# 2nd Conference on $CO_2$

Carbon Dioxide as Feedstock for Chemistry and Polymers

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## $CO_2$ as chemical feedstock – a challenge for sustainable chemistry

**7–9 October 2013, Haus der Technik, Essen (Germany)**

# Conference Journal

**1st Day, 7 October 2013**
Political framework and visions

**2nd Day, 8 October 2013**
Chemicals and energy from $CO_2$

**3rd Day, 9 October 2013**
Polymers and building blocks from $CO_2$

- Biggest event on $CO_2$ as feedstock
- Full programme of the Conference
- Scientific paper on $CO_2$ as Feedstock

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# 2nd Conference on $CO_2$

Carbon Dioxide as Feedstock for Chemistry and Polymers

## Dear participants from more than 20 countries!

The $CO_2$ economy is developing rapidly with research, technology and even already with applications and investments. It is a very particular challenge to build a bridge between the vision of an eco-friendly and infinite resource which can satisfy humankind's growing hunger for raw materials, and a technology that is still in its infancy, still too expensive and has still to prove its ecological advantages. Very possibly, technology needs to be enhanced and gain in efficiency in order to achieve all this. But it's worth to follow through, because down the road, there is a promise of a permanent solution for our civilization's crucial problems: Solar power, $CO_2$ and water together can supply all of humanity with energy and raw materials! Building this bridge will pay off.

At this three-day conference we will try to cover the full range of the $CO_2$ economy, from policy and vision, to chemistry and energy, building blocks and polymers. Come with us on a journey into the future – presentations of leading experts and strategists, an exhibition and a poster-session as well as concluding discussions at the end of each day and a dinner buffet will ensure comprehensive exchange and networking.

The nova team wishes you a lot of new insights and impulses.

Your Michael Carus
Managing Director nova-Institute

nova Institute for Ecology and Innovation

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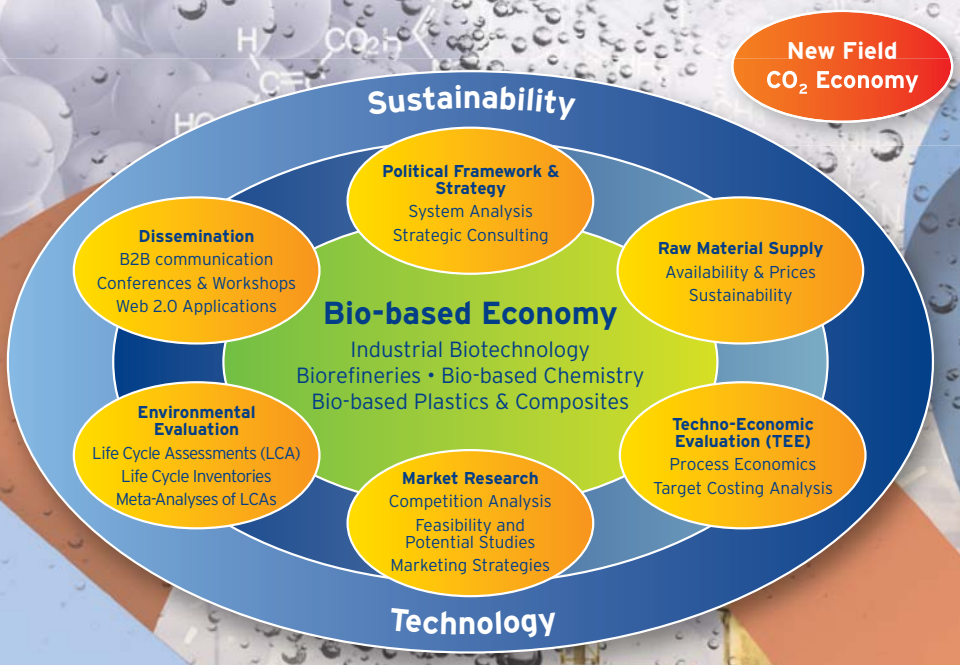



## Venue

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# 2nd Conference on $CO_2$

Carbon Dioxide as Feedstock for Chemistry and Polymers

## Preface

**Forward-looking solutions from North Rhine-Westphalia**

More than a hundred years ago, the wealth and prosperity of our economy, industry and society rested on the use of coal. In recent decades, it was the use of oil. The fact that these resources are running out, along with the adverse effects of using them in the first place, is what gives our societies the collective headache that we have today. We are confronted with these big issues, sometimes referred to as the 'grand challenges', and we must succeed in resolving them. Here, a key role is set aside for science and research. Researchers the world over are working on ways to efficiently utilise renewable energy and alternative resources such as biomass or, indeed, carbon dioxide.

The challenges we face, global warming for instance, are of such a global nature that they are unlikely to be dealt with by a single scientific discipline. Solutions can only be delivered in concert with other branches of science, in an interdisciplinary or, if you include political leaders and community representatives, trans-disciplinary approach. That is one of the key principles of North Rhine-Westphalia's research strategy, 'Progress NRW'.

The academic and research communities in North Rhine-Westphalia are in a very good place to do the job. Research is conducted at more than fifty universities and other research establishments with a focus on chemistry, process engineering or the life sciences. The research and business communities are closely linked. A combination of 700,000 small and medium enterprises, numerous large international players and research facilities have turned North Rhine-Westphalia into a living lab where local research contributes to international solutions.

The use of carbon dioxide as an economic resource is going to be big in the future. The Second Conference on $CO_2$ as Feedstock for Chemistry and Polymers is discussing two promising approaches: the chemical and the biotechnological utilisation of carbon dioxide. The idea is for this to lead to mutual synergy between sustainable chemistry and the bioeconomy.

I would like to say a big thank you to nova-Institute for organising this international conference. Let me wish you a good conference, many productive discussions and plenty of new contacts.

Svenja Schulze

*Minister of Innovation, Science and Research of the German State of North Rhine-Westphalia.*

## Patronage

### Svenja Schulze

*Minister of Innovation, Science and Research of the German State of North Rhine-Westphalia.*

Ministry of Innovation, Science and Research of the German State of North Rhine-Westphalia

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# 2nd Conference on $CO_2$

Carbon Dioxide as Feedstock for Chemistry and Polymers

## Cluster EnergyRegion.NRW amalgamates North Rhine-Westphalia's energy industry expertise

North Rhine-Westphalia has intensified its cluster activities in the energy economy domain. To create synergies, the marketing activities of the existing eight networks were being combined under the common brand name of EnergyRegion.NRW. The starting signal was given in Düsseldorf in August 2009 for the new energy industry cluster of the state of North Rhine-Westphalia.

With its unique blend of global players, medium-sized enterprises and small think tanks, not to mention the excellent research institutions, North Rhine-Westphalia provides an ideal location to cultivate forward-looking developments in the energy economy. EnergyRegion.NRW stands for innovative power, tradition, neutrality and an openness to technology. With this strong brand the outstanding achievements of the state in the energy field are given a higher profile both internally and externally. The aim is to enhance even further North Rhine-Westphalia's image Europe-wide as a forward-looking region.

The cluster manager of EnergyRegion.NRW is Dr. Frank-Michael Baumann, Director of EnergyAgency.NRW. With cross-network cluster management it is intended in future to tailor the cluster's products and services more closely to the needs of the individual actors in the energy field. And consultancy is also to the fore: "We wish to play the role of initiator even more vigorously and to launch innovative projects, which we will accompany up to market maturity", says Dr. Baumann.

According to a current study by the management consultants McKinsey, the energy economy has enormous future potential worldwide, with growth rates sometimes reaching double figures. As an important lead market this sector offers great potential which North Rhine-Westphalia wishes to exploit. The job of the state government in this area is to create reasonable framework conditions in order to facilitate a close collaboration between all the actors involved along the energy economy value chain, also extending into other sectors.

After all, in global, fast and mobile markets the classic coexistence of industry, science and public bodies is no longer sufficient. The new cluster structure and a strong cluster management will help to improve communication between the partners of EnergyRegion.NRW.

"We know the state's energy companies and institutions very well. And so we can pass on enquiries directly and promptly to the right recipient", is how cluster manager Dr. Frank-Michael Baumann explains the benefit EnergyRegion.NRW provides to its partners. These appreciate the cluster in particular as a set of neutral information and communication platforms in the energy field.

### Further information


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**Cluster EnergyRegion.NRW**

EnergyRegion.NRW
Cluster North Rhine-Westphalia

**About EnergyRegion.NRW**

The energy economy is one of North Rhine-Westphalia's most powerful sectors. The EnergyAgency.NRW was delegated by the state government of North Rhine-Westphalia to take responsibility for and manage the cluster to promote innovations and growth and to secure the settlement of new companies in EnergyRegion.NRW. 3,300 companies and institutions have joined the state's energy economy cluster. Three quarters of the companies involved are small and medium-sized enterprises. 64 universities, 107 institutes and 94 associations are members. 5,200 individuals participate in the cluster's working groups and networks. 30,000 individuals regularly receive information on the cluster's work.

The cluster's work concentrates on eight areas of the energy economy for which outstanding growth opportunities in the future are forecast. That is why there are eight networks within the Energy Economy Cluster focusing on:

photovoltaics, power plant engineering, the topic of fuel cells and hydrogen, biomass, future fuels and drives, the topic of energy-efficient and solar construction, geothermics and wind power.

In view of the heterogeneous nature of the various topic areas, the networks are at differing stages of development. One of the tasks of the cluster manager and the individual network managers is to organise the networks even more efficiently, to introduce uniform quality standards for all networks and to amalgamate all activities under the new brand name EnergyRegion.NRW. With the new set-up it will also be easier to network with clusters in other federal states and to collaborate in cross-innovations.

# 1st DAY

# Political framework and visions

## PROGRAMME OF THE 1st DAY, 7 OCTOBER 2013

**09:30** Registration and welcome coffee

**10:00** Conference Opening, nova-Institut GmbH Michael Carus

**10:15** Opening words from the Ministry of Innovation, Science and Research of the State of North-Rhine Westphalia

### POLICY & VISIONS

**Chairman**
**Prof. Dr. Ludo Diels**
Flemish Institute for Technological Research (VITO)

**10:30** Federal Ministry of Education and Research (BMBF)

**PD Dr. Lothar Mennicken**
*The German R&D Program for $CO_2$ Utilisation – innovations for a green economy*

**11:00** International Energy Agency (IEA)

**Simon Bennett**
*IEA perspectives on CCS: what role (or roles?) for $CO_2$ utilisation*

**11:30** CEFIC

**Dr. Gernot Klotz**
*A vision on $CO_2$ economy from the chemical industry*

**12:00** Lunch and press conference

**13:30** Virgin Earth Challenge

**David Addison**
*A vision of $CO_2$ utilisation's role in combating climate change*

**14:00** nova-Institut GmbH

**Michael Carus**
*Industrial utilization of $CO_2$: Suitable strategy and political framework for implementation*

### SUSTAINABILITY ASPECTS ON THE $CO_2$ ECONOMY

**Chairman**
**Michael Carus**
nova-Institut GmbH

**14:30** Meo Carbon Solutions GmbH

**Dr. Norbert Schmitz**
*ISCC Certification schemes for $CO_2$ based fuels and chemicals*

**15:00** University of Stuttgart

**Aleksandar Lozanovski**
*LCA for $CO_2$ as raw material*

**15:30** Coffee Break

### BIOELECTROCHEMICAL CONVERSION

**16:00** Flemish Institute for Technological Research (VITO)

**Prof. Dr. Ludo Diels**
*Bioelectrochemical conversions of $CO_2$ into new chemical building blocks*

### ARTIFICIAL PHOTOSYNTHESIS

**Chairman**
**Dr. René Klein Lankhorst**
BioSolar Cells

**16:30** nova-Institut GmbH

**Dr. Fabrizio Sibilla**
*Artificial Photosynthesis: a comparison with nature*

**16:40** Delft University of Technology

**Prof. Dr. Ernst Sudhölter**
*From solar energy to energy rich compounds*

**17:10** Kyoto University

**Dr. Naoki Ishida**
*Solar-Driven Incorporation of Carbon Dioxide into α-Amino Ketones*

**17:40** Discussion with speakers from the first day

**18:30** End of the first day

**19:00** Dinner Buffet

# 2nd DAY

# Chemicals and energy from $CO_2$

## PROGRAMME OF THE 2nd DAY, 8 OCTOBER 2013

**08:30** Registration and welcome coffee

**09:00** Conference Opening

### $CO_2$ PURIFICATION AND TECHNICAL PREPARATION

**Chairman**
**David Addison**
**Virgin Earth Challenge**

**09:00**

**University of Newcastle**
**Prof. Dr. Michael North**
*$CO_2$ from flue gas without purification as reactant*

**09:30**

**Aker Clean Carbon**
**Dr. John Nustard (inquired)**
*$CO_2$ capture technology by Aker Clean Carbon*

**10:00**

**SUPREN GmbH**
**Prof. Dr. Axel Gottschalk**
*INTERACT: R&D on INnovaTive Enzymes and polyionic-liquids based membRAnes as post combustion $CO_2$ Capture key Technology*

**10:30** Coffee Break

**11:00**

**Climeworks AG**
**Christoph Gebald**
*$CO_2$ Supply through Direct Air Capture*

**11:30**

**TNO**
**Dr. Erin Schols**
*From $CO_2$ capture to $CO_2$ use: hurdles and opportunities*

**12:00** Lunch

### CONSTRUCTION MATERIALS BASED ON $CO_2$

**Chairman**
**Dr. Fabrizio Sibilla**
**nova-Institut GmbH**

**13:00**

**Cambridge Carbon Capture**
**Michael Priestnall**
*$CO_2$ Mineralisation – a scalable & profitable approach to industrial CCS*

### $CO_2$ AS CARBON SOURCE FOR AN INNOVATIVE ORGANIC CHEMISTRY

**Chairman**
**Dr. Fabrizio Sibilla**
**nova-Institut GmbH**

**13:30**

**Seoul National University**
**Prof. Dr. Sang-Eon Park**
*$CO_2$ Utilization as Oxidant for Petrochemicals*

**14:00**

**University of Messina**
**Prof. Dr. Gabriele Centi**
*Trading renewable energy by using $CO_2$: A new option towards a green use of carbon dioxide*

**14:30** Coffee Break

**15:00**

**Leibniz-Institut für Katalyse e.V.**
**Prof. Matthias Beller**
*Hydrogen Storage with Carbon dioxide: Opportunities for Homogeneous and Heterogeneous Catalysis*

**15:20**

**Cluster Industrial Biotechnology CLIB 2021**
**Prof. Dr. Karl-Erich Jaeger**
*Bioprocesses enable cross-industry value chains*

**15:40**

**Tecnalia**
**Dr. José R. Ochoa-Gómez**
*Synthesis of glycerol carbonate from glycerol α-monochlorohydrin and carbon dioxide using triethylamine as both solvent and $CO_2$ fixation-activation agent*

**16:00**

**Evonik Industries AG**
**Dr. Benjamin Schäffner**
*Utilization of $CO_2$ in the production of fine chemicals on industrial scale*

**16:20** Coffee Break

### $CO_2$ AS ENERGY CARRIER

**Chairman**
**Lars Schulze-Beusingsen**
**EnergieAgentur.NRW**

**16:50**

**Technical University of Munich**
**Prof. Dr. Richard W. Fischer**
*$IC^4$ – integrated Carbon Capture, Conversion and Cycling*

**17:10**

**RWTH Aachen**
**Prof. Dr. Walter Leitner**
*Formic acid as energy carrier*

**17:30**

**Technical University of Regensburg**
**Prof. Michael Sterner**
*Generating $CO_2$ based fuels by using wind harvesting ships*

**17:50**

**Krajete GmbH**
**Dr. Arne Seifert**
*Applications of Methanogenesis for $CO_2$ Utilization and Intermittent Power Storage*

**18:10**

**Delft University of Technology**
**Dr. Wim Haije**
*$CO_2$ to fuels: enabling the sustainable energy society*

**18:30** Discussion with speakers from the second day

**19:30** Networking reception with snack

# 3rd DAY

# Polymers and building blocks from $CO_2$

## PROGRAMME OF THE 3rd DAY, 9 OCTOBER 2013

**08:30** Registration and welcome coffee

**09:00** Conference Opening

### POLYMERS BASED ON $CO_2$

**Chairman**
**Prof. Dr. Wim Soetaert**
**Bio Base Europe Pilot Plant**

**09:00**

**Bayer MaterialScience AG**
**Dr. Christoph Gürtler**
**RWTH Aachen**
**Niklas von der Assen**
*Recent developments in $CO_2$-based polyurethanes*

**09:40**

**CSIRO**
**Dr. Xiaoqing Zang**
*Opportunities of $CO_2$-based polymers in composites with biopolymers and natural fibres*

**10:10**
**The University of Sydney**
**Prof. Dr. Fariba Dehghani (inquired)**
*Better catalysts by reducing zinc levels for the production of PPC*

**10:40** Coffee Break

**11:10**

**BASF SE**
**Dr. Núria Huguet**
*Acrylates from alkenes and $CO_2$, the stuff that dreams are made of*

**11:40**

**Wuppertal Institute**
**Dr. Stefan Bringezu**
*Carbon recycling for renewable material supply: assessing the sustainability of sources of $CO_2$ and potential pathways of polymer production*

**12:10**

**University of Wageningen**
**Dr. Maria Barbosa**
*SPLASH – Sustainable PoLymers from Algae Sugars and Hydrocarbons*

**12:40** Lunch

**13:40**

**Catalan Institution for Research and Advanced Studies (ICREA) & Institute of Chemical Research of Catalonia (ICIQ)**
**Prof. Dr. Arjan W. Kleij**
*Catalytic Potential of Amino-Trisphenolate Complexes in Polycarbonate Synthesis*

### $CO_2$ FOR BUILDING BLOCKS

**Chairman**
**Michael Carus**
**nova-Institut GmbH**

**14:10**

**LanzaTech**
**Grainne Smith**
*$CO_2$ and CO fermentation, a route from waste to fuels and Chemical Building Blocks at Scale*

**14:40**
**Oakbio Inc.**
**Brian Seflon**
*Chemoautotrophic bacteria as cell factories*

**15:10** Coffee Break

**15:40**

**University of Amsterdam**
**Prof. Dr. Klaas Hellingwerf**
*$CO_2$ as the ultimate substrate for a sustainable biotech industry*

**16:10**

**Bio Base Europe Pilot Plant**
**Prof. Dr. Wim Soetaert**
*Fermentation of $CO_2$ – piloting in the Bio Base Europe Pilot Plant*

**16:40** Discussion with speakers from the third day

**17:30** End of the conference

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**Federal Ministry of Education and Research (BMBF)**

**PD Dr. Lothar Mennicken**

## The German R&D Programme for $CO_2$ Utilization – innovations for a green economy

Three major challenges for the German society are of high priority today: to impede the climate change, to prevent a shortage of resources, and to transform Germany's energy system towards renewables (Energiewende). The reduction of $CO_2$ emissions and the utilization of $CO_2$ are key components towards a sustainable future.

Hence, the German Federal Ministry of Education and Research (BMBF) supports research in this area with the funding programme „Technologies for Sustainability and Climate Protection – Chemical Processes and Use of $CO_2$" as part of the BMBF's general research programme "Research for Sustainable Development (FONA)". From 2010 to 2016 33 collaborative R&D projects between academia and industry are supported with a total funding volume of about 100 Mio. €. In addition the German industry contributes 50 Mio. €, thus reflecting the high relevance of this research area. Based on the existing excellent academic research in Germany, 18 research projects focussing on $CO_2$ utilization have been initiated. While the majority of these projects target **basic products of the chemical industry**, incl. polymers and fine chemicals, six projects aim at **energy storage** by conversion of $CO_2$ and green hydrogen ($H_2$) to synthetic natural gas (SNG) or fuels.

Common technical challenges for all projects are: How can the low energetic level and low reactivity of $CO_2$ be overcome? And can $CO_2$ be converted in a sustainable manner? **Catalysis** is a key technology in $CO_2$ utilization, therefore the development of efficient catalytic systems is a priority in many projects. Regarding the energy supply, a number of projects investigate the use of the discontinuous **surplus energy from renewable sources**. Overall, $CO_2$ utilization has evolved into an attractive and highly relevant research field with strong involvement in projects of all stakeholders.

The research projects investigating the production of high quality polymers from $CO_2$ are highly successful: Bayer opened a pilot plant for the production of $CO_2$-based polyols in 2011 and recently announced the construction of a production plant (Start of operation 2015).

The transformation of the energy system in Germany, mainly towards wind power, demands innovative approaches for energy storage. A large-scale utilization of $CO_2$ can play a significant part here: Surplus electricity is used to produce H2 by water splitting. Subsequently, $H_2$ and $CO_2$ can readily be transformed into methane or methanol. Those chemicals are efficient energy feedstocks and can easily be stored in large quantities in an already existing infrastructure.

All projects are subjected to an accompanying **carbon footprint analysis**, based on state of the art LCA methods. First evaluations have shown promising results.

In summary, the BMBF supports the **extension of the raw material base** by decreasing the dependency on fossil resources. Replacing fossil carbon feedstocks by $CO_2$ from power plants and other industrial and biological sources is a major step towards innovations for a circular carbon economy and contributes to reach the ambitious policy targets of a future green economy.

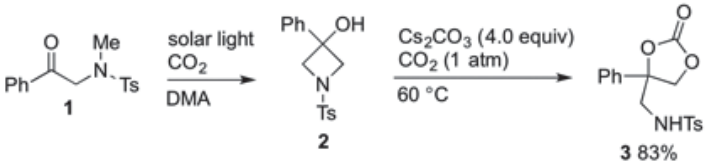
2nd Conference on CO2 Carbon Dioxide as Feedstock for Chemistry and Polymers

# Solar-Driven Incorporation of Carbon Dioxide into α-Amino Ketones

Kyoto University

**Dr. Naoki Ishida**

The manifestation of the potential risk inherent to nuclear technologies has incited a strong demand for exploration of innovative means to exploit energy from natural sources, thus increasing the need for research on sustainable energy in many scientific fields. Chemists can contribute by developing chemical systems to utilize solar light, which is undoubtedly the best source of sustainable energy available on the planet. Another imperative issue is the establishment of carbon-neutral systems. One synthetic approach to this issue is the incorporation of $CO_2$ into organic compounds as a chemical feedstock. Under these circumstances, it presents a significant challenge to simultaneously tackle the two issues mentioned above. We report herein a solar-driven process that incorporates $CO_2$ into α-N-methylamino ketones 1.[1] Amino-substituted cyclic carbonates 3, which are potentially useful ingredients in industry, are obtained. This process presents a simple model of the chemical utilization of solar energy for $CO_2$ incorporation.

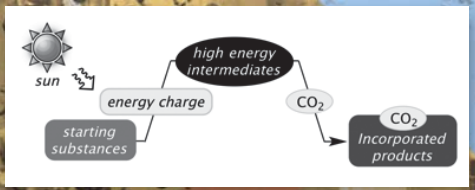



An N,N-dimethylacetamide (DMA) solution of amino ketone 1 under an atmosphere of $CO_2$ (1 atm) in a Pyrex® flask was irradiated with solar light outside on a sunny day (1st step). After 8 h, $Cs_2CO_3$ (4.0 equiv) was directly added to the reaction mixture, which was then heated at 60 °C for 10 h in a fume hood (2nd step). Quenching with 1N HCl, extraction, isolation by chromatography afforded the analytically pure cyclic carbonate 3 in 83% yield based on 1.

The first step is a photocyclization reaction of 1 forming azetidinol 2, which was originally reported to require irradiation with a mercury lamp.[2] We discovered that solar light successfully effected this reaction. The resulting azetidinol 2 possesses structural strain owing to the four-membered ring, so that the reaction is energetically uphill. The light energy drives the reaction, and is stored in 2 as the structural strain.

The second step is a base-induced $CO_2$ incorporation reaction into the azetidinol 2. The four-membered ring is opened to produce cyclic carbonate 3. The release of the energy stored in the form of the strain serves as the driving force for the $CO_2$ capturing reaction.

Thus, $CO_2$ is incorporated into α-amino ketones by sequential action of solar light and a base. The sequential process presents a model of the chemical utilization of solar energy for $CO_2$ incorporation.

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[1] N. Ishida, Y. Shimamoto, M. Murakami, Angew. Chem., Int. Ed. 2012, 51, 11750.

[2] a) N. C. Yang, D.-D. H. Yang, J. Am. Chem. Soc. 1958, 80, 2913; b) E. H. Gold, J. Am. Chem. Soc. 1971, 93, 2793.

2nd Conference on $CO_2$
Carbon Dioxide as Feedstock for Chemistry and Polymers

University of Newcastle
Prof. Dr. Michael North

## Synthesis of cyclic carbonates from waste $CO_2$

The synthesis of cyclic carbonates[1] from epoxides and $CO_2$ is one of the few large scale applications of $CO_2$ with the potential to be used as part of a carbon capture and utilization (CCU) process.[2] CCU is potentially complementary to carbon capture and storage (CCS) and could offset some of the costs associated with CCS. The reaction is highly exothermic ($\Delta$Hr = 140 kJ mol-1 for ethylene oxide and $CO_2$ to ethylene carbonate), yet current commercial processes operate at high temperatures and pressures and need highly purified $CO_2$ as a reactant. Therefore, as a result of the energy use, current commercial processes generate more $CO_2$ than they utilize. Cyclic carbonates have a large number of commercial applications.[3] In particular, they are the electrolytes used in lithium ion batteries for portable electronic devices and electric vehicles which is predicted to be a major growth area. They are also used as technological solvents and are green polar aprotic solvents which can be used as direct replacements for solvents such as DMSO, DMF, NMP and HMPA.[4]

Over the last six years, we have developed bimetallic aluminium complexes as highly active catalysts for the synthesis of cyclic carbonates from epoxides and $CO_2$ in batch reactors at room temperature and pressure.[5] The combination of these aluminium catalysts and Bu4NBr gives a rate enhancement of 10–20 fold over a range of temperatures and pressures compared to the use of commercial catalyst systems based on quaternary ammonium salts alone. The mode of action of the bimetallic aluminium catalysts has been determined[6] and the catalysts have been immobilized onto silica and used to produce cyclic carbonates in a gas–phase flow reactor at 100 °C.[7] This opened the possibility of directly utilizing waste $CO_2$ or even atmospheric $CO_2$ in these reactions, giving the technology the potential to directly reduce $CO_2$ emissions from power stations or to take $CO_2$ out of the atmosphere.

Initial studies showed that the aluminium based catalysts were unaffected by the NOx and SO2 present in simulated flue gas when used to convert ethylene or propylene oxide into ethylene or propylene carbonate in a gas–phase flow reactor, though addition of SO3 to batch reactions did irreversibly deactivate the catalyst.[8] It was subsequently shown that real flue gas produced by the combustion of coal or natural gas in a 160 kW emissions reduction test facility also had no effect on the activity of the immobilized catalyst when used in a flow reactor, though a decrease in catalyst activity was noticed in batch reactions.[9]

All of the above work employed initial $CO_2$ concentrations of around 20 % to simulate the concentration of $CO_2$ present in power station flue gas. The concentration of $CO_2$ present in the atmosphere is much lower (390 ppm) and our mechanistic studies6 had shown that the rate of cyclic carbonate synthesis catalysed by bimetallic aluminium catalysts was directly proportional to the $CO_2$ concentration. However, the catalysts are so active that by carrying out reactions at 25 bar pressure and 50 °C, even compressed air could be used as the $CO_2$ source, thus permitting the synthesis of cyclic carbonates from terminal epoxides and air.[10]

Most recently, we have extended the range of substrates to 1,2-disubstituted epoxides and shown that cyclic carbonate formation occurs with complete retention of the epoxide stereochemistry. This has been developed into a method for the overall syn-bishydroxylation of alkenes which avoids the use of toxic metals such as manganese or osmium.[10]

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**Climeworks AG**

**Christoph Gebald**

## $CO_2$ Supply through Direct Air Capture

Climeworks provides solutions for efficiently capturing $CO_2$ out of ambient air ("direct air capture", DAC). We offer location-independent and environmentally friendly $CO_2$ supply to our customers.

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## Trading renewable energy by using $CO_2$: a new option towards a green use of carbon dioxide

University of Messina
Prof. Dr. Gabriele Centi et al.

Chemical utilization of carbon dioxide[1], in contrast to carbon capture and storage (CCS), has received very limited attention as an effective option to control greenhouse gas (GHG) emissions and to contribute in the mitigation of climate changes. The motivation is the supposed limited market of the chemical products of $CO_2$ conversion, although the data on the potential amount of $CO_2$ that is not emitted should be corrected by considering the energy needed in the process of sequestration or in the case of $CO_2$ utilization the amount of avoided carbon dioxide emissions related to the use of the chemicals deriving from the utilization of $CO_2$.[2] In addition, when the products of $CO_2$ chemical conversion are energy vectors (such as methanol) allowing to transport renewable energy from remote areas, the potential market is large, potentially the same of $CO_2$ anthropogenic emissions deriving from the use of fossil fuels.[3, 4] This route enables to create also a new scenario for sustainable chemical production based on the use of the products of $CO_2$ conversion using renewable energy (light olefins, methanol, etc.) as raw materials substituting fossil fuels.[5] These aspects make this $CO_2$ conversion path using renewable energy a potential valuable approach to mitigate the climate changes.

The lecture will show that (i) there is a large untapped potential for renewable energy (RE) which needs an efficient and economical way to transport these resources to long-distance areas where a possible market exists; (ii) the conversion of $CO_2$ to methanol, a liquid energy carrier which can be easy stored and transported as well as conveniently used both in the current energy chain and as raw material in the actual chemical production (e.g. without the massive costs related to change energy and chemical production infrastructure), is the preferable solution to use these untapped RE resources; (iii) methanol can be produced from $CO_2$ by using these unexploited RE resources, particularly hydropower, at a cost which is compatible with the actual cost of methanol production from fossil fuels; and (iv) the estimated impact of this technology on mitigation of climate changes is better than that of CCS, and with a significant reduction in costs and a positive effect on the transition to a low-carbon economy.

Hydropower is the largest contribution to modern renewables, e.g. excluding traditional use of biomass for combustion. Hydropower accounts for nearly 78 % of world renewable electricity generation (about 4760 TWh) in year 2012, and still about 70 % of the estimated 6,4 PWh ($10^{15}$ Wh) produced worldwide for year 2017. A reason is that the costs of power production from hydropower will remain competitive over other solutions (wind, PV). However, there is a large untapped hydropower potential. The global technically exploitable hydropower potential is estimated at more than 16,4 PWh per year, e.g. over 80 % of the potential is still unexploited. A large part of this potential can be utilized only when effective ways to transport this RE to long-distances (>500 km) are developed. This solution offers the great opportunity to combine a cost-effective increase in generation capacity to the diversification of energy sources. Deserts and arid regions offer also a large, unexploited potential for large-scale generation of RE (PV, wind) which can be exploited only when the transport to long-distance of the produced electrical energy is solved. The potential of wind and solar energy production costing less than 50 €/MWh (in 2050) in these areas was estimated to be over 10 PWh.

There is thus a potential of over 10-15 PWh per year of electrical energy which can be produced from unexploited renewable sources and which use can be enabled from the development of effective technologies to store and transport the RE using energy vectors that well integrate within the actual energy (and chemical) production chain to avoid the costs and time related to changing the actual infrastructure. In addition, electrical energy accounts today for about one third of global consumption of energy, while RE sources produce mainly electrical energy as output. Converting electrical to chemical energy allows a more flexible use in different applications and the products find use also as base raw materials for the chemistry sector enabling a new low-carbon economy.[5] It is thus reasonable the estimation that for year 2050 there is a potential of over 10 PWh per year of additional RE which could be exploited by enabling an effective route for electrical to chemical energy conversion to store and transport RE.

10 PWh correspond to 7 Gtons of equivalent $CO_2$ emissions. Blue Map Scenario of the International Energy Agency (IEA) indicates for year 2050 CCS will contribute with a removal of about 8 Gtons of $CO_2$ to this scenario. Taking into account the additional $CO_2$ emissions due to carbon dioxide capture, transport and storage, the effective contribution is about half. The proposed path of using $CO_2$ to trade unexploited RE sources is thus potentially better of CCS in contributing to climate change mitigation. In addition, it is an economically more effective path. The $CO_2$ avoidance costs for possible new CCS plants was estimated ranging from 35 to over 90 €/ton of $CO_2$, with the upper range likely in regions such as Europe considering transport costs to storage sites. As shown below, methanol could be produced at a cost economically competitive with the actual production from fossil fuels by using cheap electrical energy produced in remote areas and by considering the avoidance of carbon taxes costs estimated in about 20 €/ton of $CO_2$. It is thus possible an economically competitive route (with respect to CCS) reducing at least to half the costs with further benefits: (i) reduced emissions of both pollutants (NOx, etc.) and greenhouse gases (use of unexploited RE sources reduces the need of new power plants as well as of extraction of fossil fuels); (ii) better diversification of energy resources (with benefits in terms of energy security) and greater flexibility in use (methanol or DME can be used to produce components for the transport sector); (iii) better flexibility in energy management to follow fluctuating energy demand, because for example methanol-fuelled turbine have a rapid switch off-on time. Methanol is considered a superior turbine fuel.

$CO_2$ conversion to liquid fuels such as methanol ($CH_3OH$) or dimethyl ether (DME, $CH_3OCH_3$) in one of the preferable routes (due to energy density and cost-effectiveness) for electrical to chemical energy conversion6 and to produce (using renewable energy) liquid energy vectors/chemicals to store and transport energy.[7] In addition, these products are fully compatible with the actual energy and chemical production value chain. We will present in the lecture the results of techno-economic assessment on the production of methanol from $CO_2$ and renewable H2, produced by water electrolysis using electrical energy produced in remote areas when local use in not possible neither transport. The methanol production cost, taking into account the benefit of avoided emissions (20 €/ ton $CO_2$), is 294 €/ton of methanol, resulting competitive against an average market value of 370 €/ton.

In conclusions, the data reported here show that the utilization of $CO_2$ to produce methanol (to be used as energy vector and raw material for chemical production) in remote areas, where cheap renewable $H_2$ could be produce from renewable sources, is a technology having a potential impact estimated to be at least comparable with that of CCS, but with advantages in terms of reduction of costs, lower impact on environment and energy security by enabling the use of unexploited renewable energy resources. Further benefits are in terms of good integration with the actual energy and chemical production value chain, and of solving the issue of intermittency in most of renewable energy sources. The technology could be extended to produce different type of products from methanol (DME, light olefins, etc.) and developments are underway to directly develop devices (indicates also as artificial leaves8) to make in a single-step what currently requires multi-steps (preserving thus future competiveness). This route has thus all the characteristics to become a new effective option to mitigate climate changes.

This work is a summary of a paper submitted to Science. The EU project NEXT-GTL (NMP-3-LA-2009-229183) and PRIN10-11 project “Mechanism of activation of $CO_2$” in the frame of which part of this work was realized are gratefully acknowledged.

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**Leibniz-Institut für Katalyse e.V.**

**Prof. Matthias Beller**

## Hydrogen Storage with Carbon dioxide: Opportunities for Homogeneous and Heterogeneous Catalysis

The sufficient and sustainable supply of energy remains one if not the most important challenge for our future. An abundant source of energy is sunlight. In the coming years it will be vital to develop efficient artificial processes to interconvert the energy of light with chemical energy. In the talk possibilities to achieve this goal will with the help of molecular-defined catalysts will be discussed. Special emphasis will be placed on hydrogen as chemical energy vector. Among the different chemical energy carriers hydrogen has received significant attention. However, the cheap and sustainable generation and storage of hydrogen remains challenging. In this respect our concept to use of carbon dioxide as storage material for hydrogen and the controlled decomposition of formic acid to hydrogen will be discussed in detail.

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2nd Conference on $CO_2$ Carbon Dioxide as Feedstock for Chemistry and Polymers

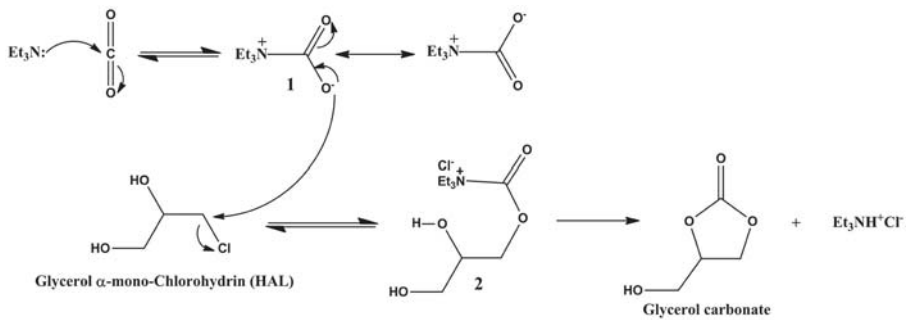
# Synthesis of glycerol carbonate from Glycerol α-monochlorohydrin and subcritical carbon dioxide using triethylamine as $CO_2$ fixation-activation agent

**Tecnalia**

**Dr. José R. Ochoa-Gómez et al.**

## 1. Introduction

Chemical industry is now interested in obtaining valuable chemicals from biomass or biomass-derived compounds such as glycerol and/or $CO_2$. Glycerol carbonate (GC) is one of such chemicals due to its physical properties and chemical reactivity leading to broad range of potential applications [1,2]. Attempts for synthesizing GC directly from glycerol and $CO_2$ have been unsuccessful from an industrial standpoint due to poor $CO_2$ reactivity [3-4]. So, currently the synthetic approaches to GC are indirect ones starting from more reactive derivatives of glycerol and/or $CO_2$ [1,2]. One of such approaches is the object of this work and starts from glycerol α-monochlorohydrin (HAL), an easily synthesizable glycerol derivative [5], and $CO_2$, in which triethylamine (TEA) is used for both $CO_2$ fixation and activation (Scheme 1).




Scheme 1: Reaction between HAL and $CO_2$ through $CO_2$ activation with TEA

## 2. Experimental

Reactions were carried out in an Autoclave Engineers model MagneDrive II equipped with 5 stainless steel vessels of 100 mL. Chemicals were analysed by GC-FID in a Varian 450-GC apparatus and a 30 m x 0.25 mm DB-WAX column, 0.25 µm, using ethylene glycol or butylene glycol as internal standards.

## 3. Results and discussion

The influence on conversions and yields of TEA/HAL molar ratio, temperature, $CO_2$ pressure and reaction time has been studied. A 100 % HAL conversion and a 90 % GC yield are obtained at 100ºC and 60 min using a 1.5 TEA/HAL molar ratio and a $CO_2$ pressure of 25 bar. Glycerol was the only by-product detected in 4–6 % yields. Temperature is the most influent variable (Fig. 1). Above 100ºC, GC yields decrease dramatically due to GC polymerization resulting in polyglycerols. GC yield is strongly and negatively influenced by water presence. Experimental evidence supports a reaction mechanism (Scheme 2) which proceeds through a zwitterionic adduct 1 between TEA and $CO_2$ which reacts with HAL through a SN2 reaction resulting in an intermediate 2 which evolves to GC either directly or through glycidol.

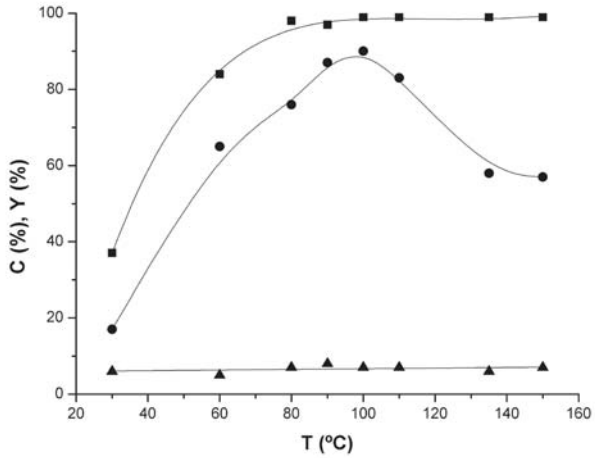
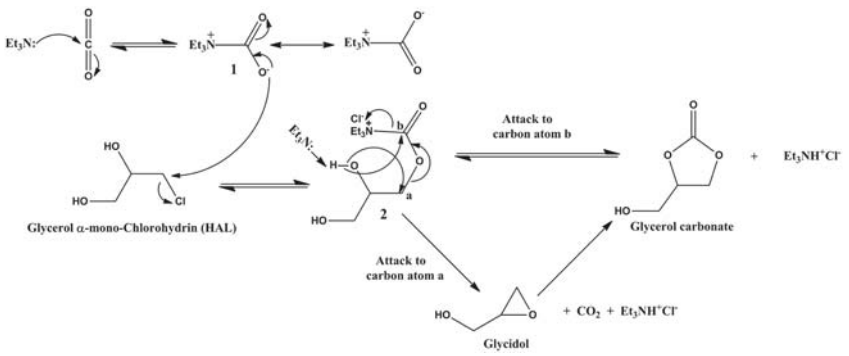



Fig.12: Variation of conversion (C, ■) and yields (Y, ●: glycerol carbonate; ▲: glycerol) with temperature ($CO_2$ pressure: 25 bar; 60 min; TEA/HAL molar ratio: 1.5).




Scheme 2: Proposed simplified reaction mechanism

## Acknowledgements

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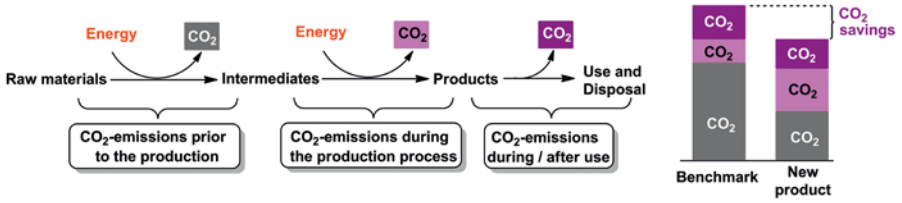
2nd Conference on $CO_2$
Carbon Dioxide as Feedstock for Chemistry and Polymers

# Utilization of $CO_2$ in the production of fine chemicals on industrial scale

Evonik Industries AG
Dr. Benjamin Schäffner et al.

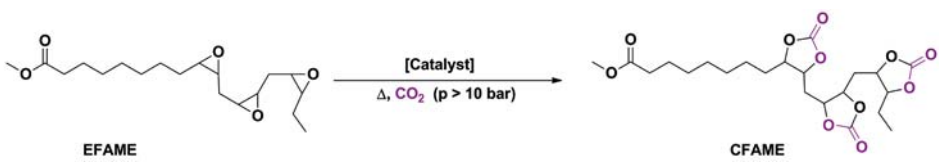
## Introduction

$CO_2$ is discussed as available, cheap and non-toxic building block for the chemical industry. Although utilization of $CO_2$ will not significantly contribute to the mitigation as greenhouse gas, its use can open up new pathways for chemicals (scheme 1). Especially for $CO_2$-utilization Life-Cycle-Assessments (LCA) are essential to prove $CO_2$ savings due to the additional need of energy intensive co-reagents or conditions (intermediates → products). However, $CO_2$ can act as enabler to obtain molecules via new pathways which can lower the environmental burden compared to established benchmarks (raw materials → intermediates).




Scheme 1: LCAs as essential part of CO2-utilizing processes in comparison to an established benchmark.

CFAME was synthesized by carbonation of EFAME with $CO_2$ in the presence of a suitable catalyst. (scheme 2). The obtained material has been tested as plasticizer and lubricant. Finally, a LCA was performed to determine the sustainability of CFAME as plasticizer.




Scheme 2: Carbonation of EFAME by using various catalysts & conditions.

# 2nd Conference on $CO_2$

Carbon Dioxide as Feedstock for Chemistry and Polymers

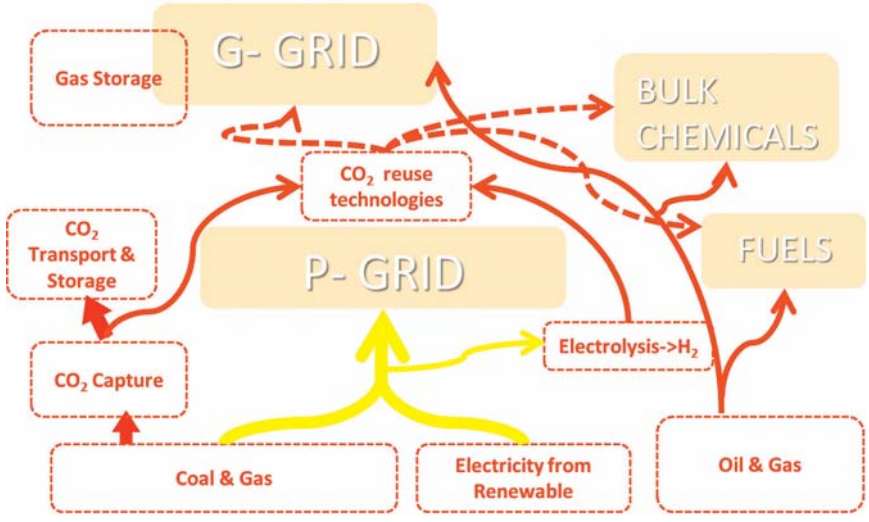

**Delft University of Technology**

**Dr. Wim Haije et al.**


## $CO_2$ to fuels: enabling the sustainable energy society

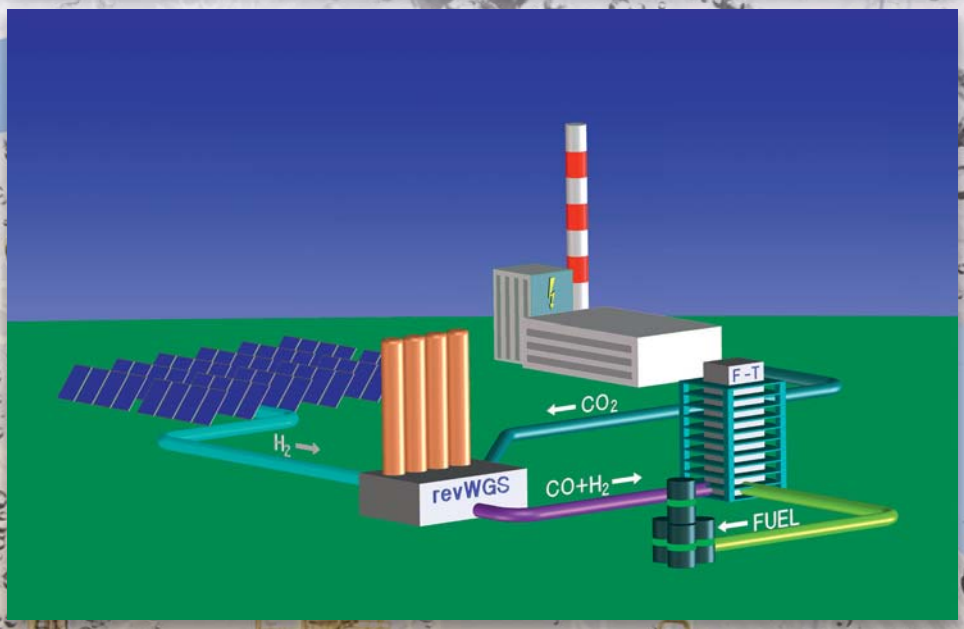
There is a clear transition apparent from regarding $CO_2$ as waste to using it as valuable feedstock for chemicals and as enabler of the introduction of large scale sustainable energy. CCU (carbon capture and use) clearly contributes to reducing net emissions of this greenhouse gas and is complementary to CCS (carbon capture and storage). $CO_2$ as raw material is therefore an upcoming field of R&D. There are three distinct R&D areas to be discerned, i.e. sustainable electricity storage, enhanced resource production and green production of chemicals:

- Using $CO_2$ in fuels production related to intermittency/variability of sustainable sources and in upgrading methane streams with high $CO_2$ content. In sustainable power production electricity storage is of utmost importance. The production of liquid fuels, methanol/DME and Fischer-Tropsch, is one of the best options (volumetric/gravimetric energy density), and for countries with a dense gas grid the formation of methane is second best.
- Using $CO_2$ at commercial scales for enhanced fossil resource recovery, which is already a fact.
- Using $CO_2$ in chemicals production, i.e. new $CO_2$ based polymers is primarily driven by the need for new green resources. It leads to new, better chemical products and a significant reduction of fossil feedstock use. This is primarily done at present by companies and research institutes in Germany, e.g. BASF, BAYER, and at a smaller scale in the Netherlands, e.g. AkzoNobel, DSM.



The first two options are the most important ones in terms of scale: e.g. $CO_2$ emissions in the power sector are about 1–2 orders of magnitude larger than carbon use in chemical industry. Replacing fossil based power plants by renewables is then the largest contribution to $CO_2$ abatement.

Carbon capture and utilization (CCU) indeed offers an attractive option to divert part of the carbon dioxide from the future transport and storage infrastructure while providing a raw material that may be used for renewable power storage, after conversion to fuels or chemicals. Especially when renewable power capacity contributes significantly to the global power production, $CO_2$ conversion technologies may find applications for small and large scale energy storage and can secure thereby power supply, fuel supply, and basic (feedstock) chemicals supply. $CO_2$ utilization technologies may provide a reliable option to recover variable surplus power produced by the renewable power generation facilities installed.




Analysis of technological bottlenecks clearly points at the need to develop process schemes that can cope with variable supply pattern and process design that allows for efficient part-load operations and rapid shut-down/ start-up procedures.

2nd Conference on $CO_2$
Carbon Dioxide as Feedstock for Chemistry and Polymers

**Bayer MaterialScience AG**
**Dr. Christoph Gürtler**

## Polyurethanes from $CO_2$ capture: A successful Story

Carbon dioxide as the basis for high-quality plastics: promising new potential applications for the greenhouse gas (GHG) were identified by Bayer and partners working together in a three-year research alliance. A polyurethane based foam was produced using the $CO_2$ captured from a coal fired power plant as part of the publically funded Dream Production project. Because the carbon dioxide replaces a portion of the petroleum from which the foam is normally made entirely, the new process contributes to the conservation of limited fossil resources.

Comprehensive testing by Bayer has even shown that the $CO_2$-based polyurethane foam outperformed in several properties its conventionally produced counterpart. Polyurethane is used in many areas of daily life, including in mattresses, upholstered furniture, shoe soles and automotive components. It is also used as an insulating material for buildings and refrigeration equipment.

### Pilot plant in Leverkusen

Bayer is initially using $CO_2$ in a pilot plant in Leverkusen to produce polyol, a key chemical precursor for polyurethanes, for testing purposes. The carbon dioxide is provided by project partner RWE, which separates it from the flue gas of a lignite-fired power plant outside Cologne. The $CO_2$ is chemically bound in the polyol and later in the polyurethane.

In early 2013, the new method was successfully converted from the production of discrete quantities to continuous production, a key intermediate step for the industrial-scale production of $CO_2$-based polyurethane, which Bayer is targeting for 2015. The company recently announced that the planning process for a commercial plant iscurrently under cinstruction in Dormagen (Germany).

### Positive eco-balance

The environmental benefits of the process were analyzed within a detailed life cycle assessment (LCA) conducted by RWTH Aachen University, another project member. The LCA analysis employs a so-called cradle-to-gate approach: provision of all feedstocks including $CO_2$ from RWE's power plant, transport processes, provision of process energy and the production process of polyols itself are all taken into account. The LCA results show that the $CO_2$–based process reduces both life-cycle GHG emissions and fossil resource depletion significantly. These reductions originate mainly from substitution of epoxides by $CO_2$.

The process became possible when Bayer found a suitable catalyst for which experts had been searching for over 40 years. The catalyst enables the efficient reaction of $CO_2$, which is normally slow to react. The special carbon dioxide catalysis process was co-developed and is being further developed in collaboration with an additional project partner, the CAT Catalytic Center. This research facility in Aachen is funded jointly by the university there and Bayer.

Dream Production was funded in part by the German Ministry of Education and Research. The funding period expired in May 2013. Bayer now continues the project and is looking for partners in the value-added chain to the consumer as the project moves to market maturity.

2nd Conference on $CO_2$
Carbon Dioxide as Feedstock for Chemistry and Polymers

# Opportunities of $CO_2$-Based Polymers in Composites with Biopolymers and Natural Fibres

CSIRO
Dr. Xiaoqing Zhang et al.

## Introduction

Utilization of $CO_2$ as a monomer in the synthesis of new biodegradable polymers has the potential to provide huge economic and environmental benefit as this will be an increasingly important part of carbon constrained economies into the future. Reaction of $CO_2$ with epoxy monomers to produce biodegradable poly(ether carbonates) has been attracting increasing interest since new catalysts have been developed in recent years with greatly improved efficiency in material manufacture. These $CO_2$ polymers would provide a sustainable way to produce alternative biodegradable polymers other than natural polymers (starch, cellulose, proteins) and synthetic biodegradable polymers (such as polylactic acid, polybutylene succinic adipate) without competing with food and energy consumption of agriculture products. $CO_2$-based biodegradable poly(propylene carbonate) (PPC) has been developed and commercially manufactured. It can contain up to 48 wt% of $CO_2$, depending on the content of the polypropylene oxide segments. A wide variety of applications of PPC are beginning to emerge, from low molecular weight monomers for organic synthesis to polymerisation into high molecular weight thermoplastics.

The polymer engineering group at CSIRO-MSE has a long history working on biodegradable polymers and biocomposites. We recently applied PPC as polymer matrix to make biocomposites with wood fibres and compared the results with those using poly(lactic acid) (PLA) as matrix. The thermal stability under processing conditions, mechanical properties of the biocomposites and bonding interactions with wood fibres were examined.

## Results and Discussion

PPC and PLA wood fibre biocomposites were produced via thermal mixing PPC and wood flour then compression moulding into sample sheets at 170 C. The bonding between PPC and wood flour was strong, and the biocomposites displayed sufficient thermal stability under thermal mixing and compression moulding conditions at 170°C; the molecular weight was only reduced slightly during 10 min thermal processing at the temperature. The mechanical properties of PPC biocomposites were relatively weaker than those of PLA biocomposites, but the gape was decreased when the wood fibre content was increased in the composites. Importantly, ductile failure mode of PPC composites was detected as compared to brittle failure mode for PLA composites as shown in Figure 1.

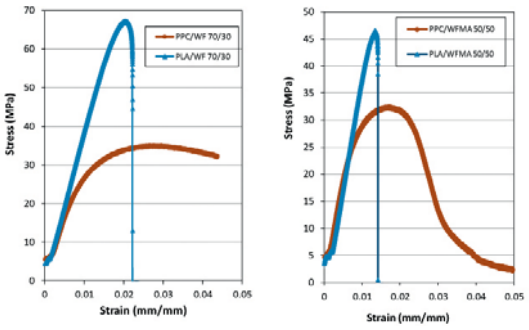



Figure 1: Failure modes of PPC and PLA biocomposites.

However, the glass transition temperature of PPC is relatively low; just around 40 °C, and this would be an issue for the dimensional stability of the composites used at high temperatures. PPC foam were also produced with density as low as 30 g/L. The low Tg of PPC also caused a stability problem for the PPC foam.

It appears that modification of high molecular weight PPC with other polymers or additives is necessary to enhance the material performance. Low molecular weight PPC might have opportunities in the application as composite binder when using suitable chain extension agents and crosslinkers to form crosslinked network. Future work will be also focused on developing new generation of $CO_2$ based co-polymers with improved properties including higher Tg, varied functionalities for designed applications, and enhanced mechanical and barrier properties.

**References:**

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## $CO_2$ and CO fermentation: A Route from Waste to Fuels and Chemical Building Blocks at Scale

**LanzaTech**

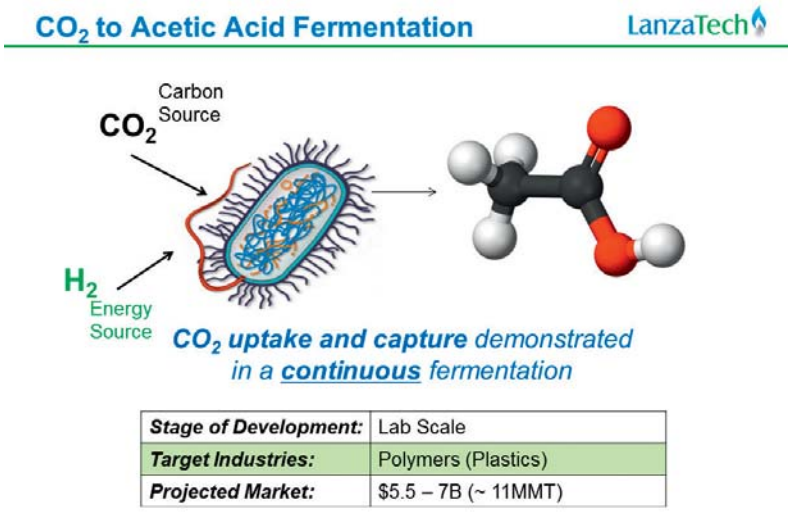
**Grainne Smith**

LanzaTech has developed a gas fermentation platform for the production of alternative transport fuels and commodity chemicals from carbon monoxide, hydrogen and carbon dioxide containing gases. At the core of the process is a proprietary microbe capable of using this broad spectrum of gases as the only carbon and energy input for product synthesis. LanzaTech's robust synthetic biology platform enables production of commercially valuable products through the synthesis of a variety of novel molecules through gas fermentation.

LanzaTech initially focused on the fermentation of CO rich industrial waste gases for fuel ethanol production and has demonstrated this at pilot scale using flue gases from a working steel mill since 2008. A pre-commercial unit processing steel mill waste gases was commissioned in China in 2012 with commercial scale operations targeted for 2013/2014.

Gasified biomass and reformed natural gas have also been used as an input gas stream for the process moving the technology beyond industrial CO-rich waste gases.

Carbon dioxide as the sole carbon source for chemical syntheis has been a more recent focus of work and LanzaTech has developed proprietary microbial catalysts capable of converting $CO_2$ in the presence of hydrogen directly to value added chemicals.




| | |
|---|---|
| ***Stage of Development:*** | Lab Scale |
| ***Target Industries:*** | Polymers (Plastics) |
| ***Projected Market:*** | $5.5 – 7B (~ 11MMT) |

The pathway entails the conversion of $CO_2$ to acetate which is subsequently converted to fuels and chemicals. The LanzaTech process can, therefore, potentially afford greater commercial opportunities for marginal or $CO_2$ contaminated gas fields via unique integration schemes that have been simulated, whilst also capturing fossil carbon in valuable products. LanzaTech is also currently working with partners to create a new process for the direct conversion of waste $CO_2$ into "drop-in" fuels through an acetates-to-lipids pathway.

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# 2nd Conference on $CO_2$

Carbon Dioxide as Feedstock for Chemistry and Polymers

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8–10 April 2014, Maternushaus, Cologne, Germany

**Highlights from Europe:** Bio-based Plastics and Composites – Biorefineries and Industrial Biotechnology

## HIGHLIGHTS FROM EUROPE:
## Bio-based Plastics and Composites – Biorefineries and Industrial Biotechnology

This conference aims to provide major players from the European bio-based chemicals, plastics and composite industries with an opportunity to present and discuss their latest developments and strategies. Representatives of political bodies and associations will also have their say alongside leading companies. For the second time, the conference will count with a third day especially dedicated to the recent achievements in research & development. One highlight of the conference will be the presentation of the first running European biorefineries and the state-of-the-art of Industrial Biotechnology.

The 7th International Conference on Bio-based Materials ("Biowerkstoff-Kongress") builds on successful previous conferences: in 2013 more than 180 participants and 10 exhibitors were represented. More than 200 participants and 20 exhibitors mainly from industry are expected!

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## Innovation Award "Bio-based Material of the year 2014"

For the seventh year running the Innovation Award "Bio-based Material of the Year" will be awarded to the young, innovative bio-based chemicals and materials industry for finding suitable applications and markets for bio-based products. The competition focuses on new developments in these areas, which have had (or will have) a market launch in 2013 and 2014, exclusively coming from Europe this time round.

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Use the extraordinary chance to present your company and your products at the conference with an exhibition stand! Prices starting at 800 €.

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The venue is 10 minutes walking distance from the central station and 30 minutes distance by train from Cologne/Bonn airport.

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Conference incl. Catering, plus 19 % VAT

| 1st Day Conference 8 April 2014 | 2nd Day Conference 9 April 2014 | 3rd Day Conference 10 April 2014 |
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For more than 14 years, the news portal "www.bio-based.eu/news" has been offering up-to-date expert knowledge about everything concerning bio-based chemistry and bio-based plastics and composites. A newsletter is published every week; the archive contains more than 12,000 reports and more than 3,000 companies.

So far, access to the portal required a fee, but starting from 1 October, it will be completely free for everyone and will grow to be the central point of information for the whole branch. This is your opportunity to place your banner, when we restart the portal:

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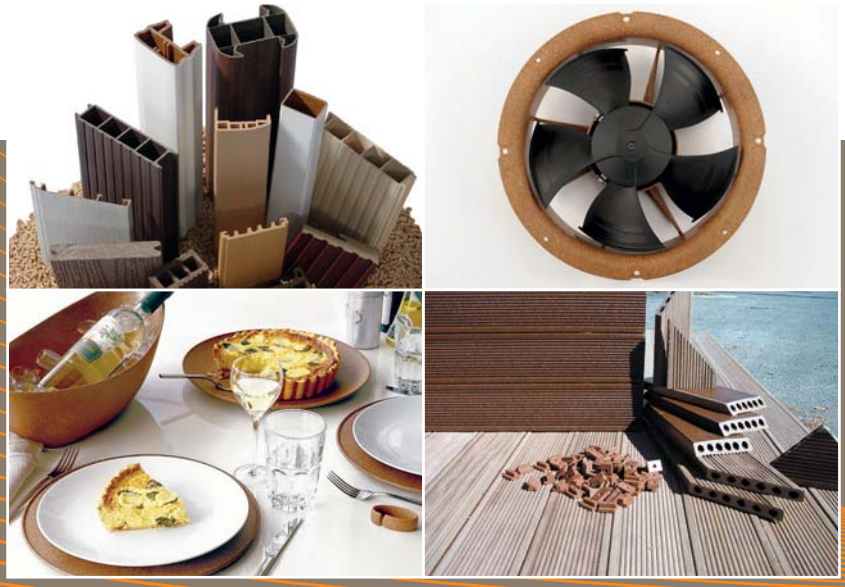

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