of criteria of assessment.

CO2 re-use technology	Uptake potential (Mt/y)	Research&Industrial engagement	TRLs
Methanol production	> 300	+ + +	**4-6**
(Carbonate) Mineralisation	> 300	+ + +	**3-6**
Polymerisation	5 < demand < 30	+ + +	**8-9**
Formic acid	> 300	+ + +	**2-4**
Urea	5 < demand < 30	+ + +	**9**
Enhanced coal bed methane recovery	30< demand < 300	+ - -	**6**
Enhanced geothermal systems	5 < demand < 30	+ + -	**4**
Algae cultivation	> 300	+ - -	**3-5**
Concrete curing	30< demand < 300	+ + -	**4-6**
Bauxite residue treatment	5 < demand < 30	+ + -	**4-5**
Fuels engineered micro-organism	>300	+ + -	**2-4**
CO2 injection to methanol synthesis	1<demand<5	+ - -	**2-4**

Table 3. Overview of the most promising European CCU technological pathways and the DG JRC CO2 reuse shortlisted technologies showing the CO2 uptake potential (based on GCCSI/Parsons & Brinckerhoff, 2011), the research and industrial engagement and the TRLs..

Criterion	Methanol production	(Carbonate) mineralisation	Polymerisation	Formic acid	Urea
Technology maturity	😐	🙂	😐	😐	🙂
Scale-up potential	😐	🙂	🙂	🙂	😐
Commercial viability	😐	🙂	😐	☹️	😐
CO2 abatement potential	☹️	🙂	🙂	☹️	☹️

Table 4. Status of the most promising technology options as selected by DG JRC depending on the technology maturity, scale-up potential, commercial viability and CO2 abatement potential (based on GCCSI/Parsons & Brinckerhoff, 2011).

II. CO_2 re-use workshop

II.1. Introductory session and key messages

The workshop introductory session provided the framework for the following presentations on CO_2 re-use.

- A panoramic overview of the current state of play of CO_2 re-use technologies in the European Union are necessary to understand and advance the maturity status of three technologies.
- DG Research and Innovation, Directorate Industrial Technologies (DG RTD), deals with the CO_2 challenge through the Horizon 2020 framework. Horizon 2020 is a powerful instrument to promote innovative approaches and climate change mitigation, and it will provide R&D opportunities for CO_2 technologies.
- CO_2 perception as a valuable resource. CO_2 re-use technologies may achieve a reduction of greenhouse gases and foster innovation. However, CO_2 re-use is a niche application: the large scale deployment of Carbon Capture and Storage (CCS) continues to be the priority for the decarbonisation of the European economy. CO_2 re-use and CCS will be complementary, and CO_2 re-use has to be seen as an option among the different technological pathways to reduce CO_2 emissions.
- CO_2 re-use technologies may provide revenues to cover part of the costs of CO_2 capture. The Commission is open for discussions with the stakeholders to understand the specific challenges from the different sectors and technologies.

Three technological pathways were chosen for in-depth analysis, as mentioned before, methanol production, mineralisation and polymer production, and were addressed through the following aspects:

- State-of-the art of the CO_2 re-use technology
- The impact of the CO_2 re-use product (i.e. methanol, carbonates and polymers) on the energy system and related markets
- The needs of each sector, related to each technology addressed, for large scale industrial deployment, and links with other technologies

II.2. Technological pathways

DISCLAIMER

The following summaries of the presentations do not represent the views of the European Commission, but only those of the authors of these presentations.

II.2.a. Renewable methanol

Kees Hettinga from Carbon Recycling International (CRI)

CRI is an Icelandic company that uses mainly CO_2 as raw material to produce a liquid fuel. Its research also comprises now the production of carbonates. The hot water from geothermal plant in Iceland contains carbon dioxide (CO_2) and hydrogen sulphide (H_2S). The CO_2, which would have been otherwise released to the atmosphere, is captured, cleaned and combined with hydrogen (H_2) to produce methanol. The product is commercialized under the name of Vulcanol. The use of hydrogen produced through renewables provides an added value to the decarbonisation of the transport sector. CRI has tested high Vulcanol blends in Flex Fuel Vehicles (E85) which requires no modification. The next phase is the production of electro-fuels and the conversion of renewable energy into a liquid fuel that will lower the CO_2 footprint. It is possible to use methanol as blending agent in gasoline, and it can be further transformed to be converted in a substitute of diesel (DME). The production of polymers is also an alternative.

In Iceland, energy and feedstock for Vulcanol production are available and can be locked in with long-term contracts for power and other utilities. Scale-up and sustained operation of a production plant has been demonstrated under industrial conditions, resulting in a scale-up risk contained and predictable. The technology is cost competitive and has a scaling potential capable of impacting the market over a long term horizon. In the medium term, producers are price takers based on current economics of 1st generation biofuels. The speaker said that the main challenge for the technology to compete in mainland EU is to take advantage of feed-in tariffs and the Renewable Energy Directive (RED) framework for electro-fuels. The value of CO_2 reductions is not sufficiently taken in the legislative framework or in the market. Nowadays, there is no satisfactory promotion of non-biological sources. The current (i.e. provisioned at that time by the EC in the proposed ILUC amendment but still to be appended to the RED) quadruple counting is a good incentive but does not translate into a quadruple price. The conversion of cars to run on methanol is estimated to cost around ~ €100 per new car. The engine control is a marginal problem and can easily be modified. However, current legislation for gasoline does not address this opportunity and the blending rate for methanol allowed is too low.

Question and answer session

- Internal renewable methanol consumption in Iceland: In order to increase the consumption, there is a need to convince the oil companies and to provide the right incentives.
- Scaling could bring revenues: Scaling up the technology could bring more revenues by just replicating the production and multiplying the technological units without involving any further R&D challenges (economies of scale).
- Energy efficiency: The use/sale of the oxygen produced by the hydrolysis of water, which now vented into the atmosphere, can improve the energy efficiency and the economics of the process.

II.2.b. Polymers development and chemical production

Polymer development: Christoph Guertler from Bayer

The Bayer Company manufactures products in the fields of health care, nutrition and high-tech materials. It is currently developing the technology for polyurethanes synthesis using CO_2, looking for the right catalyst. It has been branded as the "Dream Production". This project has an overall value of 9 M€, representing almost half of the CO2rrect project ("wind power to polymer") total sum funding (18 M€). The use of CO_2 to produce polymers is a clear alternative and competitor for polymers production using fossil fuels, which are scarce. Moreover, the production of petrochemicals requires significant amounts of energy. It is important for the polymer related industry to take this scarcity and energy consumption into account, and look for sustainable solutions, marketable and useful for the customer. For instance, the epoxide production/consumption can be decreased with CO_2 as a carbon building block. Specifically, the amount of epoxide associated with petrochemicals can be avoided. The use of CO_2 as a raw material is assessed using a pragmatic approach that considers a reasonable amount of CO_2 in the product.

The technology fits into the already existing market of polyurethanes, and there is a window of opportunity if additional efforts are taken by policy makers and industries. The reduction of the carbon footprint with regards to conventional technology is considerable and the product can be perceived as more sustainable. There is a need for fundamental research and Life Cycle Assessment (LCA). A project that is working on this respect is the B-COR project initiated by the EIT Climate-KIC between the TNO, Imperial College London, MinesParisTech, Bayer Technology Services and RWTH Aachen. However, the process is in its very beginning and there is a need for incentives and investment; considerable efforts have to be made in order to address the "valley of death": start piloting projects with a customer, or push for industrial trials and technology readiness. Commercialisation could be possible after 2015.

There is a possibility to use the excess of energy (peak loads from renewable sources, like wind) and store it in an intermediate polymer material. This is the final objective of CO2rrect project. Regarding this potential, incentives to enhance the cooperation between the energy and the chemical sector are needed, to facilitate the development of demonstration facilities.

Chemical production: Nuria Huguet from BASF and CaRLa

BASF, as chemical producer, CaRLa (Catalysis Research Laboratory of University of Heidelberg), a research centre on catalysis, and their academic partners in TUM, Univ. of Stuttgart and Univ. of Heidelberg, are currently focusing on the development of the monomer sodium acrylate from CO_2, (bio-) ethylene (as raw materials) and a base, also a "dream reaction" that currently is not feasible. The potential of this technology is a reduction of 30% in raw materials and a significant reduction in investment costs. The chemistry has not been known until the team at CaRLa started its basic research efforts. So, BASF, CaRLa and co-workers are dealing with fundamental research to obtain this new industrial process. They already have managed to create the first full catalytic cycle but, more effort is needed to increase the catalyst efficiency and lifetime. More details concerning the various chemical reactions are to be found in the presentation, see Annex.

Question and answer session

- Funding: 18 M€ have been allocated to the Bayer foam project.
- Sustainability: Promoting chemical reactions should not be exclusively intended to high volume applications.

II.2.c. Mineralisation

Michael Priestnall from Cambridge Carbon Capture Ltd.

Cambridge Carbon Capture Ltd. is a Cambridge-based, early venture company, which aims to develop and operate a mineral carbonation process to capture CO_2 into mainly magnesium carbonates. Mineral carbonation refers to the industrial ex-situ conversion of magnesium or calcium containing minerals or wastes to carbonates, mimicking the natural process by which CO_2 is removed from the atmosphere. Mineral carbonation is an exothermic process (energy-releasing) but kinetically very slow. The process sequesters CO_2 directly from flue gas, and transforms it into stable & solid mineral products; so, there is no need of a capture and storage infrastructure. On the other side, the silicates are pre-treated (alkaline digestion process) to improve the reaction rate. At small scales, mineral carbonation can deliver immediate commercial deployment of industrial CO_2-sequestration without a carbon price; it is already commercially deployed in niche applications, where revenues come from by-products. Today, economic feasibility is slowly driving worldwide mineral carbonation development.

Mineral carbonation is potentially a highly scalable CO_2 capture/utilisation option. For example, Oman, in one accessible geological deposit, has sufficient magnesium silicate to sequester 30 trillion tonnes of CO_2, if fully carbonated. USA and other countries have similar large resources. The low-value aggregate products of large-scale mineral carbonation could service existing gigatonnes scale international markets for construction aggregates. However, R&D on processes suited to large-scale application is advancing slowly and research funding is still needed. Policy mechanisms are also needed to evaluate CO_2-sequestration independently of emission reductions. There is excellent potential for a cost-reduction learning-curve based on market-driven volume growth, but it is necessary to get the support and enabling policies.

II.3. Future outlook

Peter Styring from CO2Chem Network and Edgar Hertwich from Norwegian University of Science and Technology (NTNU)

The aim of the CO2Chem Network is to bring together academics, industrialists and policy makers from the CO_2 re-use community. The speaker focused on off-setting the costs of CCS while combining the CO_2 re-use process with renewable energy storage: conversion of (extra) peak electricity production, where electricity is not used, into chemical energy. In order to facilitate the uptake of the storage potential of the technology, there is a need to design new capture agents for the captured CO_2 and especially to the atmospheric CO_2. The latter remains a main challenge.

The presentation gave also an overview of the different possibilities for CO_2 utilisation, from urea synthesis up to mineralisation (carbonates production).

The breaking of CO_2 bonds may not in some cases have a huge impact on the climate. The use of CO_2 will have an impact on the supply chain by reducing the reliance on fossil fuels and thus increasing the security of fuel supply. The commonality between all renewable sectors is the production of electricity, or simply a supply of electrons stored in the chemical process.

LCA was addressed as critical for identifying which re-use options (or under which circumstances) make sense, by the NTNU presentation. There is a need to identify the environmentally friendly options on a case-by-case basis. Thermodynamics and system analysis are key issues to conduct LCAs for CO_2 re-use technologies. The presenter analysed as example the cases of a power plant with post-combustion capture technology, enhanced oil recovery and formic acid production.

Question and answer session

- LCA: What are the different bottlenecks and financial implications as well as the LCA for the formic acid as substitute product? The expert provided the answer that the LCA was performed for the whole fuel chain, from production to pipelines. The expert mentioned that the research question was if formic acid can be produced with either higher or lower emissions of air/water/soil pollutants compared to the conventional fossil or renewable alternatives. If the emissions are comparable, then the LCA should investigate it. How does it affect the CO_2 balance in the power plant and does it make sense as a fuel. The conclusion was that it does <u>not</u> make sense.

- Renewable resource used: The main results were obtained by assuming that the CO_2 used to produce formic acid comes from a fossil fuel plant with CO_2 capture. The concentration of the formic acid obtained is so low that it requires a lot of energy to be purified.

III. Discussion of horizontal issues

- Regulatory framework: Although critics have argued that there is currently no satisfactory legislative framework for CO_2 re-use technologies, the history of EU law- making shows that there is a relatively strong tradition for amendments to existing laws to drive innovation forwards. The current framework concerning the Fuel Quality Directive, Renewable Energy Directive and the ETS were object of discussion.
- Terminology: CO_2 re-use is used as a term in order to underline the cyclic aspect of this technology.
- Funding criteria for Horizon 2020: Horizon 2020 will go closer to market activities and will use the Technology Readiness Levels (TRLs) as a reference point. However, there will be no financing of product development, even if the innovative aspect is crucial for CO_2 re-use technologies. There is also a possibility to enhance the link between innovation funding and financial instruments. This will provide a basis for a possible pooling of funds from the European Investment Bank.
- The CCS and CO_2 re-use debate: One of the drivers to consider CO_2 re-use technologies is the lack of a consolidated CO_2 storage and transportation network in the Member States. However, CO_2 storage capacity is far larger than re-use volumes, so CO_2 re-use can provide support the CCS costs. There is also a need to assess the different CO_2 re-use technologies potential, on a case-by-case basis, because of their applicability to a wide range of industrial processes and options. The cost of the captured CO_2 needs to be addressed.
- Labelling: The participants at the workshop also discussed the possibility and need to introduce one CO_2 label for CO_2 re-use technology related products, or the introduction of an eco-labelling such as EU Ecolabel to recognise the potential benefits of products made using captured CO_2.
- Energy storage potential of CO_2 re-use technologies: Electricity can be converted into chemical energy by using the excess of renewable electricity production in times of low demand. It will be converted into a liquid fuel either stored or used locally, e.g. to take an amount of energy from a waste plant and convert it into diesel which will be used to power the waste collection trucks. It means that it is possible to store the energy as a usable form, where the transportation costs are offset through the immediate use of the final product. In the case of kerosene or diesel, it is possible to cut out the refining costs. This underlines its local usability potential rather than distribution of a resource.
- Intermittent sources of energy: Some of the recurring questions were whether the wind and solar will be able to cope with the energy needs of the CO_2 re-use technologies taking into account their intermittent character as sources of energy and if this could reduce the potential of this technologies; it was established that this needs further consideration. Plants with carbon capture are capital intensive and will likely need to be operating well over 80-90% to payback capital in commercially acceptable periods of time, whereas surplus renewable energy may only be available for 10-30% of the time. The geothermal energy has strong potential as well as tidal in the UK. By the use of simple electrolysers opens the possibility to use wind energy.
- There is a need for a transparent analysis regarding the impact that different CO_2 re-use options can have on European energy system and the development of a sustainable market for CCU products (e.g. CO_2 balance; operational, cost and environmental performance; bottlenecks for technology scale-up; current and future market; and the potential market penetration)

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Annex: SETIS page for the Workshop on "CO2 re-use Technologies" and the experts presentations

European Commission

SETIS

Strategic Energy Technologies Information System

Workshop on "CO2 Re-use Technologies"

A workshop was held in Brussels on 7th June 2013 on "CO2 Re-use Technologies", organised and co-hosted by the Institute for Energy and Transport of the Joint Research Centre of the European Commission and the Directorate General for Climate Action.

The aim of the workshop was to present how the most promising pathways for CO_2 re-use are related to climate and energy technology policies, to facilitate a dialogue between stakeholders (industry, academia and policy makers) and to address the challenges for a possible large scale roll-out of CO_2 re-use technologies. Several presentations were given by experts in the field and focused on the state of the art of the technologies, the needs of the sector for large scale deployment and the impact of the CO_2re-use products on the market. In particular, the workshop focused on three promising pathways, namely: methanol production; mineralisation; and polymer production. The Summary report on the workshop and the presentations are given underneath.

Document Reference and Links:

Presentation by Kees HETTINGA.pdf

Presentation by Christop GUERTLER.pdf

Presentation by Núria HUGUET.pdf

Presentation by Michael PRIESTNALL.pdf

Presentation by Peter STYRING.pdf

Presentation by Edgar HERTWICH.pdf

Carbon Recycling International

Liquid Transport Fuel production from Renewable Energy, CO_2 and water

Kees Hettinga, EU Business Development
CO2 Reuse Workshop, Brussels, June 7 2013

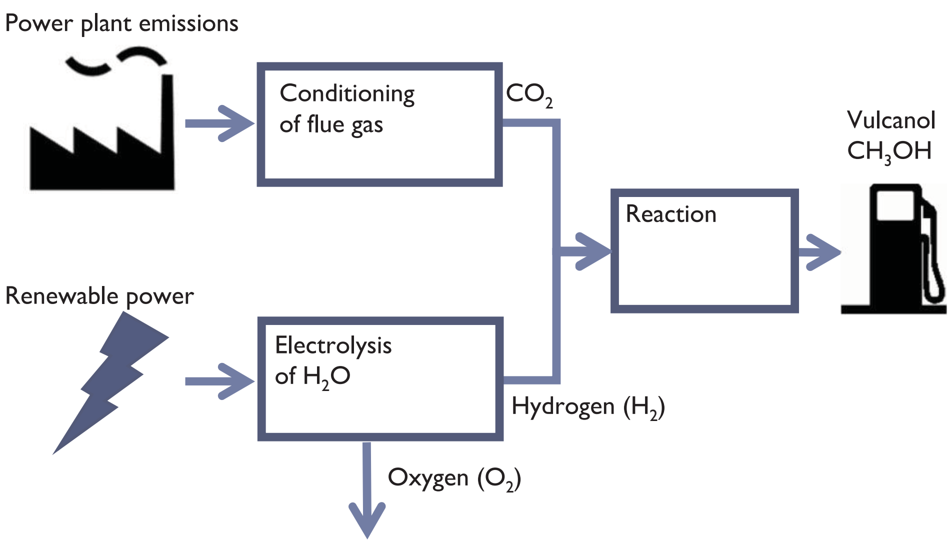
Agenda

- What is Carbon Recycling International (CRI)?
- What is CRI's Emission-to-liquids technology (ETL)?
- Is ETL ready to be deployed at scale?
- What will be the impact of ETL on in the market?
- Does CO2 re-use make a business case?
- What are the needs of this sector?
- What are the bottlenecks?

What is Carbon Recycling International?

2006	Carbon Recycling International founded in Reykjavík
2007-2010	Development of emission-to-liquids technology
2011	Construction of plant begins Grant to develop waste to fuel technology Fleet trials with oil companies
2012	Plant inaugurated ETL patent issued in US FFV fleet trials with Methanex Sales of Vulcanol to biodiesel and chemical production Dutch regulations amended to include Vulcanol Commercial contract with Argos EU grant to develop cyclic carbonates from CO2 technology
2013	Continuous operation of industrial plant Sales to Holland

What is the Emissions-to-Liquids process?



Opportunities for electrofuels

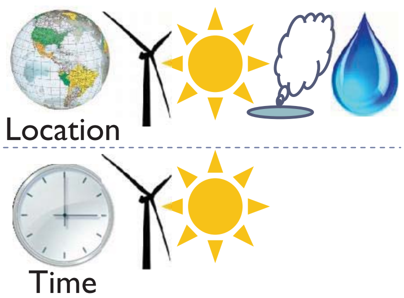
We don't face energy **shortage**: we face an energy **location** and **distribution** problem

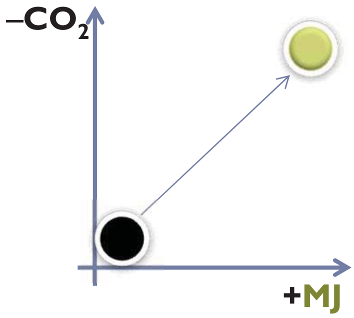
Stranded renewable energy → **Convert to green MJ** → **Lower CO_2 footprint**

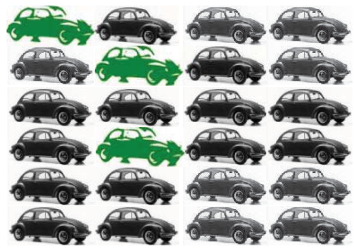
Renewable energy sources are usually either stranded "in time" – intermittent – or by location - access to distribution and market

Conversion provides green energy in liquid form which is easily stored and transported and meets targets for sustainability

Overcome location and distribution issue while reducing carbon footprint of transportation and increasing renewable energy







Svartsengi Geothermal Resource Park

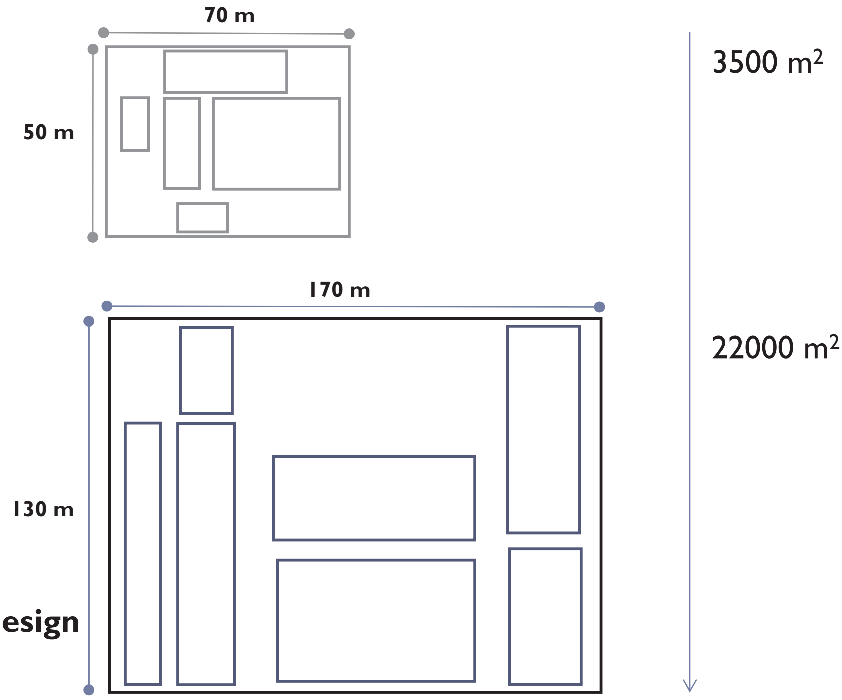
HS Orka	The Blue Lagoon	Carbon Recycling International
Water	Geothermal Spa	CO2 recycling
Disrict Heating	Skin Care Clinic	Fuel production
Power Production	Cosmetics	

How can CRI scale to 100 t/day?

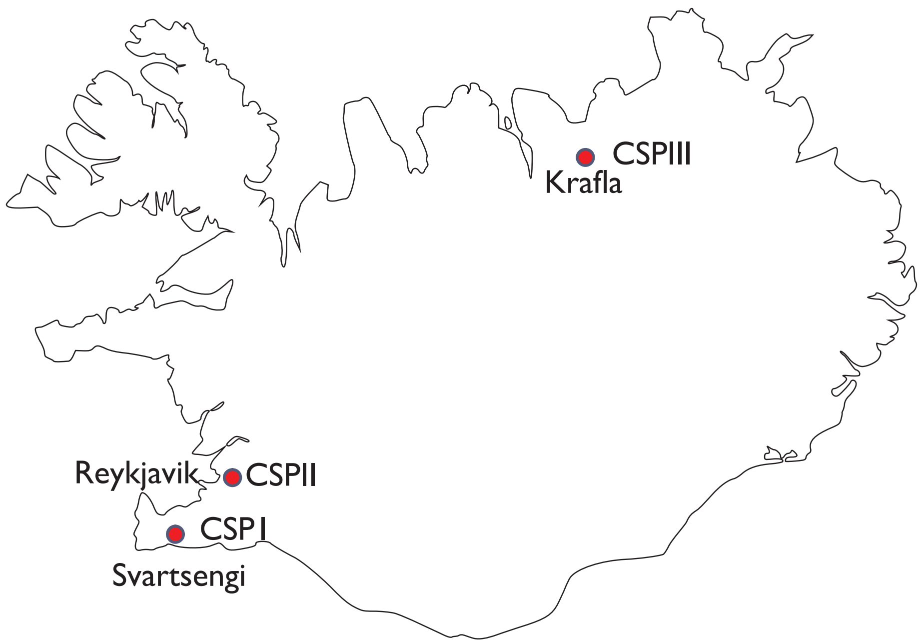
Current scale
5,400 t/yr CO_2
4,000 t/yr methanol
`~12 t/day

Commercial scale
45,000 t/yr CO_2
35,000 t/yr methanol
~ 100 t/day

Proven process
Skid based modular design
Low scale up risk



Pipeline of 100 t/day projects in Iceland



Technology is deployed at industrial scale which limits risks of going to larger scale

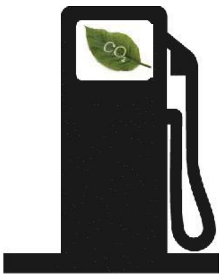
- Scale-up and sustained operation of production plant has been demonstrated under industrial conditions
- Plant is based on modular design and construction which allows scale up risk to be contained and predictable
- Energy and feedstocks available and can be locked in with long-term contracts for power and other utilities
- CRI R&D working with vendors on reducing CAPEX in larger scale plant beyond economies of scale

What is the addressable market in EU?

12 Gt/yr

2 Gt/yr

Direct gasoline blending



Now:
EN228: methanol 3 %v/v

Chemical feedstock

10 Gt/yr

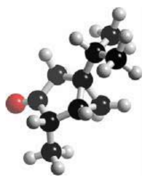
?

Fuels and blending agents

Now:
MTBE: methanol 6 %v/v
FAME/RME: methanol 15 %v/v
Future:
DME: methanol 100 %v/v

Polymers

Complex value chain
Low premia for lower CO_2



CRI has tested high Vulcanol blend in Flex Fuel Vehicles (E85) which require no modification

Engine control system already reprogrammed for higher oxygen

Fuel tank and fuel line from material already compatible with alcohol

Fuel pump and injectors already designed for more fuel throughput

Active oxygen sensor connected to engine control

FFV/E85 vehicle incremental production cost ~€100/car

Does the current policy framework promote production from non-biological sources?

Member States must ensure 10% of final consumption of energy in transport is from renewable sources

Renewable energy sources are non-fossil sources, both non-biological and from biomass and biogas

Biofuels must meet specific sustainability criteria; contribution of energy of biofuels from wastes and cellulose shall be counted twice

4. Each Member State shall ensure that the share of energy from renewable sources in all forms of transport in 2020 is at least 10 % of the final consumption of energy in transport in that Member State.

(a) 'energy from renewable sources' means energy from renewable non-fossil sources, namely wind, solar, aerothermal, geothermal, hydrothermal and ocean energy, hydropower, biomass, landfill gas, sewage treatment plant gas and biogases;

1. Irrespective of whether the raw materials were cultivated inside or outside the territory of the Community, energy from biofuels and bioliquids shall be taken into account for the purposes referred to in points (a), (b) and (c) only if they fulfil the sustainability criteria set out in paragraphs 2 to 6:

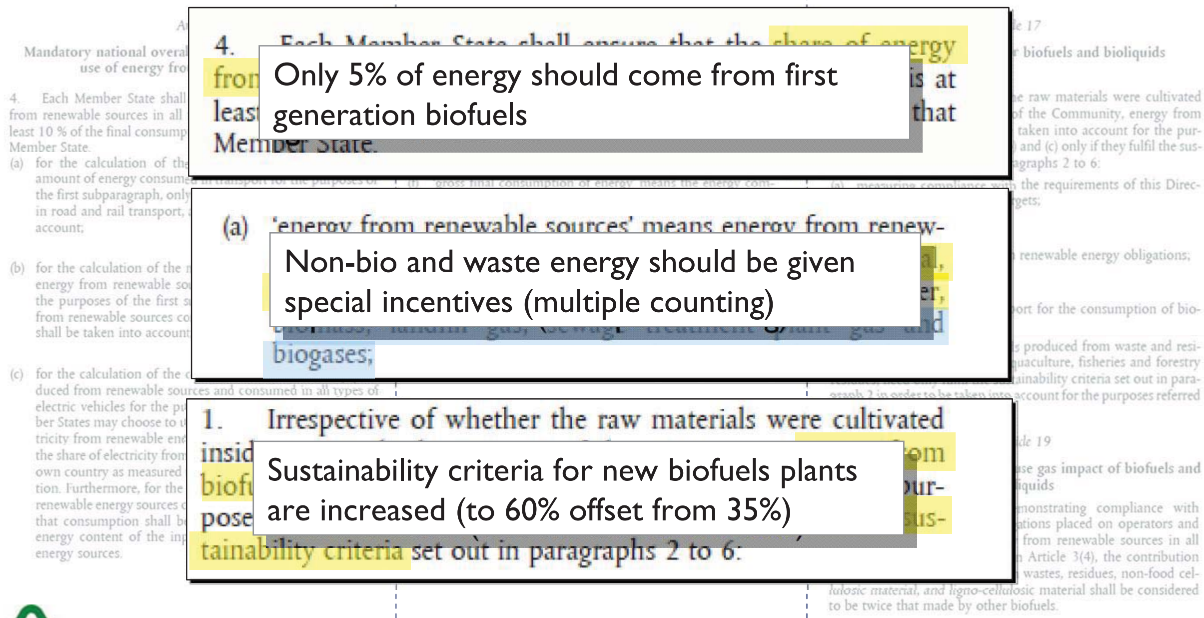
Carbon Recycling International – Do not quote without permission

ILUC amendment limits crop based biofuels and promotes more advanced renewables

Member States must ensure 10% of final consumption of energy in transport is from renewable sources

Renewable energy sources are non-fossil sources, both non-biological and from biomass and biogas

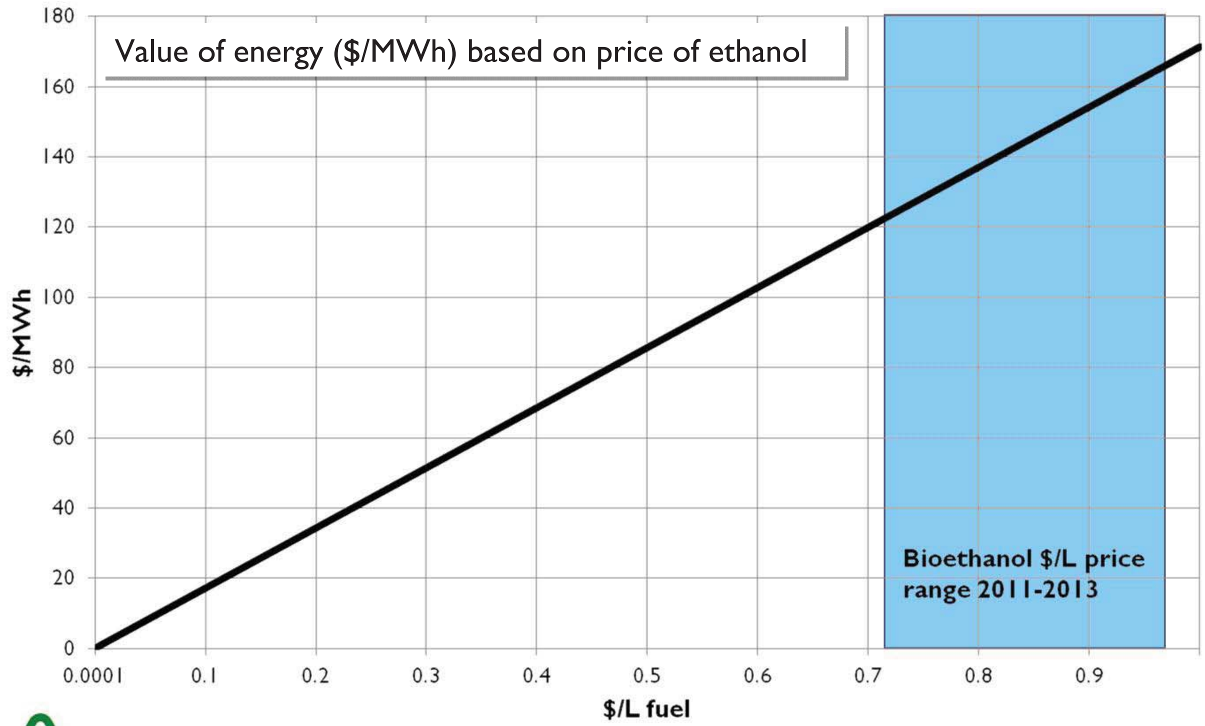
Biofuels must meet specific sustainability criteria; contribution of energy of biofuels from wastes and cellulose shall be counted twice



How will ETL impact supply and pricing

- In medium term producers are price takers based on current economics of 1st generation biofuels and €/MJ
- Technology is cost competitive and has scaling potential which will impact market over longer term horizon
- Next steps is to scale the technology at ~100 t/d in Iceland with available green energy and CO_2
- Main challenge for deployment of technology in mainland EU is to compete with feed in tariffs and RED framework on LCA for electro-fuels

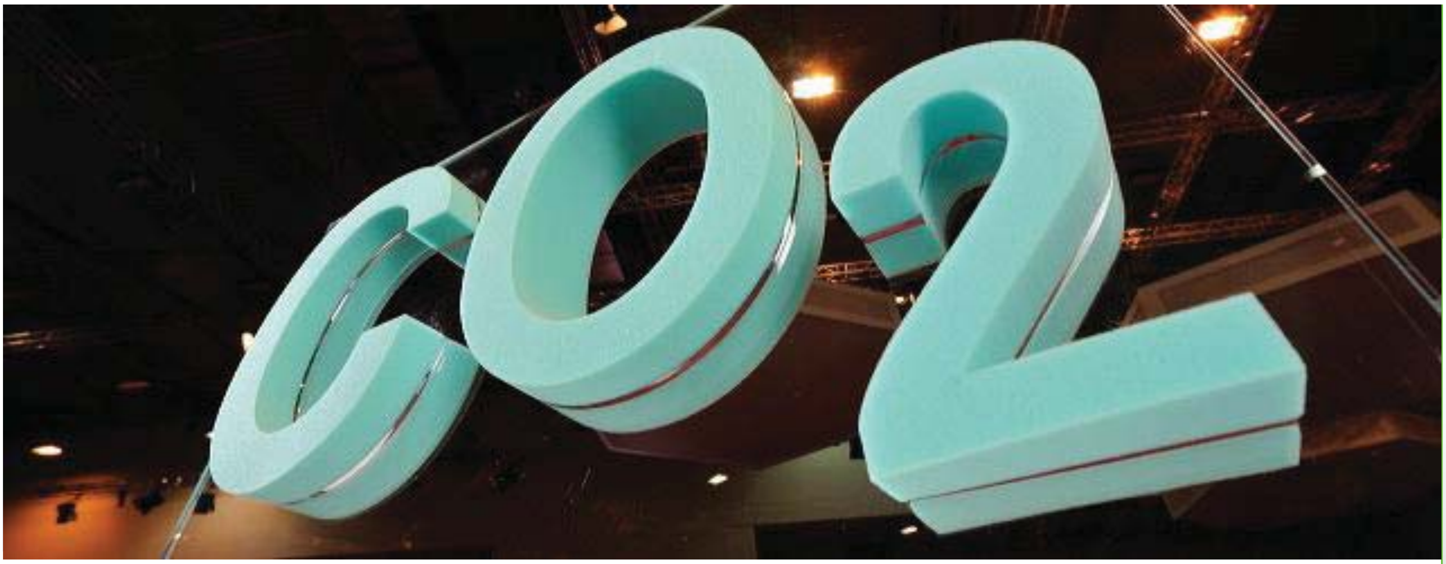
Does CO2-to-fuel reuse technology make economic sense?



Needs and Bottlenecks

- Small player in a very big market
- Barriers to entry in fuel market
  - Excise duty per liter
  - Text and regulations written for bio, e.g. Double counting currently only for biomass, RVP waiver for ethanol only
- Use of renewable electricity by means of certificates of origin
- Value in CO2 reduction not valued by market and regulations


kees.hettinga@carbonrecycling.is



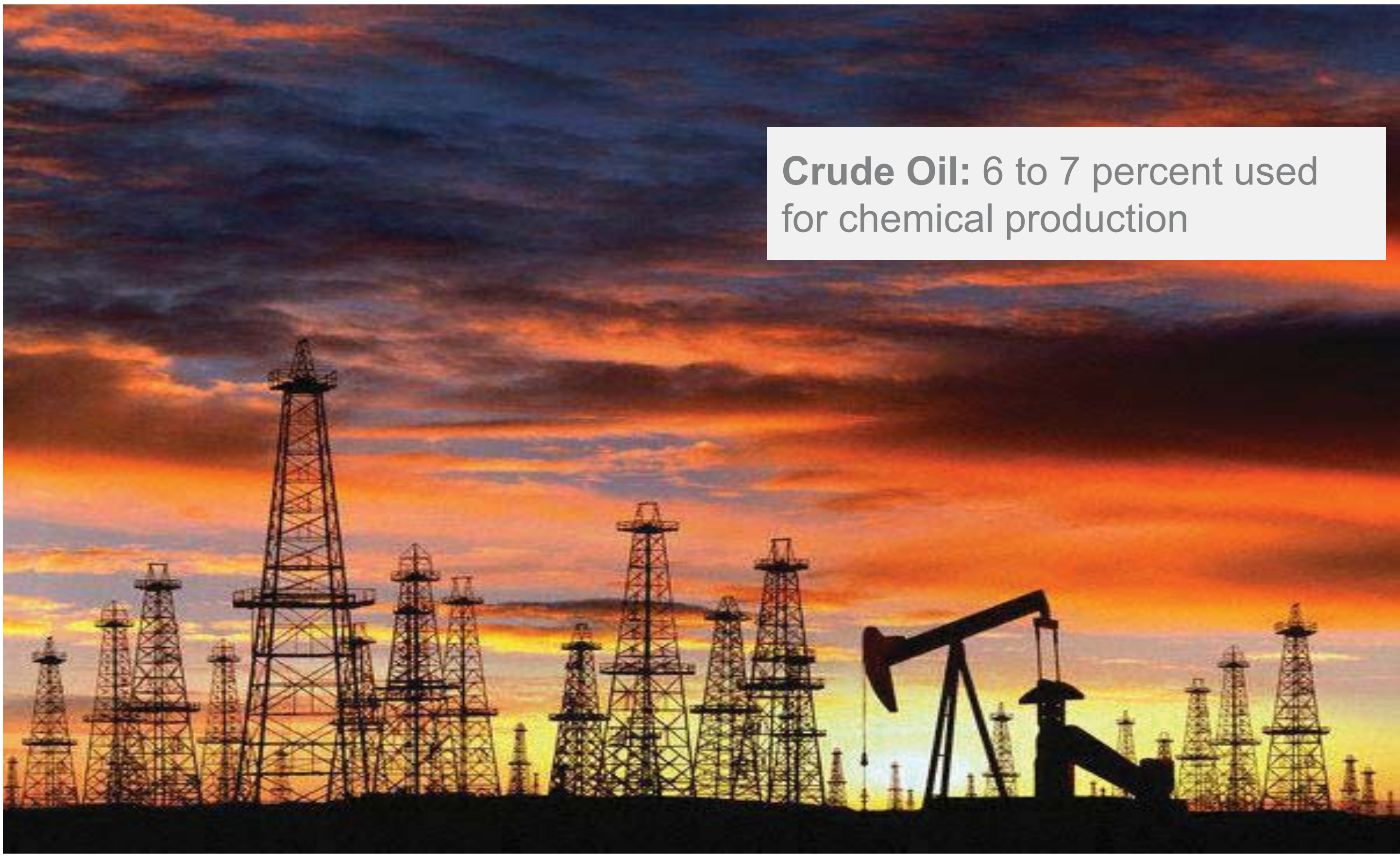
Science For A Better Life

„Dream Production“ CO_2 as raw material for Polyurethanes

Dr. Christoph Gürtler, Bayer MaterialScience AG

2013-06-07

Fossil raw materials: A part of it can be exchanged with CO_2



Alternative feedstock CO_2 – Motivation for chemical utilization

Sustainability
- Resource efficiency – less oil
- Chemical CO_2 recycling
- Climate protection

Industrial value creation
- Process improvement
- Market needs
- No food competiton
- Defined product quality – no downsides

Strategies for CO_2 conversion and utilization

Existing

Urea (80 m. t/a)

Methanol (2 m. t/a)

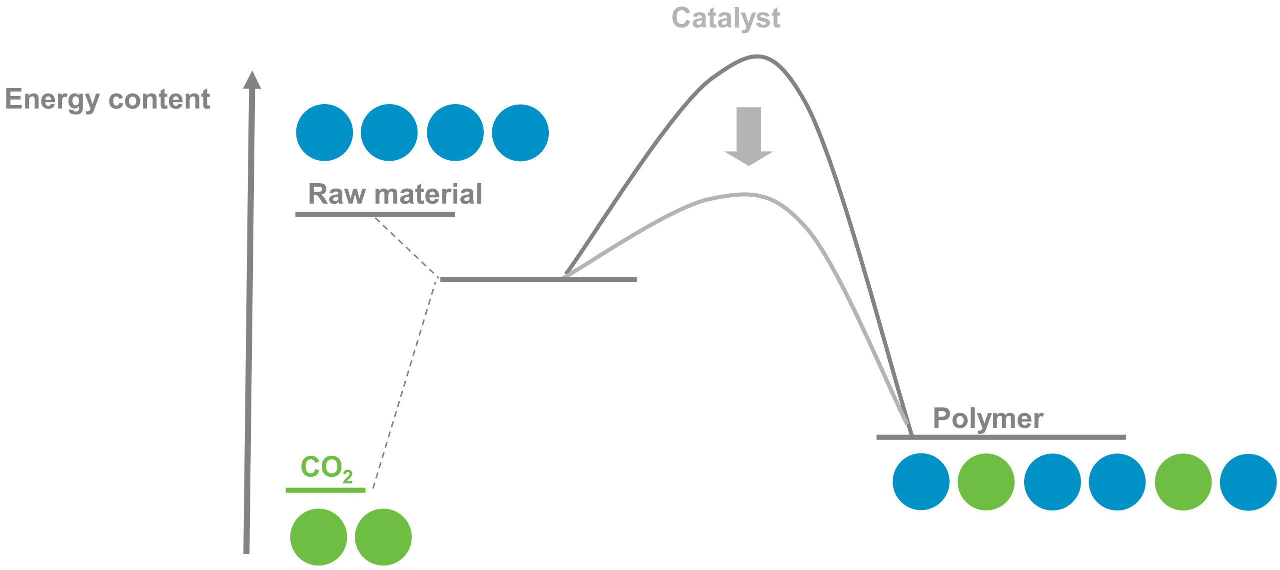
Cyclic carbonate (0.04 m. t/a)

Salicylic acid (0.025 m. t/a)

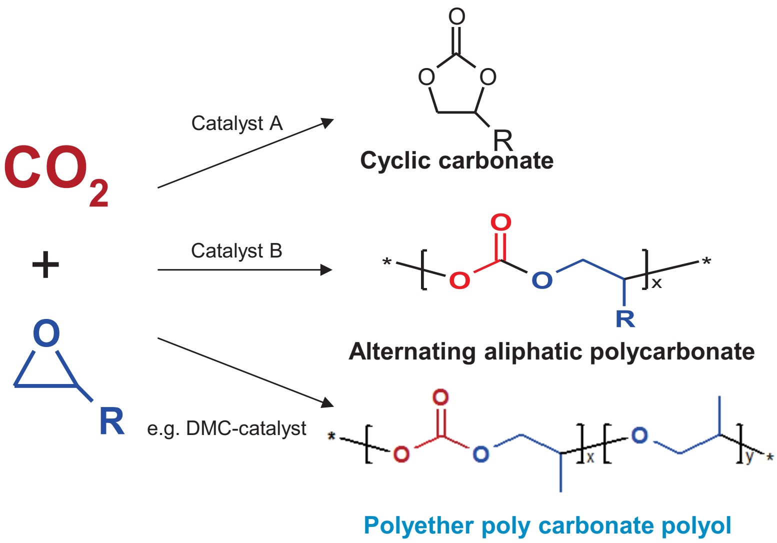
Emerging
- CO_2 based polymers
- Dry reforming
- CO_2 hydrogenation to formic acid
- Fuels (DME) etc., Intermediates
- ….

Exploratory
- Isocyanates
- Organic carbonates
- Lactone synthesis
- Carboxylic acids
- ….

CO_2 – typically sluggish in reaction Catalysis makes the difference



Industrial application of epoxide/CO_2 chemistry for carbonate syntheses



- Green solvent
- Synthesis of dimethyl carbonate

- High molecular weight
- Binders for ceramics
- Biodegradable/compostable polymers

- Low molecular weight
- Terminal **OH-functionalities** yields polyols for polyurethanes synthesis

- ▶ Selectivity is strongly influenced by the catalyst /competing reaction
- ▶ Up to 43 wt% incorporation of CO_2 (R = CH_3) possible
- ▶ Homogenous and heterogeneous catalyst suitable

Dream Production –
From power plant to polyurethane

Bundesministerium für Bildung und Forschung

BAYER

Scrubbing and supply of CO_2

VORWEG GEHEN

Process development and conversion of CO_2

Bayer Technology Services

Production and testing of polyurethanes with CO_2

Bayer MaterialScience

Fundamental research — CAT® Catalytic Center — RWTH AACHEN UNIVERSITY — **Life Cycle Assessment**

Dream Production –
Covering the value chain

BAYER

VORWEG GEHEN

CO_2-separation, bottelling and quality monitoring

Dream Production –
Covering the value chain

Bayer Technology Services

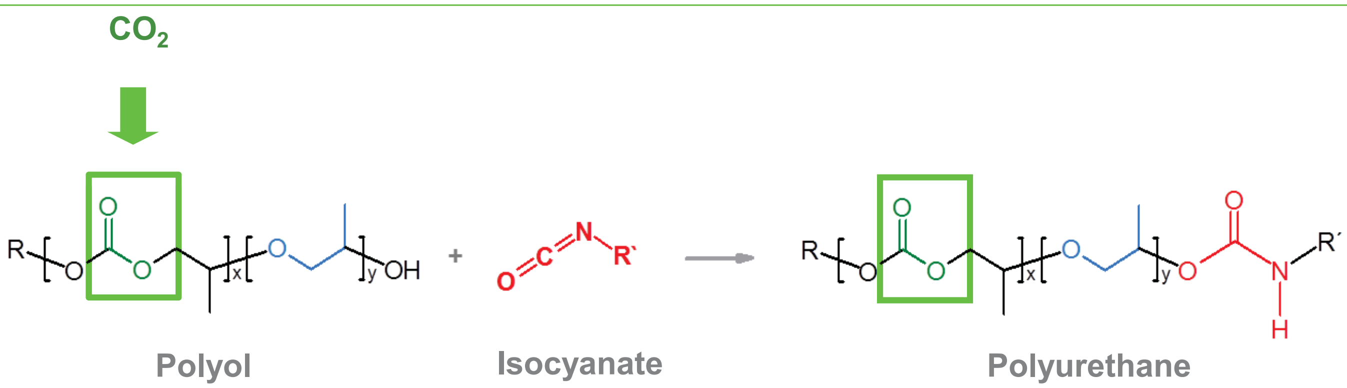
Construction and operation of a pilot-plant → Samples

Dream Production –
Covering the value chain

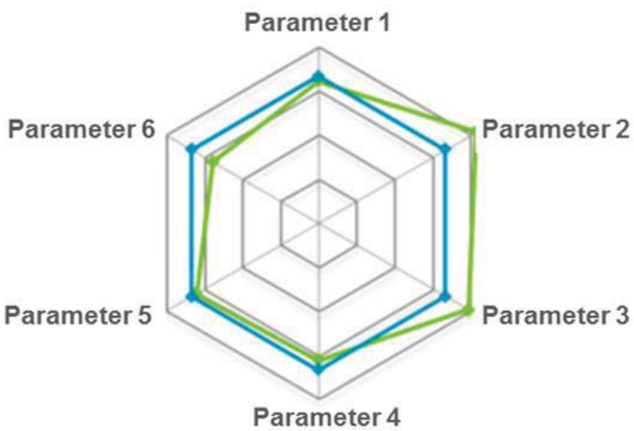
Bayer MaterialScience

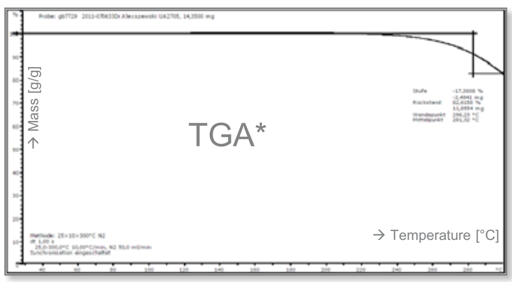
Slab stock plant for CO_2-PET testing in foams

Target product polyurethanes – Allrounder among plastics



CO_2-based polyurethanes foams -
New polyols give decent properties

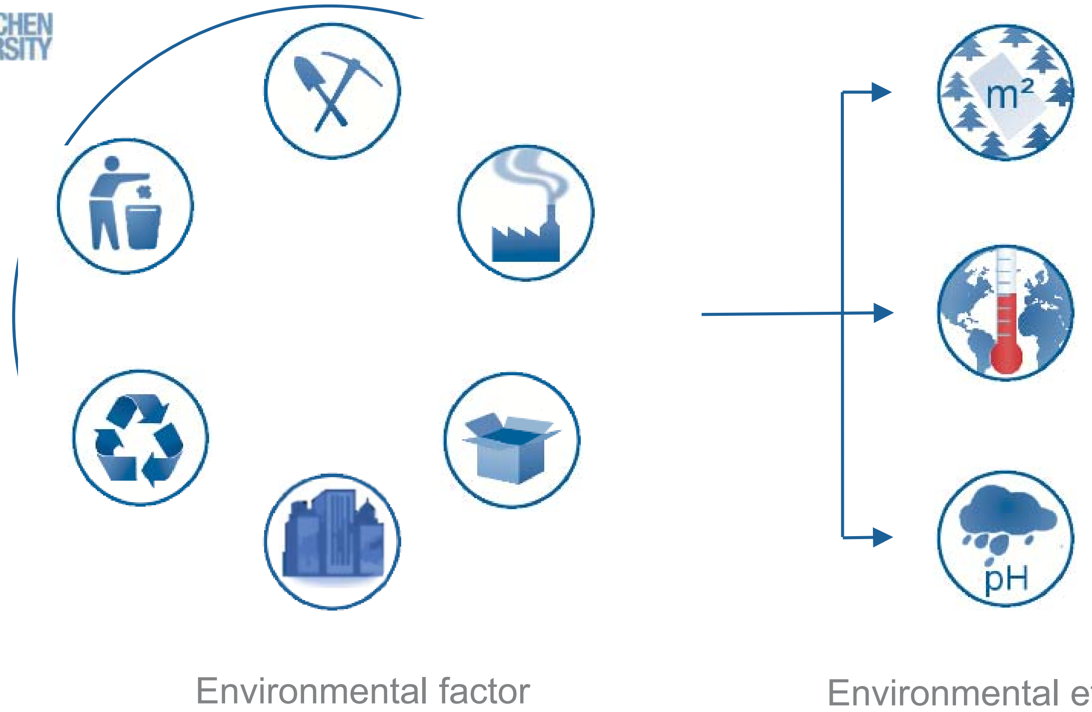




- CO_2 based polyurethanes can be used for many applications
- Properties are on the same level or even exceed conventional polyurethanes

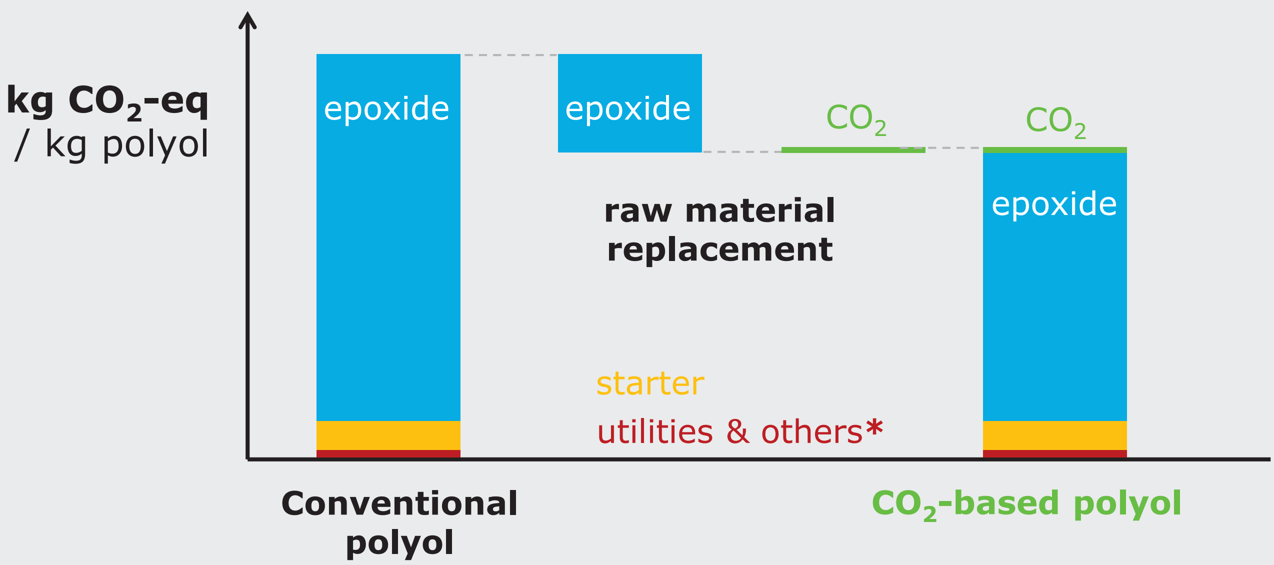
- CO_2 is chemically bound
- Stability is equal to existing products
- Lower heat of combustion

Complex LCA by RWTH University – All aspects covered



Dream Production LCA – Climate Change

Impacts on Climate Change



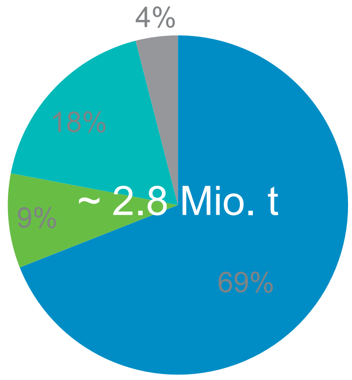
* includes process steam, electricity, cooling water, catalyst etc.

N.von der Assen and A.Bardow (**2013**). Oral presentation, ICCDU XII, Alexandria, VA, USA, *accepted*.

New CO_2-based flexible foam polyols

Targeting the largest market segment: conventional polyol

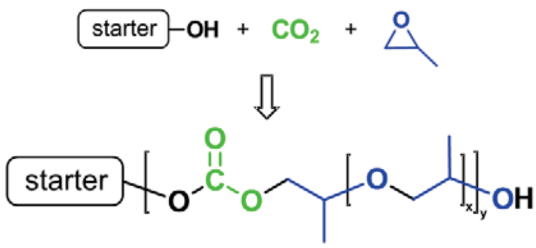
Global Slabstock
Polyol Market 2012*



Conv. Polyol | HR Polyol | All Filled Polyols | Other Polyols

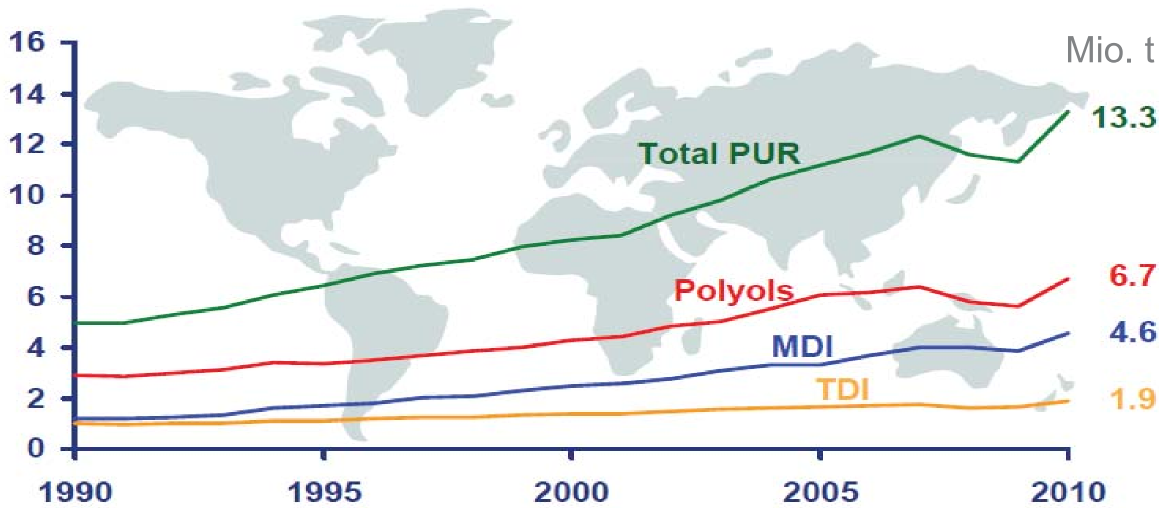
* Estimate based on IAL studies

BMS is working to expand the raw material base by introducing **carbon dioxide** – creating a new class of products: **polycarbonate-polyether-polyols**



Target market Polyurethane –

Global production exceeds 13 Mio t



MDI = diphenylmethane diisocyanate TDI = toluene diisocyanate

Bringing sustainable materials to life

CO_2 based materials fit into the triangle of sustainability

Environmental
Lower carbon footprint compared to existing materials
Collaboration with LTT, RWTH for LCA of CO_2 based products

CO_2 *Dream Production*

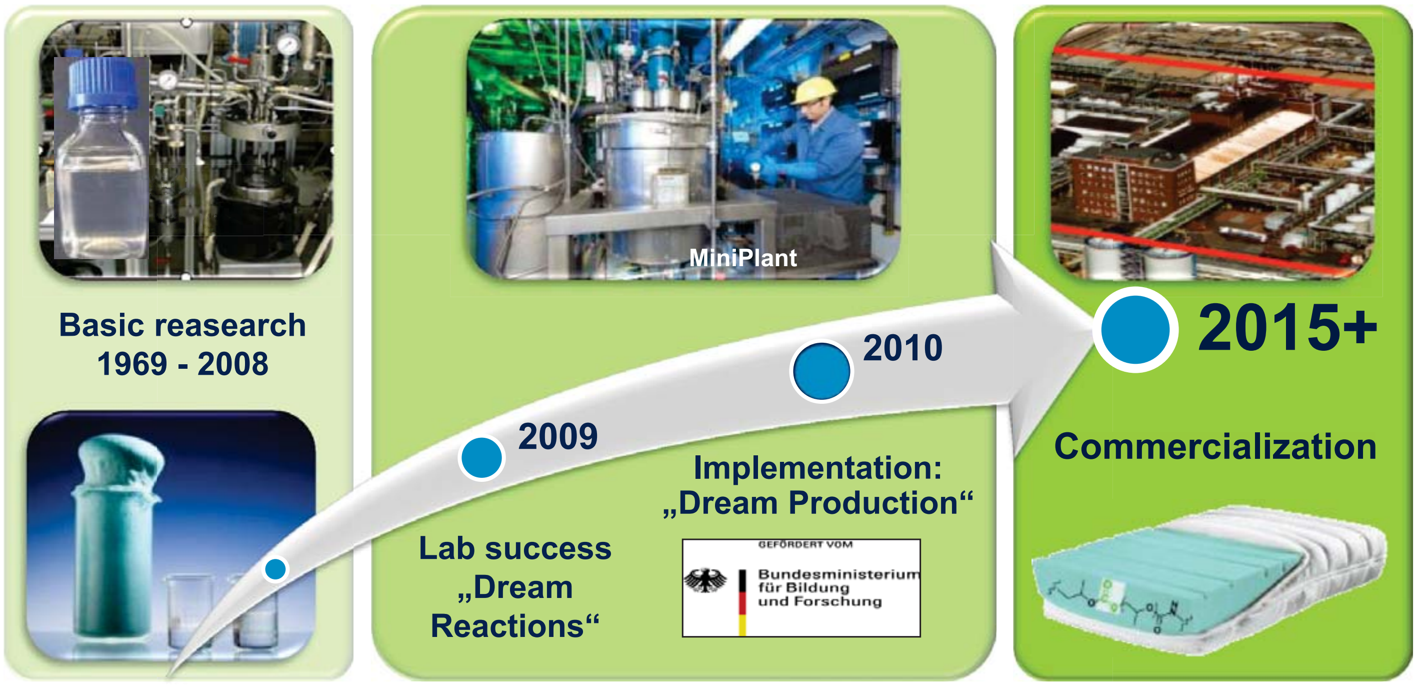
Social
Attract public interest and acceptance in sustainable materials

Economic
Initial investments in assets
Lower raw material needs can lead to a positive business case

- **Utilization of CO_2 as raw material for polymers is a clear contribution to sustainability**
- **Bridging the "valley of death" contributes to the implementation of sustainability technology**

Polyether-Polycarbonate Polyols

Investment into assets would be the next step



Bayer MaterialScience | Bayer Technology Services | CAT | RWTH AACHEN UNIVERSITY

What´s next?

Beyond Dream Production

„Dream Products“ gives access to new materials

eit Climate-KIC

CO_2 scrubbing

Process development

PUR Specialties:
- Fibers

CO_2-PET based polymers:
- Rubber like materials and blends
- Elastic coatings
- Inorganic coatings/Zeolites

Materials and testing

VORWEG GEHEN

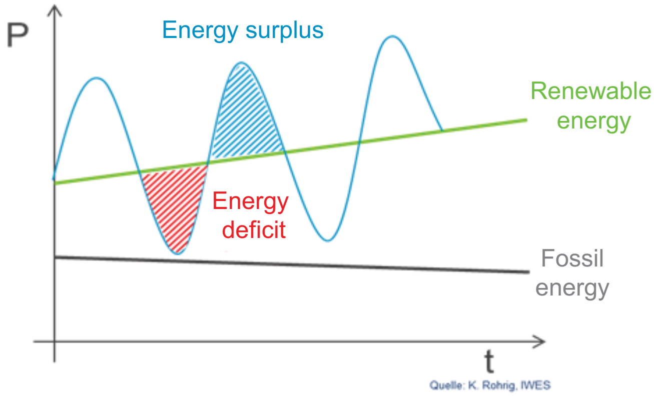
Bayer Technology Services

RWTH AACHEN UNIVERSITY, LTT, ETH, INSTITUT FÜR KUNSTSTOFFVERARBEITUNG, ITA

Fundamental research CAT Catalytic Center RWTH AACHEN UNIVERSITY **Life Cycle Analysis**

Overall funding volume: 2 *Mio* € / 2 years, start 01.01.2013

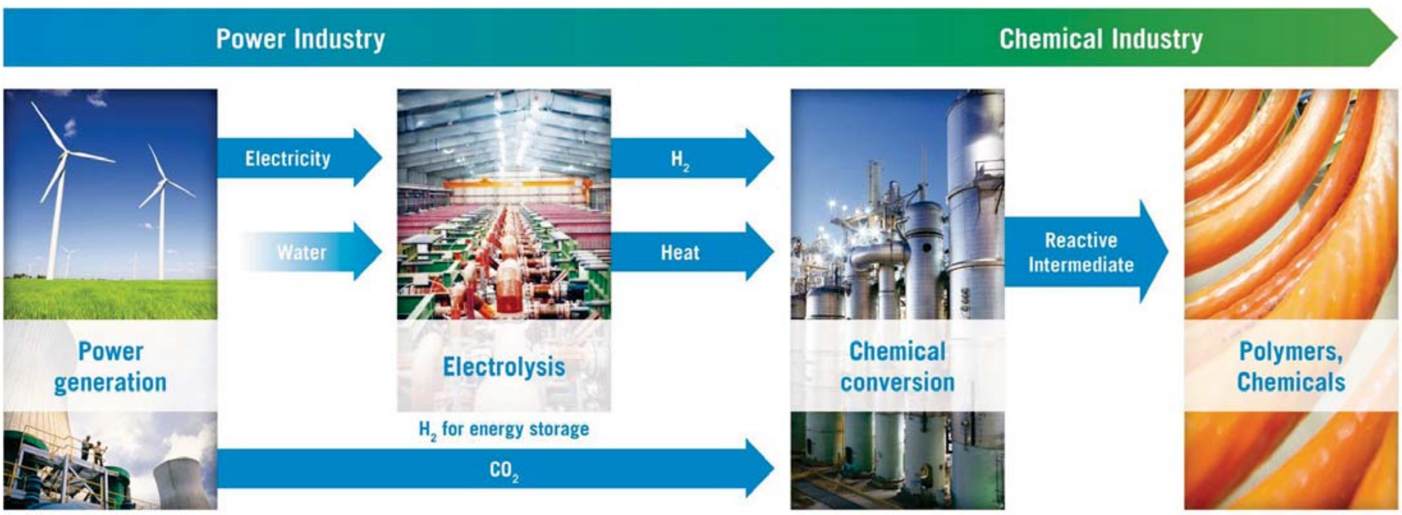
The next step –
using unsteady wind energy



Renewable energy

- First-time integration of renewable energy into chemical industry
- Making use of peak loads for CO_2-based products
- Promotes new forms of energy storage; contribution to "Energiewende"

CO_2RRECT – Wind power to polymer
BMBF Project (BTS lead) develops fundamental technology



VORWEG GEHEN SIEMENS Bayer Technology Services Bayer MaterialScience

Joint development across industry and sector boundaries for a chemical site

Summary

TODAY:

- Support for multidisciplinary research projects (EU, national)
- First examples CO_2-containing high-quality products could already be demonstrated

TOMORROW:

- Sectoral and intersectoral projects as vision for the future
- Support for scale-up and industrialization
- Stable political frame conditions for acceptance and risk mitigation

CaRLa – Catalysis Research Laboratory
CaRLa – a laboratory incorporated in the University of Heidelberg and supported by BASF

Ruprecht-Karls-Universität Heidelberg

BASF The Chemical Company

ACRYLATES FROM ALKENES AND CO_2, THE STUFF THAT DREAMS ARE MADE OF

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European Comission, Climate Action & Joint Research Centre
"CO_2 re-use workshop"
Brussels, 07.06.2013

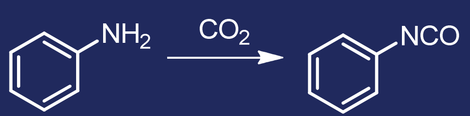
DREAM REACTIONS: UTILIZATION OF CO_2

A *dream reaction* is an economically highly attractive transformation, which is currently unfeasable due to a major scientific/technological challenge

Carboxylation of alkanes

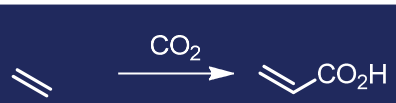
$$CH_4 \xrightarrow{CO_2} CH_3CO_2H \qquad \Delta G_R^0 = +55.0\ kJ/mol$$

$\Delta G_R^0 = +77.4\ kJ/mol$



$\Delta G_R^0 = +306.6\ kJ/mol$

Carboxylation of olefins



$\Delta G_R^0 = +42.7\ kJ/mol$

DREAMS CAN COME TRUE

Ammonia from elements

$N_2 + 3\,H_2 \longrightarrow 2\,NH_3 \qquad \Delta G_R^0 = -32.8$ kJ/mol


Carl Bosch


Historic Reactor

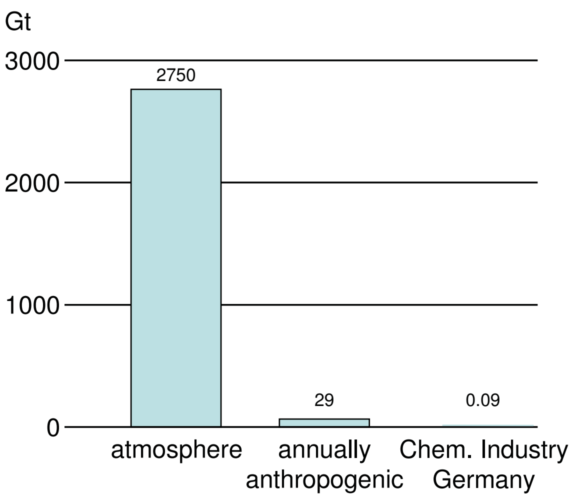

Plant Antwerp


Alwin Mittasch

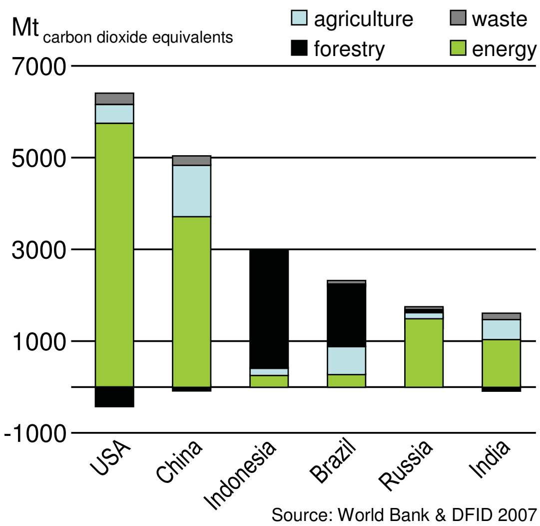
CO_2 AS INDUSTRIAL RAW MATERIAL

Availability

Quantity



Producer

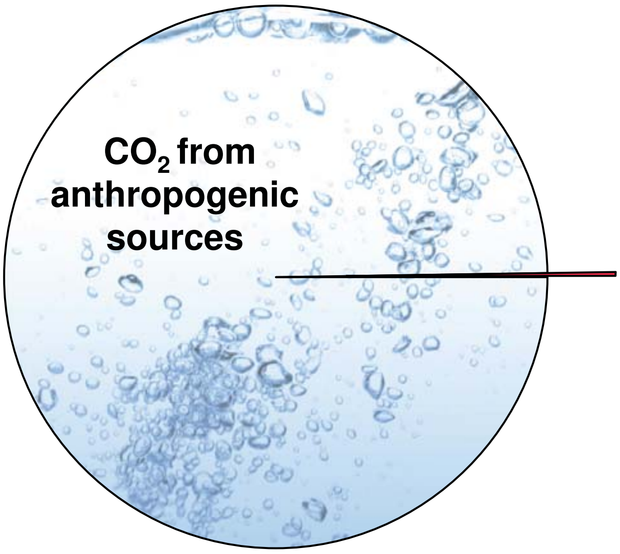


Source: World Bank & DFID 2007

Atmospheric carbon dioxide concentration increased from ~280 ppm in pre-industrial time to today 380 ppm.

Source: Dalton Trans. 2007, 2975

CO_2: USE IN CHEMICAL INDUSTRY



29 GT p.a.

110 MT p.a. = 0.4 % are presently used by chemical industry

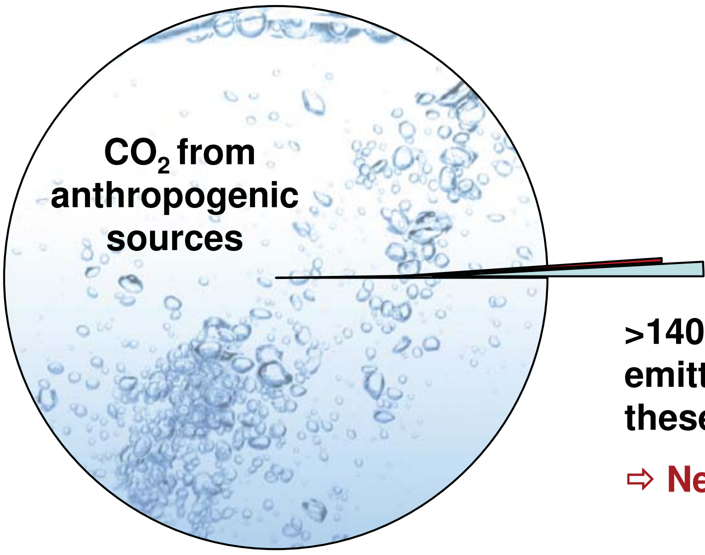
– Urea (70 MT)

– Inorganic carbonates (30 MT)

– Methanol (6 MT)

Source: US Department of Energy; DOE/EIA-0573 Dec. 2009; Data from 2007

CO_2: USE IN CHEMICAL INDUSTRY



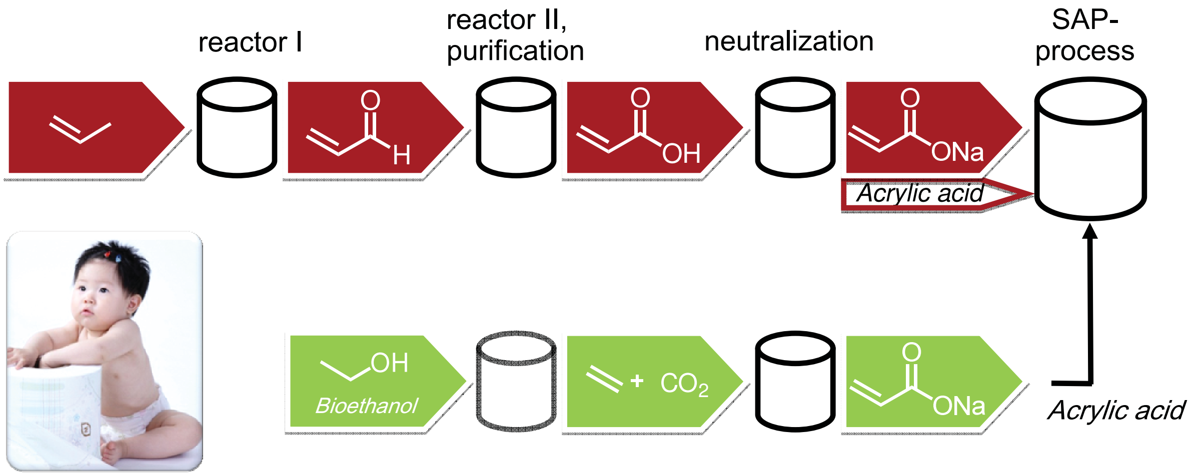
29 GT p.a.

>140 MT p.a. CO_2 are emitted while producing these compounds!

⇨ Net CO_2-production

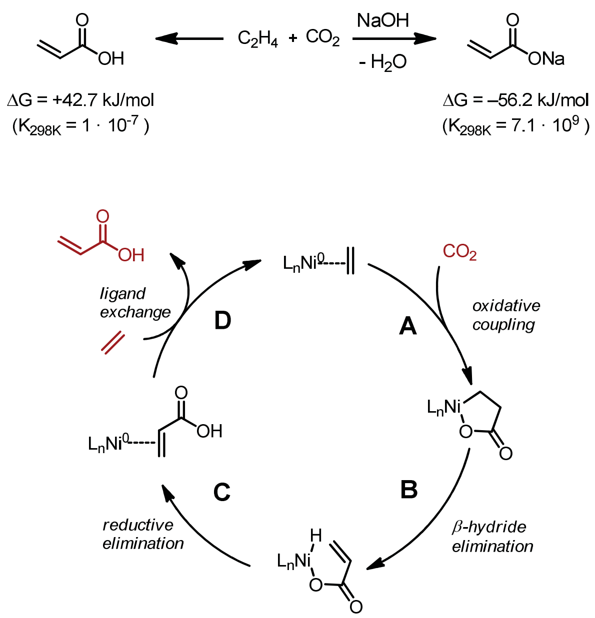
Source: US Department of Energy; DOE/EIA-0573 Dec. 2009; Data from 2007

ACRYLATES OLD & NEW: POTENTIALS



- We expect from a process based on CO_2 and (bio-) ethylen:
  - ~30% raw material advantage
  - significant reduction in investment costs ⇨ liquid phase reaction
  - simplified work-up
- But: **The Reaction does not yet exist (“dream reaction”) !**

THE CHALLENGE!



Walther *et al. Chem. Commun.* **2006**, 2510-2512.

Buntine *et al. Organometallics* **2007**, *26*, 6784-6792.

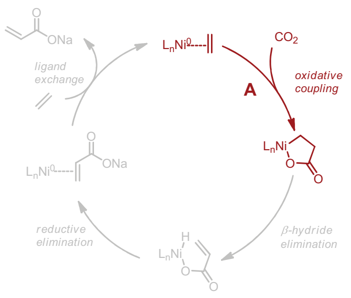
Historic survey

- Long standing problem in literature
- Uncertain mechanism (Walther *et al.*)
- *β*-H elimination as key-step
  - unfavorable thermodynamics to acrylic acid (Buntine *et al.*)
  - high, but not unbearable kinetic barriers (147 kJ/mol)

Challenge after ~30 years of research

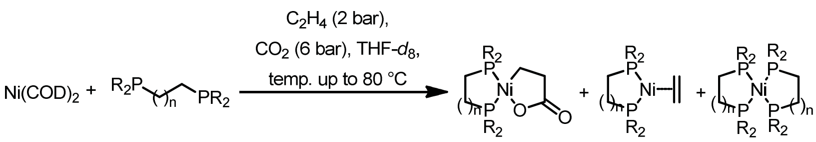
- Oxidative coupling only at –70 °C (**A**)
- No (productive) *β*-H elimination (**B**)
- Unknown Ni-acrylate complexes (**C**)
- No final ligand exchange to re-enter cycle (**D**)

COUPLING OF CO_2 AND ETHYLENE



Key facts

- oxidative coupling so far only observed for DBU as ligand at –70 °C
- selected ligands require exact stoichiometry of CO_2



1a-f **2a-f** **3a-f** **4a-f**

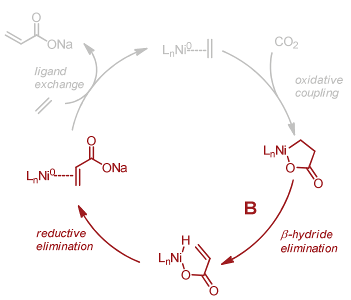
Key findings

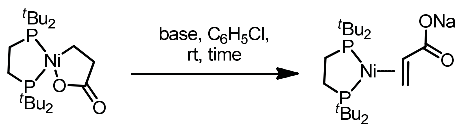
- identification of d*t*bpe ligand by systematic variation of backbone and substitution at the donor atom
- d*t*bpe ligand enables formation of lactones **2** and ethylene complexes **3**
- optimal lactone yield of 73% at 45 °C within 24 h ($p(CO_2/C_2H_4)$ = 40/5)
- **no need for low temperature** (*cf.* Hoberg)

Entry	1a-f	R	n	Yield **2a-f** (%)	Yield **3a-f** (%)	Yield **4a-f** (%)
a	dppm	Ph	0	0	0	0
b	dppe	Ph	1	0	0	65
c	dppp	Ph	2	0	0	24
d	d*t*bpm	*t*Bu	0	60 (0)[a]	40 (100)[a]	0
e	d*t*bpe	*t*Bu	1	35	62	0
f	d*t*bpp	*t*Bu	2	0	97	0

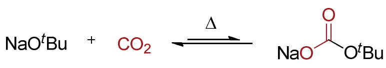
[a]Yield by ^{31}P NMR in brackets after release of CO_2 pressure.

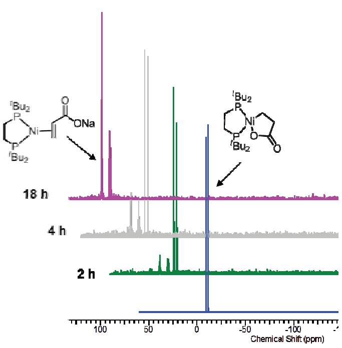
PRODUCTIVE CLEAVAGE OF LACTONES





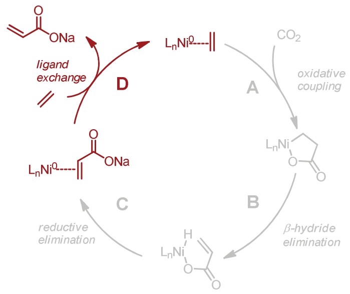
Base	Additive	Time [h]	Temp. [°C]	Yield
NaOMe	–	24	50	50
PhONa	–	72	70	0
NBu_4OMe	–	72	70	10
NBu_4OMe	NaBARF	24	50	75

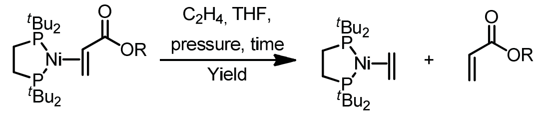




- productive cleavage of lactone with broad range of bases, if
  - anion has sufficient pK_B **and**
  - cation is Lewis acidic (*e.g.* Na^+ but not NR_4^+)
- biphasic reaction prevents polymerization of Na-acrylate, facilitates catalyst separation
  - Na-acrylate and base soluble in polar phase
  - organometallic species soluble in unpolar phase
- but: strong bases “love“ CO_2

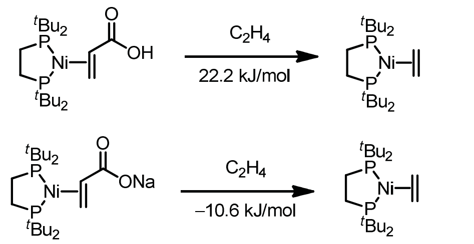
FINAL LIGAND EXCHANGE

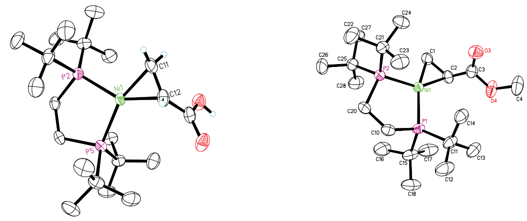




R	Pressure [bar]	Time [h]	Yield (%)
H	8	18	6
Na	8	18	93
Na	30	0.25	95

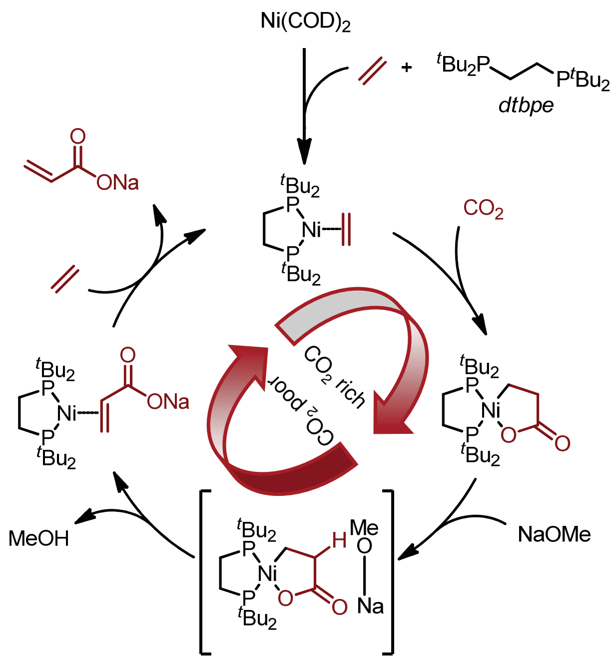
- unproductive substitution of acrylic acid π-complex via loss of CO_2 at > 60 °C
- successful substitution of Na-acrylate π-complex by ethylene

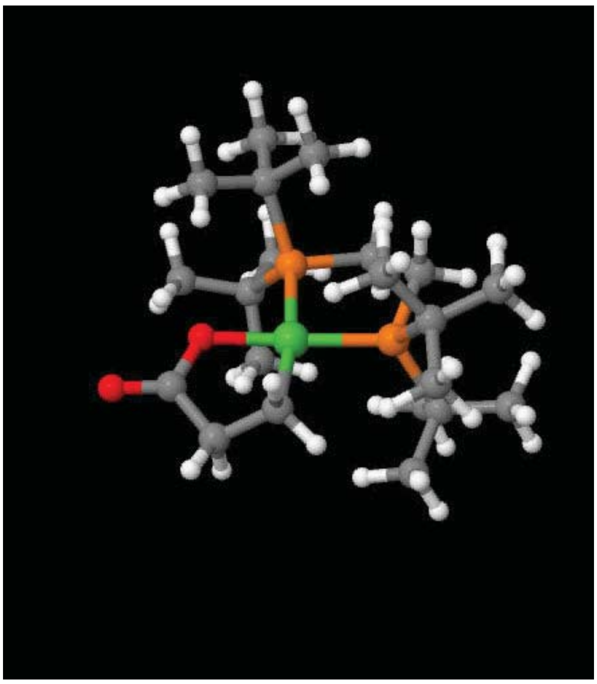




COSMO-RS BP86/def2-TZVP//BP86/def2-SV(P))

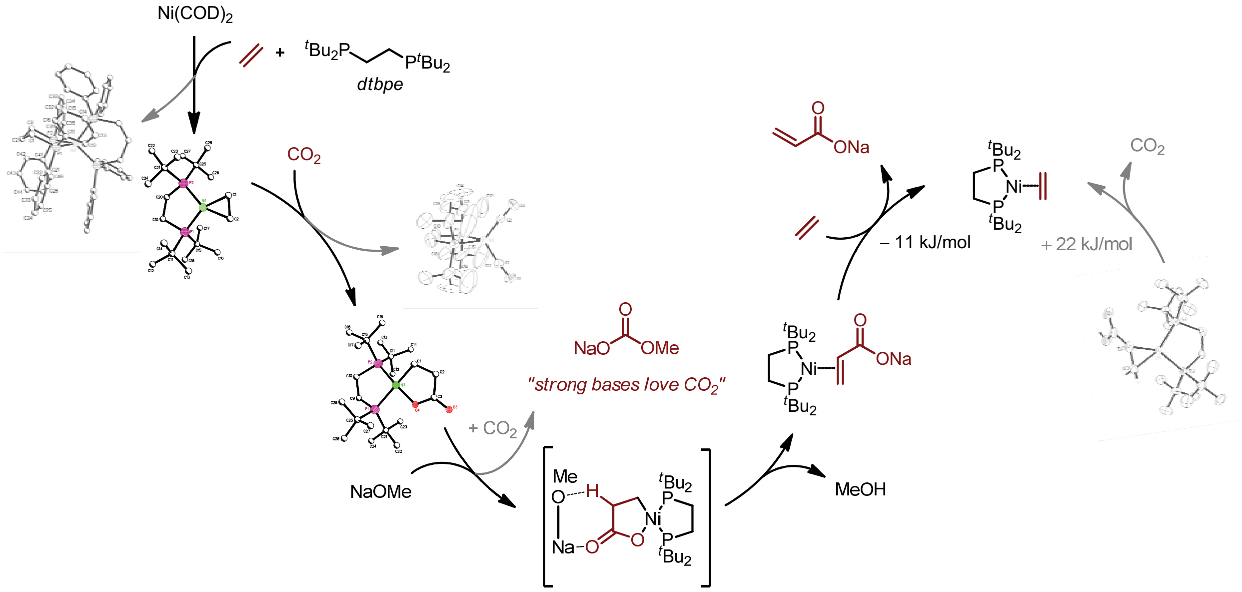
THE FIRST FULL CATALYTIC CYCLE





- Clearly catalytic reaction (TON 10) in two separate steps

HANDS ON THE ELEMENTARY STEPS



Oxidative coupling

- Rich chemistry of Nickel (*i.e.* detours and dead-ends) but
- Suitable ligand (d*t*bpe) enables selective reaction

Lactone cleavage

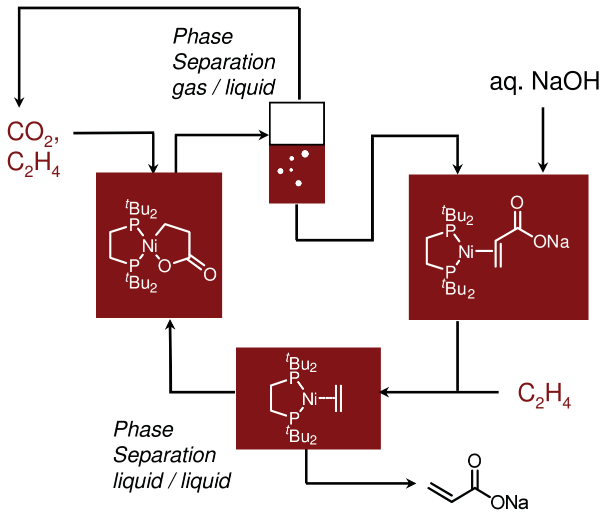
- Productive cleavage with bases, of
- Sufficient basicity **and** Lewis acidity

Final ligand exchange

- Successful substitution of π-complex by ethylene
- Loss of CO_2 from acrylic acid π-complex

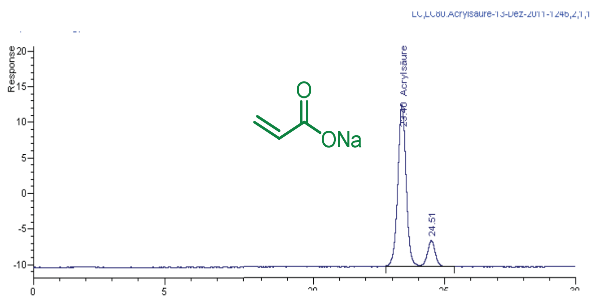
CONCLUSIONS

Process Scheme



After ~2 years of research

- Catalytic cycle closed for first time ever (TON 10, two steps) ✓
- d*t*bpe ligand enables isolation and characterization of all relevant intermediates
  - not best ligand for catalysis!
- Na-acrylate as only organic product, no need for stabilizer

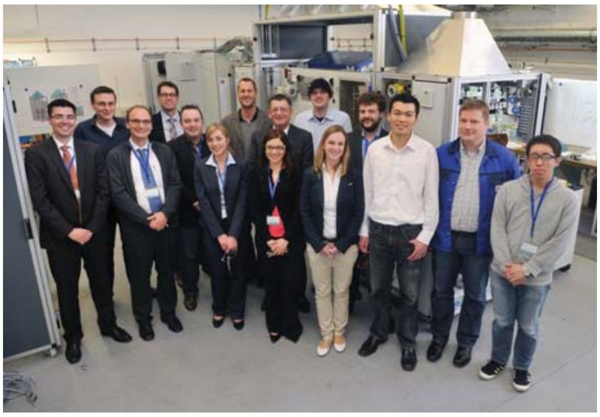


Interested in more information?

- Limbach *et al.*, *Chem. Eur. J.* **2012**, *18*, 14017 – 14025.

ACKNOWLEDGMENT

Happy (Lucky) Team



CaRLa
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S. Kraus (TUM)

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P. Hofmann (Univ. of Heidelberg)
L. Weigel (Univ. of Heidelberg)

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GEFÖRDERT VOM

CO_2 Mineralisation
- a scalable & profitable approach to industrial CCS

Michael Priestnall
CEO, Cambridge Carbon Capture Ltd
Industry Chair, Mineralisation Cluster, UK CO2Chem Network
CO2 Re-Use Workshop (JRC DG CLIMA)
Brussels, 7th June 2013

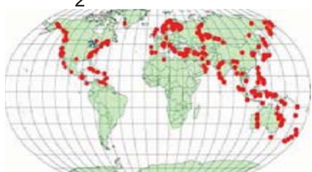
CCC is a Cambridge-based, early-stage venture company developing a unique, profitable Mineral Carbonation process to sequester flue-gas CO_2 directly & permanently as magnesium carbonates.

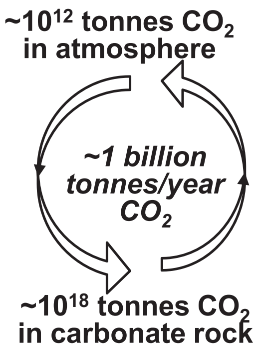
What is Mineral Carbonation ?
Earth's natural carbonate-silicate cycle

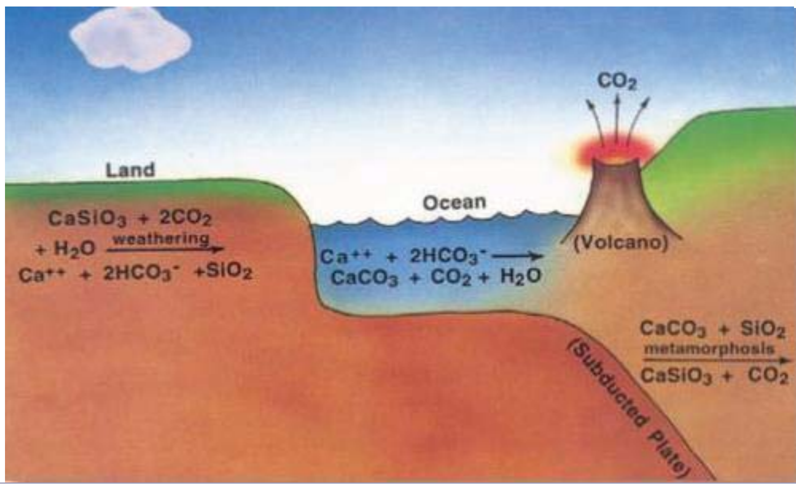
Mineral carbonation refers to the conversion of silicates to solid carbonates, mimicking the natural process by which CO_2 is removed from the atmosphere

Wollastonite:	$CaSiO_3 + CO_2 \rightarrow CaCO_3 + SiO_2$	dH = -90kJ/molCO_2
Olivine:	$Mg_2SiO_4 + 2CO_2 \rightarrow 2MgCO_3 + SiO_2$	dH = -89kJ/molCO_2
Serpentine:	$Mg_3Si_2O_5(OH)_4 + 3CO_2 \rightarrow 3MgCO_3 + 2SiO_2 + 2H_2O$	dH = -64kJ/molCO_2

- Primary process by which carbon dioxide is removed from the atmosphere
  >99% world's carbon reservoir is locked up as limestone & dolomite rock – **$CaCO_3$ & $MgCO_3$**
- Thermodynamically favourable, but kinetically slow







OMAN: 70,000km^3 of 30% olivine; sufficient to mineralise centuries of global CO_2 emissions.

KEY MESSAGES about CO_2 mineralisation

Get the support & enabling policies right & Mineral Carbonation can deliver:

- Commercial deployment of industrial CO2 sequestration, with potential for giga-tonne CO2 scale
- Learning-curve cost reduction through market-driven volume deployment with no/low carbon price
- Economically viable distributed CCS(M) across the range from car & ships to industry & power
- MC opportunity is more about a disruptive alternative to (G)CCS than “using” CO2
- Without targeted R,D&D & policy support, commercial MC will remain niche & not reduce CO2

Situation today – already commercially niche deployed, but in the *very* slow-lane:

- Niche commercial deployment based on materials valorisation models (even paying for CO2), but very few investors or customers willing to engage with development costs & technical & commercial risks
- Multiple technical approaches with different business models – dangerous to pick “winners”
- Commercial developers & academic researchers are starved of R,D,D&D funding
- Major R&D questions still to be addressed – “downhill” process, but CO2 LCA uncertain
- Increasing academic research, but weakly coordinated & communicated, & little funding

Next-step needs – demonstration funding & industry-academia R&D collaboration:

- Multiple FOAK & NOAK commercial demonstrations required (lots of small projects)
- R&D agenda defined bottom-up by industry needs rather than by top-down CCS policy – economic viability first; CO2 LCA viability second; large-scale CCSM third
- More interdisciplinary R,D&D collaborations; industry partnership critical; funding is critical – process chemists, engineers, modellers, geochemists; mining, metals, minerals, cement, steel, waste, chemicals
- R&D & industry network needed to improve knowledge sharing; more R&D centres = more processes
- Level the playing field with geo-CCS (MC is generally outside scope of CCS programs)
- Policy mechanisms needed to valorise CO_2-sequestration independently of emissions reductions

Key R, D & D Challenges – considerable work still to do

- Process engineering design to offset process energy inputs against reaction energy outputs
- LCA to accurately assess net energy usage/output, net CO2 sequestered
- Assessment of capex & opex – expert engineering design studies & demos needed to answer
- New processes that maximise kinetics of both activation of feedstock minerals and of carbonation while minimising energy/chemicals inputs; and avoiding creation of any wastes
  - Modelling of thermodynamics & kinetics of process steps
  - Particular energy intensity issues: evaporation of solvents; crystallisation/recovery of chemicals; sequential consumption of acids and bases
- Electrochemical approaches for both recovery of carbonation energy and chemicals recovery
- Development of processes optimised to use flue gas directly rather than pre-captured CO2
  - More research to investigate kinetics and thermodynamics in gas-solid and aqueous phase carbonation of magnesium (hydr)oxides and salts at low pCO2
  - Effects of flue gas impurities on product qualities
- CCSM potentially involves huge volumes of materials – better understanding of materials qualities, market requirements, volumes and prices needed versus MC process options
  - Processes optimised for different feedstocks
  - Processes optimised for different product outputs
  - Research on effects of seawater as solvent system for large-scale CCSM
  - Processes optimised for different market applications and scales of operation
- Much greater funding needed for interdisciplinary R&D and for multiple commercial demos
  - Process concepts need to be reduced to engineering practice and evaluated at pilot scale
  - Disparate R,D & D activities currently, due to sub-critical, fragmented sector, needs coordination and investment to develop a critical mass of activity; dedicated conferences and journals needed

KEY PERFORMANCE CHARACTERISTICS

Energy & CO2 balance

- Overall energy released = ~70kJ per mole CO_2 sequestered (i.e. ~20% additional to burning coal)
- Energy inputs = to speed up reaction kinetics; to recover chemical reagents (essential to minimise)
- Low-grade energy released, high-grade energy used (essential to recover energy)

Materials Inputs

- Direct dilute flue-gas *not* pre-captured CO2 (except for in-situ MC & early demonstrations)
- Wastes, minerals & chemicals that contain CaO / MgO (& some other niche options)
- Acids to solubilise Mg, Ca ions (& increase reaction kinetics)
- Alkalis to adjust pH, capture CO_2, precipitate carbonates and/or solubilise silica (& increase kinetics)
- 1-7 tonnes mineral feedstock required per tonne of CO_2 sequestered

Materials Products

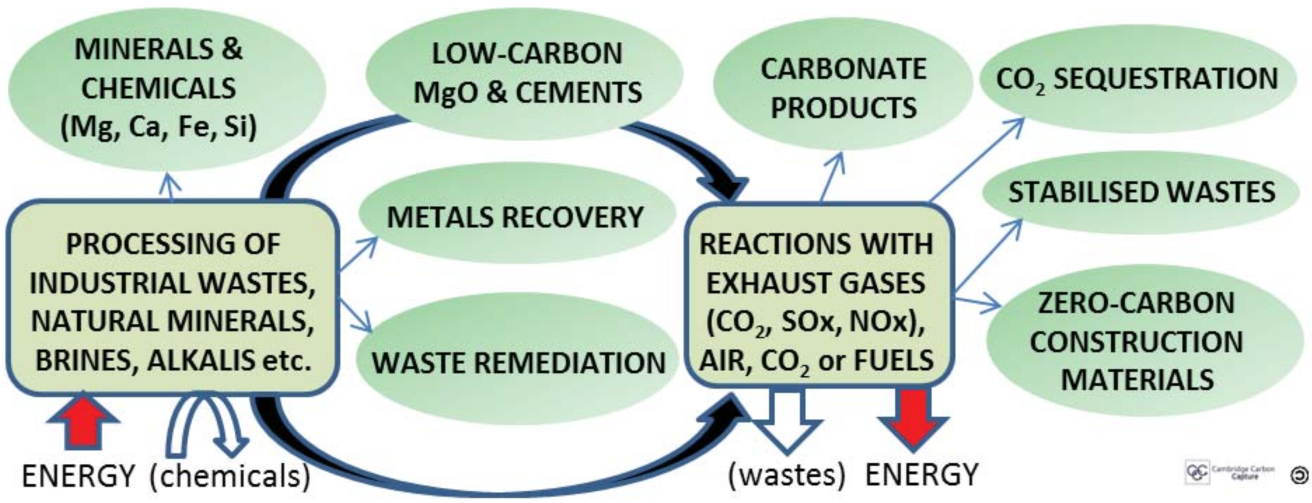
- Silica (either combined with low-value carbonate product or separated as pure high-value product)
- Magnesium (or Ca) chemicals (hydroxide, oxide, chloride, sulphate - potential process intermediates)
- Magnesium (or Ca) carbonates (low-grade mixed solids; or high-purity grades; or construction products)
- 2-10 tonnes materials products per tonne of CO_2 sequestered

Materials Values

- Feedstocks: -€100 to +€15 per tonne (-€1000 to +€30 per tonne of CO_2 sequestered)
- Silica: 0-€1000 per tonne (0-€3000 per tonne of CO_2 sequestered)
- Mg/Ca chemical intermediates: 0-€500 per tonne (0-€3000 per tonne of CO_2 sequestered)
- Carbonates: -€5 to +€500 per tonne (-€40 to +€3000 per tonne of CO_2 sequestered)

Business Case: commercial drivers for Mineral Carbonation

negative-value wastes – high-value materials & chemicals products – CO_2 sequestration




Alcoa: red mud waste stabilisation

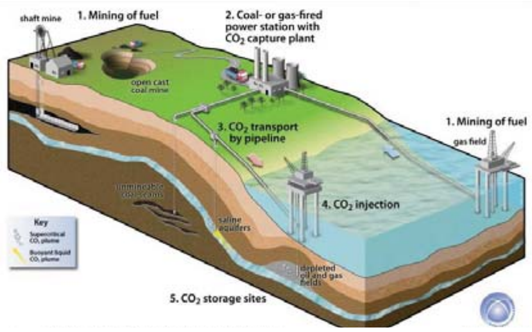

C8S: APC wastes to building blocks

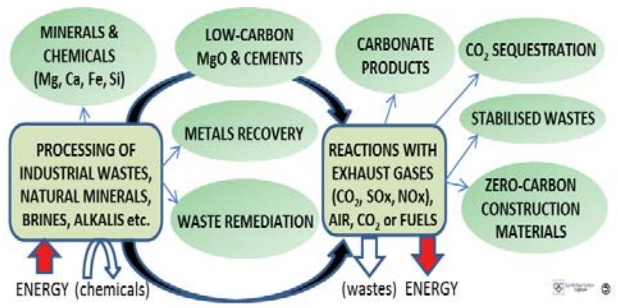
CCC: olivine-to-$Mg(OH)_2$ & SiO_2 for scalable CCS

Mineral Carbonation versus Geological CCS

Mineral carbonation is an energy-generating & scalable CO_2-sequestration alternative to the capture, separation, purification, compression, transport and storage of gaseous/liquefied CO_2 that is associated with geo-CCS.

Geological CCS	Mineral carbonation





- × 30% cost and energy penalty
- × More expensive than nuclear or on-shore wind; infrastructure dependent
- × Estimated €40-90/tonne* CO_2 versus lower ETS price
- × Public acceptance issues
- ✓ Relatively well developed & demonstrated technology

- ✓ Stand-alone without CO2 infrastructure
- ✓ Stable, safe solid products
- ✓ Product materials are commercially useful
- ✓ Wastes can be used as inputs
- ✓ Already commercially deployed in niche applications without CO2 price
- × energy intensive mineral processing steps
- × Huge materials volumes to handle/sell/store

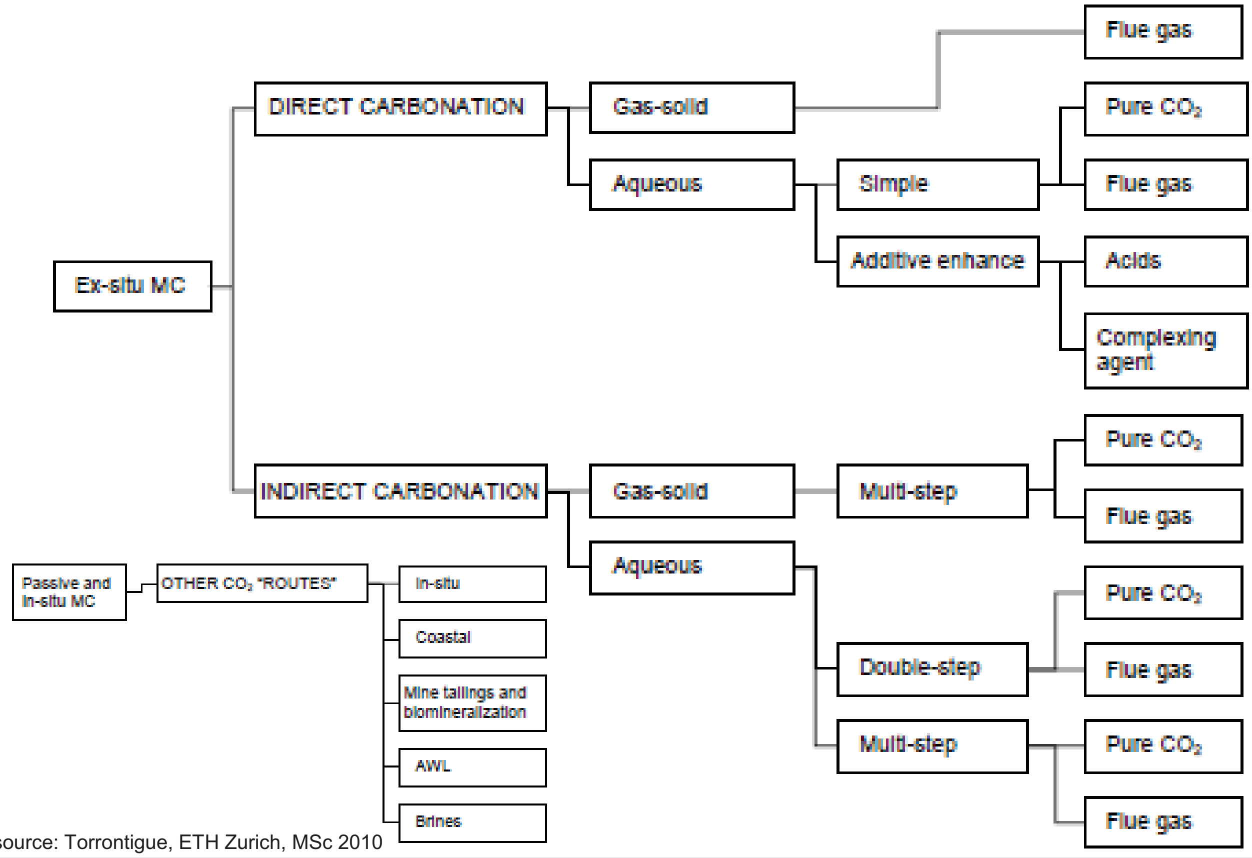
* Source: McKinsey

Giga-tonnes of Carbonate products – where would they all go?

* very approximate market data	Million tonnes/yr (USA)	$/tonne (USA)	US annual Market $billion	Global estimate $billion
Mineral fillers	100	100	10	100
Soil stabilisation	100	30	3	30
Light wt aggregate	200	40	8	80
Sand & aggregate	3000	7	21	210
cementitious materials	24	60	1.4	14
bricks	20	20	0.4	4
drywall	20	25	0.5	5
Concrete blocks	50	30	1.5	15
cement	120	80	10	100
Masonry cement	4	1000	4	40

*source: Calera, 2009

Ex-Situ Mineral Carbonation – multiple technical approaches*



*source: Torrontigue, ETH Zurich, MSc 2010

Mineral Carbonation - a range of technical approaches & 20yrs R&D

- Essentially: CO_2 + source Ca/Mg/Fe = limestone / HCO_3^-
  - pH, temperature, water, pCO2, source: phase, chemistry, size
  - exothermic, but more energy is needed to overcome kinetics
  - wastes much easier than natural rocks, but rocks more available than wastes
  - Ca much easier than Mg, but Mg (serpentine, olivine, brines) more available than Ca (wollastonite, brines)

- Gas-solid phase reactions (easiest, most developed, commercial operations):
  - mill to <75um, heat ~650C and/or acid/base digestion (~100C) required to activate serpentine for carbonation; pure CO_2(g) + activated serpentine = aggregates (slow & energy intensive)
  - dilute CO_2(g) + combustion ashes = aggregates + heat (very easy, but not scalable)
  - mine tailings: natural atmospheric carbonation 1-50 kt/CO_2/yr per mine site – rate-limited by silicate mineral dissolution & depends on local climate [Dipple, 2009 - study at four Canadian & Australian sites]

IPCC Shell

Carbon8 ltd

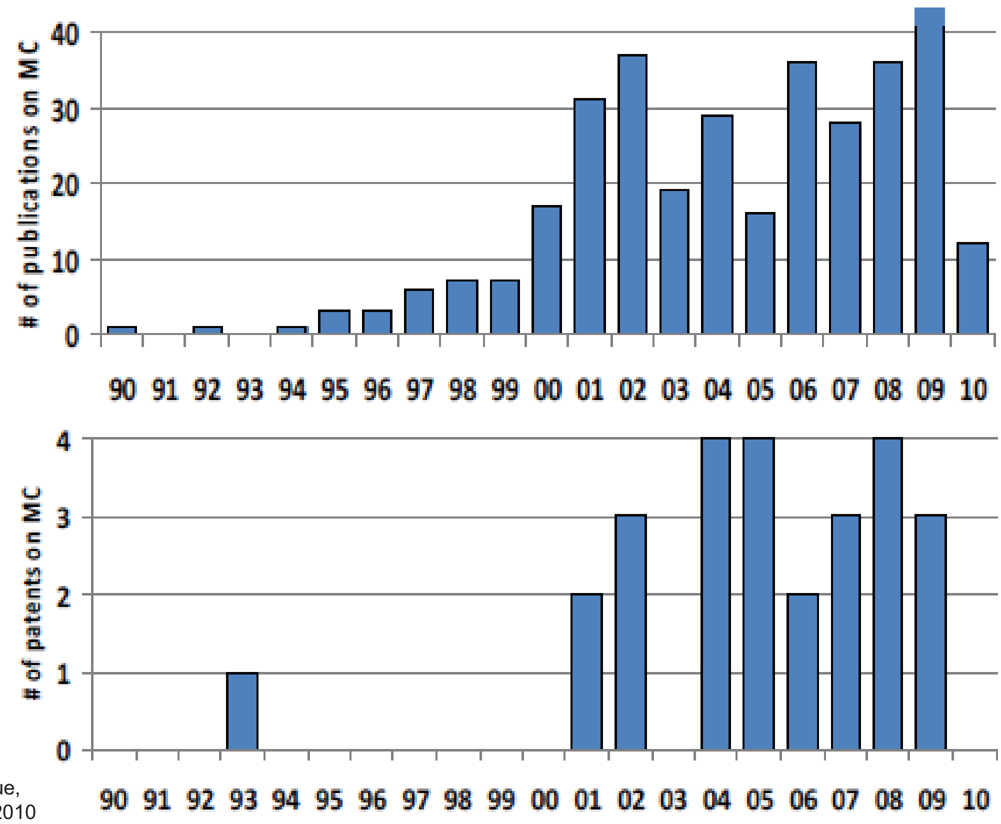
- Aqueous-phase (lowest energy, less developed, +chemicals, attractive economics):
  - chemical activation/digestion of silicates or wastes to generate Ca/Mg salts or ions
  - brines & liquid waste sources of Ca/Mg ions
  - direct capture of CO2 from flue gases into alkaline solution, brines & $Mg(OH)_2$
  - selective precipitation of product carbonates & by-products & cementitious phases
  - overall: CO_2 + water(high pH) + Ca/Mg salts = (bi)carbonates + silica + residual metals (typically ~80-150C & ambient to high-pressure)
  - closed-cycle, pH-swing ammonium bisulphate digestion at 80C & carbonation to convert $Mg_3Si_2O_5(OH)_4$ to high-purity $MgCO_3$, SiO_2 & Fe
  - direct NaOH or KOH digestion of silicates to form solid $Mg(OH)_2$ & $Ca(OH)_2$

Calera, Alcoa, CU Eng / MSM

ETI

CCC

Mineral Carbonation - small R&D base, but increasing activity



*source: Torrontigue, ETH Zurich, MSc 2010

Some Commercial Activities in Mineral Carbonation

Economic feasibility is (slowly) driving worldwide Mineral Carbonation development

- **China Huaneng & Peabody** – Xiliguole (mongolia) 1.2GWe supercritical coal using mineral carbonation (Calera technology) coupled to local building materials production
- **UK ETI** – £1m 2011-13 study on “mineralisation opportunities” (Shell, Caterpillar, BGS, CICCS)
- **USDoE** – CO_2 Mineral Sequestration working group: (ARU, ASU, LANL, NETL, PSU, SAIC, UU)
- **Shell** – 8yrs development of a flue-gas de-carbonation slurry process: heat/steam-activated serpentine powder in slurry to strip CO_2 then heat & pressure & separate carbonate solids
- **Alcoa** – Kwinana commercial plant carbonating red mud slurry waste to reduce storage costs
- **Carbon Sense Solutions** – Canadian manufacturer using CO2 to fast-cure building blocks
- **EnPro** – developing 24,000tonne CO2/yr capture into alkaline wastes project in Norway.
- **Calera** – early VC-backed California start-up developing commercial carbonation of waste hydroxides & brines; low-energy electrolysis of brine to create base for CO_2 capture; focused on selling/qualifying products for cement and construction industry; Australia (Latrobe) & Mongolia
- **Skyonic** – building $25m Texas pilot plant to capture flue gas to convert sodium hydroxide (optionally via electrolysis) to NaHCO3 (dried product for sale); life-cycle CO_2 unclear
- **Carbon8** – UK venture with simple profitable process for conversion of low-pressure CO_2 to building aggregate by direct carbonation of wet mix of hazardous APC wastes + quarry fines
- **Cambridge Carbon Capture** – CO2 sequestration via olivine-to-brucite & silica; CO2 fuel cell
- **Cquestrate / Oxford Geo-Engineering** – focused on net CO_2 capture from atmosphere as ocean bicarbonate via liming of oceans
- **Integrated Carbon Sequestration Ltd** – Australian developer of flue-gas de-carbonation via ammonia + activated serpentine (similar to Shell)
- Others – **Novacem** (Mg cement), **Calix** (MC materials), **GreenMag** (processes), **Oman** projects

(Some) UK R&D Activities in CO2 Utilisation via Mineral Carbonation

- **ETI** – £1m 2011-13 study on "mineralisation opportunities" (Shell, Caterpillar, BGS, CICCS)
- **Shell** – 8yrs development of a flue-gas de-carbonation slurry process: heat/steam-activated serpentine powder in slurry to strip CO_2 then heat & pressure & separate carbonate solids
- **Nottingham University & BGS** - partnership on CCS R&D with strong component of mineral carbonation science; recent partner with ETI mineral carbonation project
- **Greenwich University –** £1m award (2013) for EU collaborative project on carbonation of wastes
- **Carbon8** – UK venture (spin-out of Greenwich) building second commercial mineral carbonation plant (building blocks made via low-pCO_2 carbonation of hazardous wastes)
- **Cambridge Carbon Capture** – CO2 sequestration via olivine-to-brucite & silica; CO2 fuel cell
- **Oxford University / Cquestrate** – open source collaboration focused on net CO_2 capture from atmosphere as ocean bicarbonate via liming of oceans
- **Southampton University** – growing strong team in mineral carbonation; in-situ & ex-situ and ocean processes
- **Herriot Watt** – new centre of expertise in CCSM R&D with recruitment of Prof Maroto-Valer
- **Sheffield University** – R&D in cement, waste and olivine carbonation processes
- **Cambridge University** – olivine-to-brucite process; also carbonate looping
- **Novacem (Imperial spin-out)** – CO2 sequestration via magnesia cements; significant early-stage developer with industrial partners, recently went bust & assets acquired by Calix
- **Conoco Philips, BP** – major investors in Skyonic (building mineral carbonation plant in Texas)
- **Newcastle University** – novel bio-catalysis of aq-phase mineral carbonation
- **Others** – Leeds, Birmingham, West of Scotland, Arup, MIRO, Sibelco, & more…

CCC process schematic – digestion step 1

(alkaline digestion of serpentine or olivine to convert to brucite & silica)

USP: profitable, low-energy, silicate digestion process

PROCESS COSTS:
€12 0.8t olivine
€105 0.5t NaOH
(/tCO_2 sequestered)

Overall: $Mg_2SiO_4 + 2H_2O \Rightarrow 2Mg(OH)_2 + SiO_2$ dH=-12kJ dG=+9kJ

(1) $Mg_2SiO_4 + 2NaOH + H_2O \Rightarrow 2Mg(OH)_2 + Na_2SiO_3$ dH=-115kJ; dG=-68kJ

(2) $2Na^+ + SiO_2(OH)_2^{2-} \Leftrightarrow SiO_2(ppt) + 2Na^+ + 2OH^-$ dH=+12kJ; dG=+5kJ

MINERAL MINE

INDUSTRIAL WASTE

(€105) NaOH re-cycle

energy

Digestion of mineral silicates (180C, 1atm, 3hrs) (1)

Separation of Mg(OH)2 from alkali silicate (aq. filtration)

(£174) 0.7t Na_2SiO_4

Precipitation of silica & trace metals recovery (2)

TRACE METALS

€19 .2%Ni

heat

water re-cycle

$Mg(OH)_2$

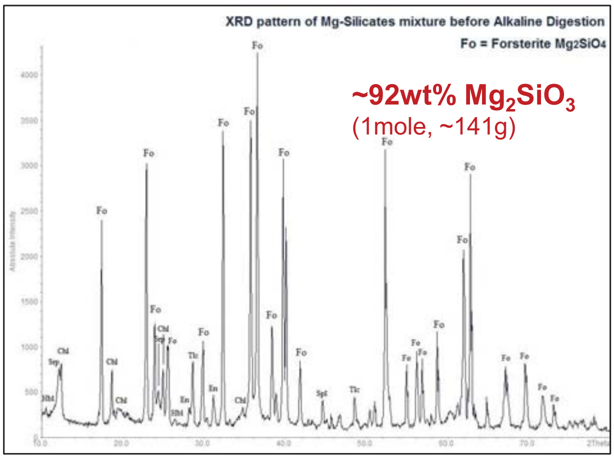
(€133) 0.7t

SiO_2

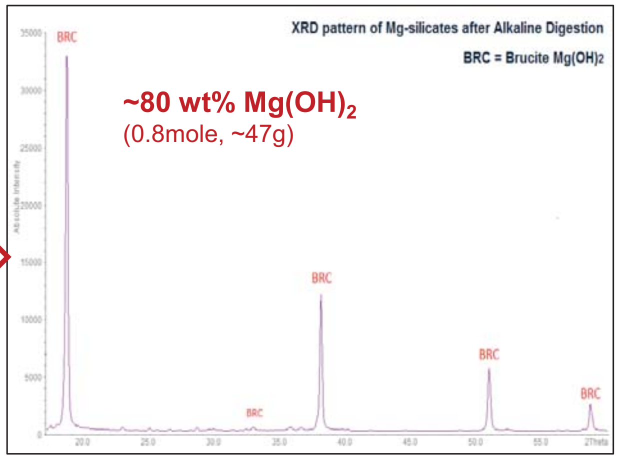
€205 0.3t APS

CCC Process: Olivine-to-Brucite conversion at high-pH

Before Digestion



After Digestion



single-step, fast, low-energy conversion of magnesium silicate to magnesium hydroxide e.g. low-carbon alternative to portlandite

Cambridge Carbon Capture

CCC process schematic – carbonation step 2

(direct carbonation of brucite (magnesium hydroxide) with flue-gas into ocean or products)

Overall: $2Mg(OH)_2 + 4CO_2 \Rightarrow 2Mg(HCO_3)_2$ dH=-268kJ dG=-140kJ

③ $4CO_2 + 4OH^- \Rightarrow 4HCO_3^-$

④ $2Mg(OH)_2 + 4HCO_3^- \Rightarrow 2Mg(HCO_3)_2 + 4OH^-$

Diesel exhaust

$Mg(OH)_2$

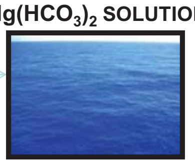
(€133)
0.7t

③ ④ Sequestration via formation of soluble magnesium bicarbonate in seawater (or reaction to solid $MgCO_3$)

decarbonised flue-gas

€35 1t CO_2

$Mg(HCO_3)_2$ SOLUTION



Heat , or

CARBON-FREE ELECTRICITY via FUEL CELL

…alternatively,

$MgCO_3$ Powder

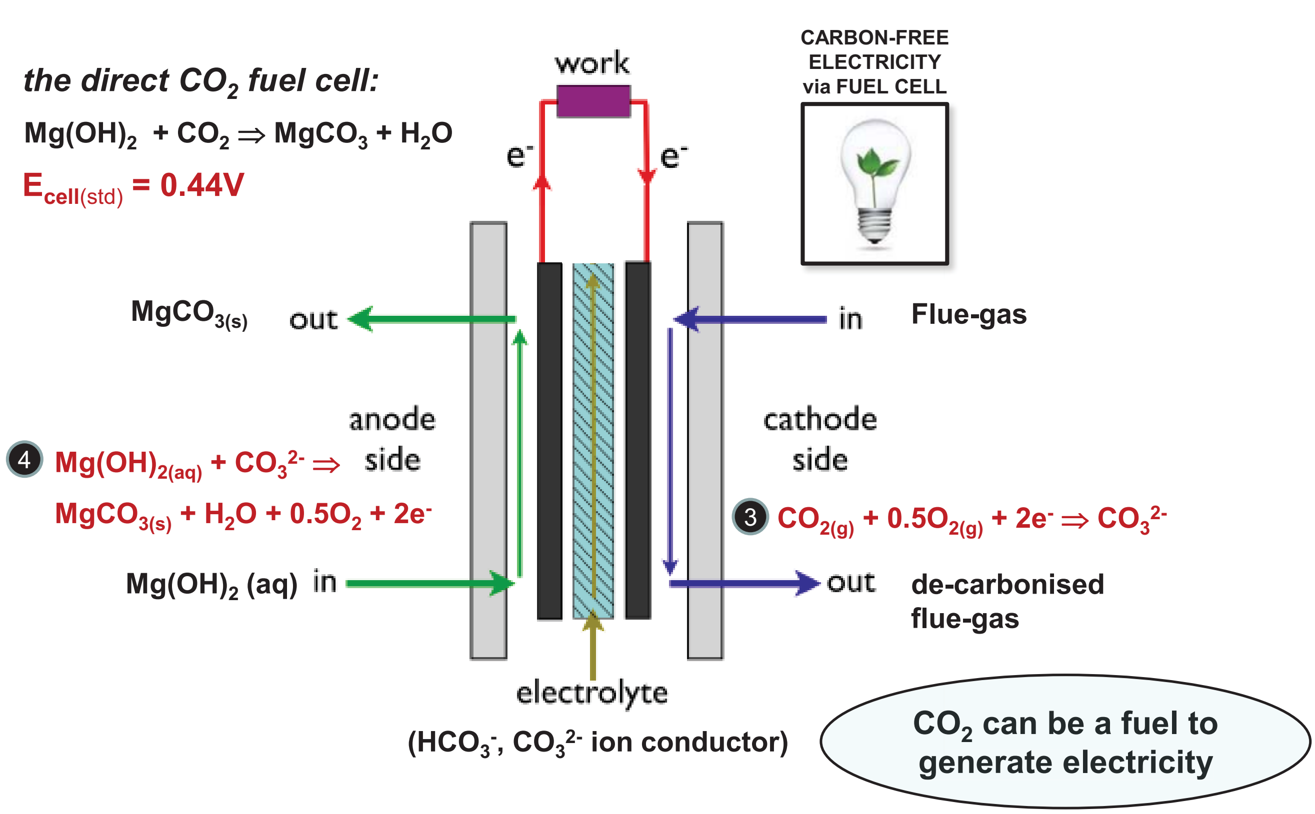
€192 1t

USP: "zero-carbon", "zero-cost" permanent CO_2 capture & storage

Cambridge Carbon Capture

Electrochemical Mineral Carbonation – option for carbonation step 2

(energy of carbonation recovered as carbon-negative electricity via direct CO2 fuel cell)



KEY MESSAGES …again

Get the support & enabling policies right & Mineral Carbonation can deliver:

- Commercial deployment of industrial CO2 sequestration, with potential for giga-tonne CO2 scale
- Learning-curve cost reduction through market-driven volume deployment with no/low carbon price
- Economically viable distributed CCS(M) across the range from car & ships to industry & power
- MC opportunity is more about a disruptive alternative to (G)CCS than “using” CO2
- Without targeted R,D&D & policy support, commercial MC will remain niche & not reduce CO2

Situation today – already commercially niche deployed, but in the *very* slow-lane:

- Niche commercial deployment based on materials valorisation models (even paying for CO2), but very few investors or customers willing to engage with development costs & technical & commercial risks
- Multiple technical approaches with different business models – dangerous to pick “winners”
- Commercial developers & academic researchers are starved of R,D,D&D funding
- Major R&D questions still to be addressed – “downhill” process, but CO2 LCA uncertain
- Increasing academic research, but weakly coordinated & communicated, & little funding

Next-step needs – demonstration funding & industry-academia R&D collaboration:

- Multiple FOAK & NOAK commercial demonstrations required (lots of small projects)
- R&D agenda defined bottom-up by industry needs rather than by top-down CCS policy – economic viability first; CO2 LCA viability second; large-scale CCSM third
- More interdisciplinary R,D&D collaborations; industry partnership critical; funding is critical – process chemists, engineers, modellers, geochemists; mining, metals, minerals, cement, steel, waste, chemicals
- R&D & industry network needed to improve knowledge sharing; more R&D centres = more processes
- Level the playing field with geo-CCS (MC is generally outside scope of CCS programs)
- Policy mechanisms needed to valorise CO_2-sequestration independently of emissions reductions

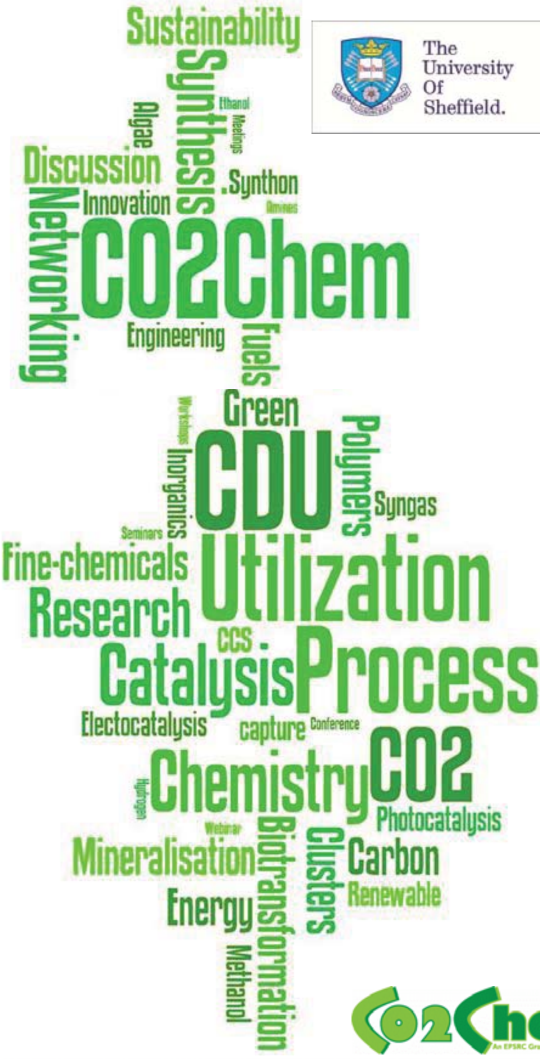
***"CCC objective:* to develop, deploy & operate profitable solutions for industrial customers to permanently sequester CO_2 via conversion of wastes into valuable minerals, metals & zero-carbon electricity"**

- University of Cambridge – Depts Materials Science & Metallurgy; Engineering
- University of Nottingham – Centre of Innovation in CCS
- University of Sheffield – Dept. Materials Science & Engineering
- University of Greenwich – School of Science

michael.priestnall@cacaca.co.uk

www.cacaca.co.uk

Cambridge Carbon Capture Limited, Hauser Forum, Charles Babbage Road, Cambridge, CB3 0GT, UK



The University Of Sheffield.

Carbon Dioxide Utilization

off-setting the costs of CCS and providing a route to renewable energy storage

Professor Peter Styring

Chemical & Biological Engineering, The University of Sheffield, UK

The top 10 emerging technologies for 2012

By: Global Agenda Council on Emerging Technologies

Feb 15th 2012 | 16 Comments

WORLD ECONOMIC FORUM

6. Utilization of carbon dioxide as a resource

Carbon is at the heart of all life on earth. Yet, managing carbon dioxide releases is one of the greatest social, political and economic challenges of our time. An emerging innovative approach to carbon dioxide management involves transforming it from a liability to a resource. Novel catalysts, based on nanostructured materials, can potentially transform carbon dioxide to high value hydrocarbons and other carbon-containing molecules, which could be used as new building blocks for the chemical industry as cleaner and more sustainable alternatives to petrochemicals.

The CO2Chem Network

- Network has 580 individual members (June 2013)
- 80% from the UK, 20% from rest of the world
- 225 different organisations are represented

  76 Academic = 34%
  103 Industry = 46%
  46 Other = 20%

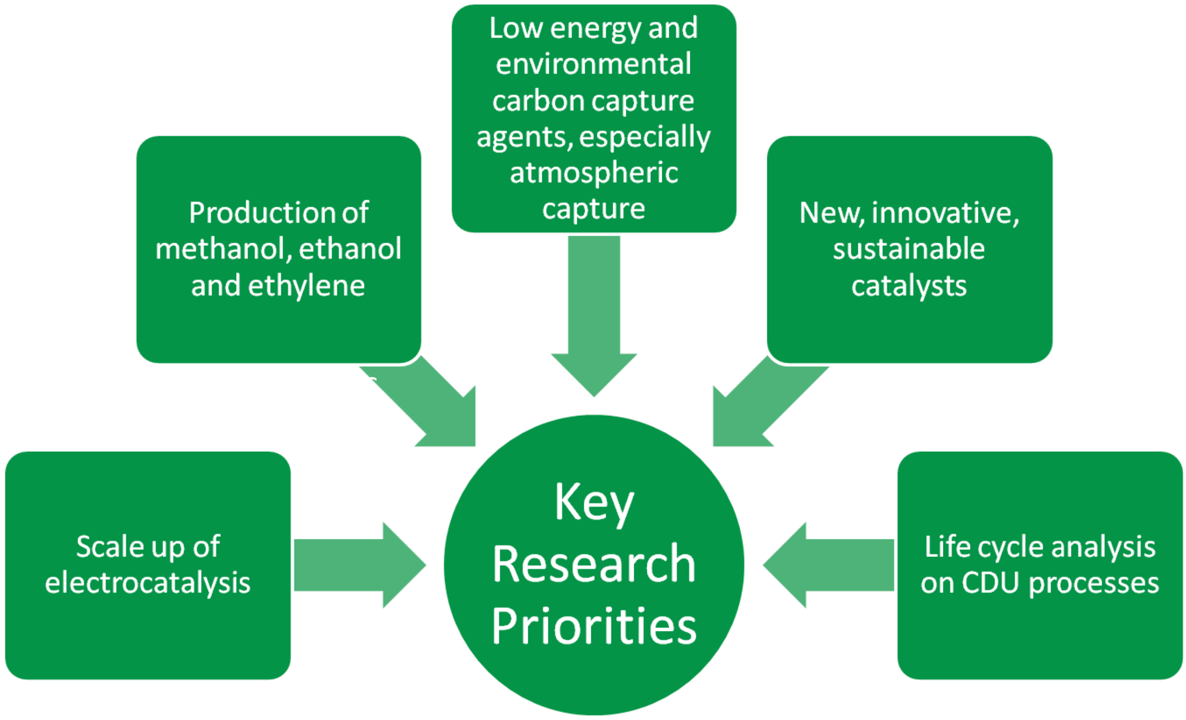
- Website at www.co2chem.com, Twitter @CO2Chem
- Website has members database, links to research papers, presentations from events and latest news
- Networking at a CO2Chem event in 2011 led to an FP7 proposal that was funded to €2.0 million. The partners had never met before that event.
- Regions of Knowledge SCOT consortium (BEL, FRA, NED, UK) now in negotiations phase with EC for € 2.6 million.

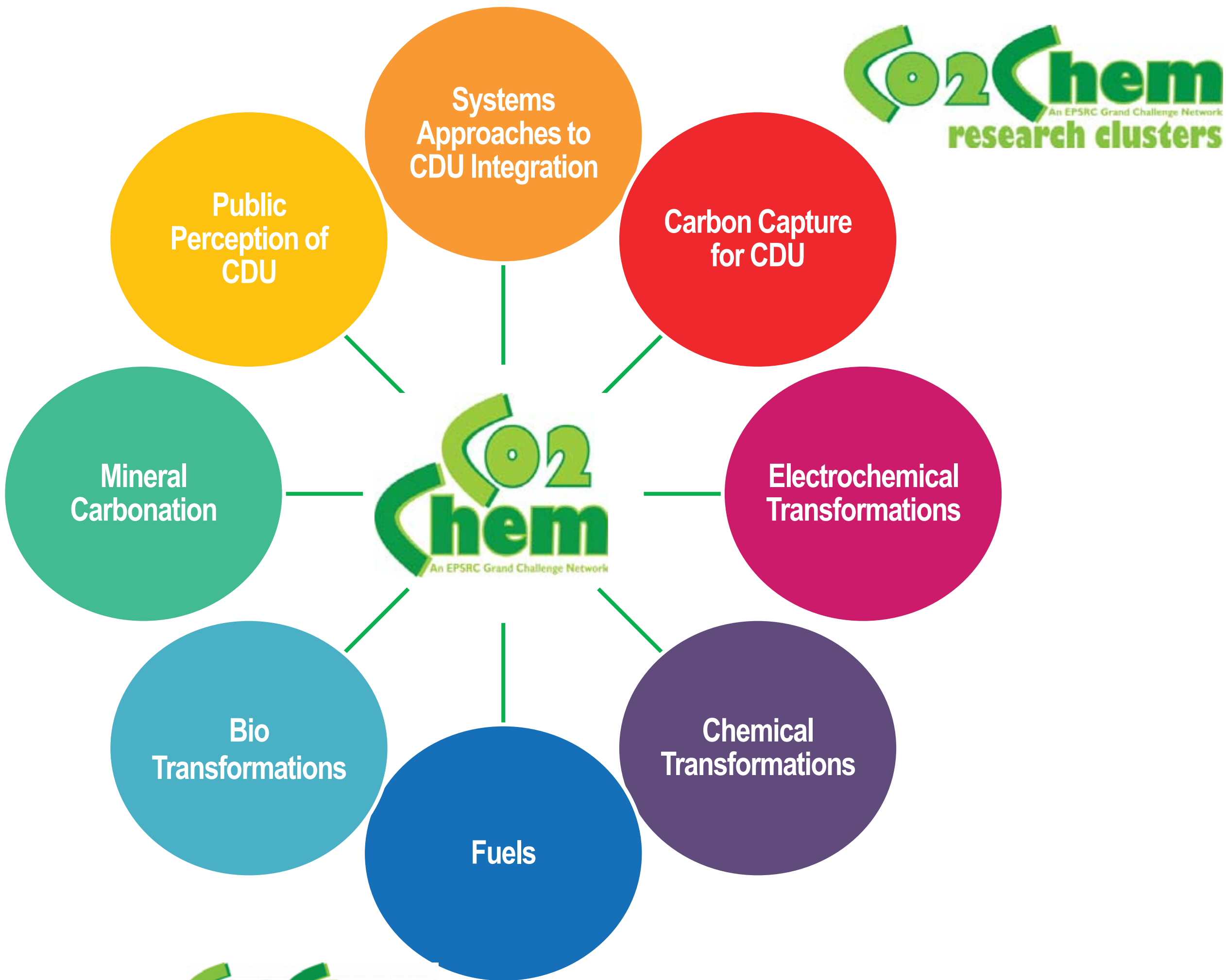
A Coordinated, Comprehensive approach to Carbon Capture and Utilisation

- Consortium of four UK universities: Sheffield, UCL, Queens Belfast, Manchester
- 7.5 M€
- 9 Post-doctoral positions and Project Manager
- Four year programme of research
- Whole System approach:
  - Life Cycle Analysis
  - Carbon Capture Reagents, ionic liquids & polymers
  - Flue Gas & AD Off-gas conversion
  - Fuels from CO2
  - Molecular Modelling

Bringing people interested in CO_2 utilization together

Key Research Priorities

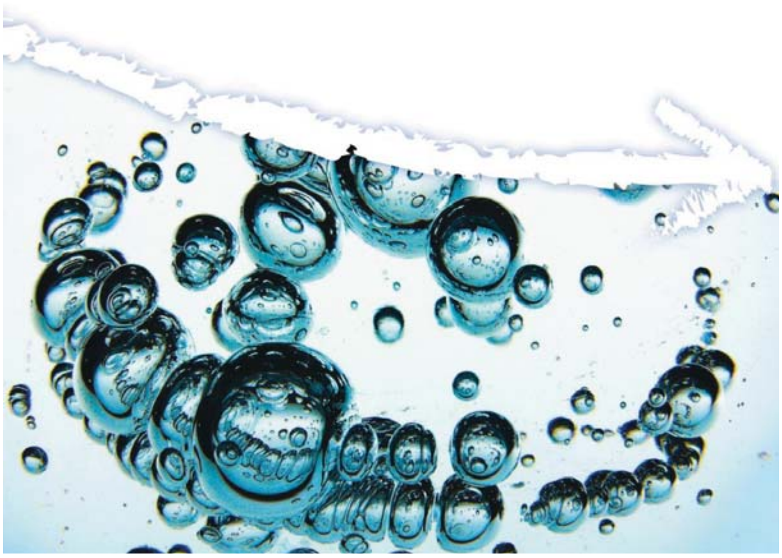




Bringing people interested in CO_2 utilization together

Carbon Capture and Utilisation in the green economy

Using CO_2 to manufacture fuel, chemicals and materials



Authors

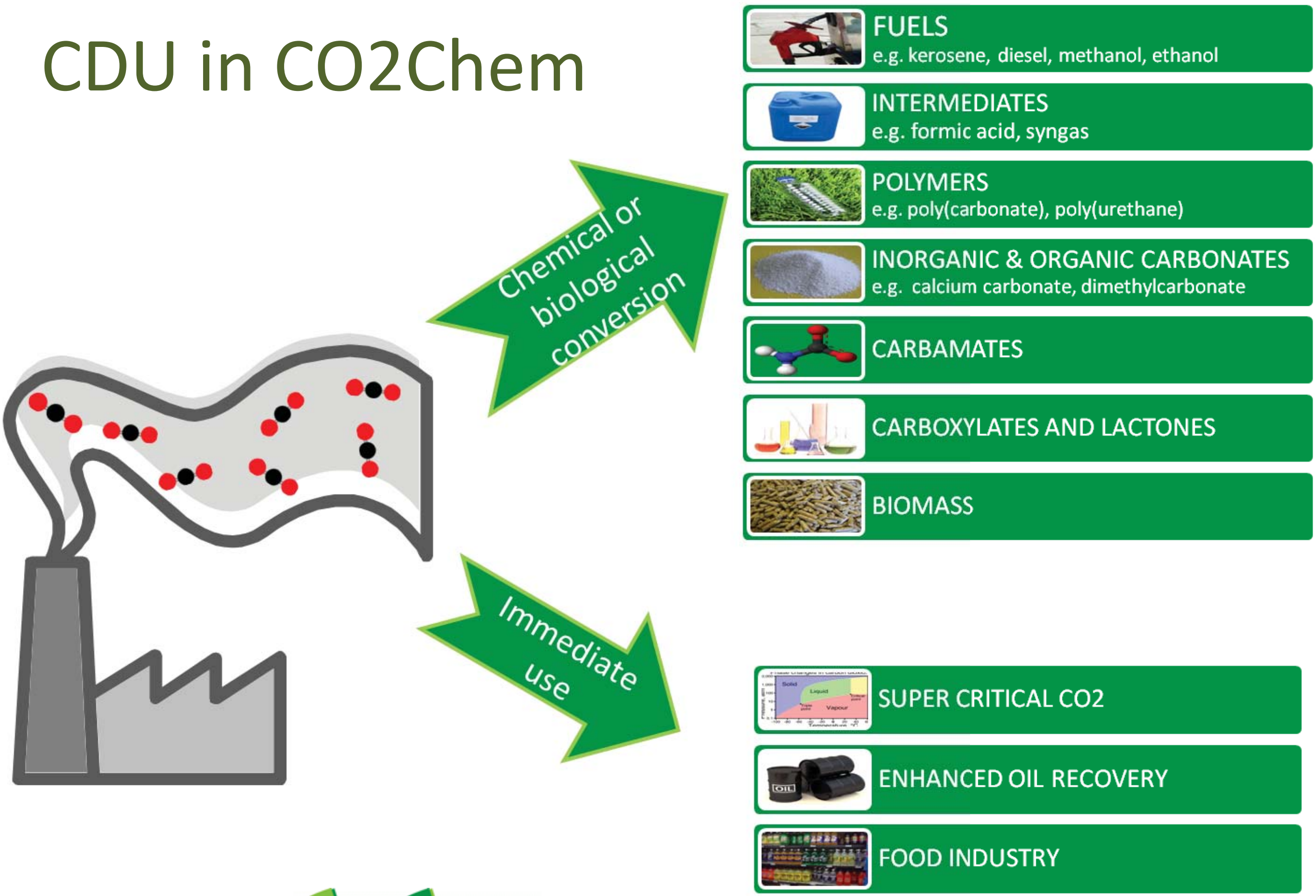
Peter Styring (The University of Sheffield), ***Daan Jansen*** (ECN)

Co-authors

Heleen de Coninck (ECN), ***Hans Reith*** (ECN),

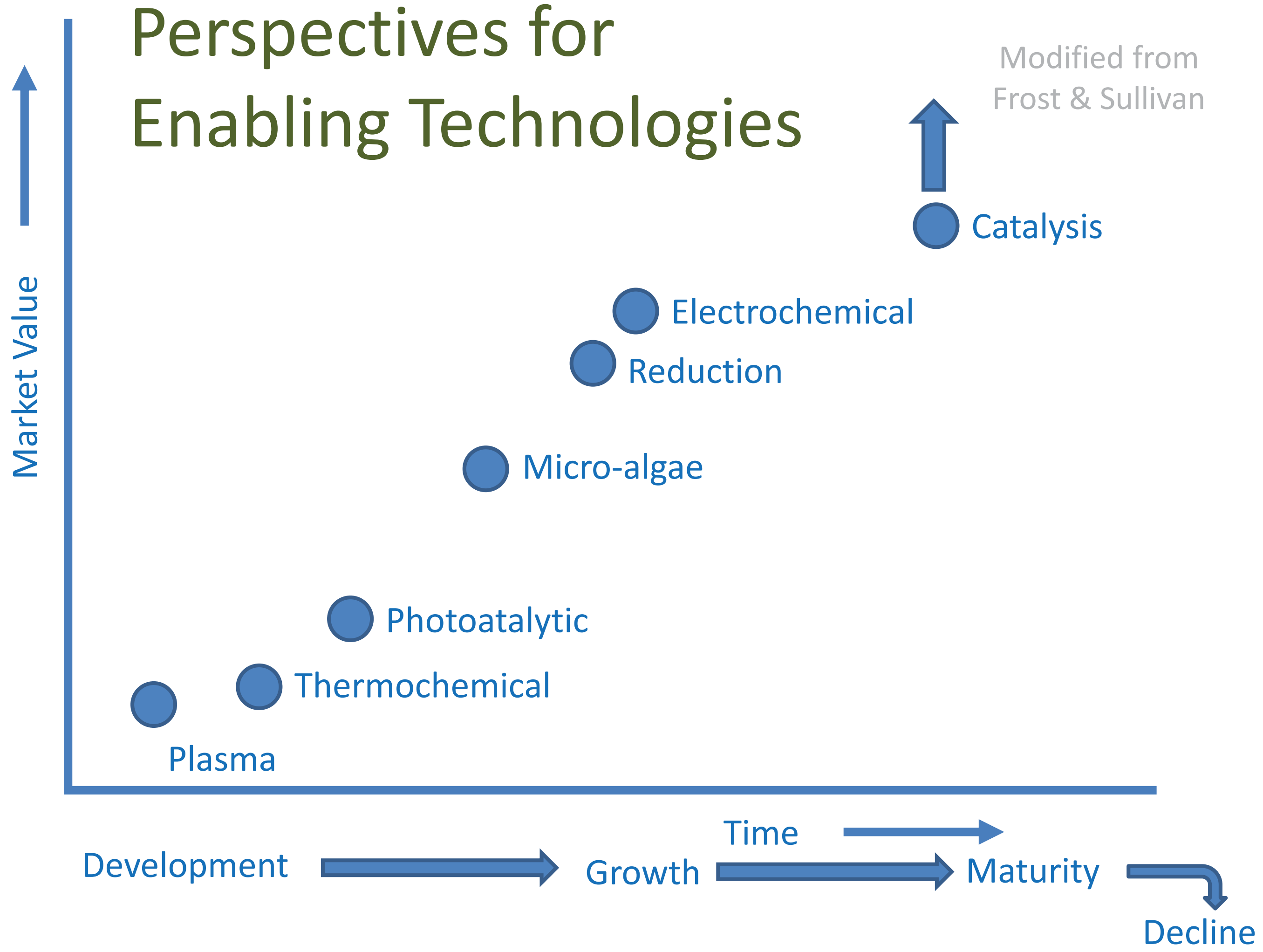
Katy Armstrong (The University of Sheffield)

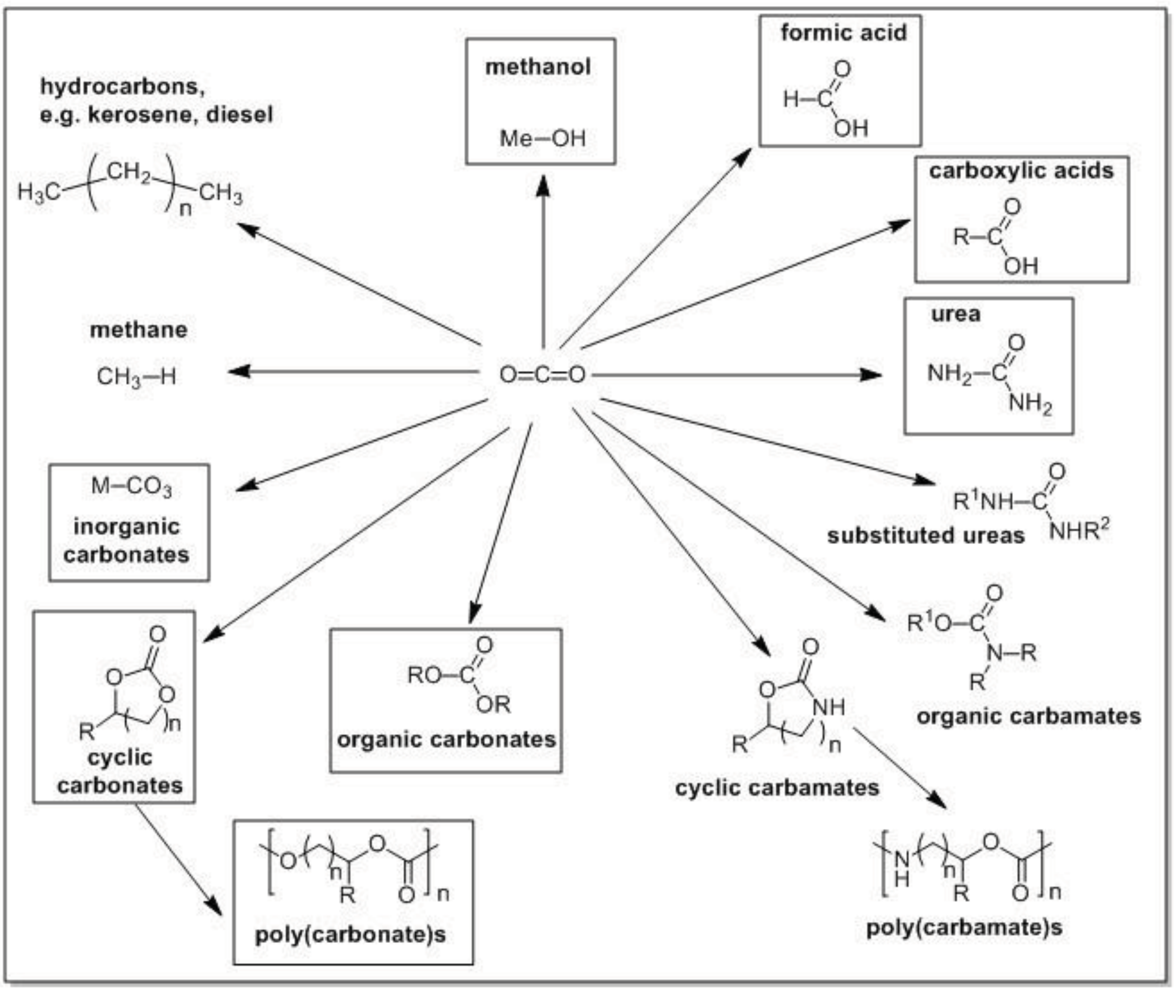
CDU in CO2Chem



Bringing people interested in CO_2 utilization together

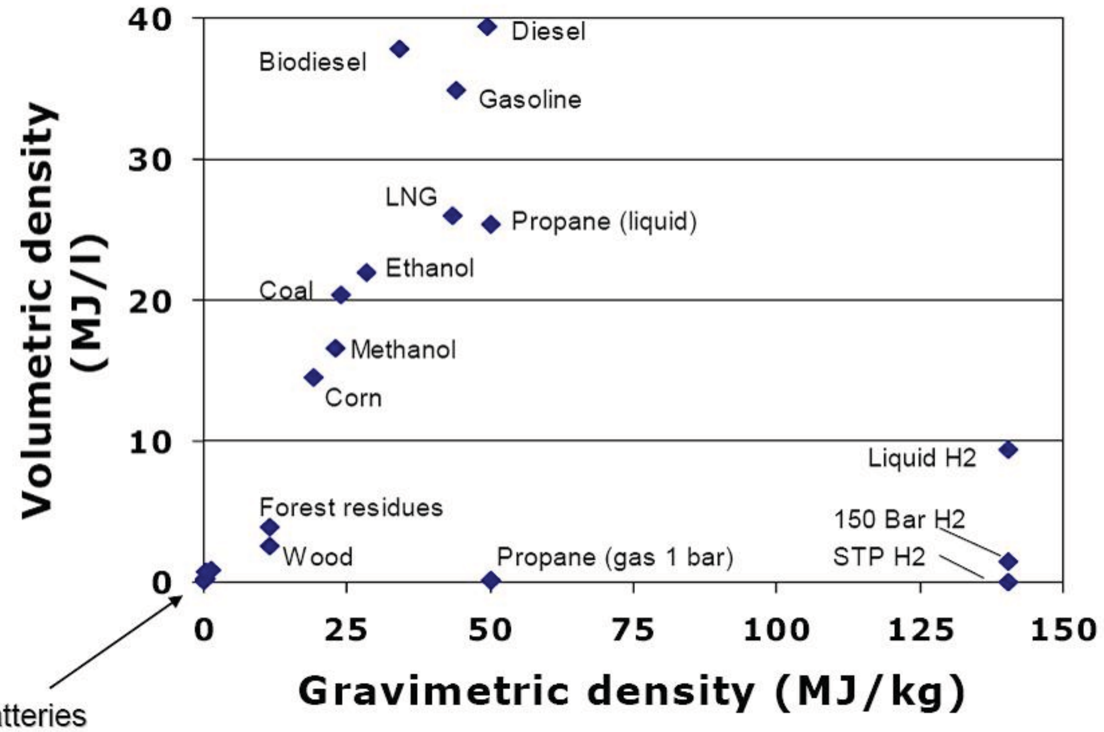
Perspectives for Enabling Technologies





Energy Density

http://www.olicognography.org/graph/energydensity.jpg

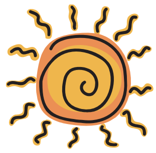


Alternative Energy Sources

• Solar	Intermittent, geographical
• Wind	Intermittent
• Tidal	Predictable
• Hydro	Geographical
• Nuclear	Political, constant output
• Geothermal	Geographical

The commonality between all these renewable sectors is the production of electricity, or simply a supply of **electrons**.

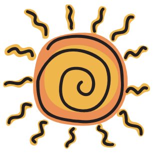
Bio- and crop-based renewables are not included above but examples include maize, sugar beet and algae



$$O{=}C{=}O + 3H_2 \rightleftharpoons H_3C{-}OH + H_2O$$

Plant	Efficiency
Plants, typical	0.1% 0.2–2%
Typical crop plants	1–2%
Sugarcane	7–8% peak

Modern photovoltaic efficiency now over 20%



20% efficiency

70% efficiency

Conversion from **solar** to **chemical** energy 10-15% which is **better than nature**!

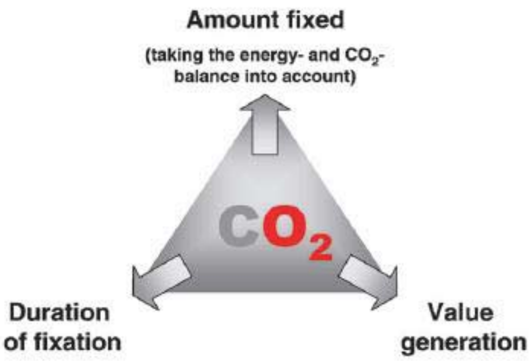
maximal achievable extraction of wind power by a wind turbine is 59% of the total theoretical wind power

Main problem is intermittency and synchronisation to peak power demand. Electricity is wasted at times of low demand.

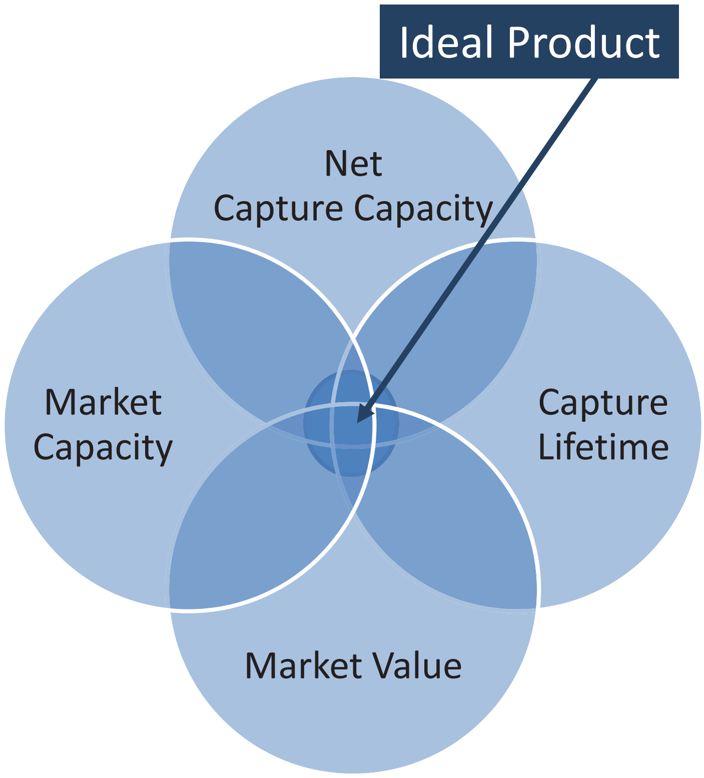
How can CDU help in renewable intermittent energy storage?

- Buffering intermittent power generation.
- Converting electrical to chemical energy which is easier to store.
- Can convert to liquid or gas. Liquids tend to have higher energy densities.
- Offers alternatives to distributed power, including remote, local conversion.
- Easier storage and transport solutions.
- Value-added product from a renewable resource.

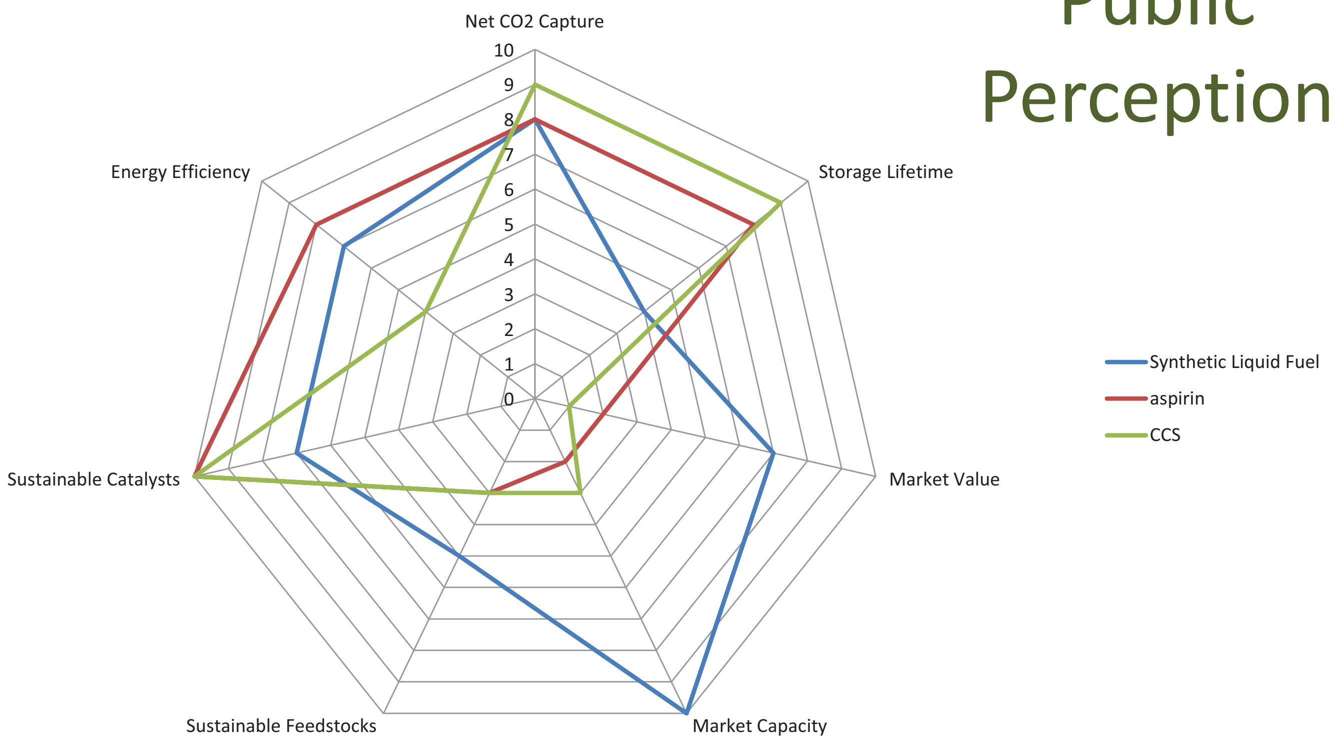
Figures of Merit



T. E. Müller, W. Leitner *et al.*, *ChemSusChem* 2011, **4**, 1216 – 1240



Public Perception



K. Armstrong, B. Robinson, P. Styring & C. Jones
To be published at ICCDU XII, Washington, June 2013

Conclusions

- CDU is an essential part of the CC portfolio that includes CCS, EOR and EGR.
- Designed capture agents are essential to reduce costs and emissions while increasing activity and selectivity.
- Integration of capture agents with catalysts offer an opportunity to intensify processes.
- Integration of with renewable intermittent energy sources offers energy storage and security as well as the possibility for remote local fuel production.
- Air capture will become increasingly important so needs to be addressed now.
- A chance to address the Sustainability and Security of fuel & chemical supplies by using renewable non-fossil feedstocks.

Free Membership at

www.co2chem.com

Life Cycle Assessment of Carbon Capture Re-Use and Storage

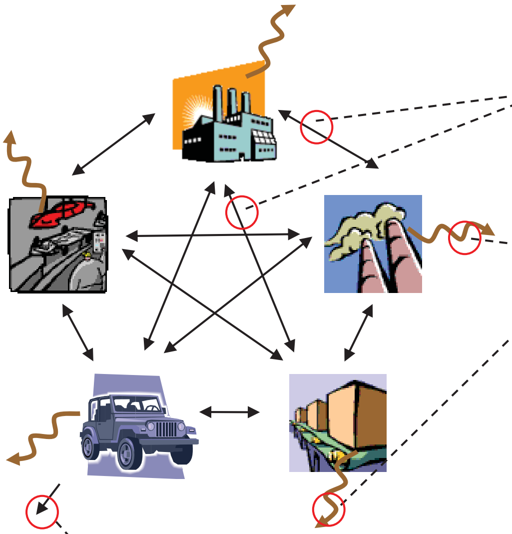
Edgar Hertwich

Industrial Ecology Programme
Department of Energy and Process Engineering
Norwegian University of Science and Technology

DG Clima, 7 June 2013

CONTENTS

Why LCA?



What is the total amount of environmental stressors connected to a comparable service?

Basis for comparison and for upscaling.

LCA of CCR and CCS

Does it make sense as a climate mitigation step?

What are the energy, chemical and infrastructure requirements and the associated GHG emissions?

How large is the emission reduction that can be achieved?

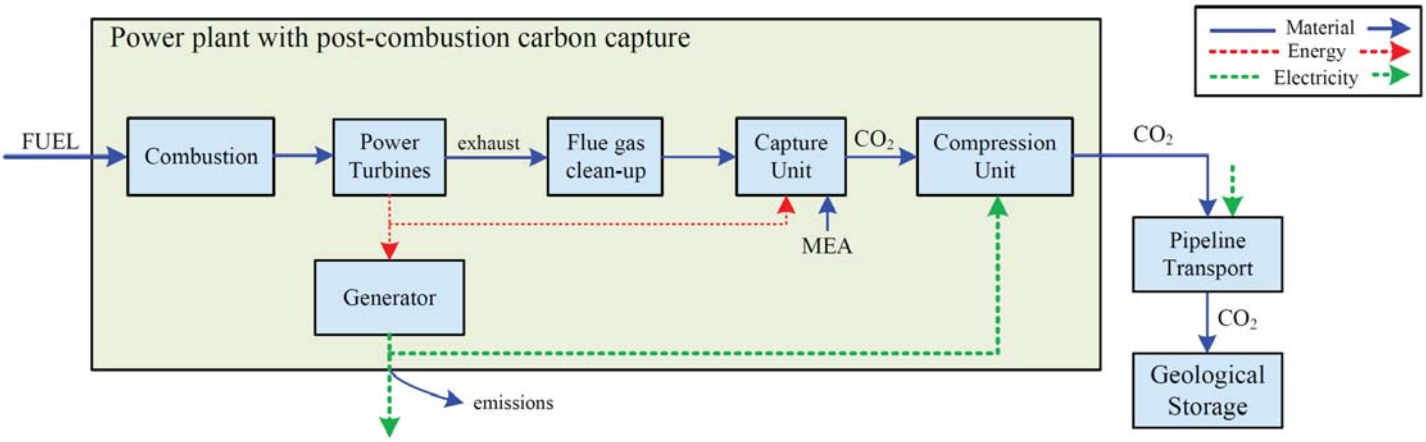
Resource and environmental trade-offs

What are the resources required?

Does the process have higher or lower emissions of air/water/soil pollutants cp to conventional fossil or renewable alternatives?

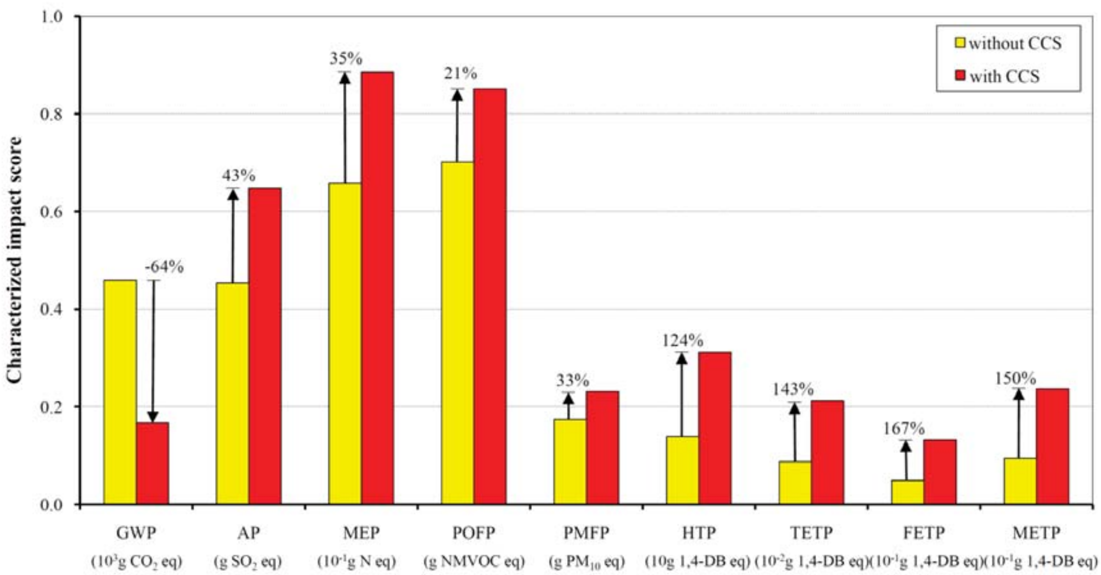
Power station with CCS

➢ ***Post-combustion capture, transport and storage system***



CCS: Trade-off between impact categories

Absolute Recipe Impact Scores for NGCC w Postcombustion CCS

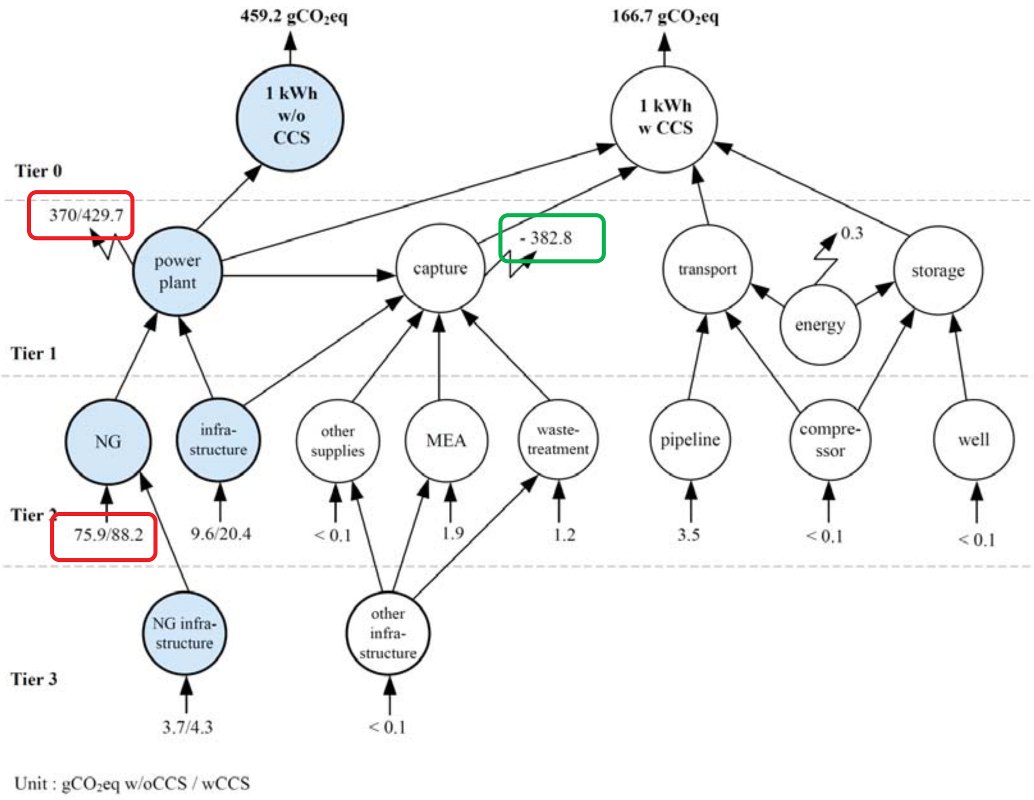


- **Increase in all environmental impacts except decrease in GHG.**

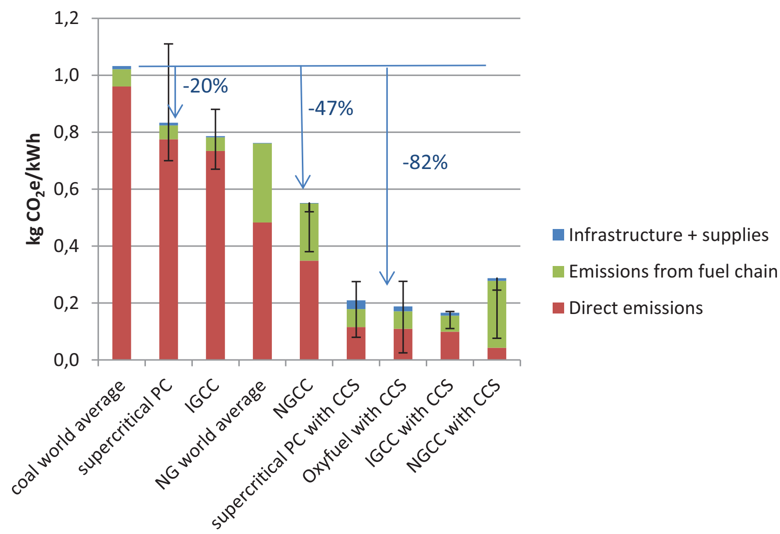
Singh, B., A. H. Strømman, and E. Hertwich. 2011. Life cycle assessment of natural gas combined cycle power plant with post-combustion carbon capture, transport and storage. *International Journal of Greenhouse Gas Control* 5(3): 457-466.

NGCC POST-COMBUSTION CCS

STRUCTURAL PATH ANALYSIS OF GWP - Contributions



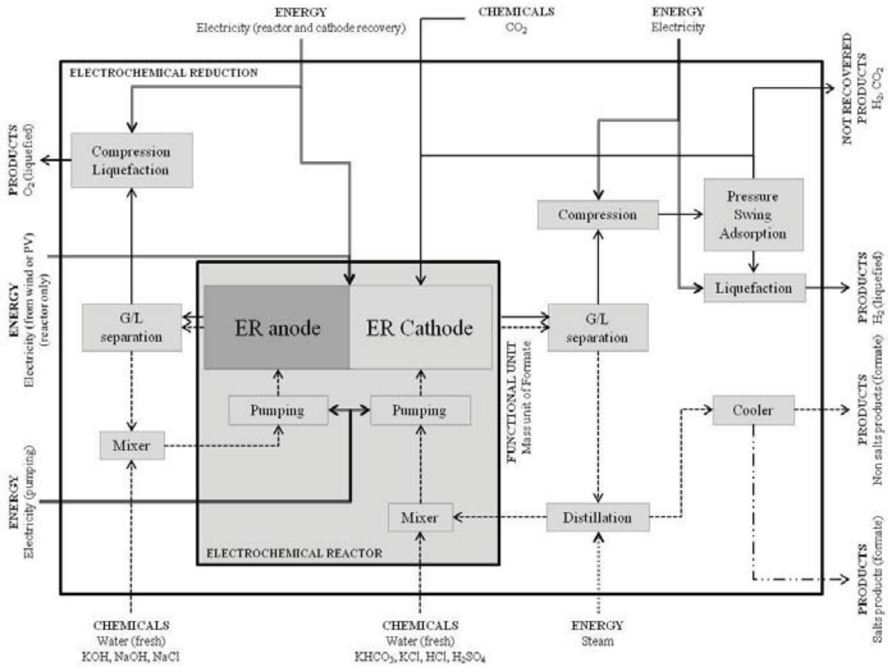
LCA of CCS – Adjusted fugitive emissions



Error bars indicate current literature range. LCA based on Singh et al. (2011) adjusted for fugitive emissions acc. to Burnham et al. (2012).

- Significant reduction of direct emissions with CO2 capture.
- More attention required to fuel chain.
- Contribution of infrastructure small.

Electrochemical Reduction



Formic acid: Preservative, antibacterial agent, tanning.

Demand: 1 Mt/y

Commonly produced from methane - methanol

Electrochemical reduction of CO_2 shown feasible in experiments; papers and patents published

LCA results for EOR

Resource inputs to electrolysis

Emissions including distillation

High requirements of electricity, chemicals

Low concentration product

Very high energy requirement for extractive distillation

High emissions given the overall inefficiency of the process.

A. Dominguez-Ramos, B. Singh, X. Zhang, E.G. Hertwich;, TCCS conference 2013

LCA of CO_2 Re-Use

Life cycle assessment is critical for identifying which options make sense from a climate mitigation perspective.

Thermodynamics and systems analysis are key for conducting LCAs of this type of processes.

European Commission
JRC86324 – Joint Research Centre – Institute for Energy and Transport

Title: Carbon Capture and Utilisation Workshop. Background and proceedings
Authors: Andrei BOCIN-DUMITRIU, Maria del Mar PEREZ FORTES, Evangelos TZIMAS, and Thea SVEEN

Luxembourg: Publications Office of the European Union

2013 – 77 pp. – 21.0 x 29.7 cm

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ISBN 978-92-79-34943-0 (print)

doi:10.2790/11560

Abstract

The utilisation of CO_2 as technological fluid or as feedstock in chemical processes and in biotechnological applications has the potential to be a very efficient tool when merged with development of innovative and feasible technologies that have less-intensive energy and materials consumption and the capacity of temporary or permanent storage of CO_2 (other than geological storage).

The Joint Research Centre of the European Commission, Institute for Energy and Transport, and the Directorate General for Climate Action co-hosted a workshop on CO_2 re-use technologies in Brussels on the 7th June 2013. The aim of the workshop was to present how the most promising pathways for CO_2 re-use are related to climate and energy technology policies, facilitate a dialogue between stakeholders (industry, academia and policy makers) and address the challenges for a possible large scale roll-out of CO_2 re-use technologies. A number of six presentations from experts focused on the state-of-the art of the technology, the needs of the sector for large scale deployment and the impact of the CO_2 re-use products on the market. In particular, the workshop focused on three promising pathways, i.e. methanol production, mineralisation and polymer production.

LD-NA-26403-EN-N

As the Commission's in-house science service, the Joint Research Centre's mission is to provide EU policies with independent, evidence-based scientific and technical support throughout the whole policy cycle.

Working in close cooperation with policy Directorates-General, the JRC addresses key societal challenges while stimulating innovation through developing new standards, methods and tools, and sharing and transferring its know-how to the Member States and international community.

Key policy areas include: environment and climate change; energy and transport; agriculture and food security; health and consumer protection; information society and digital agenda; safety and security including nuclear; all supported through a cross-cutting and multi-disciplinary approach.

Publications Office

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