3rd Conference on CO_2

Carbon Dioxide as Feedstock for Chemistry and Polymers

www.co2-chemistry.eu

CO_2 as chemical feedstock – a challenge for sustainable chemistry

2–3 December 2014, Haus der Technik, Essen (Germany)

Conference Journal

1st Day, 2 December 2014
Policy & visions + CO_2 capture & purification + H_2 generation: prerequisite for CO_2 economy

2nd Day, 3 December 2014
CO_2 based fuels + Chemicals and building blocks + Polymers & materials

- Biggest event on CO_2 as feedstock
- Full programme of the conference
- Presentation abstracts
- Poster abstracts

NEW

Newsticker on Carbon Capture and Utilization!
Free Access: www.co2-chemistry.eu/news

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Gold Sponsor
EnergyRegion.NRW Cluster North Rhine-Westphalia
www.energieregion.nrw.de

3rd Conference on CO_2

Carbon Dioxide as Feedstock for Chemistry and Polymers

Table of contents

Venue

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Germany

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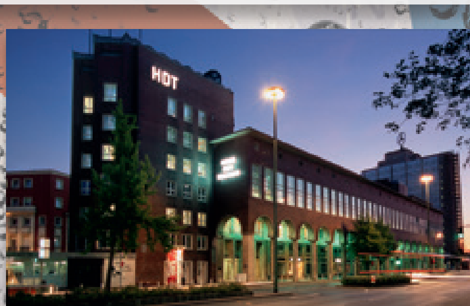
www.hdt-essen.de



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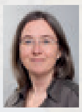

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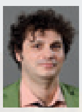

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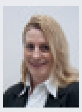

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Message of Greeting

Carbon dioxide is not just a harmful substance. It can serve as a raw material which opens up new prospects for solving global challenges. Approaches have been developed which address both climate change and the consumption of natural resources. Initial results show that this strategy has potential for the future. In mid-November, the world's first power-to-liquid demonstration plant based on a highly efficient fuel cell was opened in Germany for the production of alternative fuels and hydrocarbons for chemical refineries. We will need more such modern approaches in the future. That is why we need research to develop technologies for carbon capture and utilization (CCU).

The Federal Government attaches great importance to the promotion of innovative solutions for addressing future challenges. Since 2009, the Federal Ministry of Education and Research has been systematically supporting efforts to use carbon dioxide as a feedstock. We are providing €100 million for the world's largest CCU research programme. German industry is providing another €50 million. Furthermore, the Federal Government wants to ensure that ideas can be translated more quickly into innovations. We have adopted a new High-Tech Strategy for this purpose which involves research, industry and society. It will help us create employment and growth for a sustainable future.

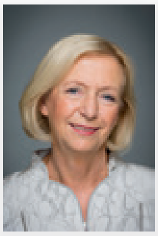
The conference "CO_2 as chemical feedstock – a challenge for sustainable chemistry" can help bring us closer to this goal. It offers representatives from science and industry an opportunity to learn about the latest research findings and engage in networking. The participation of many international experts enables a cross-border perspective on this research field.

I wish you all interesting discussions and fresh inspiration for your work. Let us focus even more strongly on the potential which carbon dioxide offers for solving future challenges.

Prof. Dr. Johanna Wanka
Federal Minister of Education and Research

Patronage

Federal Ministry of Education and Research (BMBF)



Prof. Dr. Johanna Wanka

Federal Ministry of Education and Research

3rd Conference on CO_2

Carbon Dioxide as Feedstock for Chemistry and Polymers

nova-Institut GmbH

Michael Carus

nova-Institut GmbH
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www.bio-based.eu

Dear participants,

We are happy to welcome more than 150 people from over 25 countries! During the last years, we have seen a rapid development in the area of CO_2 capture and utilization (CCU) and the related economy, spanning all the way from research activities to actual industrial applications and investments in power-to-gas installations, solar fuels and even in CO_2-based polymers such as PPC, PEC and polyurethanes. This development is, among others, based on the fact that the use of CO_2 as a resource could be the key to finding the ultimate solution for society's ever growing hunger for raw materials and energy while also significantly contributing to stopping the increase of atmospheric greenhouse gas concentration. Together with solar and wind power, water, CO_2 can cover all of humanity's needs.

However, bridging all these aspects is a very particular challenge. Before we can enter this golden age, CCU and the related economy need to be further developed, in order to be cost competitive and environmentally benign. At this two-day conference we will discuss technologies, strategies and visions that can support this development with leading experts of the field. Moreover, there will be a poster session and a dinner buffet, which will give you plenty of opportunity for personal exchange and networking.

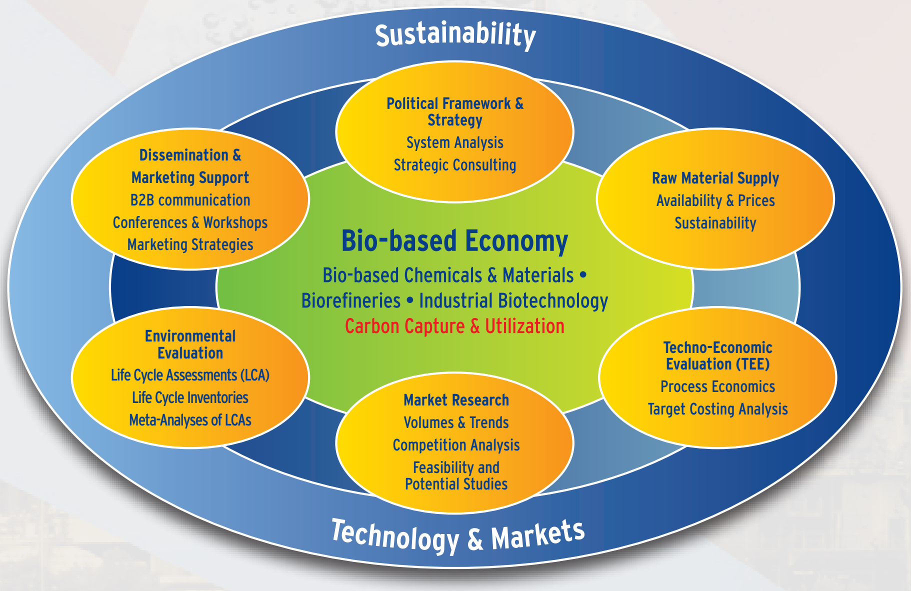
The conference is under the patronage of the Federal Ministry of Education and Research.

We hope that you will join us on this exciting journey and wish you an inspiring stay at the conference.

Your Michael Carus

Managing Director nova-Institute

Our services in the bio-based economy for companies, associations and politics



Cluster "EnergyRegion.NRW" amalgates North Rhine-Westphalia´s energy industry expertise

North Rhine Westphalia has intensified its cluster activities in the energy economy domain.

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.

"We know the state's energy companies and institutions very well. And so we can pass on enquiries directly and promptly to the right recipients", 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.

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. More than 3,000 companies and institutions have joined the state's energy economy cluster. Three quarters of the companies involved are small and medium-sized enterprises. More than 150 universities, institutes and associations are members.

The cluster's work concentrates on nine areas of the energy economy: Biomass, geothermics, the topic of energy-efficient and solar construction, future fuels and drives, the topic of fuel cells and hydrogen, photovoltaics, power plant engineering, power storage and transmission and wind power.

Gold Sponsor

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3rd Conference on CO_2
Carbon Dioxide as Feedstock for Chemistry and Polymers

Programme of the 1st Day, 2 December 2014

09:30 Registration and welcome coffee

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

Opening words of the Federal Ministry of Education and Research (BMBF)

POLICY & VISIONS

Chairwoman
Katy Armstrong
UK Centre for Carbon Dioxide Utilization

10:10

European Commission, DG Energy
Andreas Pilzecker
Carbon Capture and Use in EU Policy

10:40

Federal Ministry of Education and Research (BMBF)
PD Dr. Lothar Mennicken
Update on the German R&D Programme for CO_2 Utilisation – Innovations for a Green Economy

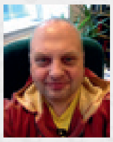
11:10

nova-Institut GmbH
Michael Carus
Industrial Utilization of CO_2: Suitable Strategy and Political Framework for Implementation

11:40 Coffee Break

12:00

Virgin Earth Challenge
Guy Lomax
'If you want to go fast, go alone. If you want to go far, go together' – an Updated Vision for CO_2 Utilisation's Role in a Sustainable Future

12:30

CO_2Chem Initiative
Prof. Dr. Peter Styring
Carbon Capture and Utilisation in the Green Economy – Activities of the CO_2Chem Network

13:00

Tecnon OrbiChem
Roger Lee
Overview of CO_2-based Chemicals Development

13:30 Press conference & Lunch Break

CO_2 CAPTURE & PURIFICATION

Chairman
Michael Carus
nova-Institut GmbH

14:45

Linde Engineering Dresden GmbH
Olaf Christoph
Industrial CO_2 Utilization in Commercial Scale – Presentation of a Project Realization

15:15

Climeworks AG
Jan Wurzbacher
CO_2 Supply through Direct Air Capture – Update on Climeworks Activities

H_2 GENERATION: PREREQUISITE FOR CO_2 ECONOMY

Chairman
Bruce Dannenberg
Phytonix Corporation

15:45

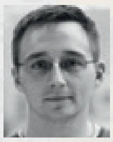
sunfire GmbH
Christian von Olshausen
Power-to-Liquids: Synthetic Hydrocarbons from CO_2, H_2O and Electricity

16:15 Coffee Break

16:45

Hydrogenics Europe N.V.
Denis Thomas
Power-to-Gas: Shifting Power with Grid-scale Water Electrolysis

17:15


University of Cologne
Prof. Dr. Sanjay Mathur, Thomas Fischer
SOLAROGENIX

17:45 Discussion with speakers from the first day, nova-Institut GmbH Dr. Fabrizio Sibilla

20:00 Dinner Buffet

Programme of the 2nd Day, 3 December 2014

CO_2 BASED FUELS

Chairman
Lars Schulze-Beusingsen
EnergyAgency.NRW

09:00

bse Engineering Leipzig GmbH
Christian Schweitzer
Integrated Concept to utilize Biochemical generated CO_2 for Thermochemical Fuel Production; Technical Feasibility – legal Challenges – Commercial Viability

09:30

Technical University of Denmark
Prof. Dr. Mogens Bjerg Mogensen
Production of Green Fuels using Solid Oxide Electrolysis Cells: Status and Perspectives

10:00

NewCO_2Fuels
Julie Horn
Converting CO_2 and H_2O into Syngas using high Temperature Heat

10:30 Coffee Break

11:00

Lanza Tech
Grainne Smith
Carbon Recycling for Sustainable Fuels and Chemicals

11:30

Phytonix Corporation
Bruce Dannenberg
Direct Photobiological Conversion of Carbon Dioxide Feedstock into Renewable Chemicals and Fuels

CHEMICALS & BUILDING BLOCKS

Chairman
Dr. Christoph Gürtler
Bayer MaterialScience AG

12:00

Politecnico di Torino
Prof. Dr. Guido Saracco
High Efficiency Photo-electron-chemical Reactors for Solar Fuels Production

12:30

UK Centre for Carbon Dioxide Utilization
Katy Armstrong
Smart CO_2 Transformation (SCOT): Defining a Strategic European Research and Innovation Agenda

13:00 Lunch Break

14:00

Avantium
Dr. Klaas Jan Schouten
Biorefinery Chemicals using Photo-electrochemical CO_2 Reduction in the Eco^2CO_2 Project

POLYMERS & MATERIALS

Chairman
Prof. Dr. Peter Styring
CO_2Chem Initiative

14:30

Bayer MaterialScience AG
Dr. Christoph Gürtler
CO_2-based Polyurethanes on the Way to Commercial Scale

15:00 Coffee Break

15:30

Econic Technologies Ltd.
Dr. Rulande Henderson
Econic Catalyst Systems for Polycarbonates and Polyols from CO_2

16:00

Novomer Inc.
Simon Waddington
Carbon Dioxide-Based Polycarbonate Polyols for Polyurethane Systems; Commercial Applications of CO_2 based Polyols

16:30 Networking reception with snack

Federal Ministry of Education and Research (BMBF)

PD Dr. Lothar Mennicken

Update on the German R&D Programme for CO_2 Utilization – Innovations for a Green Economy

Today, the Chemical Industry relies heavily on fossil resources like oil or gas. But not only as an energy source: Roughly 80 % of all chemical products are made out of crude oil as a raw material. Furthermore, the transportation sector depends almost completely on petroleum to produce petrol, diesel and kerosene. Even in the future it is unlikely that the transportation sector will be free of carbon-based fuels; airplanes and the cargo ships will be in need of these high-density energy carriers. CO_2 utilisation opens new pathways to chemical storage of renewable energy.

In order to reduce the dependency of the German economy on fossil raw materials by substitution the Federal Ministry of Education and Research (BMBF) supports R&D in this area with the funding measure *„Chemical Processes and Use of CO_2"*, part of BMBF's framework programme *"Research for Sustainable Development (FONA)"*. The replacement of crude oil also significantly reduces CO_2-emissions in a two-folded way: 1) CO_2 is directly incorporated into products and 2) fossil-based raw materials are replaced by CO_2-based raw materials. Currently, in Germany 33 collaborative projects with more than 150 partners are supported with a total funding volume of 100 Mio. € (2009–2016). An additional investment has been made by the industry of app. 50 Mio. €.

The funding measure has already proven very successful: Two projects are already very close to a market implementation of their newly developed processes. In the project "Dream Production", Bayer is currently constructing a production plant for alternative foam plastics after proving successful on a pilot scale level. The worldwide first Power-to-Liquids-pilot plant "sunfire fuel-1" was recently opened in Dresden, Germany by the Federal Minister of Education and Research, Johanna Wanka.

Projects that have already been proven successful in the lab and are seeking the way into the market via demonstration plants can be supported by the novel funding measure "r+Impuls". BMBF will also keep on supporting R&D-projects in the CO_2-utilisation field.

After five years of R&D in the worldwide largest single CCU-Programme, many projects show very promising results and a preliminary evaluation has shown that there significant effects on CO_2-emission reduction and many innovations towards a "green economy" are on the way. Final results from this programme will be presented in Berlin, 21st and 22nd April, 2015.

Industrial Utilization of CO_2: Suitable Strategy and Political Framework for Implementation

nova-Institut GmbH

Michael Carus

The presentation will discuss challenges related to the development of a suitable framework for the fast implementation of CCU. Among others, it will tackle questions such as:

- Which barriers and prejudices against CCU can be identified and how to overcome them?
- What is the latest status of policy integration of CCU in the Renewable Energy Regulations?
- How can the perception of CCU in the public, environmental and political discussion be influenced?

Since the success of CCU is directly linked to the solar and wind industry, the presentation will also give an up to date overview of their volume and cost development. Moreover, a comparison between biomass utilization and CCU with regard to their land efficiency will be presented and discussed. Finally, the presentation will touch upon the potential combination of biogas and bioethanol production with CO_2 utilization.

Tecnon OrbiChem

Roger Lee

Overview of CO_2-based Chemicals Development

Carbon dioxide is not promising for industrial chemical use, due to its thermodynamically stable state, but it is receiving increasing attention due to the need to abate CO_2 emissions. CO_2 from energy generation from fossil fuels is of low cost and indeed may become of zero or even negative cost as abatement measures become obligatory. There are several approaches to compensating for the low energy state of CO_2 which may be classified as follows:

1. Combine CO_2 with energy rich reactants that provide the thermodynamic drive to complete a reaction. Examples already in widespread use are the production of methanol from CO_2 and natural gas or of urea from CO_2 and ammonia. Accompanying CO_2 with hydrogen can facilitate complex reactions. The key in such processes is often having the presence of a suitable catalyst which, however, then requires the use of purified CO_2.
2. Preserve a **–CO–O–** linkage in the final molecule, such that the energy required for conversion is limited. Examples are the use of CO_2 to produce diethyl carbonate or polycarbonates and production of polyether carbonate polyols for the manufacture of polyurethane products.
3. Employ CO_2 as a co-reactant in metabolic processes. The energy needed comes from the action of microorganisms on an energy-rich substrate, typically a sugar. One example is the fermentation of lignocellulosic sugar hydrolysate using modified E. coli strains, in the presence of CO_2 to produce succinic acid.
4. Accompany the CO_2 reaction with external energy input, as in electro-catalytic or photo-catalytic activation. An example is the reaction of CO_2 with water in an algae bioreactor exposed to sunlight, when a photosynthetic reaction takes place under the action of chlorophyll-containing algae. Such a reactor can be designed to produce ethanol or biodiesel, while generating animal feed.

This presentation will cite case studies of companies that have been developing technologies in this space, including some already in the commercialisation phase. It will explore challenges and opportunities associated with the chemical markets and supply chains that these companies would want to compete in. Tecnon OrbiChem will also provide perspectives on the current supply/demand situations for several petrochemical-based and bio-based chemical intermediates, and look at how CO_2-based chemicals could fit into their market dynamics.

www.orbichem.com

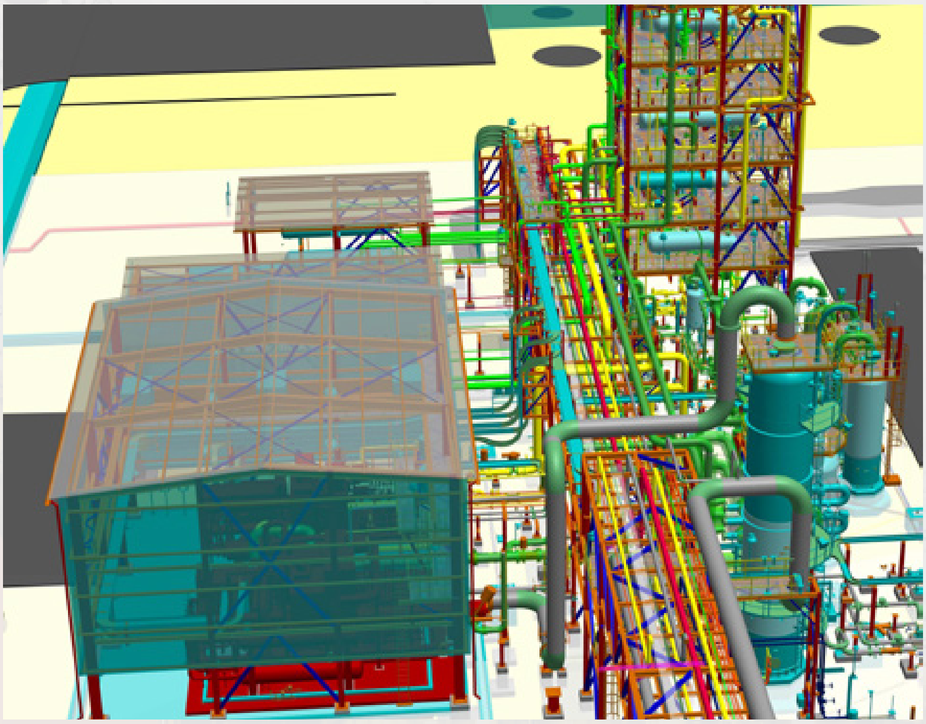
Industrial CO_2 Utilization in Commercial Scale – Presentation of a Project Realization

Linde Engineering Dresden GmbH
Olaf Christoph

Current Status and Challenges of the Project

The utilization of carbon dioxide (CO_2) is a viable option if undertaken in the correct setup and size. Nevertheless connecting different chemical plants by utilizing CO_2 is not a challenge if surrounding parameters are considered properly. We like to present the overall setup of the world's largest CO_2 purification and liquefaction plant project, which was awarded to the Linde Group in June 2013 by Jubail United Petrochemical Company (UNITED) in Jubail Industrial City, Saudi Arabia. Linde Engineering Dresden has the LSTK responsibility for the facility. The plant is currently under erection and the mechanical completion is set to be achieved in 2015. It is designed to compress and purify around 1,500 tonnes per day of raw CO_2 coming from nearby ethylene glycol plants. The purified gaseous CO_2 will be pipelined to three affiliated companies for enhanced methanol and urea production. The plant will also be capable of producing 200 tonnes per day of liquid CO_2 with food grade quality, which will be stored and thereafter supplied by truck to the beverage and food industry.

In summary, an estimated 500,000 tonnes of CO_2 emissions will be saved each year. The plant is the first CO_2 utilization project of this size to be realized in Saudi Arabia. The reduction of the CO_2 emissions is an important aim in the national and Linde's sustainability strategy.



Climeworks AG

Jan Wurzbacher

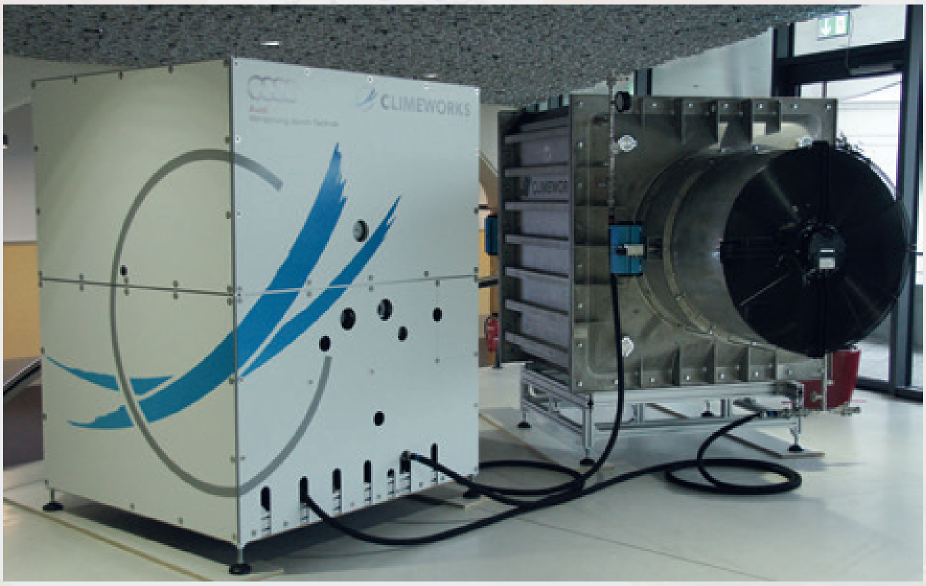
CO_2 Supply through Direct Air Capture – Update on Climeworks Activities

Climeworks provides solutions for efficiently capturing CO_2 from ambient air. Our CO_2 capture plants enable the production of carbon-neutral renewable fuels allowing for efficient storage of renewable energies within a closed carbon cycle. The Climeworks CO_2 capture technology is based on a cyclic adsorption/desorption process on a novel amine-based filter material (sorbent). The process is mainly driven by low-grade heat at below 100 °C. This enables utilization of waste heat, for example if the CO_2 capture plant is coupled to a renewable fuel synthesis plant.

Further applications include CO_2 supply to the food and beverage industry as well as for greenhouse fertilization. On-site CO_2 capture from the air is particularly attractive if long-distance transportation can be avoided or a constant gas quality and supply security are an issue.

After successful operation of a 1 ton per year CO_2 capture demonstrator for over 20 months, Climeworks has commissioned a full-scale, industrial CO_2 capture module (**CO_2 Collector**) with a nominal CO_2 capture capacity of 50 tons per year in August 2014. The CO_2 Collector was presented to the public at the Swiss Energy and Climate Summit, Bern in September 2014 together with Audi, Climeworks' partner in the mobility sector. At the same time, Audi and Climeworks announced an ongoing R&D collaboration to accelerate the technological development towards serial production and facilitate the production of renewable fuels from atmospheric CO_2.

In 2015, Climeworks will build up production infrastructure for the manufacturing of 20 CO_2 collectors, which will be contained in a first commercial CO_2 capture plant. Industrial CO_2 capture plants consist of arrays of CO_2 Collectors and therefore feature a modular design to meet various application needs.



Climeworks CO_2 Collector

www.climeworks.com

8. Biowerkstoff-Kongress

8th International Conference on Bio-based Materials

13–15 April 2015, Maternushaus, Cologne, Germany

Special Topics: Bio-based 3D Printing – 3rd Day Dedicated to High-Potential Start-Ups

HIGHLIGHTS FROM EUROPE AND ASIA:

BIO-BASED PLASTICS AND COMPOSITES – BIOREFINERIES AND INDUSTRIAL BIOTECHNOLOGY

This conference aims to provide major players from the European and Asian 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. Due to the huge response for the second time the conference will count with a third day especially dedicated to start-ups.

The 8th International Conference on Bio-based Materials ("Biowerkstoff-Kongress") builds on successful previous conferences: More than 200 participants and 20 exhibitors mainly from industry are expected!

PROGRAMME: HIGHLIGHTS OF EUROPEAN AND ASIAN LEADING COUNTRIES IN BIO-BASED ECONOMY

1st Day (13 April 2015): Policy and Industry

- Policy and markets
- Commercial biorefineries
- Innovation Award "Bio-based Material of the Year 2015"

2nd Day (14 April 2015): Industry

- Biopolymers and building blocks
- Bio-based 3D printing
- Microplastics in the environment: Sources, impacts and solutions

3rd Day (15 April 2015): Start-Ups

- Start-ups with partners

Entrance Fee

Conference incl. Catering, plus 19 % VAT

1st Day Conference 8 April 2014	2nd Day Conference 9 April 2014	3rd Day Conference 10 April 2014
475 €	425 €	400 €
775 €		
	725 €	
950 € (+ exhibition booth if desired - limited offer)		

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sunfire GmbH

Christian von Olshausen

Power-to-Liquids: Synthetic Hydrocarbons from CO_2, H_2O and Electricity

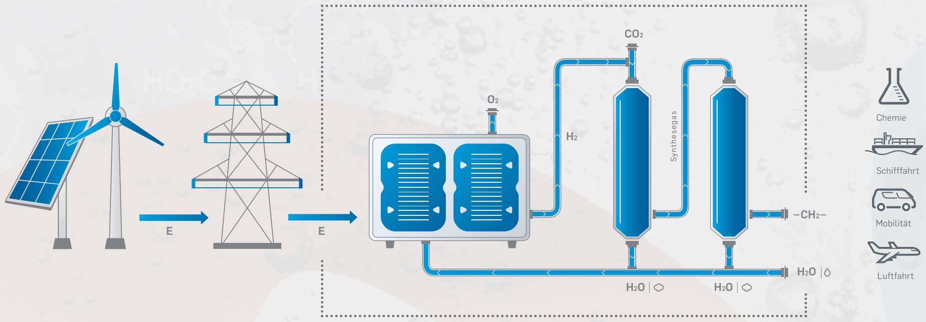
Introduction

Today's transportation and chemical sectors mostly depend on the use of fossil hydrocarbon resources. To enhance the utilisation of renewable sources while omitting the negative impact on social and ecological aspects of biomass-based fuels (e.g. food-fuel debate), electricity from renewable sources can be converted into hydrocarbons. Most concepts for so called "Power-to-Gas" (PtG) or "Power-to-Liquids" (PtL) processes are based on water electrolysis (PEM or alkaline) and a subsequent hydrocarbon synthesis, using CO_2 as the carbon source.

Methods

The company sunfire GmbH developed a new PtL process with increased efficiency. Using a solid oxide electrolysis cell (SOEC) in combination with a Fischer-Tropsch synthesis (FT),

65 to 70 % of the applied electrical energy is converted into liquid hydrocarbons (LHV-based).



Results

PtL product, named "BlueCrude", can be considered as renewable crude oil. Thus, highly developed technologies can utilise it and a broad market as well as the related infrastructure are already established.

Additionally, as CO_2 and H_2 cannot directly be used for a FT-synthesis, CO_2 firstly needs to be converted to CO by using an electric reverse waster-gas-shift reactor (eRWGS), developed by sunfire. Using the eRWGS also for FT-purge gas recycling, increases the carbon conversion efficiency of the presented PtL process from 55 % to over 95 %.

Discussion

In 2013 and 2014, sunfire constructed a PtL demonstration plant, co-funded by the Federal Ministry of Education and Research, to validate the whole process. Commissioning has started in August 2014. It is expected that first product batches will be produced until early 2015.

Conclusion

The herewith proposed presentation will give an introduction to sunfire's PtL technology. First results of the demonstration plant will be presented. Furthermore, the current and future economics of PtX technologies will be discussed.

Power-to-Gas: Shifting Power with Grid-scale Water Electrolysis

Hydrogenics Europe N.V.

Denis Thomas

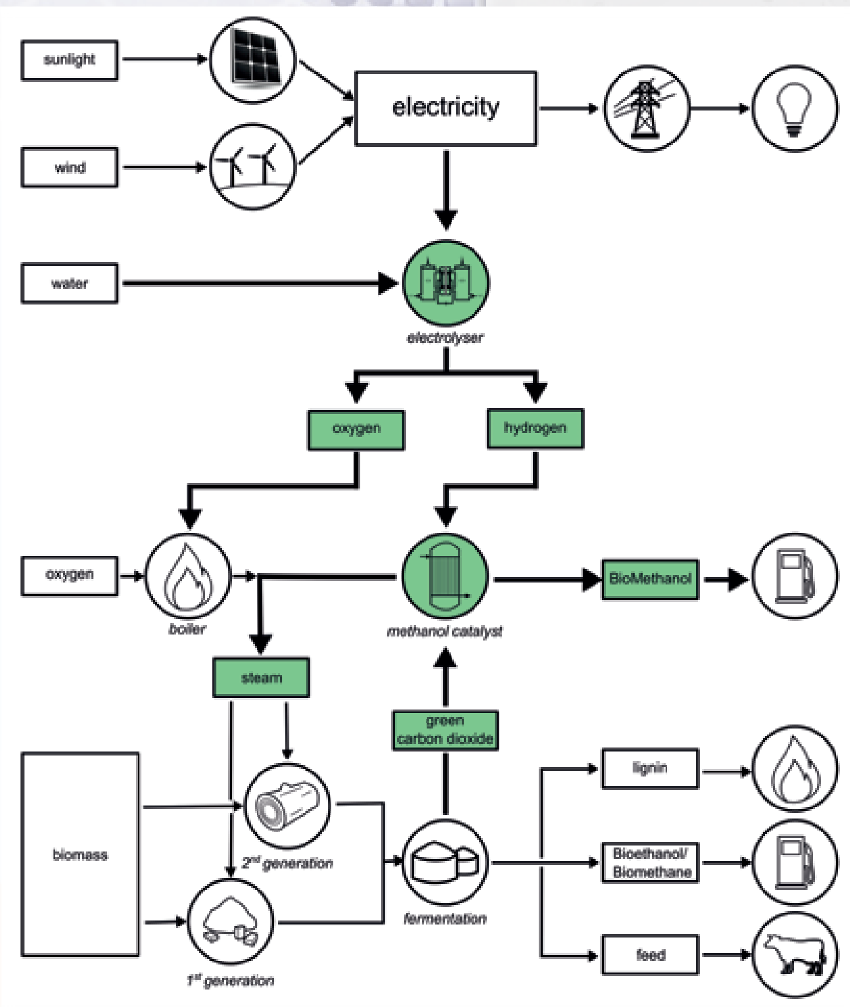
There is already in some European regions a significant share of the electricity produced from intermittent renewable energy sources such as wind and solar. The share of these will further increase in all countries in order to reach the European energy and climate goals by 2030. Curtailments are already taking place to avoid congestions on the electricity grid infrastructure and there is today a need for energy storage applications. This need will further increase in the coming decades. Power-to-Gas can play a major role by absorbing the surplus of renewable electricity and by converting it into a valuable energy carrier such as hydrogen (by water electrolysis) or methane (after a methanation process). Power-to-Gas represents a very promising solution which allows the interconnection of the four main energy silos: electricity, heat, mobility and industry. This interconnectivity creates an enormous potential for the further deployment of renewable energy and a mainstream tool to decarbonize the heat, mobility and industrial sectors. Hydrogenics has realized several Power-to-Gas projects worldwide and is leading the way in this technology. Hydrogenics has developed recently a new cell stack in the MW range based on its PEM technology which will be implemented in Hamburg (Germany) in December 2014.

bse Engineering Leipzig GmbH

Christian Schweitzer

Integrated Concept to utilize Biochemical generated CO_2 for Thermochemical Fuel Production; Technical Feasibility – legal Challenges – Commercial Viability

Over the past years, the energy sector has been shifting more and more toward renewable energy sources. Today, the main portion of renewable energy is produced decentralised and intermittent. The challenge of the future energy sector is the management of using the fluctuated power supply (wind, solar) to replace fossil fuels. Beside the batteries and power to heat, the option is to create a chemical energy storage which should be also used in the transport sector, and should be transportable, with high energy density and existing value chain. This is reachable by using waste green carbon dioxide from biological fermentation.



Huge amounts of energy are required in the transport sector and at specific times in areas of high population density. The resulting challenge for the energy sector is quite complex. It involves the coordination of energy availability to populations at the right time, which necessarily involves storage; the expansion of power grids and capacities; and political considerations as a further significant factor.

One approach to manage this complex challenge is to use energy for the production of chemical energy carriers using common renewable resources, particularly ones which are convenient for implementation in existing infrastructures and technologies.

BSE has done a pre-engineering to evaluate the opportunities for a realistic solution on the technical level under the view of the political aspects and commercial viability. The result is the CO_2mbined Plant.

The CO_2mbined Plant uses CO_2 streams from biological fermentation processes to produce e-Methanol. The plant directly faces the specific problem of fluctuated energies with the utilization of green CO_2 for fuel production most notably in regard of GHG-Emissions, fluctuated energy supply, power grid stability and sustainability of biofuels excluding without any additional land requirements.

CO_2mbined Plant will be installed in order to process continuous green CO_2 of biochemical origin (biomass) under fluctuated electrochemical conditions in a thermo chemical process to produce Methanol. The interconnection of the different process units creates a high efficient energy and resource cascade in the pilot plant. www.bse-engineering.eu

Technical University of Denmark

Prof. Dr. Mogens Bjerg Mogensen

M.B. Mogensen, S.D. Ebbesen, C. Graves, X. Sun, A. Hauch, S.H. Jensen, M. Chen, T. Jacobsen

Production of Green Fuels using Solid Oxide Electrolysis Cells: Status and Perspectives

Solid oxide cells (SOCs) can be used as solid oxide electrolysis cells (SOECs) as well as solid oxide fuel cells (SOFCs). The cell is fully reversible both for H_2O/H_2 and CO_2/CO as well as for mixtures of these reactants. Production of syngas (H_2 +CO) by co-electrolysis of $H_2O + CO_2$ using SOEC in the temperature range of 600–1000 °C opens the possibility of producing hydrocarbons from renewable electricity by catalytic conversion of syngas into hydrocarbons using well established commercial catalytic conversion technologies. Hydrocarbons, which can be used as transportation fuels as well as substitutes for natural gas and liquefied gas, may be produced. Furthermore, the fuels produced in SOEC mode can be converted back to electricity using the same SOC stack.

Therefore, the SOC technology can provide both fuels and on-demand electricity from intermittent renewable electricity and could be a long-term solution for achieving high penetration of renewable energy. Greatly increased research activity on the application of the SOFC in SOEC mode during the recent decade has been taking place. Exciting performance results have been achieved and disappointing degradation rates have been observed.

The presentation will briefly review cell performance and limitations, and explain mechanisms behind cell degradation to some extent. Various phenomena have been observed when the electrolysis and fuel cell polarization/current density brings the cell materials on the verge of their stability. Phenomena such as oxygen bubble formation in the electrolyte near the O_2 electrode, reduction of zirconia into Zr or Zr-containing-alloys at the fuel electrode, and carbon precipitation in the fuel electrode during electrolysis was observed. The presentation makes it clear that these processes are probably more dependent on the electrode potential rather than on the current density, even though a mechanism depending on the current density is also known. Also, a difference in cell polarization resistance between SOEC and SOFC mode has been observed and is related to differences in actual cell temperature, which seems to be of significant importance.

Converting CO_2 and H_2O into Syngas using high Temperature Heat

NewCO2Fuels

Julie Horn

D. Banitt, J. Horn

NewCO2Fuels (NCF) is developing an innovative, high efficiency, self-sufficient system to produce fuel from CO_2 and renewable energy. The core technology is a high temperature driven process that dissociates CO_2 and water to produce syngas (mixture of CO and H_2), from which different synthetic fuels can be produced. The 40% overall efficiency, from the thermal energy at the input of the system to the chemical energy in the Syngas, is the basis for this economically attractive solution. The system comprises of innovative reactors, power generation, buffers, gas conditioning and advanced control means.

NCF system can significantly help energy intensive industry to reduce CO_2 emission by using the industry's excess heat and providing a highly profitable fuel. The produced syngas can directly be used by the steel industry or further converted to many types of fuels or chemicals.

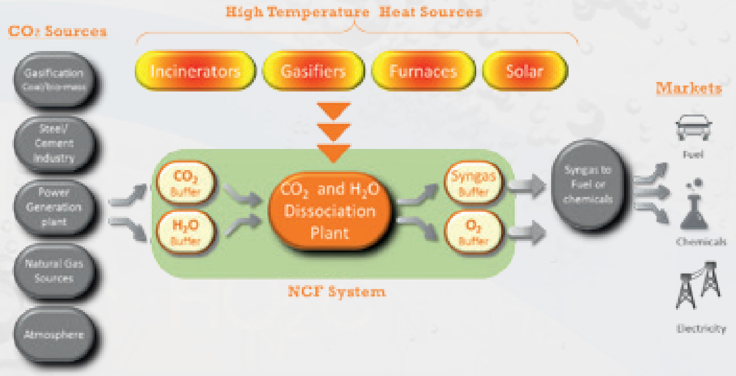


Figure 1: NCF product, feedstock, heat sources and markets

Status

To date, NCF has constructed and successfully tested a small scale prototype to demonstrate the viability of the technology and its commercial attractiveness.

Since initial tests in 2010 at the laboratories of the Weizmann Institute of Science in Israel the dissociation rate of the NCF system has increased in a single apparatus by a factor of 800 and the cost was reduced by a factor of 34. This performance was reached when conducting continuous tests over hundreds of hours' proof of concept setup simulating the excess heat configuration from high intensity industries, producing CO at the rate of ~10Kg/day.

Independent assessment of the technology by WorleyParsons in September 2013 confirms the high standard to which the prototypes have been designed, engineered and installed, with successful initial proving trials of the excess heat source configuration.

An MOU was signed during Q1 2014 with one of the world's largest steel making companies and two international engineering firms to set up a pilot to demonstrate NCF's system integration with the steel industry where the required heat for the process will be extracted from excess heat source on the facility.

Another collaboration agreement was established with a Europe-based global conglomerate to partner on product development for the integration of NCF product in other industries.

Carbon Recycling for Sustainable Fuels and Chemicals

Lanza Tech

Grainne Smith

LanzaTech is pioneering an innovative biological process for the conversion of carbon-rich waste gases and residues into renewable fuels and chemicals.

Fuel production offers a novel approach to carbon capture and utilization and through production of chemicals LanzaTech presents a route to carbon sequestration. The carbon in the waste gases and residues is sequestered into a new product-an example being the production of 2,3 butanediol from waste steel mill gases, a chemical intermediary used for the production of nylon.

LanzaTech's feedstock flexible gas-to-liquid platform enables regional production of low-cost energy from local wastes and residues, capturing carbon from gases as varied as industrial flue gas, gasified biomass wastes and residues and other CO_2 and/or methane-rich waste gas streams resulting in a growing portfolio of commodity chemicals, omega-3 fatty acids, ethanol and hydrocarbon fuels, including jet fuel.

Phytonix Corporation

Bruce Dannenberg

Direct Photobiological Conversion of Carbon Dioxide Feedstock into Renewable Chemicals and Fuels

Phytonix Corporation is a prototype stage renewable chemical and biofuel technology company. The firm is developing and commercializing a unique technology and production process that photobiologically (photosynthetically) directly converts carbon dioxide feedstock, along with solar energy and water, into renewable chemicals and fuels. The initial chemical to be produced in our pipeline is n-butanol, a valuable industrial intermediate which can also be used as a “drop-in” gasoline replacement fuel or fuel additive. The lifecycle analysis of biobutanol, utilized as a biofuel “drop-in” gasoline replacement, from production through combustion, is carbon neutral. Our carbon-negative n-butanol production process replaces an existing fossil-based, carbon-intensive process. The company estimates that its biobutanol production cost at full commercial scale will be approximately US$ 1.35 per gallon, compared to the current fossil-based production cost of around US$ 5.00 per gallon. Our development partners at Uppsala University’s Angstrom Laboratory (Sweden) have produced cyanobacterial “butanol organisms” that act as fuel and chemical production platforms, directly secreting butanol (and potentially other target chemicals such as pentanol and long chain fatty acids) via a modified photosynthetic process, utilizing carbon dioxide as the sole feedstock, and producing oxygen as a by-product. Colleagues at South Dakota State University are developing our special phytoconverter/photobioreactor (PBR) design. Our comprehensive core technology and process is patented in the USA and patent-pending in the EU and globally, and includes a unique biosafety approach that will prevent genetically modified bacteria from surviving in the natural environment. Our continuous process production systems will consist of modular and scalable arrays of soft-sided phytoconverters (culturing systems) co-located with an industrial waste carbon dioxide emitter. Phytonix’s process is expected to eliminate via conversion one metric tonne of CO_2 for every 138 gallons of n-butanol produced. Phytonix utilizes a distributed and collaborative business model to achieve breakthrough results with a minimum of capital and is based in Asheville, North Carolina, U.S.A., with development laboratories in Sweden, Virginia, and South Dakota.

www.phytonix.com

Biorefinery Chemicals using Photo-electrochemical CO_2 Reduction in the Eco^2CO_2 Project

Avantium
Dr. Klaas Jan Schouten

Avantium is performing research within the framework of the European research project Eco^2CO_2. The aim of this project is to exploit a photo-electro-chemical (PEC) CO_2 conversion route for the synthesis of methanol as a key intermediate for the production of fine chemicals, such as fragrances and flavorings, in a lignocellulosic biorefinery.

One of the key steps is the development of a PEC reactor capable of converting CO_2 into methanol by exploiting water and sunlight. The targeted conversion efficiency should exceed 6% and the expected durability should be more than 10.000 h. Avantium is investigating the (electro)catalysts needed for the reduction of CO_2 to methanol and intermediate products, such as formic acid. The extensive experience of Avantium in the combinatorial preparation, screening and optimization of catalysts can speed up and simultaneously improve the development of (photo-)electrocatalysts. We are developing equipment for the screening of electrocatalysts for the reduction of carbon dioxide under industrially relevant conditions. It is known that metals with a high overpotential for hydrogen evolution and a very low CO adsorption strength, such as Sn, In, Tl, Pb, Hg, Bi, and Cd, catalyze the conversion of CO_2 to formic acid. However, the overpotential for these catalysts is high. We are reporting on an electrode system where CO_2 is selectively reduced at lower overpotentials and high current densities.

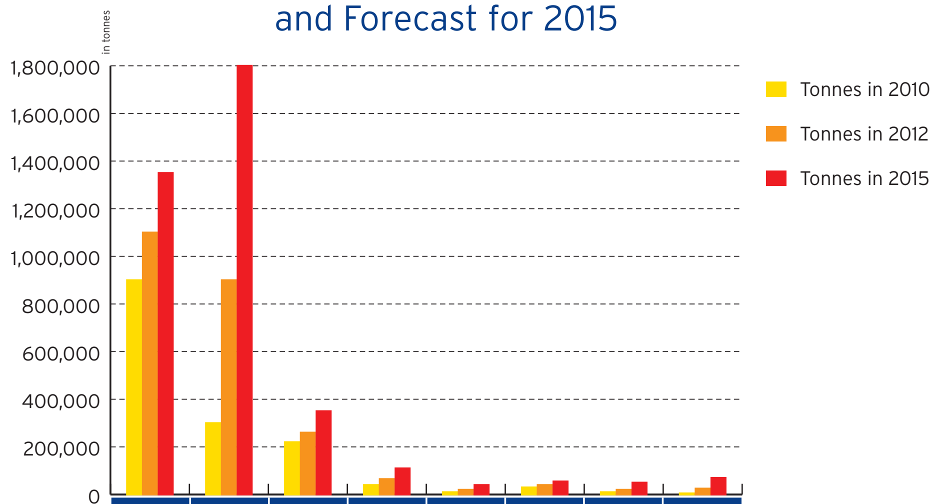
Next to the development of a new PEC reactor, catalytic reactions of methanol and furfural to produce perfuming agents via partial oxidation and optionally methylation are investigated to achieve cost effective production of green fine chemicals. Using Avantium's proprietary hardware and software platforms to screen and evaluate catalysts, the oxidative methylation of furfural is being explored.

WPC/NFC Market Study 2014-03

Wood-Plastic Composites (WPC) and Natural Fibre Composites (NFC): European and Global Markets 2012 and Future Trends

Authors: Michael Carus, Dr. Asta Eder, Lara Dammer, Dr. Hans Korte, Lena Scholz, Roland Essel, Elke Breitmayer

Global Production of WPC in 2010 and 2012, and Forecast for 2015



	North America	China	Europe	Japan	Russia	South East Asia	South America	India
2010	900,000	300,000	220,000	40,000	10,000	30,000	10,000	5,000
2012	1,100,000	900,000	260,000	65,000	20,000	40,000	20,000	25,000
2015	1,350,000	1,800,000	350,000	110,000	40,000	55,000	50,000	70,000

The market study gives the first comprehensive and detailed picture of the use and amount of wood and natural fibre reinforced composites in the European bio-based economy.

The full report can be ordered for 1,000 € plus VAT at:
www.bio-based.eu/markets

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Upgrading CO_2 into Chemicals via Fermentation of Engineered Microbes

Industrial Microbes
Derek Greenfield

[Presentation cancelled]

Derek Greenfield, Elizabeth Clarke, Noah Helman

The key to utilizing CO_2 as a feedstock is identifying high-value products that can be economically manufactured using CO_2 as a raw material. Industrial Microbes is developing a biological solution to combine CO_2 and methane into malic acid, which is a building block chemical that can be easily converted into a variety of valuable materials.

Biological fermentation is the best method to inexpensively and efficiently remove massive amounts of CO_2 from the atmosphere. Plants, algae, and bacteria already sequester 57 billion tons of CO_2 annually, 10-fold more carbon than emitted by all human activities. Unlike the energy-intensive conditions in industrial chemical plants, life evolved to assimilate CO_2 into biomolecules at atmospheric temperature and pressure with minimal energy input. Using the tools of modern synthetic biology and metabolic engineering, researchers have begun engineering enzymes and pathways in industrial microorganisms to convert CO_2 into commercially useful molecules.

Methane is an attractive energy source to power CO_2 fixation because it is low-cost, energy-dense, and available year-round. Methane makes up most of natural gas and can also be produced renewably from biogas sources such as landfills and wastewater treatment plants. Methane has a cost advantage over hydrogen, and methane can drive carbon fixation faster than photosynthesis.

Malic acid is a valuable product that requires low energy inputs for production. It was identified by the U.S. Department of Energy as a top 12 feedstock chemical that can be converted into a diverse array of products such as plastics, resins, fibers, and rubber. Malic acid is a four-carbon dicarboxylic acid in a family of related chemicals that also includes succinic and fumaric acids, which can be easily interconverted using well-known biological and chemical processes.

Production of malic acid using our process reduces CO_2 emissions in two ways: CO_2 is removed from the atmosphere or an emissions source and fixed directly into malic acid product, and a preliminary life-cycle analysis indicates that our process results in significant CO_2 emissions reductions compared to traditional petroleum-based malic acid production.

Econic Technologies Ltd.

Dr. Rulande Henderson

Econic Catalyst Systems for Polycarbonates and Polyols from CO_2

CO_2 is a low cost and abundant renewable feedstock offering a distinct sustainability advantage as well as high-value product characteristics in new classes of polymers not easily manufactured from petrochemicals. Whilst impact on global CO_2 concentrations may be modest, the products are expected to significantly improve the economics of carbon capture and storage[1], and reduce the polymers' carbon footprint by means of avoided petrochemical feedstock production[2].

The current global status of CO_2-based polymer technology is briefly reviewed, and the key challenges for successful market penetration outlined.

Central to process adoption in the existing polymer industry is the development of effective catalysts that enable a polymerisation process with overall economics comparable or better than incumbent – petrochemical based – processes, preferably utilising existing production assets with minimal capital expenditure.

Product adoption requires effectiveness and flexibility of the catalyst systems with a range of feedstocks and process conditions to produce a broad range of product properties; significant product and process development effort all the way down the supply chain; and consumer acceptance aided by public communication engendering a favourable political and regulatory backdrop.

Feedstock adoption requires development and qualification of carbon capture technologies and CO_2 supply logistics, where the economics are again in part dependent on the catalyst system, namely in terms of robustness to CO_2 contamination levels.

Econic Technologies currently focuses primarily on catalysts for the polyurethane polyol industry, with technology development and commercial strategy addressing each of these three challenges. Key to Econic's and our customers' optimal time to market is supply chain collaboration enabling largely simultaneous activities in catalyst technology validation, polymer process adaptation, polymer properties tailoring and application development. Econic is further starting to engage in collaboration with stakeholders in industry, academia, certification organisations and governments to facilitate public awareness and consumer understanding of CO_2-based polymers in the portfolio of "green product" offerings.

[1] MacDowell et al., Energy Environ. Sci. 2010, 3, 1645-1669

[2] von der Assen & Barlow, Green Chem., 2014, 16, 3272–3280

Carbon Dioxide-Based Polycarbonate Polyols for Polyurethane Systems
Commercial Applications of CO_2 based Polyols

Novomer Inc.

Simon Waddington

By Anna Cherian
Senior Scientist Applications Development, Novomer Inc.

PPC polyols are a sustainable, low-cost option with performance properties exceeding those of conventional polyols in polyurethane RHM adhesives.

Traditional polyurethane reactive hot-melt (RHM) adhesives make use of blends of polyester, polyether, and in rare cases, conventional petroleum-based polycarbonate polyols. Although polyesters and polyethers contribute properties to RHM adhesives such as good workability and rapidly building strength, polyesters have poor hydrolytic stability and polyethers are prone to oxidation under UV light. Conventional petroleum-based polycarbonates have excellent performance properties in these areas but come at a much greater cost, making them suitable only for specialty applications.

Due to their high carbon dioxide (CO_2) content, polypropylene carbonate polyols are a sustainable and cost-effective option with performance properties that exceed those of conventional polyols in polyurethane RHM systems. CO_2-based polyols are formed by the copolymerization of epoxides and CO_2. This results in aliphatic polycarbonate structures, the most common of which are polypropylene carbonate (PPC; from propylene oxide, PO), and polyethylene carbonate (PEC; from ethylene oxide, EO). The degree of CO_2 incorporation is controlled primarily by the reaction catalyst, where perfectly alternating material has the highest CO_2 content (43 wt% for PPC, 50 wt% for PEC).

The technology to perform this copolymerization has been around since the early 1970s. The development of new catalyst and production processes has resulted in the availability of commercial high-molecular-weight specialty materials since the mid 1990s. However, low-molecular-weight CO_2-based polyols are a new development made possible by key advances in catalyst technology.

Control of other reaction parameters can give CO_2-based polyols with a wide range of molecular weights and functionalities. The technology can even be used to make block copolymers.

RHM Adhesives

RHM adhesives are polyurethane systems with terminal isocyanate end groups. Solid at room temperature, these adhesives require heating to 110–140 °C prior to application. Initial strength is achieved quickly as the adhesive cools and hardens, while moisture curing over the next several days leads to full strength. Typical formulations consist of a diisocyanate (commonly MDI), a crystalline polyol (typically with a melting point of approximately 50–70 °C) and an amorphous polyol, as well as moisture curing catalysts and other additives.

Polyester polyols are often chosen for the crystalline component of RHM formulations, and polyether polyols may be selected for the amorphous component. This combination of material properties leads to the good workability of the molten adhesive, as well as the rapid build of initial strength.

Both classes of materials have drawbacks, however, particularly in stability under harsh environmental conditions. Polyesters are prone to poor hydrolytic stability; polyethers are vulnerable to oxidation under UV light (see Figure 1). Conventional petroleum-based polycarbonate polyols offer many performance advantages, including high hydrolytic and oxidative stability; however, the high price point makes them prohibitive for all but the most demanding specialty applications. If the value of a particular class of polyols is considered as a function of both performance and cost, the value of CO_2-based PPC surpasses all other polyol classes in RHM applications.

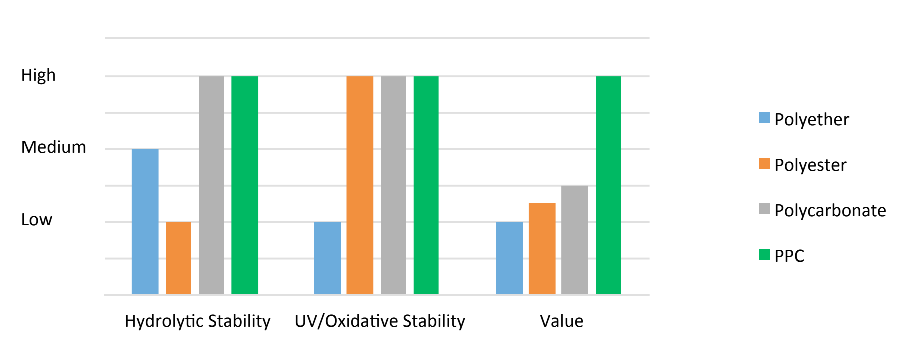

Figure 1: Performance Characteristics of Polyether, Polyester and Polycarbonate Polyols

Sustainability

The demand for raw materials sourced from renewable feedstocks has risen steeply in the last decade. Many sustainable materials are derived from plant sources (e.g., bio-based acids and diols, natural oil polyols, etc.). CO_2-based polyols do not rely on agricultural processes, but rather use CO_2 from industrial waste (waste CO_2 emissions from fermentation or chemical processes), contributing up to 50% of the polymer mass. This process results in a polyol production process with a carbon footprint reduction of up to 65% compared to traditional polyols (see Figure 2). Although sustainability is an important feature for generating interest in a new product, the market still demands a product that meets or exceeds performance and cost standards.

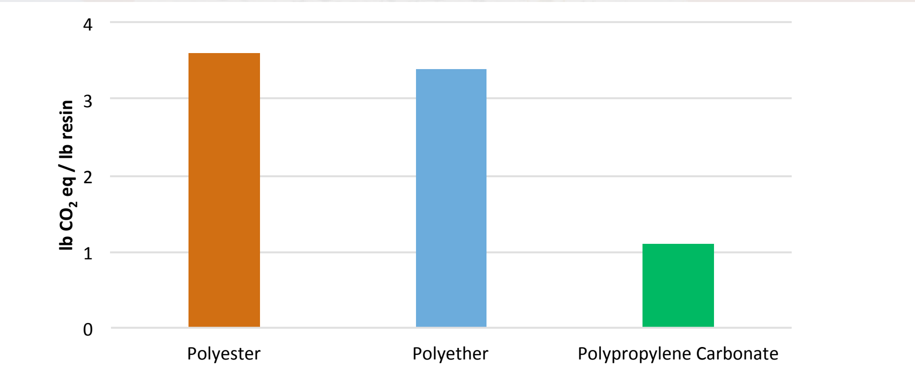

Figure 2: CO_2 Footprint in Manufacturing of Various Polyol Types

Performance

Performance in a given application is arguably the most important feature of any new product. CO_2-based polyols with the highest CO_2 incorporation have 100% polycarbonate linkages, which add substantial rigidity to the polymer backbone. Molecular weight can be carefully controlled, with narrow polydispersity indexes (PDIs) of < 1.1.

Diols with a perfect functionality of 2.0, triols with a perfect functionality of 3.0, and even higher functionality polyols can be prepared. These materials are viscous liquids or amorphous solids at room temperature, and are easily processable at elevated temperatures of 50–100 °C. They can be incorporated into traditional polyether and polyester polyurethane formulations.

When reacted with MDI and a crystalline polyol (typically HDO/adipate polyester), PPC imparts improved adhesive strength compared to RHM adhesives prepared with conventional polyesters and petroleum based polycarbonates. Cured RHM adhesive made from PPC and polyester also has a significantly higher Shore D hardness compared to polyester/polyether RHMs.

Green Strength

PPC-based RHM adhesives feature a high initial strength (green strength) reaching > 450 psi within 60 minutes. Adhesives with high green strength enable higher manufacturing line speeds by reducing the time that parts need to be clamped together, which allows for faster assembly and increased productivity.

Green strength is due to the inherent physical strength of the adhesive raw materials once the adhesive has cooled to room temperature, while moisture-curing over days or weeks leads to a very high final strength polyurethane material. RHM adhesives made with PPC show remarkable green strength, far exceeding that of conventional polyester/polyether systems (see Figure 3).

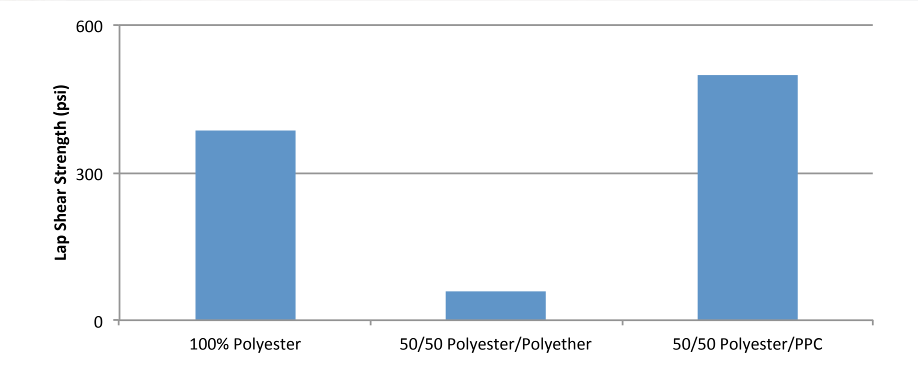

Figure 3: Comparative Adhesive Strength of RHM Adhesives Made with Different Polyol Types after 1-Hour Cure (Green Strength)

Tensile Strength

The bond strength (lap shear strength) of cured RHM adhesive made from PPC and polyester is very strong, with substrate failure occurring in many cases. Materials such as metals and certain plastics can be difficult to bond. RHM adhesives made with PPC show improved adhesion on aluminum, maple, and thermoplastic polycarbonate compared to those made with a polyester/polyether blend or polyester alone (see Figure 4).

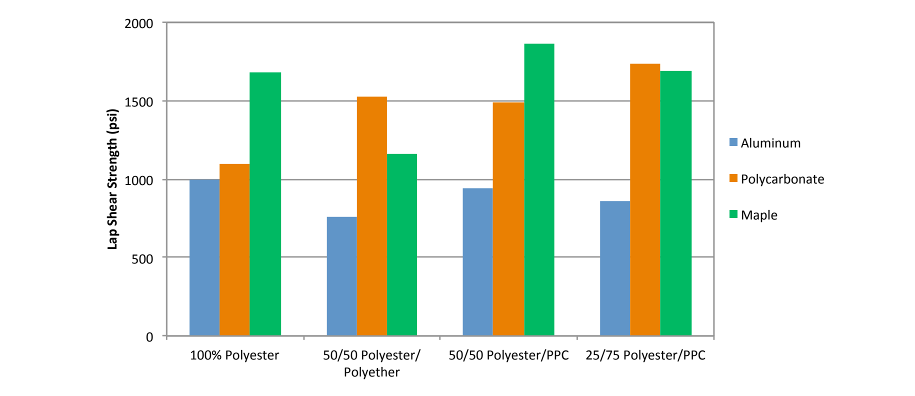

Figure 4: Comparative Adhesive Strength of RHM Adhesives Made with Different Polyol Types on Various Substrates after 1-Week Cure

Tensile strength is a key performance property of any adhesive. RHM adhesives composed of PPC polyols have both high tensile strength on notoriously difficult substrates, such as aluminum, and they also have high green strength. These observed product improvements will have a noticeable impact on end-use customers, who can depend on rapid line speeds and exceptionally strong final bonds.

Environmental Resistance

After adhesive application, many joints encounter harsh conditions such as exposure to high temperatures and elevated humidity, extreme weather, UV exposure, laundering, and/or chemical exposure. While polyester polyols typically perform well in most other categories, they exhibit poor stability in extreme conditions.

An experiment simulating accelerated wet aging (adhered polycarbonate pieces submerged in H_2O at 80 °C) showed that adhesive made with a 50/50 polyester/ PPC blend had roughly the same retention of tensile strength after 3 weeks as a 50/50 polyester/polyether adhesive (see Figure 5). Both were substantially better than 100 % Polyester. Increasing the amount of PPC to 75% drastically improved the hydrolysis resistance to > 70 % retention of strength after 3 weeks submerged at 80 °C.

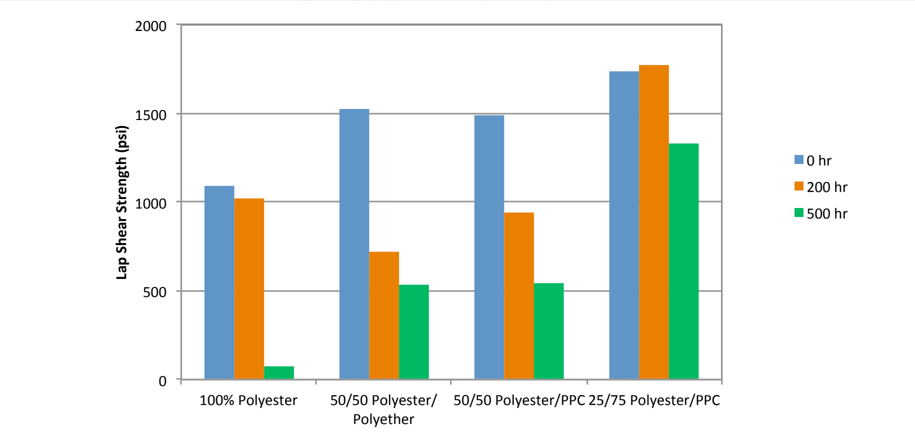

Figure 5: Comparative Hydrolytic Stability of RHM Adhesives Made with Different Polyol Types after 1-Week Cure on Thermoplastic Polycarbonate Strips Submerged in H_2O at 80 °C

Conventional petroleum-based polycarbonate polyols have high resistance to moisture, heat, and chemicals, but their high price point makes them suitable only for select high-end markets. PPC polyols share these high stability features inherent in the polycarbonate backbone, but the pricing can be significantly more attractive to end users because they are manufactured from commodity feedstocks (CO_2 and EO/PO).

Cost

The low cost of CO_2 feedstock has made CO_2-based polyols of commercial interest for some time. Compared to PPG (PO homopolymer), PPC (CO_2/PO copolymer) results in more than 40% savings in PO raw materials (see Figure 6). Although CO_2 and catalyst raw materials reduce some of these savings, poor catalyst efficiencies have made the manufacturing process prohibitive until recently. Advances in new catalyst technology have dramatically improved productivities, which have been proven at semi-commercial scale and promise a cost-competitive process at large-scale commercial production.

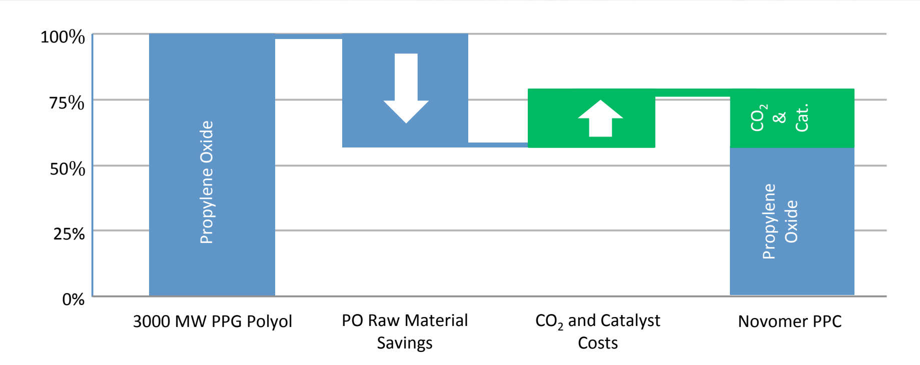

Figure 6: Raw Material Cost Comparison between PPG Polyols and CO_2-Based PPC Polyols

A Viable Option

The introduction of new CO_2-based polypropylene carbonate polyols has been well received in a number of polyurethane applications, particularly in RHM adhesives. PPC contributes all-around superior performance: exceptional green strength and final bond strength better than polyesters, and hydrolytic stability like polyethers. Through the incorporation of high percentages of a low-cost CO_2 feedstock, PPC polyols are uniquely positioned as a sustainable, competitively priced option with performance properties exceeding those of conventional polyols in polyurethane RHM adhesives.

www.novomer.com

Poster abstracts

Novel Process for the Synthesis of Dimethyl Carbonate via Urea Methanolysis

Joon Hyun Baik, Gook-Hee Kim, Jinsoon Choi, Dong Jun Koh

Recently, dimethyl carbonate (DMC) has attracted much attention as an environmentally friendly chemical. It is used as a 'green' solvent, an electrolyte within lithium ion batteries, and mostly as a raw material of polycarbonate which is produced via non-phosgene process. The commercialized processes for DMC synthesis are the transesterification of ethylene carbonate (or propylene carbonate) and the oxidative carbonylation. These conventional processes have disadvantage on the use of expensive and explosive petrochemical-based materials. On the other hand, the urea methanolysis is an emerging technology as an alternative process. The reactions are as follows: carbon dioxide reacts with ammonia to produce urea, which can be used for DMC synthesis under the reaction with methanol. During the course of the reaction, ammonia is produced as a byproduct, and then it can be sold or recycled to urea production plant.

In the present study, we developed novel process for the synthesis of DMC using urea and methanol as a raw material. The liquid-phase catalysts were developed and the reactor system has been optimized to maximize the yield of DMC. Based on the technology developed, pilot plant has been designed and operated. The pilot plant consists of reactor and distillation systems to produce and separate high purity of DMC. We operated the plant continuously for 600 hours and the DMC yield and purity was 85% and 99.9%, respectively. It has been demonstrated that this process is ready to commercialize in view of technical and economical analysis. It is believed that this process is one of promising way to utilize carbon dioxide for the production of high value added chemicals.

Clean Coal Chemicals Research Project, Research Institute of Industrial Science & Technology (RIST)

Joon Hyun Baik

Wageningen UR Food & Biobased Research

Carmen Boeriu

Synthesis of Formic Acid by Enzymatic CO_2 Reduction with in situ Cofactor Regeneration

Livia N. Corîci[1], A.E. Frissen[1], H. Verhoeven[2], J. Beekwilder[2], Carmen G. Boeriu[1]

Utilisation of carbon dioxide (CO_2) as feedstock to produce chemicals, polymers and fuels represents, along with the use of renewable resources and waste, is one of the most promising technological solutions that contribute to carbon recycling and to reducing the use of fossil resources. In the past years, new technologies integrating chemistry and biotechnology were developed to produce alcohols and base chemicals from the carbon dioxide captured from flue gasses, industrial processes and directly from atmosphere.

In this paper, we describe the direct enzymatic conversion of CO_2 into formic acid using NADH-dependent formate dehydrogenase (FDH) from *Candida boidinii*, with in situ regeneration of NADH. Two different cofactor regeneration systems were tested for enzymatic production of formic acid from CO_2 catalyzed by FDH. NADH regeneration by glucose oxidation to gluconic acid catalyzed by glucose dehydrogenase (GDH) from *Pseudomonas sp*. was superior to regeneration of NADH by lactate oxidation catalyzed by lactate dehydrogenase (LDH). The reactions with NADH regeneration by GDH system produced three times more acid than the regeneration system using LDH and the experiment without regeneration, while the control reaction without enzyme showed no product formation. Glucose and gluconic acid showed no inactivation effects on FDH up to 900 mM. The FDH-catalyzed CO_2 reduction to formate with in situ NADH regeneration using GDH was optimized in terms of temperature, pH, CO_2 concentration and pressure, NADH concentration and enzyme concentration. At optimal conditions, a molar ratio formate/NADH = 3.1 and a ratio formate/glucose = 0.94 were obtained.

Formic acid is currently used as a feedstock chemical, as food preservative, in leather processing and in textile industry, but worldwide demand for formic acid is expected to increase due to its application as hydrogen storage material and in biomass refinery.

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Conversion of CO_2 to Liquid Fuels and Chemicals by Acetogenic Bacteria

PROFACTOR GmbH
Marianne Haberbauer

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Biological conversion of CO_2 using acetogenic microorganisms offers the possibility to generate renewable and valuable chemicals and fuels at once. Acetogenic bacteria convert CO_2 and H_2 via the Wood-Ljungdahl pathway into numerous metabolites like alcohols (for example ethanol, 2-propanol, butanol, acetone and hexanol) and organic acids (for example acetate, butyrate, lactate, propionate, acrylate) within moderate conditions [1,2,3].

However, to bring this technology to a market level certain challenges have to be solved. The aim of this work is to screen a diversity of acetogenic bacteria to determine the capability of this process, to analyse the produced organic compounds and to choose the most applicative reactor type for these experiments.

Clostridium autoethanogenum, Clostridium carboxidivorans, Clostridium ljungdahlii and *Clostridium ragsdalei* were all obtained from DSMZ. Enrichment of the pure cultures was performed in the corresponding medium according to DSMZ under N_2/CO_2 atmosphere. For adaptation the sugar components in the modified ATCC media were omitted and the gas phase was exchanged to a mixture of CO_2 and H_2 (20%vol CO_2 and 80%vol H_2). Batch experiments were performed in one liter transfusion bottles filled with 200 mL medium at 37 °C and 100 rpm.

Clostridium autoethanogenum was used as model bacteria for the mesophilic fermentation (at 37 °C) in a trickle bed reactor. Medium circulated with a rate of 150 mL/min. The counter current flow of the gas mixture of 80%vol H_2 and 20%vol CO_2 was constant at 100 mL/min.

References

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Wieland Hoppe

Comparison of GWP between Conventionally Produced and CO_2-based Natural Gas used in Transportation versus Chemical Production

Wieland Hoppe[1], Stefan Bringezu[1,2], Yang Liu[1]

Today both car transport and the production of organic chemicals are largely based on fossil fuels. In Germany, against the background of the “Energiewende” (transformation of the energy system) and policies to enhance resource efficiency and substitution of fossil carbon sources in industry, the capacities for renewable SNG (synthetic natural gas) are going to be expanded significantly. Pilot plants are underway to use surplus renewable power, mainly from wind, for electrolysis and the production of hydrogen, which is methanised or directly fed into the existing extended gas pipeline grid. The most advanced pilot projects aim at the energetic use of the SNG for households and for transport in particular gas fueled cars. On the other hand, it could be used in the chemical industry for the production of platform chemicals.

This raises the question of whether SNG should be better used for mobility needs or the production of chemicals. The presentation focusses on the comparison of the global warming potential of the production of natural gas and CO_2-based natural gas and its usage for mobility needs or chemical products, for the example of synthesis gas. The power supply for electrolysis was assumed to come from wind converters. The CO_2 was assumed to be sequestered from a biogas plants fermenting waste.

The assessment is preliminary, as it was mainly based on a literature review, data from Ecoinvent 3.0, and data from documented industrial processes. The calculation was done by Umberto NXT LCA.

The results indicate that both in mobility and in chemical production less CO_2-equivalents would be emitted in the life-cycle of SNG compared to natural gas. The preliminary data indicate slightly higher savings for the use as a car fuel, however, sensitivity analysis shows a potentially wide variation, and further analysis is conducted to validate the key factors.

The research aims to contribute to a higher security of sustainable supply of material and energy resources and increased independence from fossil raw materials.

References

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Novel Process of Catalytic Hydrogenation of Carbon Dioxide to Methanol

HES-SO Haute école spécialisée de Suisse occidentale, Ecole d'ingénieurs et d'architectes de Fribourg

Roger Marti
Pauline Sanglard
Ennio Vanoli

Carbon capture and utilization (CCU) is an ingenious manner to answer the rise of CO_2 concentration in the atmosphere and as well the depleting of oil reserves if CO_2 is transformed in an "energetic material". Methanol, the simplest alcohol, can be used as a chemical, an additive to gasoline or directly as a fuel corresponding to a novel methanol economy.

The hydrogenation of CO_2 to methanol through syngas is a well know process but require high pressure and temperature (200–320 °C, 40–120 bar). Milder conditions are possible with homogeneous catalysis. We developed a two-step homogeneous hydrogenation process to synthesize methanol from CO_2 absorbed on a secondary amine. In the first step using a Cobalt catalyst we synthesized the corresponding formamide. This formamide is isolated and further hydrogenated to methanol with a ruthenium catalyst (Figure 1). We obtained an overall yield of 48% of pure methanol from CO_2 on multi-gram scale.

Our new process has the great advantage of using captured CO_2 instead of pure and compressed CO_2.

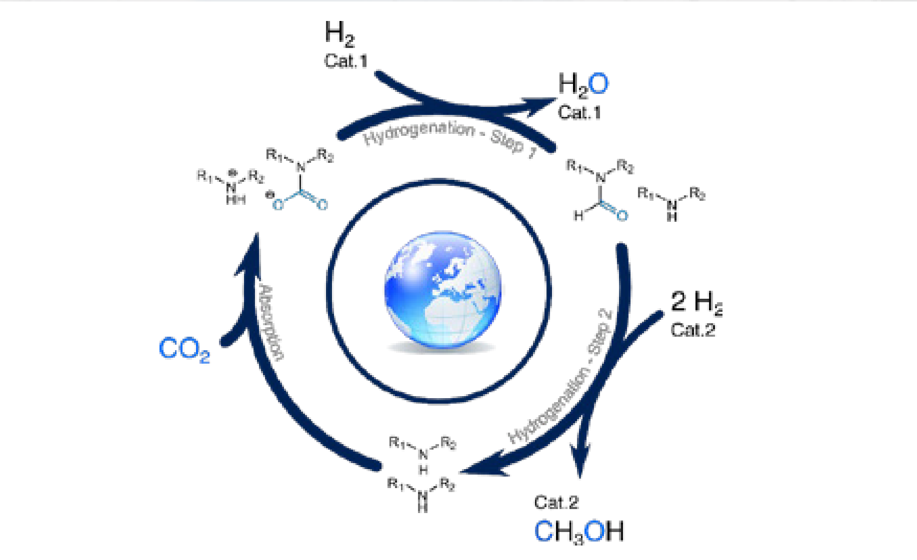


Figure 1: Carbon dioxide to methanol hydrogenation cycle

Performance Benchmarking and Process Development for Converting CO_2 into useful Chemicals

Department of Chemical Engineering, Imperial College London, South Kensington Campus

Nilay Shah
Naresh Susarla

It is now a consensus that CO_2 capture and utilization is imperative to prevent the anthropogenic climate change. In this regard, utilization of CO_2 as a carbon feedstock in the chemical production chain is a promising approach to reduce emissions of greenhouse gasses. Among the available options, converting CO_2 to fuels is an attractive alternative as it has a significant potential to reduce CO_2 emissions. However, synthesis of fuels such as methanol (MeOH) and di-methyl ether (DME) from CO_2 are both difficult and energy intensive. Thus, the intuitive environmental benefits are not obvious and require detailed analysis through performance benchmarking and developing efficient process alternatives.

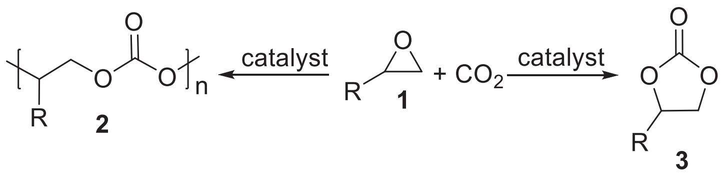
In this presentation, we focus on two primary objectives: developing efficient process alternatives for converting CO_2 into MeOH and DME, and compare them against the established processes to quantify the environmental benefits. For this, we investigate a number of potential synthesis routes for these valuable products using CO_2 as a feedstock. We compute the energy and process efficiencies of the identified process alternatives. Through life cycle assessment technique, we determine their environmental impact. In addition, we present a set of important performance indicators, which reflect the environmental impact of a typical CO_2 utilization process. Finally, we establish benchmark values for such performance indicators from the relatively mature industrial technologies.

Green Chemistry Centre of Excellence, Department of Chemistry, University of York

Michael North
Jose A. Castro-Osma
Xiao Wu

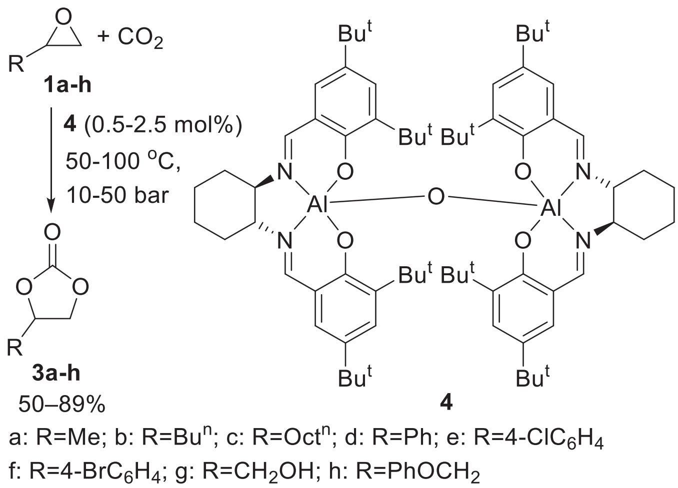
Unprecedented halide-free Aluminium Catalyst for the Synthesis of Cyclic Carbonates from Epoxides and CO_2

Carbon dioxide is a cheap, abundant and non-toxic sustainable carbon source for chemical industries. Therefore, the development of new catalytic processes that use carbon dioxide as feedstock has generated great attention in recent years [1]. Among these processes, the reaction of epoxides **1** and carbon dioxide can afford either polycarbonates **2** or cyclic carbonates **3** and is a 100% atom-economic transformation (Scheme 1). Cyclic carbonates are the thermodynamic product of the reaction and have many applications including as electrolytes for lithium ion batteries, solvents and chemical intermediates [2].



Scheme 1: Synthesis of poly- and cyclic carbonates

In this contribution, we describe kinetic studies on the use of the bimetallic aluminium(salen) complex **4** and tetrabutylammonium bromide as a catalyst system for the synthesis of glycerol carbonate **3g** at temperatures of 25–100 oC, carbon dioxide pressures of 1–100 bar and catalyst loadings of 0.1–2.5 mol%. A key finding of this study was that there was an optimal carbon dioxide pressure (50 bar) for the reaction (Figure 1). Under these optimal conditions, we were able to show that complex **4** is catalytically active in the absence of any cocatalyst. To demonstrate the utility of this process, eight cyclic carbonates **3a–3h** have been prepared from terminal epoxides **1a–1h** and carbon dioxide under solvent free conditions, at temperatures of 50 to 100 oC, carbon dioxide pressures of 10–50 bar and complex **4** concentrations of 0.5–2.5 mol%. The importance of these results is that they simplify the catalyst system for cyclic carbonate synthesis and avoid the cost, corrosion and purification issues associated with the use of ammonium halide or basic cocatalysts.



Scheme 2: Synthesis of cyclic carbonates **3a–3h** using catalyst **4**

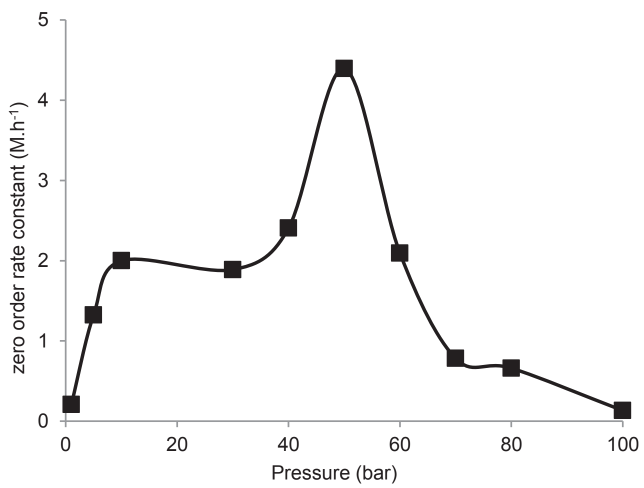


Figure 1: Influence of CO_2 pressure on reaction rate

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Bio Base Europe
Pilot Plant

Saskia Vander Meeren

Carbon Capture and Utilisation: the Role of proper Piloting

Since the industrial revolution, human activities contributed to the climate change by adding carbon dioxide to the atmosphere faster than natural processes can remove it. Different green house gases exist, like carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and fluorinated gases, but carbon dioxide is by far the most abundant. The main source of this carbon dioxide is the combustion of fossil fuels (coal, natural gas and oil) for energy and transportation.

To lower this amount, logically the amount of fossil fuel consumption needs to be reduced. Other extra measurements are carbon capture and storage (CCS) or carbon capture and utilisation (CCU). The goal of carbon capture is capturing waste carbon dioxide from large point sources, such as fossil fuel power plants. This can be transported to a storage site for a long term, for example in deep geological formations or in the form of mineral carbonates. However, economically it is more interesting to use the waste carbon dioxide to produce valuable products, like bulk chemicals or bio-fuels. The conversion can take place with a chemical catalyst, via electrolysis or with micro-organisms.

Bio Base Europe is mostly focused on the microbiological conversions, to produce bio-chemicals in an efficient way starting from carbon dioxide. This is a rather new technology and brings a lot of problems and questions like: What is the requested purity of the gas? How can the solubility of the gas be increased? What about the safety? Etc. These conversions ask for specialized and expensive equipment, which are typically available in pilot facilities. The role of piloting is diverse in developing such a process from scratch. First, the idea needs to be evaluated on lab scale, tested in a small fermentor and optimized and subsequently thoroughly validated on a pilot and demonstration scale. Furthermore, the isolation and purification of the product out of an aqueous environment such as a fermentation broth is also a challenge that can be tackled by a pilot plant, by using the flexible and large amount of available equipment. In addition, pilot tests will provide accurate date in order to be able to make a techno-economical evaluation of the process.

Although the CO_2 accumulation in the atmosphere has been heavily debated in recent years and is considered as being one of the most important environmental threats for the current generation, little efforts have been made so far to bring CCU technologies that are being developed at laboratory scale to a demonstration scale. Action needs to be taken.

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Ennio Vanoli
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Ionic Liquids, Key to sustainable Energy Production?

The level of CO_2 in the atmosphere is rising dramatically, reaching for the first time in May 2013 the level of 400 ppm in Mauna Loa (Hawaii). Thus a great effort is made to find solutions to reduce greenhouse gas (GHG) emissions and especially its major contributor, CO_2. Instead of treating CO_2 as a waste, it can also be considered as a chemical raw material. For example it can be recycled in the food industry or used as chemical feedstock in the synthesis of chemicals (urea, salicylic acid, cyclic carbonates). This approach is known as carbon capture and utilization (CCU) and it is the most promising and energetically "useful" approach.

Conventional solvents for the capture of CO_2 (amines solutions such as monoethanolamine – MEA, methyldiethanolamine – MDEA, or diethylamine – DEA) allows the sequestration of CO_2 but high energy is needed to recover CO_2 from them and they lack stability over time because of the evaporation of water

Ionic liquids (ILs) are efficient solvents for the selective removal of CO_2 from flue gas. Conventional, off-the-shelf ILs are limited in use to physisorption, which limits their absorption capacity. Adding a chemical functionality, like amines or alcohols, allows chemisorption of CO_2. By carefully choosing the anion and the cation of the IL, equimolar absorption of CO_2 is possible (instead of a 2:1 for amine solutions).

We synthesized different ILs in the purpose of capturing CO_2 and transforming it in methanol by hydrogenation. For its price, availability and greenness we chose choline as cation and prepared a variety of ILs with anions, such as amino acids and phenol derivatives. All these ILs were tested on their CO_2 absorption capacity. Stability and viscosity were the two main qualities that we looked for in our ILs as this is important for further industrialization.

We obtained up to 20 weight percent CO_2 absorption in our ILs, which is among the highest reported in literature.

Ecole d'ingénieurs et d'architectes de Fribourg
Hochschule für Technik und Architektur Freiburg

Ionic Liquids, key to sustainable energy production?

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Ing. Pauline Sanglard, Dr. Ennio Vanoli

Research Topic

Green energy

Keywords

Carbon dioxide absorption, Ionic liquids, Energy

Ionic Liquids – basics

- Salts that melt below 100°C
- Very low vapor pressure
- Physical and chemical properties depend on anion and cation

Advantages of ionic liquids (ILs) for CO_2 capture:

- No losses of ILs through evaporation
- Stability

Two modes of absorption:

1. Physisorption
   CO_2 weakly bound to the IL
   Low absorption capacities
2. Chemisorption
   CO_2 chemically bound to the IL
   Equimolar absorption possible

In the two cases, the anion plays a major role

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Context

- CO_2 concentration is rising in the atmosphere! (*Figure 1*)
- Need to find sustainable energy supply

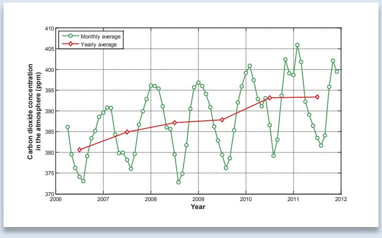
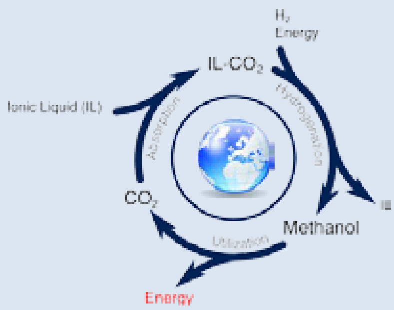


Figure 1 : Evolution of CO_2 concentration in the air in Hohenpeissenberg (D)
ftp://ftp.cmdl.noaa.gov/ccg/co2/flask/event/

Goal

Extending the carbon life cycle



→ Ionic liquid (IL) as the vector of CO_2

Results

Requirements for the IL :

- Low price
- Easy to synthesize
- High CO_2 chemisorption capacity (*Table 1*)
- Easy desorption
- Good stability
- Low viscosity

Choice of cation:
Choline: low price, large availability, good stability

Choice of anion:
Amino acid: not stable for absorption if water:

$$[Z^+][H_2N-CHR-COO^-]+H_2O \xrightarrow{CO_2} [Z^+][HCO_3^-]+[H_3^+N-CHR-COO^-]$$

p-methoxyphenolate (*Figure 2*): good absorption (*Table 1*), stable upon recycling (*Figure 3*), but high viscosity → dissolution in PEG

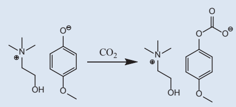


Figure 2 : Reaction of CO_2 capture by [Cho][p-MeO-PhO]

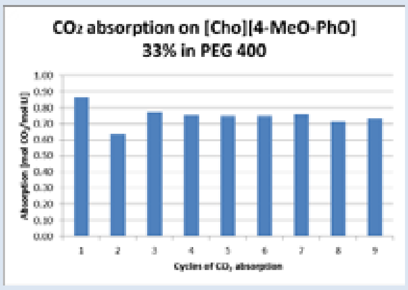


Figure 3 : Cycles of CO_2 absorption by [Cho][p-methoxy-PhO in PEG 400

Table 1: CO_2 absorption capacitiy of the ILs synthesized

Cation	Anion	Absorption (mol CO_2/mol IL)
PBu_4	Lys	1.0
PBu_4	2-cyano-Pyr	0.9
PBu_4	p-methoxy-PhO	0.9
PrMIM	Lys	1.0
PrMIM	p-Cl-PhO	0.6
PrMIM	p-methoxy-PhO	0.7
PrMIM	Ala	0.7
PrMIM	Gly	0.9
Cho	Gly	0.8
Cho	Ala	0.8
Cho	Pro	0.7
Cho	Sar	0.6
Cho	Lys	1.3
Cho	Met	1.3
Cho	p-methyl-PhO	0.9
Cho	p-methoxy-PhO	0.9
Cho	Pyr	0.8

Valorization

Using CO_2 as building block will stabilize its concentration in the atmosphere
ILs permits to bring CO_2 to a liquid phase which facilitate subsequent conversions

- For energy production
- For chemical synthesis

Hes·so Haute Ecole Spécialisée de Suisse occidentale University of Applied Sciences and Arts Western Switzerland

Heatric,
Division of Meggitt

M. R. Vujicic

High Temperature Electrolysis, Power Cycle, Methanol production and Diffusion Bonded Technology

This paper includes heat exchanger technology that is key technology for the process combining three individual processes i.e. hydrogen and oxygen production using high temperature steam electrolysis; Power cycle that use oxygen produced by the high temperature steam electrolysis providing heat to the high temperature steam electrolysis reducing electricity requirement and methanol production where CO_2 produced by Power cycle is used as feedstock that enable methanol and electricity production with 100% carbon capture.

Industrial hydrogen has been used in many different applications e.g. oil refineries, ammonia and methanol production with demand that has been increasing continuously and expect to rise in days to come. To date, Steam Methane Reforming (SMR) process where methane (natural gas) reacts with steam at high temperature in an endothermic reaction has been adopted as the conventional way to produce industrial hydrogen.

However, there are other processes developed to produce hydrogen with electrolysis of steam being one of them. Steam electrolysis includes few different cell types with Solid Oxide Electrolysis Cell (SOEC) that operates at high temperatures being considered in this paper. It needs to be noted that hydrogen produced by steam electrolysis is of highest purity.

As steam electrolysis requires electricity which can be provided by either renewable or non-renewable energies, this paper is considering electricity provided by renewable energies (wind, solar or hydro), so hydrogen is produced without Green House Gas (GHG) emission.

To reduce electricity requirement for steam electrolysis a diffusion bonded heat exchanger is employed to use heat from exhaust gas after combustion of natural gas (Power cycle) and heat realized during hydrogenation of CO_2 in methanol production.

Keywords: Hydrogen, Printed Circuit Heat Exchanger (PCHE), Formed Plate Heat Exchanger (FPHE), Hybrid Heat exchanger (H^2X), High Temperature Steam Electrolysis, Power Cycle, Methanol

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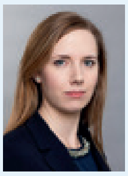

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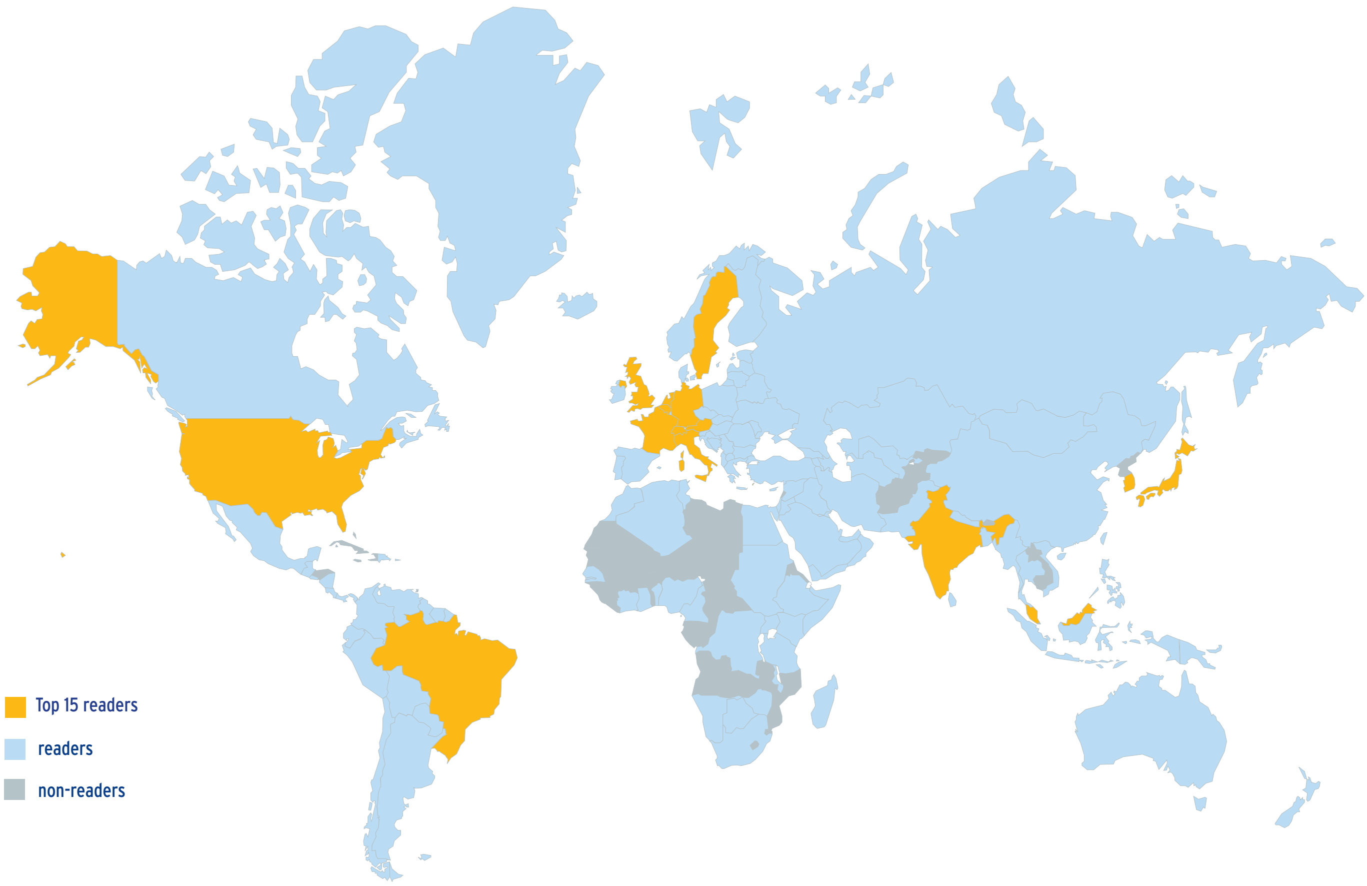

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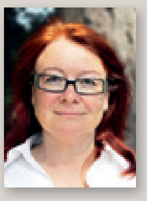

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