Federal Ministry
of Education
and Research

FONA
Research for Sustainable
Development
BMBF

Technologies for Sustainability and Climate Protection – Chemical Processes and Use of CO_2

Final Conference | www.chemieundco2.de

Contents

Projects Status „CO_2 Utilisation Projects“ 30

Project Status „Energy Efficiency Projects“ 45

Concluded Projects 63

Preface

How can chemical processes and procedures be improved in such a way as to reduce emissions of carbon dioxide and transform the climate killer CO_2 into a resource for use in the chemical industry? We must consider this question in the context of the transition to renewable energy, climate protection and resource efficiency. We sought answers with the "Technologies for Sustainability and Climate Protection – Chemical Processes and Use of CO_2" call for proposals under the "Research for Sustainable Development – FONA" framework programme. The focus was on using carbon dioxide in base chemicals, the chemical storage of renewable energy and energy efficiency in processes with a high potential for reducing emissions.

The Federal Ministry of Education and Research (BMBF) has supported a total of 33 collaborative projects in this area since 2010, providing funding of approximately one hundred million euros. The last projects are due to end this year. German industry has contributed an additional 50 million euros in own funding, making the programme the world's largest R&D programme on the industrial use of CO_2. One important guarantee for success is the close cooperation and networking between industry, innovative small and medium-sized enterprises and research institutions. This type of collaboration also serves as a stimulus for fostering young scientists.

I am delighted that the conference to mark the end of the BMBF's funding measure will provide an opportunity to present the programme's results and describe its potential economic and ecological leverage effects. The results show that research and innovation can successfully contribute towards reducing CO_2 emissions in the chemical industry. Furthermore, the smart use of CO_2 provides an opportunity to broaden the industry's resource basis, making it possible in the long term to create a sustainable substitute for the fossil resource of mineral oil.

The results of the BMBF's funding measure are all the more important in the context of the Energiewende and the associated increasing need for storage technologies for renewables. The BMBF will therefore continue to support creative approaches in research and innovation and at the same time expand cooperation with its European partners.

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

Looking Back: Five years of the German R&D initiative in CO_2 utilization

Today, more than 70 % of all chemical products are made out of crude oil. This includes medicines, plastics, insulating material for buildings and even commodities like cosmetics. Furthermore, basically almost all of our fuels are of fossil origin. This highlights two major challenges that we are facing today: The use of fossil resources is causing a vast amount of greenhouse gas emissions, and we are fully relying on a depleting, unsustainable raw material base.

Germany has already begun to transform the energy system in a more sustainable manner and has set high targets: Until 2050, 60 % of our energy should come from renewable sources. But transforming the energy system alone is not sufficient for a green economy. We also have to change the raw material base for one of our most important industrial areas – the chemical industry. Many value-added chains start from the chemical industry. Changing the raw material base of this major supplier will provide ample opportunities for green development.

The Federal Government has adopted that challenge in the New High-Tech Strategy. Here, research and development towards a sustainable economy and sustainable energy is one of five major focus areas. With the 3rd edition of the framework programme "FONA-Research for Sustainable Development" (2015) the Federal Ministry of Education and Research (BMBF) takes up that lead and prioritizes the need for a green economy.

With the funding measure "Technologies for Sustainability and Climate Change – Chemical Processes and Use of CO_2", BMBF started a new initiative in 2009. The measure focusses on the need for a more sustainable raw material base of the chemical industry as well as on the increased demand for energy storage, resulting from a changing energy system. Furthermore, energy intense processes have been investigated and solutions for new processes with low greenhouse gas emission have been developed.

With 33 collaborative projects, the funding measure has proven immensely successful. On a technological level, many breakthrough results have been achieved and so-called "dream reactions" have become reality.

But also on an economical level projects of the funding measure have demonstrated that the newly developed technologies can compete with long-established processes.

For the first time academic junior research group leaders have been funded with a focus on CO_2-utilization to establish that important field of research in the academic landscape. Three excellent young investigators have been selected in the fields of organocatalysis, photocatalysis, and electrocatalysis. Awards, like the recent DECHEMA award for Dr. Mayrhofer of the Max-Planck Institut für Eisenforschung show that this relatively young field of research has by now not only been acknowledged by the scientific community but also has been recognized as a trendsetting field in research for sustainability.

Of the 33 research projects, the majority was coordinated by industrial partners. In total, industry has contributed with app. 50 Million Euros additionally to the 100 Million Euros governmental funding. This demonstrates that the strong industrial base of Germany, particularly the chemical industry, is focusing on future-directed developments, especially in a sustainable and resource-efficient way.

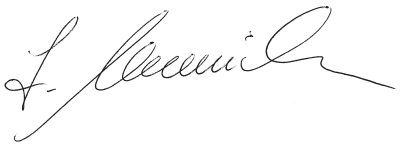
Over the past years, there were many highlights to note. Remarkably, a project called "Dream Reaction", coordinated by Bayer has proven that CO_2 can be used as a raw material for plastic production. A consortium of academics and industry found a working catalytic system to directly convert CO_2 into a so-called polyol, a building block for polyurethane foams, used for example in mattresses. The project was so successful, that a second project, the "Dream production" was started. In this project the first comprehensive life cycle assessment (LCA) of a CO_2-utilization project has been achieved. This LCA showed that not only the direct CO_2-utilization has a positive impact on the carbon footprint, but additionally, the reduced application of fossil-based raw materials evokes a second, even bigger impact on the carbon footprint. With this knowledge, Bayer is now going into production: Next year the first commercial products based on CO_2-plastic foam will enter the market.

Another highlight was last autumn's opening of the worldwide first Power-to-liquid pilot plant "Fuel1" based on a high temperature steam electrolysis in combination with a Fischer-Tropsch-reactor. It was opened in November 2014 by Federal Minister Prof. Wanka at the sunfire site in Dresden. A consortium of academia and industry, led by the sunfire company has developed a highly efficient process for water electrolysis and has combined core German technologies in a unique manner to produce fuels like kerosene or diesel but also a naphta equivalent for the chemical industry basically from CO_2, water and renewable energy. During the event, sunfire has also teamed up with Boeing and Audi in new collaborations. The transportation industry is looking for new and more sustainable fuels avoiding competition with the food industry for arable land (tank vs. table) and reducing the carbon footprint of fuels significantly.

In the area of new technologies for energy efficient processes, many promising results have been achieved. One achievement was the development of a novel nanofiltration system to remove solvents from products after chemical reactions. This is generally achieved by a high temperature process, resulting in a high demand for energy. The nanofiltration method, developed in the project "OPHINA", coordinated by Evonik, is a cold separation technique that can potentially lead to a massive reduction in energy demand and subsequently in greenhouse gas emissions.

But not only is the chemical industry involved in CO_2-utilisation strategies. In the project "Solid and fluid products from gas (FfPaG)", a consortium of BASF, Linde and Thyssen Krupp, together with other industrial and academic partners is looking for ways to integrate CO_2-utilisation pathways within the steel industry and the chemical industry. This project has started in the second half of 2013 and shows already now promising results for the future.

Many promising solutions have been found and many new technologies have been developed. Furthermore, new pathways and application methods have been detected and the potential of CO_2-utilisation has proven to be manifold. In future, we will focus on strengthening the German role as a technology leader in CO_2-utilisation, and ensure that promising R&D results are brought into the market. With the funding measures "r+Impuls" and "CO_2Plus", BMBF continues to support this future-oriented field of sustainable research to provide renewable raw materials for a green economy.



PD Dr. sc. Lothar Mennicken
Federal Ministry of Education and Research,
Division Resources and Sustainability

When Dreams come true...

If mankind is producing and emitting too much carbon dioxide (CO_2) which is known to imbalance the natural carbon cycle of our planet – why not trying to turn the greenhouse gas into something useful?

It is the researcher's dream to find reactions for using CO_2 as a building block for new materials. The chemical industry dreams of carbon dioxide based products to become more independent of petrol based chemicals. And the society and politicians are longing for a way to reduce the anthropological carbon footprint and preserve the earth for future generations.

Everything starts with a dream... and so it did at Bayer MaterialScience.

Initiated by a call from the German Federal Ministry of Education and Research (BMBF) over ten years ago, a project team was assembled to face the challenge of "Dream Reactions". The central question for the researchers was how to convince the very unreactive compound carbon dioxide to do chemical reactions in an efficient way. Catalysis was the answer and after finding the one right catalyst in a comprehensive screening first results on small scales in the laboratory were achieved.

But can the "Dream Reactions" be scaled up and the products be used in the preparation of new polymeric materials? The answer is yes: The follow-up project "Dream Production", also funded by the BMBF, established a catalytic process to incorporate CO_2 into polyol, which is one of the two essential components for polyurethane. This material is present in everybody's daily life: as soft foam in car seats or furniture, as rigid foam to insulate buildings and cooling devices.

In need of a larger quantity of this new kind of polyol, a pilot plant was built in Leverkusen at the beginning of 2011. With a larger amount of material at hand it

Fig. 1: Dreaming of a sustainable future with CO_2. (© Bayer AG)

was possible to do necessary tests and analyses which showed high potential and gave the direction for a first target product: mattresses made with a CO_2-based polyol. In the second step, Bayer MaterialScience is now building a production line in Dormagen in order to produce the new material on a larger scale. It is scheduled to come on stream in 2016.

So the reseracher's and industry's dreams are coming true. But the new material does also contribute to a more sustainable future.

Because the new polyols are consisting of roughly 20% carbon dioxide, the amount of petrol-based compounds to produce the same amount of material is reduced. But that does not necessarily lead to a decreased environmental impact. Researchers at the RWTH Aachen University looked in detail at the carbon footprint of the new products. This Life Cycle Assessment confirmed that the production of the CO_2-based polyols needs considerable less energy and less petrol resources compared to the conventional production.

And even further energy and petrol savings are imaginable.

This is what another project – "Dream Polymers" – is aiming at, again made possible with the help of the BMBF. Investigations are targeting on the synthesis of polyols by using up to 40% alternative raw materials. The project consortium follows two approaches to achieve their goal. Firstly, by directly binding CO_2 into the polyol and, secondly, by incorporating chemicals which are derived from CO_2. In total the portion of alternative raw materials in the final product will be increased significantly.

In addition, the catalyst system and process design allow for the incorporation of further functionalities. Therefore, a wider freedom in polymer design and the tuning of polymer properties is gained. As a result, the number of polyurethane plastic materials that can be produced using carbon dioxide based polyols is increasing. It is now also possible to manufacture thermoplastic polyurethanes, films and casting elastomers in this way. Such plastics are used in a large number of applications, including car interiors, cable sheathing and sporting goods such as ski boots.

Has the dream come true? Pioneering results have been achieved to include CO_2 into the catalogue of building blocks for the polymer industry. But Bayer MaterialScience is aware that it is an ongoing process to adapt the production of high-quality polymers from fossil resources to alternative raw materials. A process which the company wants to face in close contact with the scientific community and supported by the public sector all around the world.

Even though Bayer MaterialScience developed a first application of CO_2 in polymers, there are still further challenges to come on the way to close the carbon cycle. We are not lacking in dreams....

Contact:

Dr. Klaus Schäfer
Head of Production and Technology
Bayer MaterialScience AG
E-mail: klaus.schaefer@bayer.com

sunfire – Liquid fuel from CO_2 and H_2O through the integration of renewable energies

The sunfire project began in May 2012 and follows two main goals:

1. Construction and operation of a High-Temperature Electrolyser, which reaches an electrical efficiency level (LHV_{H2}/kW_{el}) of well over 90% (for $10kW_{el}$) under pressure.

2. Construction and operation of a pilot plant for the production of hydrocarbon from CO_2 and H_2O with an efficiency level of >65% (LHV_{H2}/kW_{el}).

The full process of the production of hydrocarbon consists in (1) Steam-electrolysis, (2) CO_2-RWGS-conversion [1] and (3) Fischer-Tropsch-Synthesis. After thorough lab-tasting of the process, the sunfire pilot plant was erected and presented to the public on 14 November 2014 in the presence of Minister Prof. Johanna Wanka.

Since the inauguration on 14.11.2014, the launched operation is now gradually moving forward. The strengthening of the high-temperature pressure insulation required greater revision after the thermal conductivity increased more than expected due to pressure influence.

In parallel to the technical developments underway, an economic analysis of the concept's whole supply chain has been undertaken by the University of Stuttgart. A report of the current state of the pilot plant has already been completed. This will be used to gage the ecological impact of the production of fuel on an industrial level.

In completing this project, the first steps will be made towards the industrialization of the Power-to-Liquids processes for the production of liquid fuels (Petrol, Diesel, Kerosine) compatible with various kinds of infrastructure through the use of the highly efficient steam electrolysis. Through this approach, for each ton of fuel produced, up to 3,14 tons of CO_2 can be saved. Furthermore, the process can serve as a balancing power for the stabilization of the electricity network and can enable decentralized, regional added value coupled with a greater security of supply.

5 companies and 5 scientific institutes, specializing particularly in the fields of material development and process characterization, are working hand in hand on this project. In total so far, 11 Final-Year projects and Master theses have been written about this project.

During the project, the reversible fuel-cell/electrolyzer has been successfully operated and proves ground- breaking research results. This RSOC (Reversible Solid Oxide Cell) unit could become the pioneer of the PtX-business model, in that it is able to supply electricity in time of energy penury. As a result, a new source of income will be secured and the usage of the power plant will increase.

Fig. 1: First introduction of CO_2 executed by Minister Wanka

Fig. 2: High-Temperature electrolysis pressure tank

Fig. 3: Overall view of the sunfire Fuel 1 – power plant

[1] Reverse Water-Gas Shift Reaction: Endothermal reduction of CO_2 to CO under oxidation of H_2 to H_2O

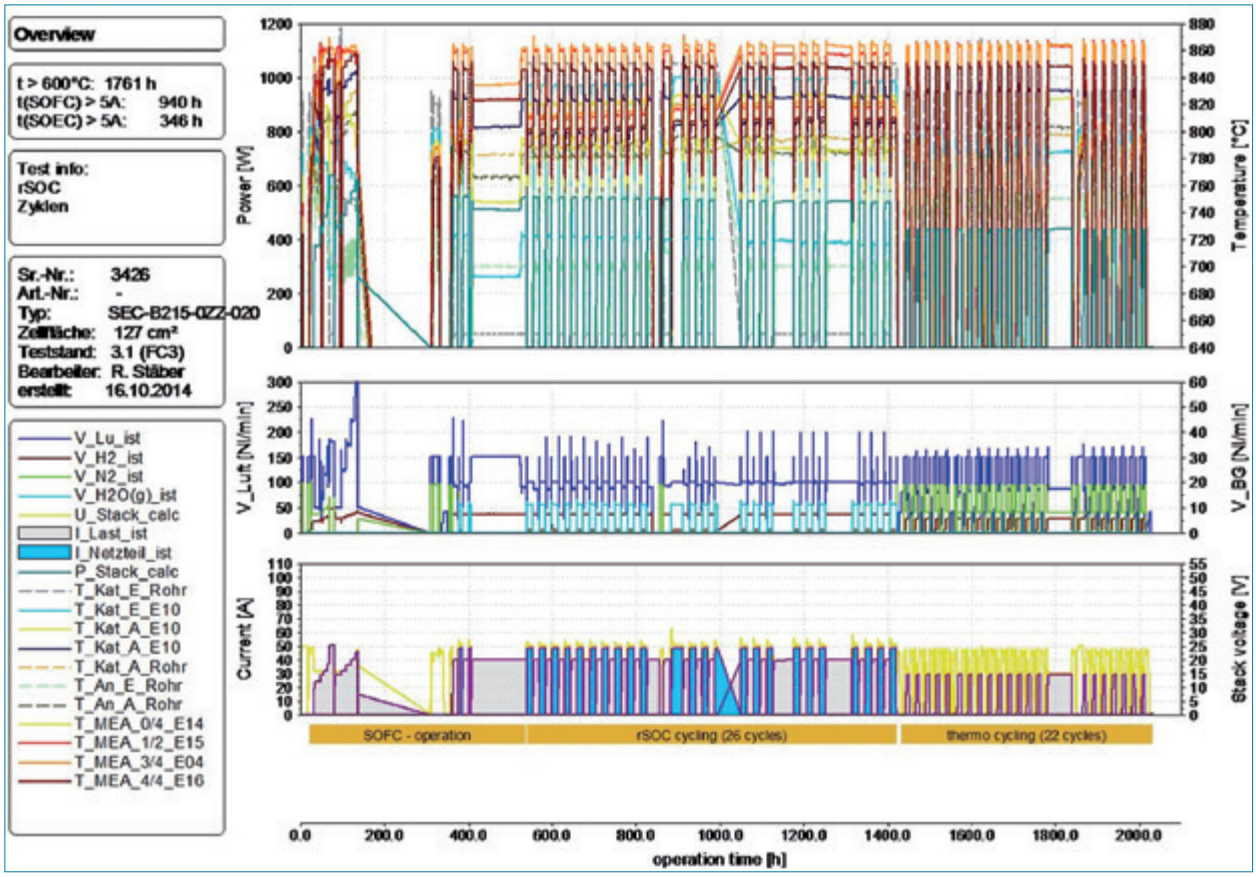
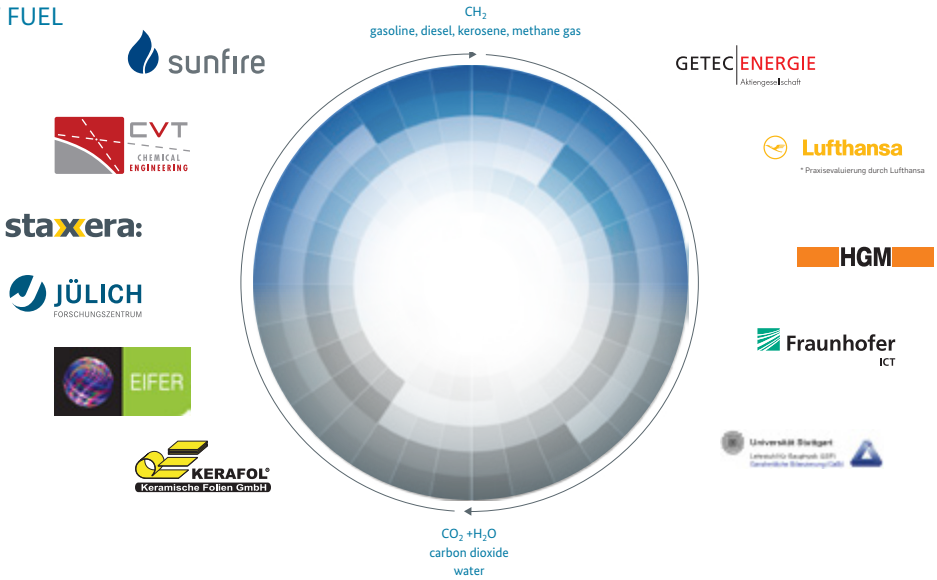


Fig. 4: Reversible cycles of the Fuel-Cell/Electrolyser (source: sunfire GmbH)

SUNFIRE – PRODUCTION OF FUEL FROM CO_2 AND H_2O



Contact:

Christian von Olshausen
CTO
Sunfire GmbH
E-mail: christian.vonolshausen@sunfire.de

Phoenix rising – Transforming CO_2 into value for a rejuvenated sustainable European economy

The chemical conversion of CO_2 – the only carbon resource that is available in abundance in Europe - has the potential to define a new landscape and business opportunities for the European industry in the next decades, and would contribute to address major challenges Europe is facing such as resource efficiency and low carbon energy.

The utilization of CO_2 as a feedstock by the European chemical industry to produce more sustainable materials, chemicals and fuels could be a key option to reduce use of fossil feedstock, reduce EU's dependence on imports of fossil resources and improve security of supply of carbon feedstock, while reducing pressure on biomass, land use and other environmental stressors. In addition, some CO_2 conversion technologies have the potential to provide solutions for large scale renewable energy storage, and thus increase the share of renewable energy in Europe.

The chemical valorisation of CO_2 has therefore the potential to contribute to meeting ambitious policy targets, and to be a key element for the development of a circular economy and leadership of Europe in sustainable technologies.

CO_2 conversion has been a scientific research topic for a long time. The knowledge created has now to be turned into value for the European society. Several European companies are working on the development of CO_2 conversion technologies at medium to high technology readiness levels. Further research and innovation developments in CO_2 conversion technologies can create new opportunities for the European industry.

Many specific activities related to CO_2 utilisation have already been initiated at national and regional level in Europe, and the results of the German funding programme dedicated to CO_2 valorisation "Sustainability and Climate Protection Technologies – Chemical Processes and Use of CO_2" are already impressive.

The European Commission is supporting various projects through different funding programmes. Topics addressing CO_2 conversion are included in various work programmes of Horizon 2020, and introduced in some sections of the new Strategic Energy Technology and Innovation Integrated Roadmap from the European Commission.

However a more coherent and coordinated approach across Europe and across public and private sectors is needed to complement the existing dispersed efforts and create the critical mass for the next steps in this long term engagement and competition with other global regions. Such a dedicated public-private partnership, would address both the financial support for technology development, as well as the non-technological barriers through an appropriate policy framework (e.g. recognition of CO_2 as renewable resource).

In the framework of an European economy that needs breakthrough technologies to address its societal challenges within a global competition, the European industry has the opportunity to put forward a proposal to contribute to "A New Start for Europe" with an integrated project of European interest on the utilisation of CO_2 as a renewable carbon resource. Such an approach, going beyond a mere financial instrument, should also engage and stimulate European investors under a common initiative supported by leaders from both public and private sectors.

Global race has started with other regions which have significant programmes and budget dedicated to CO_2 conversion technologies. The moment to take action in Europe and for Europe is now.

Contact:

Dr. Gernot Klotz
Cefic (European Chemical Industry Council)
Senior Advisor for Research & Innovation
E-mail: gernot.klotz@gkl-consulting.com

POWER-2-X – Challenges and Opportunities at the Interface of the Energetic and Chemical Value Chain

The increasing installation of renewable energy systems requires novel strategies for the storage and utilization of fluctuating electricity. At the same time, there is a growing demand for alternative carbon sources to replace fossil feedstocks as energy carriers and in chemical production. The German “Energiewende” and the strong commitment of the German Chemical Industry to a Sustainable development may provide a competitive basis to respond to this challenge and exploit possible synergies for innovation as opportunity in the global competition.

The present talk will highlight possible options to integrate these two developments and evaluate their potential to contribute to a sustainable development in the energy and chemical industry.

Three criteria will be applied as guiding principles for this analysis:

1. Usage of renewable energy at the highest level of exergy
2. Minimisation of the C-footprint of the material value chain
3. Economic revenue from the usage of the energy and carbon sources

For selected approaches, the presentation will also discuss the technology readiness levels and identify research targets for future developments.

Contact:

Prof. Dr. Walter Leitner
Institut für Technische und Makromolekulare Chemie
RWTH Aachen University
E-Mail: leitner@itmc.rwth-aachen.de

Energy carriers and materials based on CO_2 – Audi e-fuels and e-materials

The sustainable mobility of the future – as part of the world we want to live in - will heavily depend on clean, renewable energy. Cars running on green electricity and maybe also on renewable hydrogen are part of this scenario, but they will not be able to cover all mobility needs. So - what will happen to the cars, long distance buses and trucks still making use of an internal combustion engine? In twenty or thirty years they will continue to represent the main part not only of the fleets on the road but also of the new car registrations, experts say. Thus it makes sense to move this long leverage. How can GHG emissions of these vehicles be substantially reduced apart from further efforts to improve efficiency? Audi's push towards the development and production of climate-friendly synthetic fuels ("Audi e-fuels") and plastics ("Audi e-materials") addresses these questions. In general OEMs may look beyond traditionally manufacturing vehicles and expand horizons into developing the access to sustainable resources and energy carriers for vehicles.

The future will not be carbon free – nature is not carbon free neither. The vision is to regard CO_2 as a carbon source and to develop fuels or materials with emission-binding potential. One of Audi's key paths to balanced CO_2-neutral mobility is through the e-fuels strategy, which includes the e-gas, e-diesel, and e-ethanol projects. The Audi Power-to-Gas plant in Northern Germany producing renewable synthetic methane ("Audi e-gas") and connecting electric and gas grid is one concrete example showing clearly that mobility can be part and enabler of the energy turnaround we need in order to fulfil the emission reduction targets and to have a power system with up to 100% renewables.

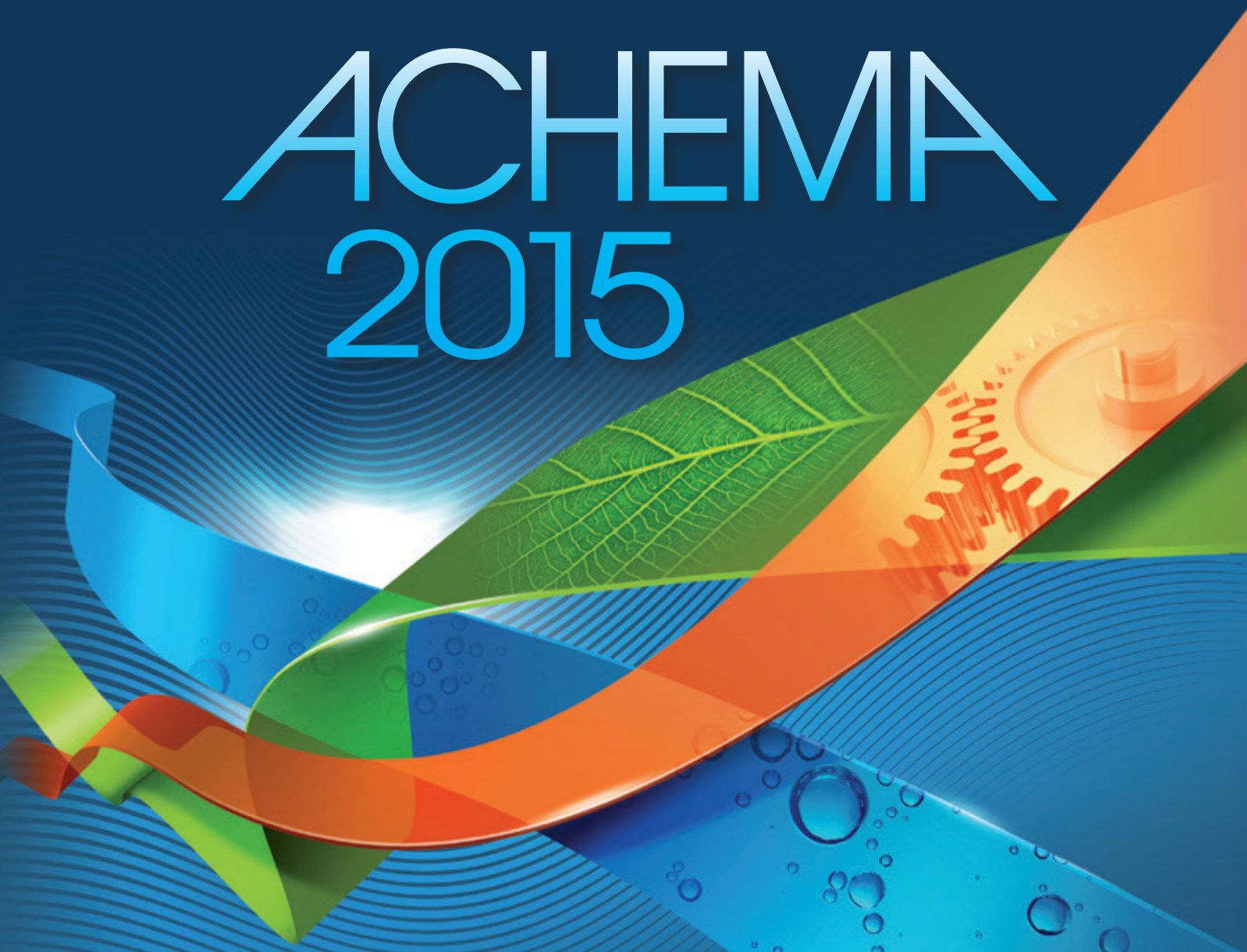
Given the fact that mobility is tightly linked to energy, there is the need for OEMs to think beyond the automotive value chain towards other industries, such as the energy sector, to jointly share knowledge, gain expertise, and develop solutions for sustainable mobility and green power supply towards the future. Audi has firmly positioned itself on this path towards sustainable mobility through leading the way in building a chain of sustainable energy sources, which is coupled with its continued developments in powertrain and drive technologies, lightweight approaches, and associated technology advancements. For all OEMs it is important to look beyond tailpipe emissions to the lifecycle of their products and maintenance of eco energy balances. And on this pathway the capturing, storage and recycling of carbon dioxide will be a key discipline.

Contact:

Reinhard Otten
Umwelt Produkt
AUDI AG
E-mail: reinhard.otten@audi.de
Homepage: www.audi.com

Frankfurt am Main · 15 – 19 June 2015

ACHEMA 2015



15. – 19. June 2015

BMBF Funding Programme

Technology for Sustainability and Climate Protection – Chemical Processes and Use of CO_2

Please visit us

Hall 9.2 / Stand E46

More information on www.chemieundco2.de

www.achema.de

iC^4 – Intergrated Carbon Capture, Conversion and Cycling

CO_2 as a Building Block for Efficient, Sustainable Energy Storage Technology

BMBF is providing 6.3 million euros in funding for the iC^4: Integrated Carbon Capture, Conversion and Cycling consortium project. The goal is to efficiently capture CO_2 from a variety of sources including biogas plants, power stations and the iron & steel and cement industries (carbon capture) and synthesize the gas into methane or other chemical building blocks such as formic acid, methanol, higher oxygenates and hydrocarbons (conversion). The technologies developed during the project could make a very substantial climate-neutral contribution to re-use of CO_2 in the energy and material streams (cycling).

The current status of the four iC^4 subprojects – COOMem, AdCOO (CO_2 capture), COOMeth and PhotoCOO (CO_2 utilization) is summarized below.

COOMem

The goal of the COOMem subproject is to develop innovative composite carbon capture membranes. Membrane technologies are used in the iC^4 cluster for gas separation, e.g. to capture CO_2 emissions from power plants and CO_2/CH_4 gas mixtures from biogas plants. The project team is conducting in-depth research on the membrane materials, membrane production and simulated system integration, and they are also carrying out an economic and environmental assessment of the technology. The composite membranes consist of a selective layer on a support membrane. Silicon elastomers with intrinsically high gas permeability are used as the support material for the hollow-fiber membranes. Polyelectrolytes with high CO_2 selectivity were chosen as the base material for the selective separation layer. Based on the development work done by the project team, large scale production of asymmetrically micro-porous hollow-fiber membranes is now feasible, and it is possible to make separation layers with CO_2/N2 selectivity of approximately 60.

The research team on the COOMeth subproject is trying to derive economic value from CO_2 by using renewable hydrogen for methanation. The technology is highly dependent on the availability of hydrogen and CO2 at an affordable price. Especially the electrolytic production of hydrogen is very costly and therefore economically limiting. Even though the costs of CO_2 separation are minor and therefore of less impact, is still is reasonable to optimize the processes.

AdCOO

Existing post-combustion capture techniques based on wet scrubbing with reactive amine reagents are very expensive and not particularly efficient. A technical/economic feasibility study is being carried out in the AdCOO subproject to determine whether solid sorbents in combination with suitable process technology can improve energy efficiency. Therefore, various solid sorbents have been produced and characterized. Some are made using different combinations of support materials impregnated with suitable receptor molecules while others are non-impregnated sorbents which have a defined pore structure such as zeolites and mesoporous silicas.

The acquired analytical data is used by the technology partner Siemens Energy to assess the economic feasibility of alternative process technologies such as fixed bed and fluidized bed reactors. The project team is also looking at the suitability of various solid sorbent options under pre-combustion conditions for next-generation power station technologies.

As things stand now, the results indicate that under fixed-bed based post-combustion capture conditions, there are no substantial energy efficiency or economic advantages compared to advanced wet scrubbing techniques. While solid sorbents do have the advantage of greatly reduced heat capacity, lower heat transfer means that compared to wet scrubbing, extraction of absorption heat for the subsequent desorption stage requires sophisticated and expensive heat exchanger technology.

As a result, the emphasis is on acquisition of data for assessing the economic feasibility of using solid sorbents in a fluidized-bed process or with structured reactor geometry. Based on the principles and tools generated in the project, concepts for the separation of CO_2 from power plant exhausts were established and evaluated. The process details and costs for a fixed bed and a staged fluidized bed were investigated in detail. A general problem for CO_2 separation techniques are the very low

prices for CO_2 certificates but under other economic conditions, the generated knowledge can help implementing future processes for the separation of CO_2 from the atmosphere. Therefore, subsequent project should be considered to proceed with this very promising work.

COOMeth

Work on the COOMeth subproject is proceeding on schedule. During catalytic screening, nickel- and cobalt-based catalysts with various promoters have been produced at TUM using a variety of fabrication techniques. Nickel catalysts look very promising and have been studied in detail. A multi-reactor system used for catalytic screening has been transferred to TUM where it is now operational. The researchers have conducted experiments to assess the reaction kinetics based on benchmark catalysts, and they have also evaluated kinetic models for describing the experiment results. Pilot-scale trials have shown that under optimized reaction conditions, in-spec product gas suitable for feed-in can be produced in a single pass operation. In a screening procedure, modifications have been identified which improve hydrothermal catalyst stability and increase the activity also at lower reaction temperatures. These materials were up-scaled by Clariant are under investigation at MAN for further improvement of their properties.

Assuming that 10TWh of chemical energy storage will be needed by 2050, CO_2 methanation could be expected to save a maximum 3,900 kto of CO_2. The improvement in energy efficiency resulting from the envisioned CO_2 methanation process improvements (reactor/catalyst optimization and heat coupling) is estimated to be 4.8 MWh/to SNG. In a regenerative scenario, CO_2 capture (COOMem and AdCOO) in combination with CO_2 methanation does not produce any additional CO2 mitigation, but ideally it does make CO_2 capture economically feasible by reducing specific energy consumption. The largest impact on CO_2 emission reduction might be the availability of an efficient seasonal energy storage system as precondition of the implementation of renewable energy sources.

PhotoCOO

Researchers are investigating various aspects of photochemical CO_2 reduction. Calculations based on quantum mechanics provide indications of possible reaction paths, activation energies and equilibrium states. Experiments can then be set up to test the theoretical models, initiating an iterative process. The team has synthesized various rhenium and iridium complexes which can be used to investigate the kinetics of selective CO_2 reduction to CO. The researchers have gained an in-depth insight into the electron transfer mechanism and the deactivation steps. They have developed systems which are capable of making a large portion of the sunlight spectrum available for the reduction process. Photochemical water splitting is an additional aspect which is being investigated using GaN/ZnO based heterogeneous catalysts. Through selection of particle composition and size along with suitable promoters (Pt, Pd and Ag), the team is attempting to determine the reaction kinetics and thermodynamics. Initial results indicate that this approach is very promising. An Xe/Hg lamp which simulates sunlight is being used to make a detailed study of oxygen and hydrogen evolution. There are strong indications that promoter cluster size is crucial. With the aid of a DEMS (differential electrochemical mass spectrometer), the researchers are carrying out investigations on photoelectric CO_2 reduction to make various products such as formic acid, formaldehyde and methanol with the aid of decorated silicon surfaces. The results indicate that covalent bonding of organocatalysts on the silicon surface tends to increase the activity of CO_2 reduction.

Project partners:

- Technische Universität München
- MAN Diesel & Turbo SE
- Wacker Chemie AG
- Fraunhofer-Gesellschaft zur Förderung der angewandten Forschung e.V.
- Linde Aktiengesellschaft
- Siemens Aktiengesellschaft
- Clariant Produkte (Deutschland) GmbH
- E.ON New Build & Technology GmbH

Contact:

Prof. Richard Fischer
Technische Universität München
Lehrstuhl für Technische Chemie
E-mail: richard.fischer@tum.de

CO_2RRECT – Utilization of CO_2 as a Carbon Building Block Mainly Using Renewable Energy

Challenges and Goals

The goal of the CO_2RRECT project is to use hydrogen produced with renewable energy together with CO_2 to make high-grade chemical products. A research alliance including Bayer, RWE, Siemens and ten partners from academia is working on the concept.

Conventional power stations are demand-driven whereas generation from alternative resources fluctuates depending on weather conditions (e.g. wind and sunlight). Many EU countries want to greatly expand the use of renewable energy, thus, electricity storage systems can be used to balance supply and demand. Pumped storage power stations are currently the most widely used technology. Chemical energy storage is another option, for example production of hydrogen using water electrolysis. Hydrogen can be stored in large volumes.

Scope and Emphasis

Research on this project was organized into 5 work packages. Siemens designed a PEM electrolysis system for hydrogen production. Trials were run on a prototype with a peak rating of 300 kW at the Niederaußem power station during the CO_2RRECT demonstration phase. Bayer developed a reactor concept and catalysts for the reaction of hydrogen with CO_2 captured from the power station emissions to produce carbon monoxide for use as a reactive intermediate. The source of the carbon dioxide is RWE's lignite power station at Niederaußem near Cologne, where the gas is extracted, purified, liquefied and filled. At the end of the project, Bayer and Invite validated the reactor concept at a pilot-scale plant in Leverkusen, which is operating since the end of 2014.

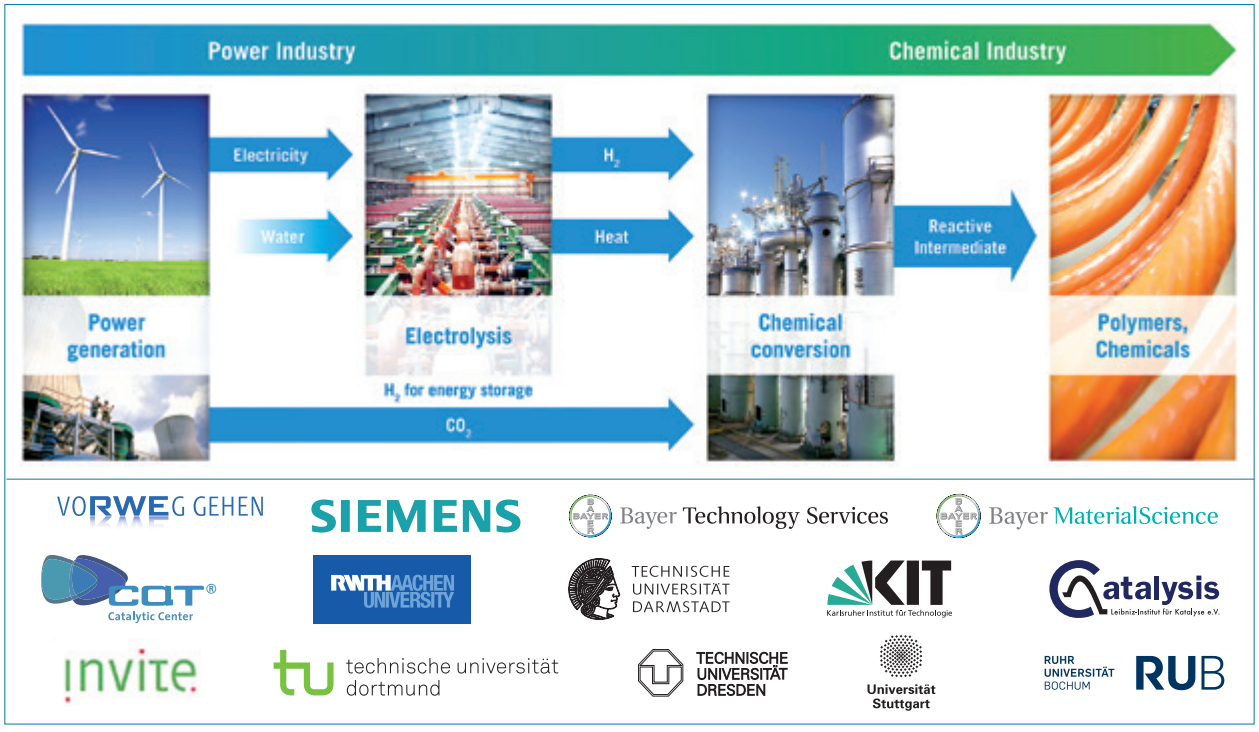


Fig. 1: Using hydrogen produced from renewable resources, CO_2 can be converted to useful products in the chemical industry (photo: Bayer)

A special catalyst is needed to activate the CO_2. Other project partners are contributing their expertise in catalyst research, process technology, reactor optimization and holistic process analysis. The consortium includes universities in Aachen, Bochum, Dortmund, Dresden and Stuttgart along with the Max Planck Society, the Leibniz Institute for Catalysis at the University of Rostock (LIKAT), the Karlsruhe Institute of Technology and the INVITE research center.

In addition to the engineering and economic aspects, the researchers also evaluated the potential for further reductions in greenhouse gas emissions compared to current process technology.

Application, Exploitation of the Results, Economic and Environmental Benefits

All of the technical goals for the project were achieved. However, technical and economic analysis shows that a very large amount of low-cost renewable energy will have to be available for the technology to be economically viable. Realization is not expected before 2020 at the earliest. The main advantages of the project are as follows: meaningful use can be made of excess electricity from wind power, and CO_2 which is otherwise treated as a waste product can be used as a new feedstock and an alternative to feedstock produced by the petrochemical industry.

High-performance plastic polycarbonate can be made from the intermediate which is synthesized from CO_2 for the production of items such as DVDs, LEDs, computer enclosures and eyeglasses. Isocyanate, a major constituent of polyurethane foam, can also be produced. The foam is found in many everyday products such as furniture, shoes, cars and building insulation material.

Fig. 2: Prototype Siemens electrolyzer with a peak rating of 0.3 MW at the RWE Niederaußem power station site near Cologne (Photo: Siemens/RWE)

Contact:

Dr. Stefanie Eiden
Bayer Technology Services GmbH
E-mail: stefanie.eiden@bayer.com

SEE – Storage of Electrical Energy from Renewable Resources in the Natural Gas Grid – H_2O Electrolysis and Gas Component Synthesis

Electricity output from wind and solar generation fluctuates significantly over time but feed-in and demand in the electricity grid must always be in balance. As more and more electricity is generated from renewable sources, there is an increasing need for highly flexible electricity storage and retrieval systems. The available capacity provided by existing electricity storage systems will not be sufficient to meet medium and long term needs. The goal of this consortium project was to develop technology to help manage the fluctuating supply of electricity from wind and solar power by storing energy as SNG (Substitute Natural Gas). CO_2 acts as the carbon source.

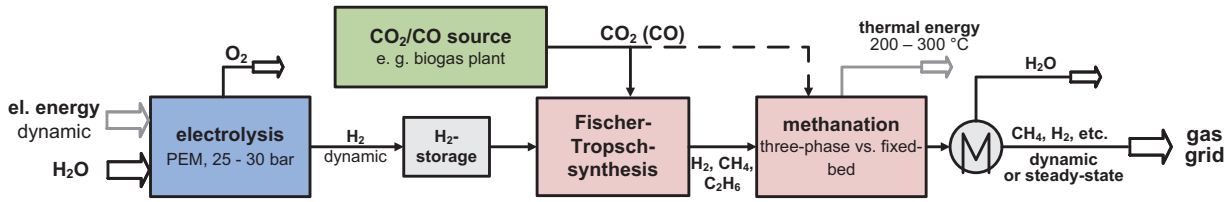


Fig. 1: Power-to-Gas process chain for the production of SNG from excess electricity and CO_2

In the proposed Power-to-Gas process chain (Fig. 1), a PEM pressure electrolyser with highly dynamic responding behavior produces hydrogen, which is subsequently transformed into CH_4 utilizing CO_2:

$$CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O\ (g) \qquad \Delta_R H^0 = -165\ kJ/mol$$

Germany has an excellent natural gas storage and distribution infrastructure. The country's pore and cavern natural gas reservoirs have a working gas volume of approximately 23 Gm^3 which is equivalent to about 250 TWh (chem) (the figure for pumped storage power stations is approx. 0.04 TWh (el)). Additional storage facilities with a volume of 7 Gm^3 are currently under construction or at the planning stage. Leaving aside the natural gas grid, storage capacity of at least 326 TWh (chem) will then be available, which is roughly seven times the total amount of electricity generated from wind power in 2012.

For the reaction of CO_2 and H_2 to CH_4 (methanation reaction), a novel reactor concept called *three phase methanation* can be used. Three-phase (slurry) reactors could have advantages compared to the two-phase methanation which has been the predominant pathway in the past. The reaction of gaseous educts takes place at a solid catalyst, suspended in a special heat transfer fluid (e.g. heat transfer oil or ionic liquids (IL)) – see Fig. 2. Because the fluid has high heat capacity, a three-phase system is well suited for dynamic operation. As an alternative, the team worked on fixed-bed methanation in a staged reactor, looking particularly at the cost-effectiveness of small to medium size systems.

Adjustment of the caloric value is needed following SNG production. Liquid fossil gas has been used up to this point for that purpose. To eliminate the dependency on fossil fuel in the process sequence, the intention is to produce C_2 - C_4 hydrocarbons from H_2/CO_2 feedstock using Fischer-Tropsch synthesis.

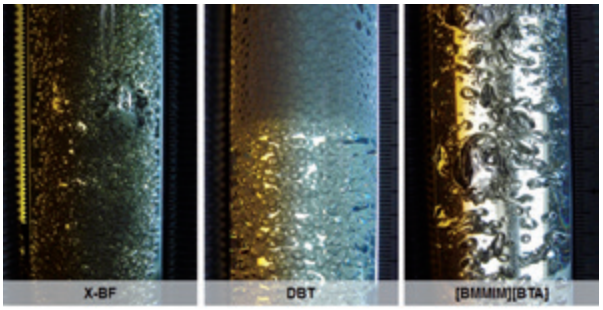


Fig. 2: Bubble formation in a three-phase reactor with various fluids at 200 °C and 1 bar (X-BF: silicon oil, DBT: dibenzyltoluene, [BMMIM][BTA]: ionic liquids (IL))

Based on this approach, a consortium made up of experts from various branches of the industrial and research community has taken on the challenge of designing a process which is technically and economically viable.

h-tec GmbH has built a PEM electrolyzer. Fraunhofer ISE was carrying out dynamic operational control analysis in order to optimize the system. The DVGW Research Center at the Engler-Bunte-Institut, which is part of Karlsruhe Institute of Technology (KIT), was carrying out investigations on methanation in a slurry reactor and was also in charge of the project. IOLITEC Ionic Liquids Technologies was responsible for IL development and synthesis. Outotec had responsibility for methanation in a fixed-bed staged reactor, and the Chemical Energy – Fuel Technology team at the KIT Engler-Bunte-Institut was in charge of syngas conditioning to adjust the calorific value. The three research institutes had joint responsibility for the dynamic performance of the overall system. EnBW Energie Baden-Württemberg, a potential user, was evaluating the economic viability and was looking at possible sites for demonstrators.

The project successfully ended in summer 2014. Support for three doctoral dissertations and more than 20 Bachelor's / Master's theses were being provided on the project.

Contact:

Dr.-Ing. Manuel Götz
DVGW-Forschungsstelle at the Engler-Bunte-Institut
of the Karlsruhe Institute of Technologie (KIT)
E-mMail: goetz@dvgw-ebi.de

From Dream Production to Dream Polymers

People are becoming more and more aware that carbon dioxide (CO_2) is much too valuable to just be released into the atmosphere, and thus worsen the greenhouse effect. CO_2 is a valuable resource due to the contained carbon, which is an important element needed for the production of plastics. Thus, the traditional source of carbon, petroleum, can be – at least in part – replaced. Bayer MaterialScience wants to exploit this possibility and has become a pioneer of using CO_2 for polyurethane materials.

Dream Production – scheduled to deliver commercial products soon

The Dream Production project, well established for some time now, focuses on using carbon dioxide to produce polyols, a crucial component of polyurethane foam. Bayer MaterialScience has developed a process for the production of polyethercarbonate polyols, using CO_2 as building block[1]. The new material is scheduled to be launched in 2016. A pilot plant with a capacity of 6.000 t/y is currently being built. The first target products are mattresses with a CO_2 content in the new polyol of about 20 mass-percent.

For the reaction of carbon dioxide with epoxides a detailed life-cycle assessment[2,3] by the LTT of RWTH Aachen University recently showed environmental benefits for conversion of carbon dioxide to polyols for polyurethane production.[4] In this specific reaction, *CO_2 replaces epoxides* as feedstock leading to reduced environmental impacts. For the new CO_2-based material as compared to the conventional polyol this leads to a reduction of about 20% (global warming impact in kg CO_2-equivalents) for a polyethercarbonate polyol with a CO_2 content of ca. 20 wt% CO_2 content.

Fig. 1: CO_2 based polyethercarbonate polyols as sustainable materials for polyurethanes

Dream Polymers – follow up with a two-pronged approach

While the environmental potential of direct utilization of CO_2 for polyethercarbonate polyols has thus been demonstrated, CO_2 can also be utilized indirectly for many intermediates in the chemical supply chain of polyurethanes. For example, CO_2 can be converted to methanol and subsequently to formaldehyde and further on to its polymer, polyoxymethylene diol, which constitutes a potential building block for polyols.

Methanol based on CO_2 is subject to many efforts in the industry, and it is already commercially available.[5] This technology is currently being developed to yield linear polyols. The idea is to increase the proportion of

[1] J. Langanke, A. Wolf, J. Hofmann, K. Böhm, M. A. Subhani, T. E. Müller, W. Leitner, C. Gürtler, *Green Chem.*, 2014,16, 1865-1870.
[2] N. von der Assen, P. Voll, M. Peters, A. Bardow, *Chem. Soc. Rev.*, 2014, 43, 7982
[3] N. von der Assen, J. Jung, A. Bardow, *Energy Environ. Sci.,* 2013, 6, 2721
[4] N. von der Assen, A. Bardow. *Green Chem.*, 2014, 16, 3272-3280.
[5] A. Goeppert, M. Czaun, J. P. Jones, G. K. S. Prakash, G. A. Olah, *Chem. Soc. Rev.*, 2014, 43, 7995.

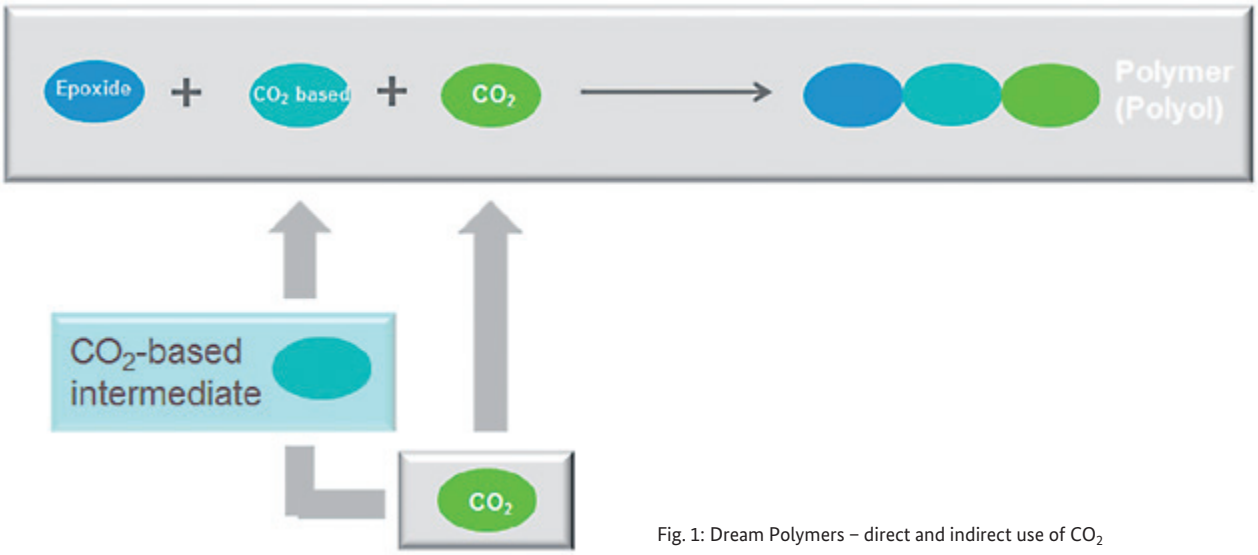


Fig. 1: Dream Polymers – direct and indirect use of CO_2

alternative raw materials to 40 percent. Initial applications for the new precursor would be thermoplastic polyurethanes, films and casting elastomers.

First, CO_2 is incorporated directly into a new kind of precursor (polyoxymethylene carbonate polyol), replacing 20 percent of the epoxide. Second, CO_2 is also used indirectly, producing a chemical that is also incorporated into the precursor for a further 20 percent saving in petroleum. As the amount of fossil material drops and building blocks based on e.g. CO_2 or conventional methanol take their part, we observe another drop in carbon footprint – primarily due to the amount of high-energy propylene oxide that can be saved.

Conclusion

In summary, even though the field of research is hardly new, the use of CO_2 as a raw material is still one of the most interesting and visionary technologies for the future. Since fossil resources are finite, using CO_2 as chemical feedstock is a promising approach to global carbon management. LCA investigations show, that there is a clear ecological benefit for the polyethercarbonate polyols as compared to the conventional ones. This can even be improved on following the approach of the direct and the indirect use of CO_2. The Bayer projects “Dream Production” and “Dream Polymers” offer great chances to implement the chemical utilization of CO_2 for the production of polyethercarbonate polyols on an industrial scale in a few years’ time.

Financial support for both the Dream Production and the Dream Polymers project by the German Federal Ministry of Education and Research is gratefully acknowledged.

Project partners:

- Bayer Technology Services GmbH
- RWTH-Aachen – Fachgruppe Chemie – Institut für Technische und Makromolekulare Chemie (ITMC)
- Leibniz-Institut für Katalyse e.V. an der Universität Rostock
- Fraunhofer-Institut für Chemische Technologie (ICT)
- Bayer MaterialScience AG

Assoziierter Partner:

- RWE Power AG

Contact:

Dr. Christoph Gürtler
Bayer MaterialScience AG
E-mail: Christoph.Guertler@bayer.com

GtF&S – Gas to Fluids and Solids

The goal of the project is the development of breakthrough technology for the production of cost competitive hydrogen at significantly reduced carbon footprint on industrial scale. In addition, a CO_2 utilization process is investigated to produce synthesis gas based on hydrogen and CO_2.

Three main process elements are involved:
- pyrolytic decomposition of natural gas into hydrogen and carbon
- carbon formulation for applications in coke and steel production and
- CO_2 utilization based on catalytic conversion of hydrogen and CO_2 to produce synthesis gas (CO_2 activation).

Based on these three elements – as shown in Fig. 1 – gas is converted to fluid and solids (GtF&S). The process comprises methane pyrolysis, carbon formulation and catalytic CO_2 activation using the reverse Water-Gas Shift Reaction. The conceptual design of a pilot unit for all three process elements is targeted for the 3-years R&D-project.

Hydrogen can be used either directly or as synthesis gas within the chemical industry and in fuel production. Solid carbon is potentially a high value-add input material for a variety of coke and steel production applications.

Utilization of the carbon
- reduces coal consumption in the coking and blast furnace process, leading to a carbon footprint advantage of the overall process (see below), and
- enhances competitiveness of the new technology through commercial benefit.

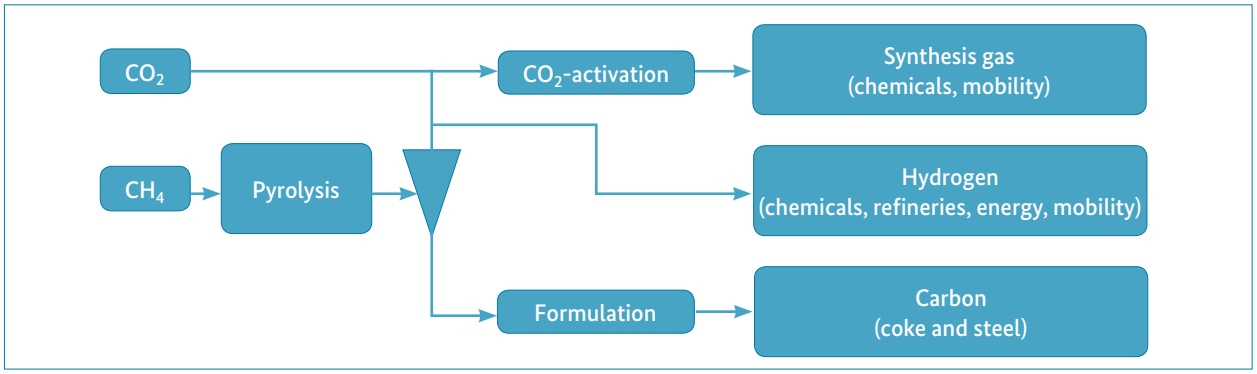


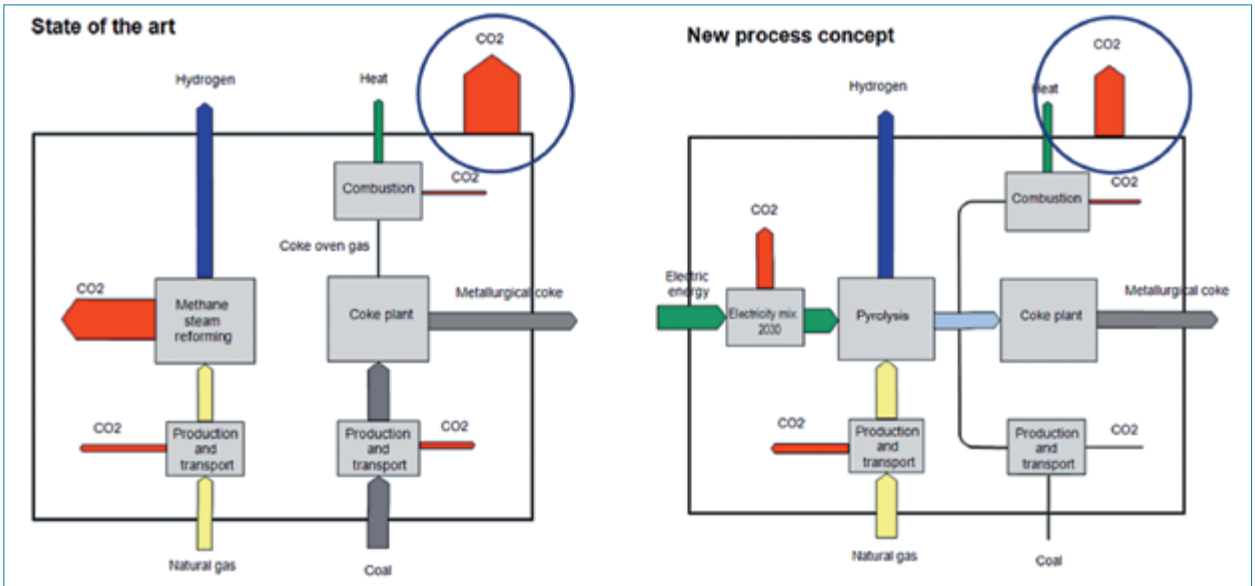
Fig. 1: Block diagram of the GtF&S process

Cross-industry collaboration ensures that a carbon product which meets the requirements of the coke and steel industry will be a suitable replacement for coal. If energy integration can be optimized to minimize CO_2 emissions resulting from the supply of energy for the endothermic pyrolysis process, the CO_2 mitigation factor will be in the region of 50% for hydrogen production. Fig. 2 depicts the qualitative result of carbon footprint calculation: State of the art and new process concept are compared regarding CO_2 emissions of the process steps (within the frame) and regarding system emissions (in circles).

Global demand for hydrogen and synthesis gas is approximately 50 million t/a and 220 million t/a respectively. The solid carbon produced in methane pyrolysis will also be utilized. Coke is currently the most widely used form of carbon. Worldwide demand for coke is currently estimated at around 1 billion t/a. The quantity of carbon produced is sufficient for industrial utilization, for example as a blending agent for coke assuming it meets the quality requirements.

Several experimental units are already in operation (Fig. 3) providing experimental data for the pyrolysis reaction, carbon samples, reactor design elements and catalytic CO_2 activation.

The innovative technology protects and enhances the competitiveness of participating companies in the hydrogen and synthesis gas market. Plant engineering and construction, catalyst production and sales, engineering and scientific service activities provide job security. The technology creates the need for new types



Up to ~50% of CO_2-emissions at the same produktion of hydrogen, metallurgical coke and heat.

Fig. 2: Sankey chart (qualitative) representing the calculation of carbon footprint for methane pyrolysis for hydrogen production combined with coke production for the steel industry. State of the Art (left) and New process concept GtF&S (right).

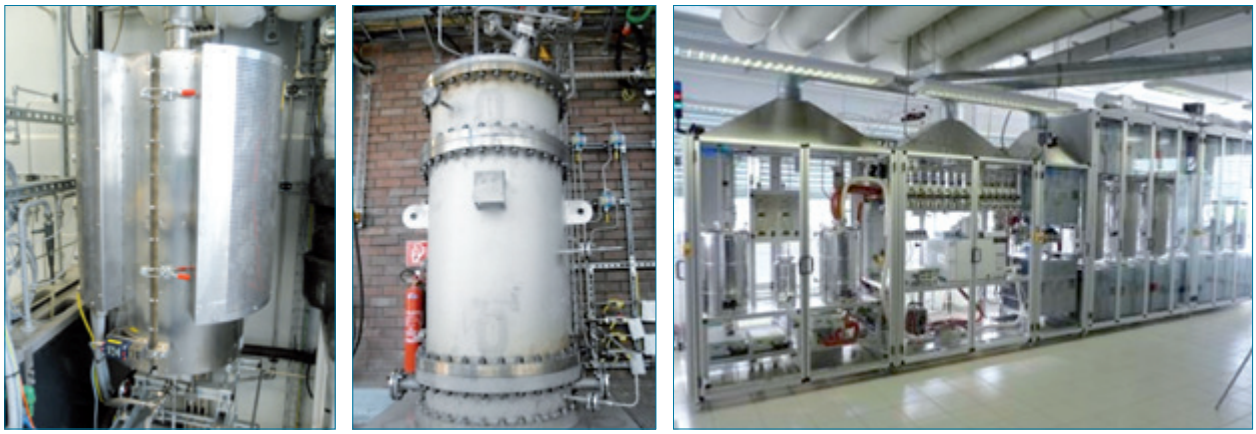


Fig. 3: Experimental units for high-temperature pyrolysis (left), heat input (middle), and catalyst development (right)

of systems and instrumentation. The list includes reactors, temperature measurement, infeed and discharge systems and carbon formulation equipment, much of which will be developed by mid-tier companies. Marketing on a broad scale can be expected to create new market opportunities. From the scientific perspective, utilization involves coke, iron and steel, chemical engineering and process engineering and enhances interaction between these disciplines.

Project partners:

- BASF SE
- hte AG
- Linde AG
- ThyssenKrupp Steel Europe AG
- ThyssenKrupp Uhde GmbH
- Technische Universität Dortmund, Lehrstuhl für Chemische Verfahrenstechnik
- VDEh-Betriebsforschungsinstitut

Contact:

Dr.-Ing. Andreas Bode
BASF New Business GmbH
E-mail: andreas.bode@basf.de

PhotoKat – Development of active and selective Heterogeneous Photocatalysts for the Reduction of CO_2 to C1 Building Block

The goal of the research project is to find ways of reducing atmospheric CO_2 by using sunlight in a photocatalytic reaction to recycle CO_2, producing C1 building block products for the chemical industry, in particular methanol and methane. The researchers are working on development of catalyst systems which are based on semiconducting oxide composites and have high photon yields. The catalysts need to be durable, readily available and suitable for industrial-scale applications. The preferred starting materials are TiO_2 and ZnO which are tested in catalyst systems that have varying structures and compositions.

During the initial phase of the project, the team investigated in detail the physical and chemical properties of the known photocatalyst system consisting of isolated titanate species on SiO_2 (TiO_x/SiO_2). Also, the system was modified using gold as the co-catalyst. In photocatalytic test reactions, evidence was found for the importance of the Ti-O-Si linkages for photocatalytic activity.. Deposition of isolated zinc oxide species improved the potentially insufficient adsorption of CO_2 on the titanium species. Using literature data as the basis, the team also developed and built a gas phase photo reactor with an improved design at the Laboratory of Industrial Chemistry (Fig. 1). With this reactor, they were able to carry out investigations under ultra-pure conditions and collect reliable product formation data. Using gas chromatography, it is possible to quantify hydrocarbon concentrations down to a few ppm. Initial measurements on the known TiO_x/SiO_2 photocatalyst made it very obvious that meticulous photocatalytic cleaning of the samples is essential to prevent formation of products from contaminants. Overall, the quality of the photocatalytic measurements that can be performed in Bochum has seldom been equaled anywhere in the world.

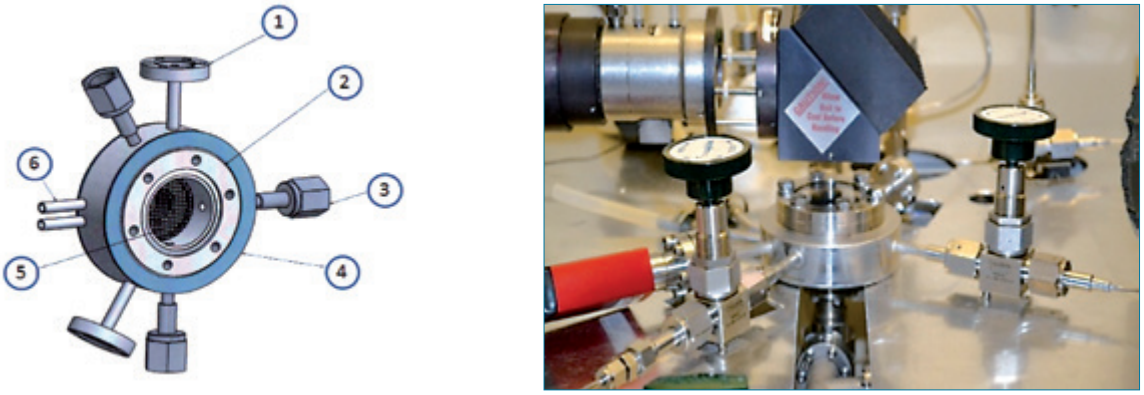


Fig. 1: Left: schematic diagram of the complete metal-sealed gas phase photo reactor with CF flanges (1), quartz window (2), VCR connections (3), cooling jacket (4), sample compartment (5) and cooling circuit connections (6); right: photo of the actual reactor with valves and 200 W HgXe lamp.

The results of activity measurements on photocatalytic reduction of CO_2 demonstrate that TiO_2 and titanium dioxide based systems generally produce higher hydrocarbon yields than ZnO and the zinc oxide based systems which have been tested so far. As a result, the scientists concentrated their efforts on trying to improve the activity of titanium oxide based systems. With a maximum yield of around 100 ppm after 7 hours reaction time, methane was the main product on all tested systems.

The yields are comparable with those reported in the literature by other working groups. Methane formation was normally accompanied by the formation of small amounts of other hydrocarbons. Methanol or other oxygenates were not found. In a second CO_2 reduction experiment without intermediate purification, hydrocarbon yields appeared to be higher (Fig.2a). The explanation for this appears to be that stable surface intermediates form on the $TiOx/SiO_2$ during the first run.

Using infrared spectroscopy, formaldehyde and paraformaldehyde were identified as intermediates by their typical vibration bands and high thermal stability (Fig. 2c). Deposition of gold on the TiO_x/SiO_2 system doubled the activity. Twice the amount of methane was formed in the same reaction time. More long-chain hydrocarbons (ethane, propane, butane) were also detected. Less intermediates accumulated on the catalyst surface. It was found that the titanate species form titanium-rich shells around the gold (Fig. 2b). Those shells improve the electron transfer in photocatalytic test reactions.

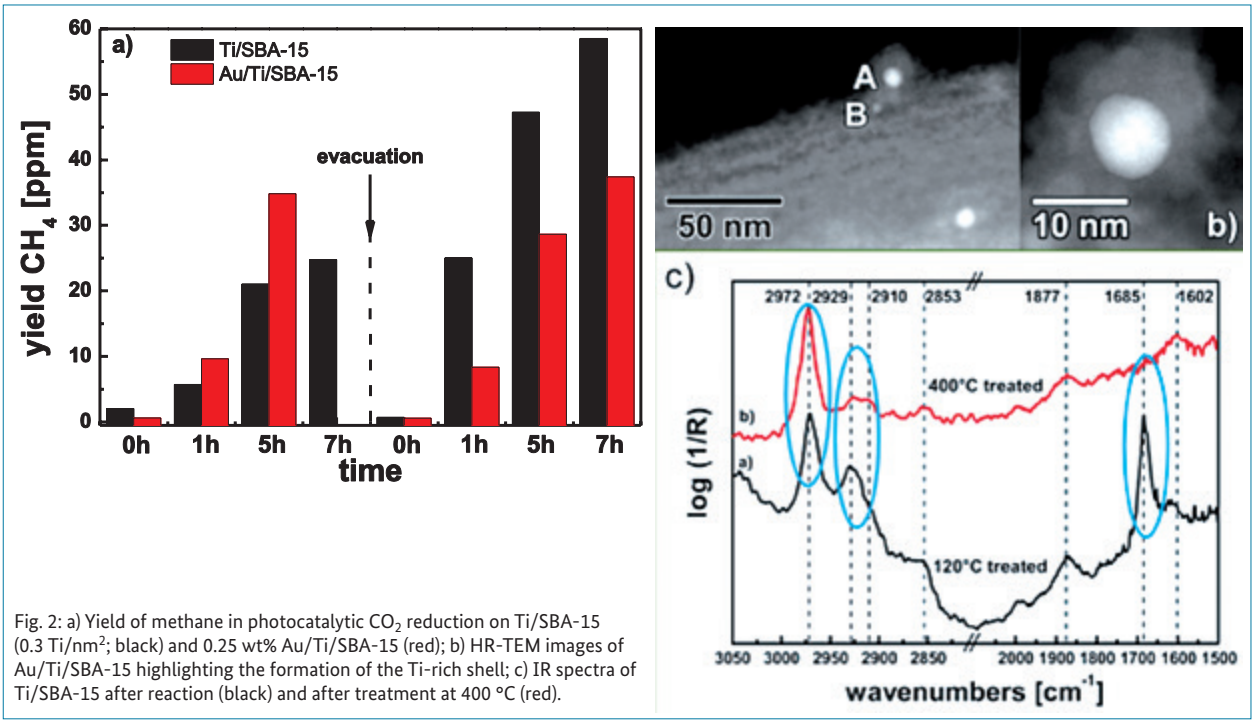


Fig. 2: a) Yield of methane in photocatalytic CO_2 reduction on Ti/SBA-15 (0.3 Ti/nm^2; black) and 0.25 wt% Au/Ti/SBA-15 (red); b) HR-TEM images of Au/Ti/SBA-15 highlighting the formation of the Ti-rich shell; c) IR spectra of Ti/SBA-15 after reaction (black) and after treatment at 400 °C (red).

Modifying the titanium system with zinc oxide also has an influence on activity, but an increase in activity is only observed if the ZnO is present in large aggregates and is not isolated. This would seem to indicate that the exact combination of zinc oxide and titanium species has a crucial effect on activity. With regard to reaction design, the team was able to demonstrate that for all TiO_x/SiO_2 systems a significant excess of CO_2 has a positive effect on the hydrocarbon yield.

Because the yields shown by commercial titanium dioxide are similar in magnitude to TiO_x/SiO_2, the researchers are looking at surface doping to improve charge carrier life and increase activity. Another objective is to stimulate activity in visible light. They were able to demonstrate that surface doping with Sn^{2+} produces hole transfer sites on the surface which have a positive effect on dye degradation and facilitate absorption of visible light. TiO_2 with Sn^{4+} and photo-deposited Rh on the surface is a highly active catalyst which promotes the production of hydrogen from an aqueous methanol solution. Researchers are currently investigating the activity of these photo catalysts in the reduction of CO_2.

The results were presented in one completed doctoral dissertation and in two others which are currently being written. They were also published in international scientific journals and discussed at conferences. There is currently a need for basic research on photocatalytic CO_2 reduction. Because the reaction could help reduce CO_2 emissions, it is the subject of intensive international investigation, but the yields so far are not sufficient for industrial-scale applications.

Contact:

Dr. Jennifer Strunk
Lehrstuhl für Technische Chemie
Ruhr-Universität Bochum
E-mail: jennifer@techem.rub.de
Homepage: www.techem.rub.de

Evaluation of economic and environmental potentials of using CO_2 in chemical processes

The research cluster "Technologies for Sustainability and Climate Protection" is part of the German High-Technology strategy and an element to support industry to reach the ambitious climate goals in Germany. The Federal Ministry of Education and Research funds more than 30 projects with a total budget of 100 million Euros to investigate in new technologies dealing with reduction option as well as use option of CO_2 emissions. The co-funding from industry is of a similar magnitude. Next to an increase in energy efficiency of the chemical sector, the development of technologies to use CO_2 in products and the disclosure of new functional liquids to store CO_2 offer innovative ways to mitigate climate change.

The study presented here analysed the potential environmental and economic benefits of that research cluster. Each project carried out a life cycle based assessment or evaluation of the environmental impacts associated with the new products or technologies. The

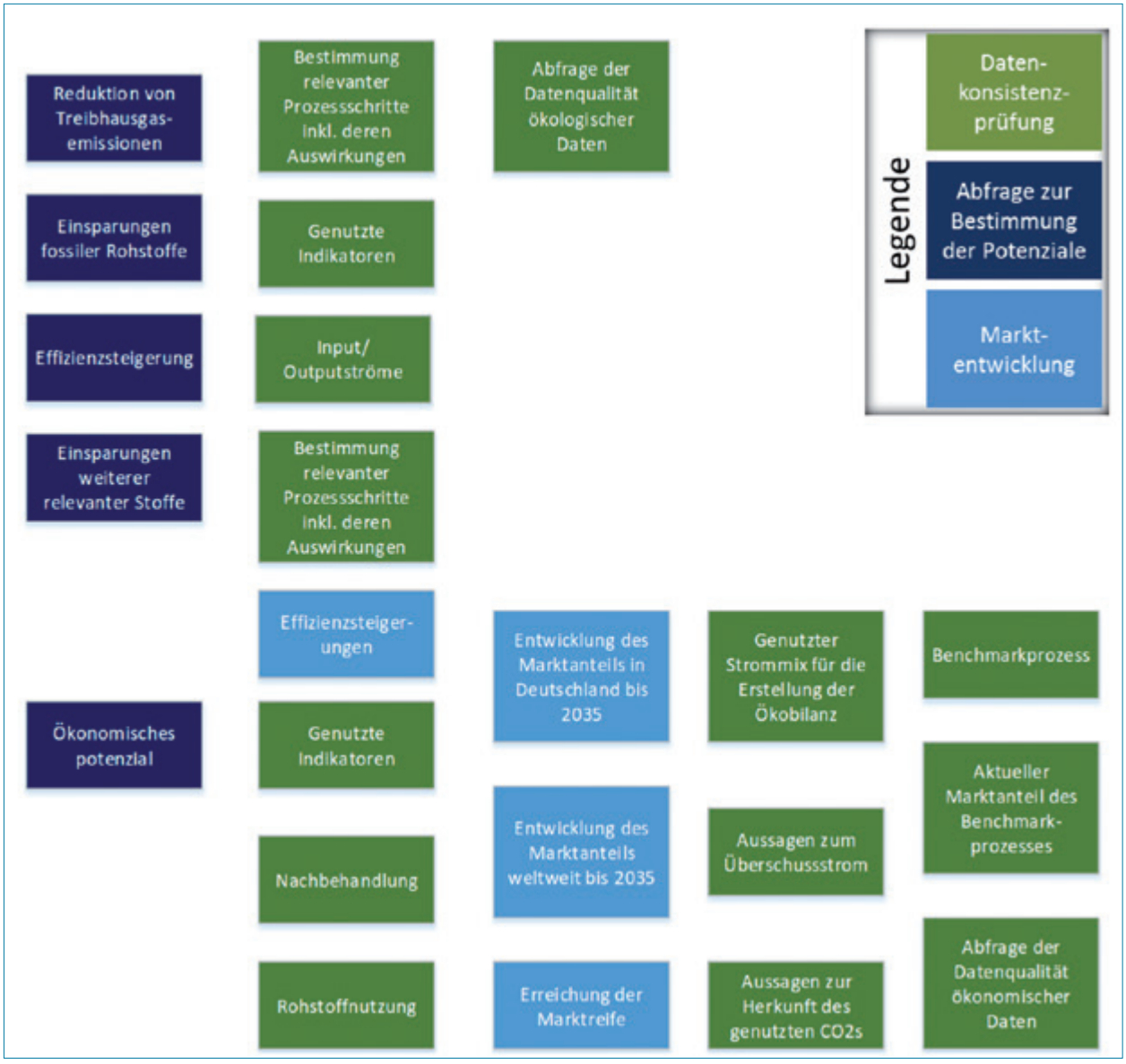


Fig. 1: Content of the different questionnaires

results contribute to a consolidated evaluation with respect to the three themes: CO_2 as raw material, new functional fluids and energy efficiency. Three questionnaires (Figure 1) were developed and served as the basis to obtain the data from the individual projects in respect to self-evaluation of data quality, market development for the new technology or product, saving potential on greenhouse gases, fossil fuels and energy consumption. This ensures a standardised methodological approach to evaluate the potential environmental savings. The delivered primary data from the different projects are used to assess the efficiency measures compared to the benchmark process. Although, a common procedure was used, individual communication with the different project leaders were needed to check data consistency and to validate the delivered results. 61% of all questions were answered on a quantitative basis, useable for the assessment, and 18% on a qualitative basis. 21% of the questions have not been answered.

The results from the assessment show a potential of saving greenhouse gas emissions up to 6.2 Mt CO_2e./a in the year 2020 and up to 25.6 Mt CO_2e./a in 2030, respectively. The saving potential for fossil fuels is calculated up to 4.0 Mtoe/a in 2020 and up to 7.30 Mtoe/a in 2030, respectively.

The data quality on a scale from 1 (very good) to 5 (very poor) was judged with 2.2 in average. Energy efficiency savings of 20% to 50% were identified compared to the respective benchmark process. Although, for some projects the market penetration still needs time, the potential economic benefit is high due to the long-time perspective and registered patents. The results for the total contribution of the cluster with regard to the sustainability goals of the research strategy will be presented.

Contact:

Dr. René Scheumann
Lisa Winter
Prof. Dr. Matthias Finkbeiner
Technische Universität Berlin
Chair of Sustainable Engineering
E-mail: rene.scheumann@tu-berlin.de

Carbon Dioxide Utilisation Research in Europe

We stand at a crossroads in energy use where we retain an ever increasing demand for energy yet at the same time need to reduce anthropogenic carbon dioxide emissions. We have a trilemma: the need for CO_2 mitigation, the need for energy (and chemical resource) supply security and the need for all this at low cost. The main focus has been on mitigation through the geological sequestration of emitted CO_2 and considerable funding has been directed towards it. In recent years there has been a realisation that CO_2 is a valuable resource that can be converted into value added products. This has led to a resurgence in carbon capture & utilisation (CCU) or carbon dioxide utilisation (CDU) with Europe being amongst the front runners.

Aresta *et al.* carried out pioneering work in the early 1970s but it is really in the last few years that CCU has had a renaissance. To a great extent this has been led by the foresight of BMBF in Germany through its investment first in fundamental research and then in the translation of some of that research into commercially viable processes. In part this has been a result of the move away from CCS processes, freeing resources for the more commercially attractive CCU.

The potential for CCU has been underestimated for a long time. It was been stated that CCU cannot compete with the capacity for CO_2 mitigation offered by CCS. But is this really the case? How much CCs capacity really exists in Europe and indeed globally? Likewise, how much CCU is currently deployed and what are its prospects in the future? Figure 1 shows some scenarios for CCU and compares them with CCS targets globally and in Europe.

This pre-supposes that a number of chemicals and polymers, together with key fuels can be manufactured at a certain global percentage through CCU.

European research in CCU is developing at an incredible rate and this is being recognised at a parliamentary level. The European Commission have funded a series of techno-economic studies of five CCU processes however these are yet to be reported publically. These

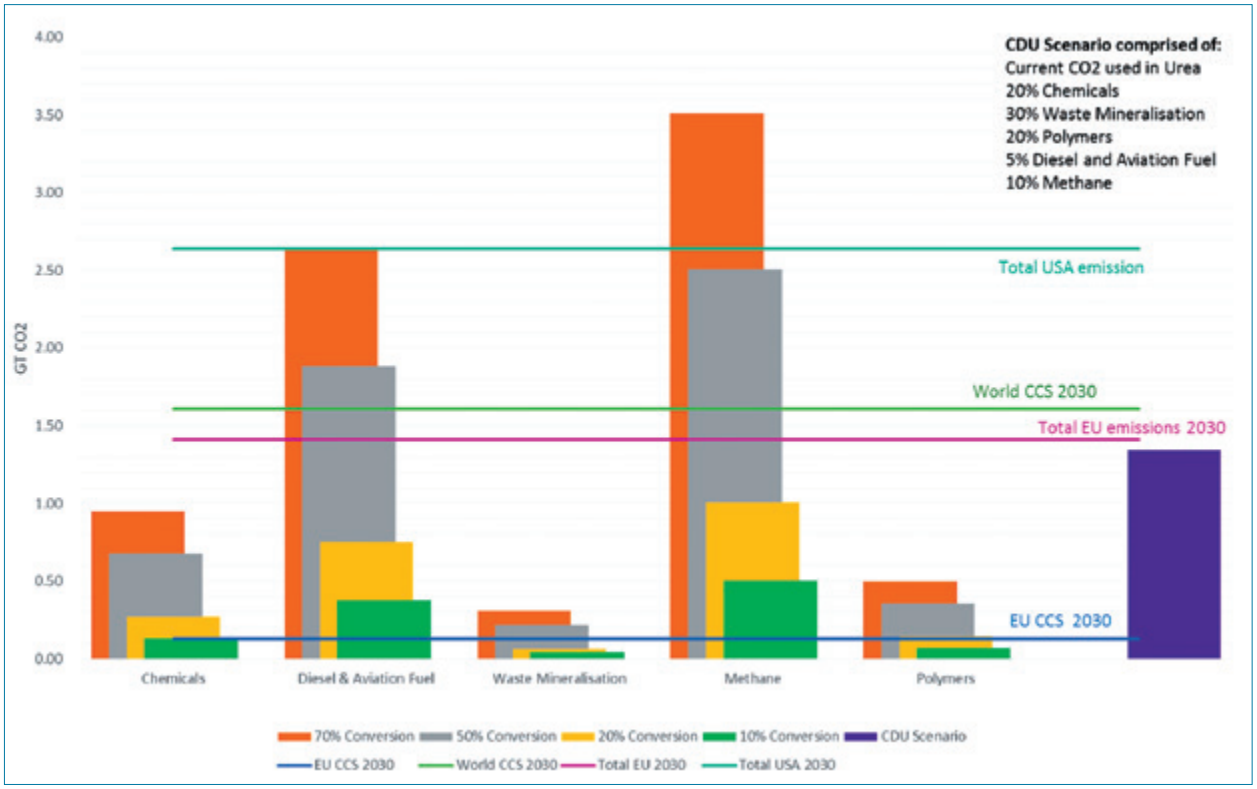


Fig. 1: CO_2 utilisation potential against emissions reduction (Armstrong & Styring, Frontiers in Energy Research, 2015, 3, 8)

studies will report on processes using a common CO_2 input feed, but implies that there will be a pre-use capture and purification step. It is not clear yet what the final boundary condition is what implications this will have for comparative studies.

The CO_2Chem Network is an EPSRC Grand Challenge that aims to bring together researchers not only in Europe but world-wide (www.co2chem.com). It is the largest and most active carbon dioxide network globally and has a membership fast approaching 1,000. It's recent successes have been in the award of small (€5k) seedcorn grants which have been translated into substantial follow-on grants; and the publication of a multi-authored textbook on the subject from CO_2Chem members (Carbon Dioxide Utilisation: Closing the carbon cycle, Elsevier; ISBN: 9780444627469).

The SCOT (Smart CO_2 Transformations) project has been established by the Committee of the Regions to develop a Strategic European Research and Innovation Agenda (SERIA) and a Vision 2030 road-mapping document. The key output will be a Joint Action Plan (JAP) which will make recommendations for future research directions and funding across European Member States. It will also aim to provide a unified approach to CCU across all EC DGs to ensure that recommendations are implemented in the most economic and effective manner (http://scotproject.org/).

DG-Clima have established that there will be a European Incentive Prize that will allow a ground-breaking process to be developed at a European level. This prize is presently in the development stage with an announcement being made later in the year.

The need for CO_2 capture (or otherwise) also needs to be considered. The capture process is often the economic and environmental hotspot in any system. If this can be eliminated through direct conversion of CO_2-containing flue gas with a co-reactant then this is an advantage. However, a number of CCU technologies involve the production of fuels from CO_2. When used these will obviously release CO_2 back into the atmosphere. Therefore, direct air capture (DAC) of CO_2 at atmospheric concentrations also needs to be considered. Is it possible that the DAC technology can also be incorporated into the CO_2 conversion technology? This would certainly reduce costs.

This talk will look at current European efforts in CCU and look towards a vision for 2030 where low carbon technologies must start to show an impact on industrial processes and products if we are to be in a position to realise targets for 2050 GHG emissions reductions.

Contact:

Prof. Peter Styring
UK Centre for Carbon Dioxide Utilisation
and CO_2Chem Network
Chemical & Biological Engineering
Sir Robert Hadfield Building
The University of Sheffield
E-mail: p.styring@sheffield.ac.uk

ACER – Sodium Acrylate from CO_2 and Ethene (Acrylates ex Renewables)

Challenges and Goals

The goal of the project is to utilize CO2 as a feedstock through catalytic synthesis of sodium acrylate from CO2, ethylene and a base. Sodium acrylate is an important basic material for high-performance polymers. Superabsorbers used in diapers are the most obvious example. Millions of tonnes of superabsorber polymers are produced annually worldwide.

Acrylic acid is currently made in a two-stage reaction from propylene which is produced from straight run gasoline (Fig. 1). The technology, which is fossil-based (oil), has been refined over a period of many years, and it is the benchmark against which the material and energy aspects of a potential new process will be measured.

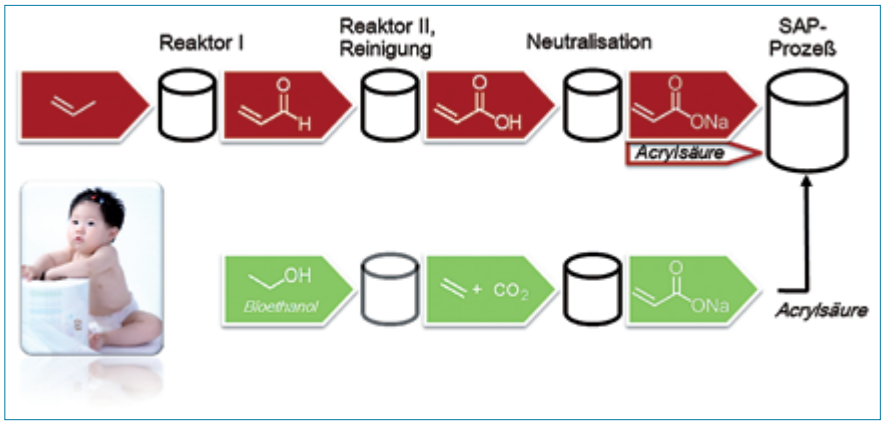


Fig. 1: Current state-of-the-art sodium acrylate synthesis process and the production process under investigation in the ACER project

Project status

Since January 2011, researchers at the Catalysis Research Laboratory (CaRLa) which is supported by BASF, hte AG (part of BASF), TUM in Munich and the University of Stuttgart have been working together on the ACER project (Acrylates ex Renewables) to find ways of using CO_2 on an industrial scale for the production of sodium acrylate. The process must be viable from both the economic and environmental standpoint. Creating this "dream reaction" is no easy undertaking. From the engineering perspective, it is a "hard nut to crack". 30 years of intensive academic and industrial research has failed to provide an answer.

In the first year of the project, the team which included catalyst researchers, theoretical chemists and chemical engineers identified a nickel-based catalyst which

Fig. 2: Catalyst screening system

makes it possible for the first time to combine CO_2 and ethylene feedstock under industrially relevant conditions. Various homogeneous and heterogeneous candidate catalysts and process conditions were evaluated and optimized during high-throughput screening. Different analytical techniques were employed to gain a deeper understanding of the critical reaction steps. Continuous improvements are being made to catalyst performance and life. Initial superabsorber samples were produced using representative reaction products, and their properties were evaluated.

Application, Exploitation of the Results, Economic and Environmental Benefits

The German Ministry of Education and Research (BMBF) is providing 2.2 million euros in funding for the project. BASF and hte are contributing an additional 1.7 million euros over a period of three years.

If the results of the ACER project can be transferred to industrial scale production and assuming a market volume of around 4 million tonnes, roughly 2.4 million tonnes of CO_2 could be utilized as feedstock. Because an established process for making ethylene from renewable bioethanol already exists, complete changeover of acrylate synthesis to a renewable feedstock base would be feasible. The bioethanol feedstock can contain two CO_2 equivalents, so a maximum 7.3 million tonnes of CO_2 could be utilized along this value-add pathway if total global demand for acrylic acid were satisfied using this technology. In addition, migrating synthesis from propylene to ethylene could substantially reduce material, energy and fossil-based feedstock consumption and drive down investment costs.

An expedient patent portfolio for the entire acrylate value-add chain, from the catalytic process to polymerization, is being put together to protect the knowledge gained during the project. The doctoral and post-doctoral candidates involved in the project regularly present their scientific results at national and international conferences. Significant findings are published in leading scientific journals.

Information on the project is regularly shared with international opinion-making bodies from government and industry.

Project partners:

- BASF SE
- Universität Stuttgart
- Technische Universität München
- hte GmbH the high throughput experimentation company

Contact:

Dr. Thomas Schaub
BASF SE
E-mail: thomas.schaub@basf.com

COOBAF – CO_2-Based Acetone Fermentation

Project goal

The goal is to develop a fermentation process for biotechnology production of acetone using acetogenic microorganisms along with carbon dioxide (CO_2) as the sole carbon building block. To the extent possible, the CO_2 should be supplied from industrial waste gas streams and used to produce acetone which is an important base product in the chemical industry. Industrial waste gas streams which contain carbon monoxide (CO) and hydrogen (H_2) as well as CO_2 are particularly well suited for cost-effective, sustainable production of acetone in a fermentation process. Microbiological production of acetone from CO_2-laden waste gas streams could be an economically viable and environmentally friendly alternative to the petrochemical production pathway.

Project status

The first step in the project was to select suitable strains of bacteria. The strains had to tolerate the gas mixtures including the toxic constituents and convert as much of the CO_2 in the gas as possible into natural metabolites (e.g. acetic acid). The researchers tested 39 strains and identified suitable candidates in a two-stage process. The graph in Fig. 1 shows the results of biomass-specific and volumetric acetate productivity of autotropic cultivation for a) H_2/CO_2 and b) an industrial waste gas stream. The results were used among other things for strain selection.

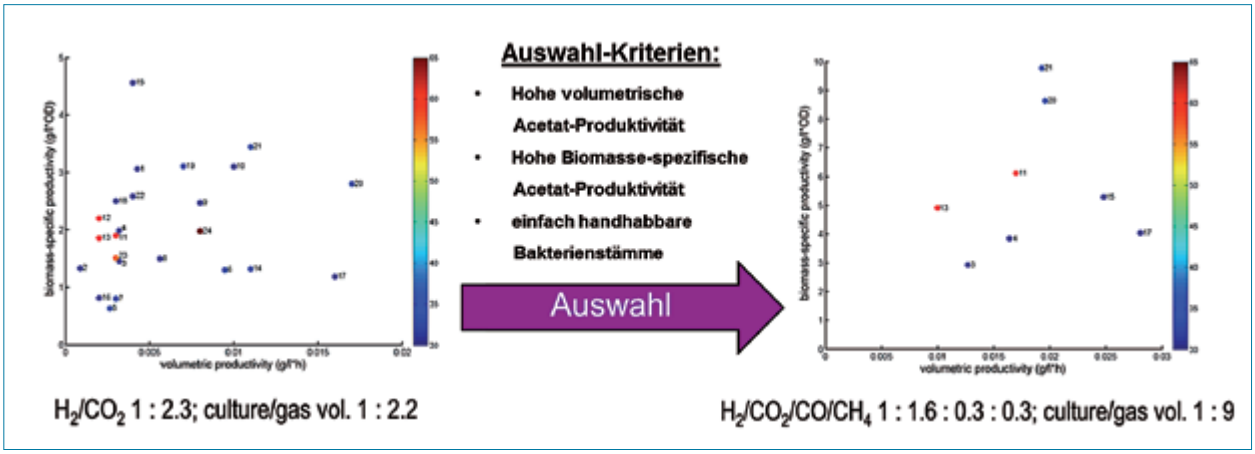


Fig. 1: Strain screening of acetogenic bacteria strains

The next step was to insert the genes needed for acetone production into the selected strains, creating new recombinant strains capable of producing acetone from CO_2. C13-marked CO_2 was used to ensure that the acetone is actually produced from CO_2 rather than from other media constituents.

The next step in development of a production strain was strain optimization to enhance acetone productivity. This work is currently still in progress and will continue right through to the end of the project.

Work proceeded in parallel on development and optimization of the fermentation process. The researchers succeeded in transferring the fermentation process from shake flasks to lab reactor scale and they also increased the amount of acetone produced by an order of magnitude (see Fig. 2).

Cost-effective downstream processing which produces optimized yields is a critical factor in a biotechnology-process, so work on this particular aspect began at an early stage of the project. A methodology was developed for recovery of the acetone from the fermentation broth, and an initial process simulation was carried out. Modifications to the downstream process over the course of the project improved yields to the point where industrial feasibility could be envisioned.

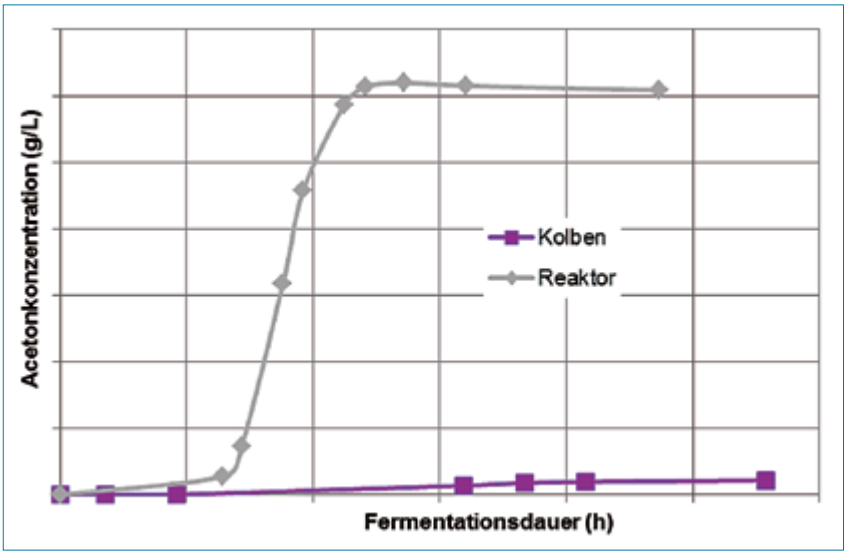


Fig. 2: Comparison between cultivation of a recombinant acetogenic strain (with CO_2 as the only carbon source) in a shake flask and a lab fermenter

The economic viability of acetone production using CO_2 as the sole carbon building block and H_2 as an energy source will depend heavily on the productivity of the overall process. The researchers have continuously improved acetone productivity during the project, but before the process can be used in industry, a further substantial productivity increase will be needed. The acetone productivity and selectivity of the CO_2 based acetone production process will have to be further optimized to make industrial scale-up feasible. That will have to take place systematically on a pathway leading from lab bench and test systems to pilot and industrial production. Besides process enhancement, more work will be needed to improve the genetically modified strain.

Economic, environmental and societal leverage effect

Leaving aside yields, substitution of thermal energy and the cost of biotechnology production, the process has the potential to eliminate 1.7 kg CO_2/kg acetone. If only 10% of current annual acetone production (6 million tonnes) were migrated to the CO_2 process, CO_2 emissions could be reduced by more than 1000 kt. An initial lifecycle analysis (LCA) of the biotechnology process taking the factors mentioned above into account indicates an overall reduction of CO_2 emissions. Compared to the existing petrochemical process, emissions would be cut by at least 0.3 kg CO_2/kg acetone even in a conservative scenario. Once again, the size of the emissions reduction is directly related to acetone productivity.

8 Bachelor's theses and 3 doctoral dissertations are expected to be completed during the course of the project.

Project partners:

- Universität Rostock
- Universität Ulm

Contact:

Dr. Jörg-Joachim Nitz
Evonik Industries AG
E-mail: joerg-joachim.nitz@evonik.com

$ECCO_2$ – Electrochemical CO_2 Reduction Project – High-Throughput Search for new Electrocatalysts

The team of scientists on the $ECCO_2$ Project is exploring electrochemical pathways for conversion of CO_2 into high-grade chemical products for energy storage and synthesis of building block chemicals. The project is funded by the German Ministry of Education and Research. Practical demonstrations have shown that production of methane and methanol using this technique is feasible in principle, but how reaction conditions and the materials used affect fundamental reaction mechanisms is not sufficiently understood. The research team is attempting to significantly improve catalyst performance beyond the current state of the art by using special high-throughput electrochemical screening which enables them to run a large number of experiments in a short space of time. This is essential due to the very large range of operating parameters, which is typical of electrochemistry in general and CO_2 reduction in particular. Beyond enhancing the speed and reliability of the investigations, the team is using additional complementary techniques, for example combining electrochemistry with online element analysis, to generate more detailed data. Based on this new approach, the researchers are trying to gain an in-depth understanding of electrochemical CO_2 reduction and also oxygen evolution which is the other half-reaction. They intend to use the results to develop new active, stable, selective catalysts.

Project Status

During the first two years of the project, the team developed a new high-throughput catalyst screening and online analysis setup (Fig. 1). The core element is an electrochemical cell (Scanning Flow Cell) with flow system and fully automatic positioning. The SFC can be used to scan the surface of a sample and carry out local electrochemical investigations. This makes it possible to quickly evaluate different operating conditions with minimum effort using a homogeneous sample and ensure that the starting conditions are the same by repositioning the cell. This is important if, for example, corrosion or poisoning alters the surface of the catalyst during the course of the reaction. With the cell, it is also possible to carry out combinatorial investigations on material libraries under comparable operating conditions, for example to quickly identify ideal catalyst compositions. The ability to evaluate the activity of catalyst materials along with their stability in electrolytes

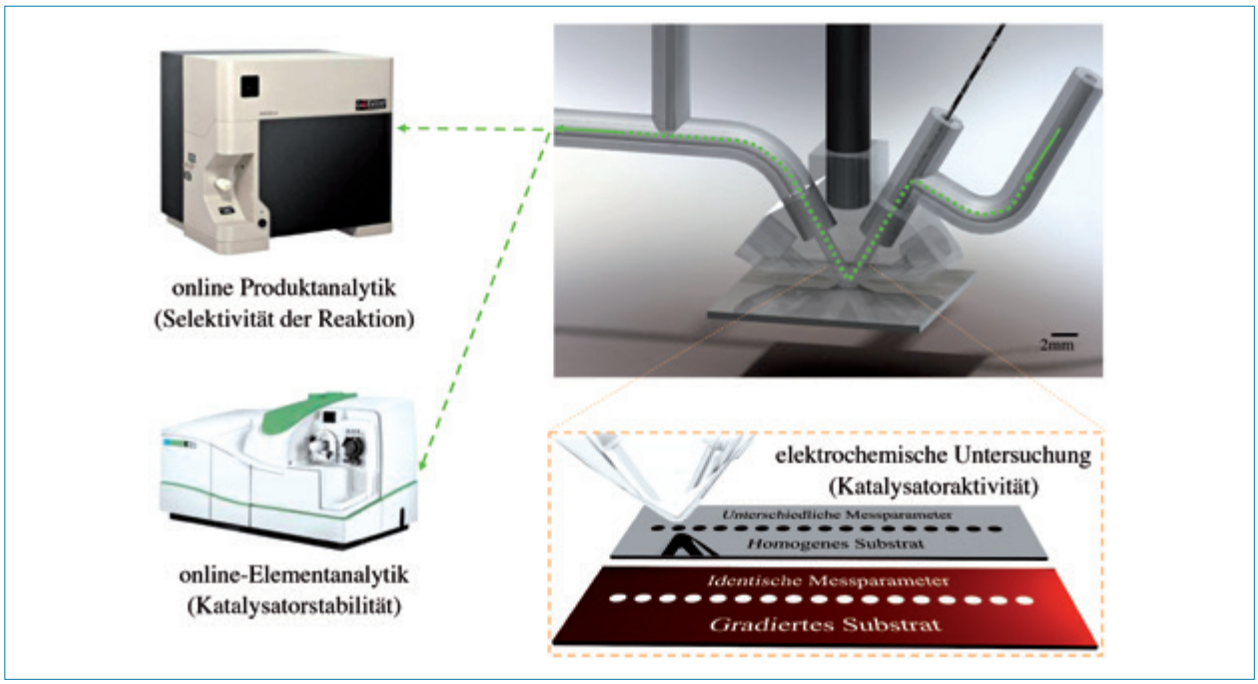


Fig. 1: Schematic representation of the new experimental setup using an electrochemical flow cell (top right) for high-throughput screening (bottom right) coupled with online electrolyte analysis (left).

and their selectivity for the desired reaction products is a particularly attractive feature of this technology. This is accomplished by directly linking the SFC to instrumentation which analyzes the product stream. Element analysis using inductively coupled plasma (ICP-MS) is a unique development.

Fig. 2 shows a small excerpt from the very extensive set of results delivered by this approach. The effect of the applied voltage on reduction of CO_2 to methane and methanol on a copper catalyst and the stability of copper in dilute acidic electrolytes can be seen in these examples. The SFC is currently being used to test different material libraries under varying conditions to gain an understanding of the complex interrelationships. Based on the results, the researchers will evaluate the best catalysts which they have found by running individual tests in actual reactors.

Future Potential

Given the initial starting point, this project is by necessity focused on basic research. As a result, it is not yet possible to estimate the potential economic, environmental and societal effects of CO_2 utilization based on this technology. The technical developments and results to date show the enormous benefits of this approach for achieving a deeper understanding of important electrochemical processes. It also highlights the benefits which further investigation could have for important related areas of technology such as energy conversion (e.g. water electrolysis and fuel cells) and corrosion in general. A number of high-profile articles have been published in leading international journals such as *Angewandte Chemie* and *Science*. The project has given a number of young scientists the opportunity to work on their Master's theses and doctoral dissertations. They will be able to pass on the knowledge they have gained to industry. In addition, by bringing new knowledge to the attention of the general public, the project promotes the development of various sustainable technologies.

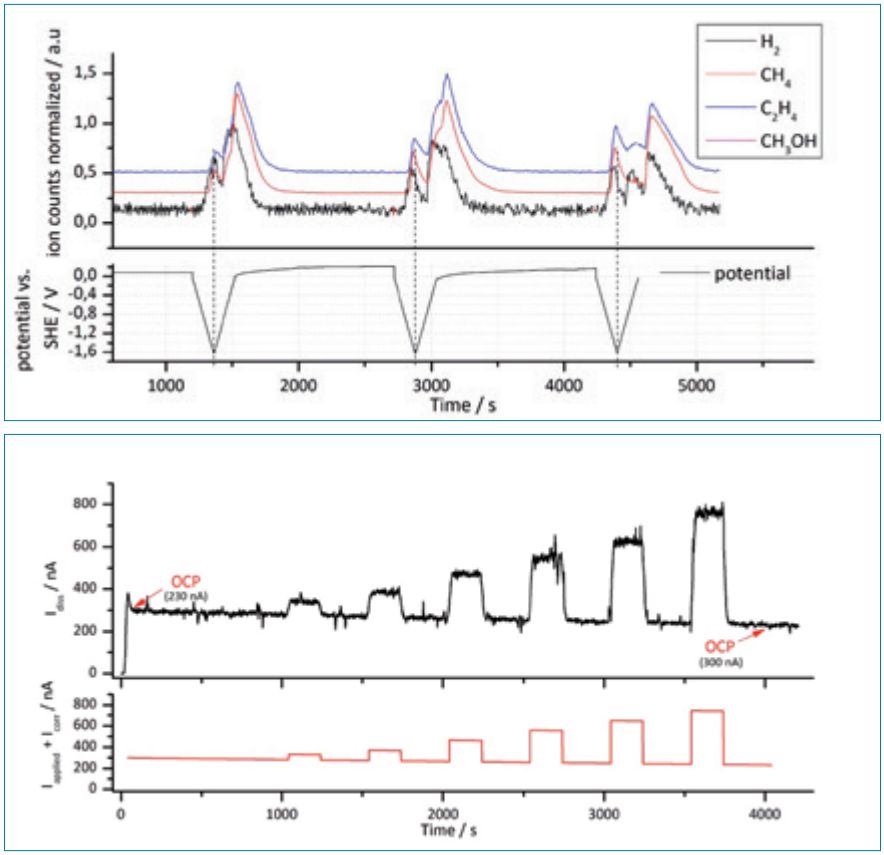


Fig. 2: Top: Product analysis of hydrogen, methane, ethylene and methanol evolution during cyclic voltammograms at a copper electrode. Bottom: Example of element analysis showing the dissolution behavior of a copper electrode

Contact:

Dr. Karl J.J. Mayrhofer
Abteilung für Grenzflächenchemie und Oberflächentechnik,
Max-Planck-Institut für Eisenforschung GmbH
E-mail: mayrhofer@mpie.de

OrgKoKAT – New Organocatalysts for Utilization of CO_2 as a Building Block for Chemical Synthesis

The objective of the OrgKoKat project is to find ways of using carbon dioxide as an alternative, sustainable C1 source for high value-add industrial products. The main emphasis is on development of highly active and selective catalyst systems for chemical fixation of CO_2.

The researchers carried out intensive investigations on different catalysts in four sub-projects: cyclic carbonic acid esters (SP1), polycarbonates (SP2), β-Keto and β-hydroxy carboxylic acid derivatives (SP3) and α-unsaturated carboxylic acids (SP4) - see Fig. 1.

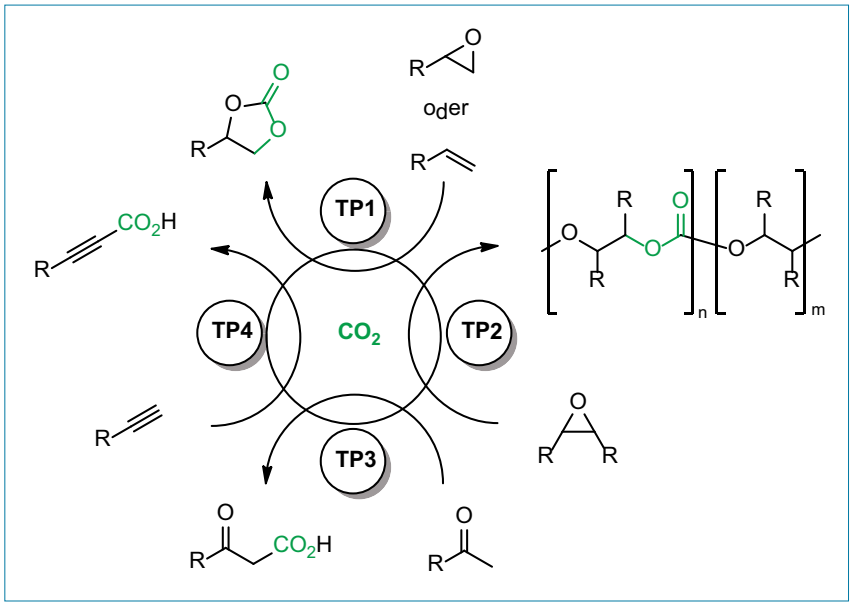


Fig. 1. Utilization of CO_2 through direct chemical fixation. See posters TP1: *Hydroxy-Phosphoniumsalze – Aktive Organokatalysatoren zur Synthese zyklischer Carbonate*, H. Büttner, T. Werner*, 08 April 2014, Königswinter; TP2: *Entwicklung neuer Katalysatorsysteme zur Synthese von Polycarbonaten*, A. Pommeres, W. Desens, T. Werner*, 08 April 2014, Königswinter; TP3: *Carboxylierung CH- acider Verbindungen mittels zwitterionischen Imidazoliumcarboxylaten*, W. Desens, T. Werner*, 08 April 2014, Königswinter.

The results so far from sub-project 1 look very promising. The catalyst used for synthesis of cyclic carbonates has two different functionalities in the molecule. The bi-functional organocatalysts are particularly active and in contrast to their mono-functional equivalents they are able to promote synthesis of cyclic carbonate under very mild reaction conditions. Two classes of bi-functional organocatalysts have been identified. Lifecycle analysis using the most active catalyst was carried out to assess the possible environmental impact of glycerol carbonate methacrylate (GCMA) synthesis. This product is of interest to industry because it is an excellent polymer building block.[1]

Lifecycle analysis is focused particularly on the Global Warming Potential (GWP) of the greenhouse gas emissions expressed in kg CO_2e per kg of product. Stoichiometric analysis shows fixation of 148 g CO_2 per kg GCMA in the target compound. Looking at the carbon footprint, utilization of CO_2 equates to between 3% - 6% of total emissions depending on the epoxide source.

[1] a) D.-W. Park, J.-Y. Moon, H.-J. Jang, K.-H. Kim, React. Kinet. Catal. Lett. 2001, 72, 83–92; b) N. Kihara, T. Endo, *Makromol. Chem.* 1992, 193, 1481–1492.

[2] Bifunctional one-component catalysts for the addition of CO_2 to epoxides", H. Büttner, K. Lau, A. Spannenberg T. Werner, *ChemCatChem*, 2015, 7, 459-467

[3] Phosphorous based bifunctional organocatalysts for the addition of CO_2 and epoxides", T. Werner, H. Büttner, *ChemSusChem* 2014, 7, 3268–3271.

[4] Hydroxyl-functionalized imidazoles: Highly active additives for the KI catalysed synthesis of 1,3-dioxolan-2-one derivatives from epoxides utilizing CO_2 as a C1 building block", T. Werner, N. Tenhumberg, H. Büttner, *ChemCatChem* 2014, 6, 3493–3500.

Besides a number of different terminal epoxides, the researchers also investigated the formation of cyclic carbonates from internal epoxides and CO_2 [2, 3, 4, 5, 6]. Fatty acid carbonates are ideally suited as plasticizers in plastics as well as for biomedical applications and they are also regarded as potential fuel additives[7].

The researchers also developed a cooperative catalyst system which delivers high throughput and high selectivity for the desired target compounds. The system is relatively simple and commercially available. The researchers are currently investigating the immobilization of catalysts for insertion of CO_2 into epoxides. It is easier to recycle the catalysts if they are deposited on suitable carriers, and catalytic activity remained nearly the same in ten successive reactions. The heterogeneous catalysts are particularly well suited for transfer from batch reactors to a micro reactor.

During the course of the project, 2 degree theses and 1 Bachelor's Thesis have been completed and work on 3 doctoral dissertations is in progress. There were also three postdoctoral internships.

Project partners:

- Bayer Technology Services GmbH
- Creavis Technologies & Innovation

Contact:

Dr. Thomas Werner
Leibniz-Institut für Katalyse e. V.
an der Universität Rostock
E-mail: thomas.werner@catalysis.de

[5] Synthesis of cyclic carbonates from epoxides and CO_2 catalyzed by potassium iodide and amino alcohols", T. Werner, N. Tenhumberg, *J. CO_2 Util.* 2014, 39–45.

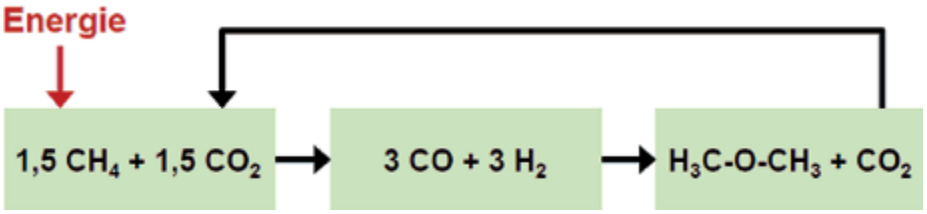
[6] Umsetzung von epoxidierten Fettsäuren oder Fettsäureestern zu den entsprechen-den Carbonaten", B. Schäffner, M. Blug, T. Werner, H. Büttner, N. Tenhumberg, DE 10 2013 206 167 A1 (2013)

[7] a) K. M. Doll, S. Z. Erhan, J. Agri. Food Chem. 2005, 53, 9608–9614; b) G. Rokicki, *Prog. Polym. Sci.* 2000, 25, 259–342; c) J. Langanke, L. Greiner, W. Leitner, Green Chem. 2013, 15, 1173–1182; d) B. Schäffner (Evonik Industries AG) Presentation at 2nd International Scientific Forum on CO_2 Chemistry and Biochemistry, Lyon, September 27–28, 2012.

DMEexCO_2 – Integrated Dimethyl Ether Synthesis from Methane and CO_2

Project goal

The goal of the project is to develop a single-stage, heterogeneous catalyzed process for synthesis of dimethyl ether (DME) from carbon monoxide rich syngas which may contain CO2. The process design will include substance and energy integration into the upstream syngas stage. "Dry" (CO_2) reforming of methane is one of the assumptions made in the process simulation for this stage. The large amount of hydrogen needed to activate the CO2 is already present in the process in the methane feed component and does not have to be supplied from an external source. The diagram below shows the process concept in highly simplified form:



Due to reduced energy demand resulting from the process thermodynamics, the new technology has a CO_2 mitigation potential of around 30% (125 kg CO_2 per tonne of DME) compared to the current state-of-the-art process with an intermediate methanol stage. Taking into consideration the specific process energy and heat consumption and elimination of the need for an energy-intensive supply of pure oxygen, dry reforming and utilization of the CO_2 increase the CO_2 mitigation potential by an additional 125 kg CO_2 per tonne of DME. The process can be expected to reduce total specific CO_2 emissions by around 60% compared to the current state of the art.

Project status

Two catalyst formulations were identified during high-throughput screening, and catalyst molds have been fabricated. Since Q4/2013, the researchers have been running long-term tests on a new tube reactor test bed. Several hundred hours of testing have confirmed the screening results. In parallel with catalyst screening, complete material and heat integrated process simulations were run for the new process and for current 2-stage state-of-the-art DME synthesis. The catalyst design reflects the simulation results, particularly as they relate to the optimal temperature operating window.

Single-stage synthesis of DME from syngas is a markedly exothermic reaction. The research team is looking at running the reaction in a slurry bubble column reactor which creates the option of isothermal operation. A pilot system to explore that possibility as well was started up in Q4/2013. Initial results indicate that this process variant is feasible, but a final evaluation has not yet been completed.

Basic mechanistic research is underway to determine the best way of fabricating the multi-function catalyst system. The options include a physical mixture of multiple catalysts and catalysts in which the various functions are atomically dispersed right next to each other.

Economic, environmental and societal leverage effect

The only way to significantly reduce anthropogenic CO2 emissions is to change our consumption of fossil fuels which contain carbon. Due to its physical properties profile, dimethyl ether appears to be a good candidate. It is already widely used in Asia as an LPG substitute. Due to its combustion characteristics, DME is a very good alternative to diesel and it has much lower soot particle emissions (www.aboutdme.org). Compared to the 2-stage process using the methanol pathway, CO_2 emissions from a DME plant with a capacity

of 1 million tonnes which uses the single-stage process could be reduced by up to 0.25 million tonnes.

The CO_2 footprint of the process could be further reduced by obtaining the energy needed for the process from renewable sources. The process can be coupled to biomass-based syngas production. Production of a CO/H_2 mixture through gasification is conceivable as well as direct upgrading of biogas (CO2/CH4) in place of biomass gasification, utilizing both C sources. Utilization of CO_2 in the dry reforming material stream would eliminate the need for costly separation of the CO_2 from the biogas.

The project has provided a framework for three doctoral dissertations on process simulation, kinetics and catalyst development at partner academic institutions. One Master's Thesis has already been completed. A number of students have supported or added to the project with their scientific contributions.

Fraunhofer UMSICHT

Linde

hte the high throughput experimentation company

BASF The Chemical Company

Contact:

Dr. Ekkehard Schwab
Chemicals Research and Engineering
BASF SE
E-mail: Ekkehard.Schwab@basf.com

Fuels from Water, CO_2 and concentrated sunlight

Solar radiation is the largest indigenous energy resource worldwide. It will gain a significantly more relevant role in covering the energy demand of many countries when national fuel reserves fall short and when demand increases as is expected within the next 10 years. If solar energy is transformed into heat by concentrating and absorbing the radiation, energy can be stored easily. Thermal energy from mirror fields that focus solar radiation not only is able to generate electricity but also can be used to generate storable heat, to desalinate salt water or to synthesize fuels from water and/or carbon dioxide and other feedstock to store, transport or use them on-site.

Solar thermochemical fuel production using a redox material is a promising route to convert concentrated solar energy into storable chemical energy. These so called solar fuels are primarily hydrogen or carbon monoxide produced by splitting water or carbon dioxide, respectively. The redox material, which is used in this two-step thermochemical process, is cycled between a reduced and an oxidised state. Until now, ceria has been identified as the most promising redox material. Beside the redox material development, several challenges are to be overcome to reach high efficiencies with technically feasible process concepts. Critical barriers have been identified for the development of receiver-reactors because of conflicting design and operation requirements for the processes of solar absorption, heat and mass transfer, and the chemical reaction. In addition, thermodynamic studies have indicated the need of solid phase heat recuperation in order to reach high process efficiencies, which adds further complexity to the design. Balancing out the multitude of constrains while respecting technical limitations is a very difficult but necessary task. The project has addressed this challenge with the development of a new process concept which includes a solid phase heat recovery approach. The concept is based on decoupling the different process steps by using a particulate redox material in combination with a particulate heat transfer material.

In the project SolarStep a novel concept was developed, which consists of three cycles. In the first cycle a particulate heat transfer medium is heated in a solar receiver [1]. It provides the thermal energy for the endothermic reduction of the redox material. The removal of the released oxygen in the reduction reactor is realized using vacuum pumping that avoids the use of a flushing gas. This redox material, also in form of particles, is transported in the second cycle between the reduction and oxidation reactor. Due to the temperature swing principle of the redox process, the redox material must be heated and cooled between the oxidation and reduction temperature. Therefore, again a heat transfer medium is used to recover the high temperature heat in a third cycle. The advantage of a solid heat transfer medium is that despite of temperatures up to 1500°C no phase change occurs. In addition, its chemical inertness avoids re-oxidation of the redox material. The advantage of this proposed concept is that all parts, the solar receiver, the reduction, and the reactor can be optimized independently. For instance, the residence time should be minimized in the solar receiver, to reduce thermal losses. However, in the reactor it must be long enough to reach the desired reaction extent. Extended with a thermal storage, a continuous and flexible operation is possible, independently from fluctuating solar irradiation.

The performance of the concept was numerically analysed for the solar receiver, the reduction reactor, the heat recovery system as well the combination of the completely system. Dependent on the boundary conditions, peak efficiencies of the system between 15% and 30% were calculated which is in the same range of a direct system. Additionally, with a multi stage reactor design, where the pressure in each stage was optimized, the efficiency could be further boosted by 20%. The heat recovery system consists as well of different stages to reach a quasi-counter current design. Heat recovery rates of 70% utilizing six stages were calculated [2].

[1] S. Brendelberger, J. Felinks, M. Roeb, C. Sattler, Solid Phase Heat Recovery and Multi Chamber Reduction for Redox Cycles, Proc. ASME. 45868; Volume 1: Combined Energy Cycles, CHP, CCHP, and Smart Grids; Concentrating Solar Power, Solar Thermochemistry and Thermal Energy Storage; Geothermal, Ocean, and Emerging Energy Technologies; Hydrogen Energy Technologies; Low/Zero Emission Power Plants and Carbon Sequestration; Photovoltaics; Wind Energy Systems and Technologies, V001T02A016, June 30, 2014, ES2014-6421.

[2] Jan Felinks, Stefan Brendelberger, Martin Roeb, Christian Sattler, Robert Pitz-Paal, Heat recovery concept for thermochemical processes using a solid heat transfer medium, Applied Thermal Engineering, 73 (2014), 1004-1011.

Fundamental to the calculation of the concept is the heat transfer between particulate materials, the heat transfer medium and the redox material. It bases on direct contact in a mixture of both, which was experimentally investigated. Therefore, an experimental set-up was developed to determine the heat transfer coefficient in a batch-wise experiment up to temperatures of 1250°C. All three basic steps (mixing, heat transfer, and separation) were implemented. Using statistical methods, the dependency of the diameter of the redox particles, the diameter of the heat transfer spheres, the mixing ratio, the contact time, and the temperature were investigated. Heat transfer coefficients up to 300 W/m^2 K were determined.

Though thermodynamic and process efficiency studies have shown that such thermochemical cycles meet the metric of potential viability compared to benchmark technologies like electrolysis powered by solar electricity, it is clear that further research efforts are needed for the achievement of these targets in practice [3]. The two main research tasks are in one hand the improvement of solar interfaces and integrated heat recovery schemes and in the other hand solving the main materials-related issues and further developing the right functional materials at reasonable costs.

Contact:

Dr. Martin Roeb
Deutsches Zentrum für Luft- und Raumfahrt e.V.
Institut für Solarforschung
E-mail: martin.roeb@dlr.de

[3] Christos Agrafiotis, Martin Roeb, Christian Sattler, A review on solar thermal syngas production via redox pair-based water/carbon dioxide splitting thermochemical cycles, Renewable and Sustainable Energy Reviews 42 (2015) 254–285.

Materials For The 21st Century: Can Carbon Come From CO_2?

Carbonic dioxide and its relevance to climate change currently receive worldwide attention. That is why considerations are taken to use CO_2 more intensely as a C1 component for high-value products.[1] With regard to the range of polymeric materials the lecture focuses on aliphatic polycarbonates (*ali*-PC), which can be catalytically produced from epoxides and carbonic dioxide.

The first part of the lecture deals with the mechanisms of polymerization of different catalyst types which differ fundamentally from the olefin polymerization reaction: whereas one catalyst center controls olefin polyinsertion processes, bi-functional catalysts are required in the CO_2/epoxide-copolymerization sequence.[2] Here, a novel concept of bi-functional Zn(II)-based catalysis will be introduced, that moves the reactivity determining step away from ring opening to the CO_2-insertion reaction.[3]

The second part focuses on some fascinating material features of the ali-PC and discusses the potential of this class of materials.[4] As a very recent finding blends of polypropylene carbonate (PPC) and interestingly polyhydroxybutyrate (PHB) will be presented, which for the first time afford properties that resemble those of purely oilbased plastics, like ABS and even PS.[5]

Contact:

Prof. Dr. Bernhard Rieger
WACKER-Chair of Macromolecular Chemistry
Technische Universität München
E-mail: rieger@tum.de

[1] a. Klaus, Lehenmeier, Anderson, Rieger Coord. *Chem. Rev.*, 2011, 255, 1518; b. Rieger, Herrmann, Kühn, *Angew. Chem.*, 2011, 123, 8662.

[2] a. S. Kissling, M. Lehenmeier, P. Altenbuchner, A. Kronast, M. Reiter, P. Deglmann, U. Seemann, B. Rieger Chem. Commun., 2015, 51, 4579; Lehenmeier, Kissling, Altenbuchner, Bruckmeier, Deglmann, Brym, Rieger* "Flexibly Tethered Dinuclear Zinc Complexes: A Solution to the Entropy Problem in CO_2/Epoxide Copolymerization Catalysis?" *Angew. Chem. Int. Ed.* 2013, 52, 1 – 7.

[3] a. Eberhardt, Allmendinger, Luinstra, Rieger, *Organometallics* 2003, 22(1), 211; b. Luinstra, Haas, Molnar, Bernhart, Eberhardt, Rieger, Chem. Eur. J. 2005, 11, 6298; c. Vagin, Reichardt, Klaus, Rieger, J. Am. Chem. Soc. 2010, 132, 14367; d. Klaus, Lehenmeier, Herdtweck, Deglmann, Ott, Rieger, J. Am. Chem. Soc., 2011, 133, 13151; e. Lehenmeier, Bruckmeier, Klaus, Dengler, Deglmann, Ott, Rieger, Chem. Eur. J. 2011, 17, 8858

[4] Luinstra, Polym. Rev. 2007, 48, 192.

[5] Bruckmeier, Rieger, Lehenmeier, Reithmeier, Herranz, Kavakli, Dalton Trans., 2012, 14, 5026-5037.

InnovA² – Innovative Equipment and System Design for Increased Production Process Efficiency

Project goals and content

Design and operation of energy and resource efficient processes is a core engineering challenge in all sectors of the process industries. In this context, innovative equipment and plant design may become the enabling technology to exploit new process efficiency potentials. Heat integration is a well established technology to increase the energy efficiency of a given production process. However, implementation of heat integration measures requires the availability of heat transfer equipment capable of transferring heat at the given temperature levels and process conditions in a stable and cost efficient way. Innovative heat transfer equipment may open new energy saving potentials as it allows for smaller temperature differences, lower pressure drop or increased economics compared to the standard plain cylindrical tube. Therefore, the collaborative research project "Innovative Equipment and Plant Design for Increased Production Process Efficiency – InnovA²" has investigated three innovative designs for heat exchangers for evaporation and condensation services: low-finned tubes, pillow-plate heat exchangers and a multi-stream plate condenser. The project consortium comprised of 12 research partners plus five associated partners, represent-ing market players along the whole value chain: Equipment manufacturers, engineering service providers, turn-key contractors, production process operators as well as research institutes. Innovative equipment design – like the ones addressed in InnovA² – typically face the challenge of entering the market with no long reference list of past successful applications in the back. Additionally, no shortcut design methodology is available in the open literature thus disabling engineering service providers or potential applicants to assess the efficiency potential of the new technology for their processes. Within the InnovA² project an innovation pipeline for new equipment technologies was implemented consisting of three core pillars: feasibility studies at laboratory scale at the university partners, pilot scale experiments at the respective facilities of the industrial partners Linde Engineering and BTS GmbH as well as theoretical work to establish shortcut design methods, an approach to identify potentially beneficial applications as well as the economic and ecological assessment of the new technologies.

Fig. 1: Test facility for pillow-plate thermosiphon reboiler (© ICTV TU Braunschweig)

Feasibility studies at lab scale

Experimental investigations were started with feasibility studies of the different new technologies at lab scale. This comprised of fundamental investigations of single phase heat transfer, evaporation and condensation at the single tube and single plate level. It was then extended to "lab scale" plant experiments with up to three parallel tubes or plates in the reboiler or condenser apparatus. Fig. 1 shows the test rig for the pillow-plate thermosiphon reboiler at TU Braunschweig.

The equipment typically had a heat transfer area of 0.5 to 1 m², allowing maximum heat flows of 20 to

30 kW. Project partners agreed on a standard procedure for operating the equipment and conducting the experiments, extraction of the experimental raw data, processing of the data to establish consistent and comparable mass and heat balances as well as the technical assessment of fluid dynamic and heat transfer performance of the different equipment types. Also standard component systems were defined, representing typical relevant single components and binary mixtures. Standard approaches were also agreed to extract characteristic dimensions for the complex geometries of structured tubes and pillow-plates. This allows for a comparison of the operational performance of the new equipment technologies with the reference standard of plain cylindrical tubes. It also facilitates the application of commercial rating and design tools for heat exchangers to the innovative equipment in a transparent and well-document manner.

Pilot scale test

Pilot scale experiments were conducted for combined evaporation and condensation services at the respective facilities of Linde Engineering using structured tubes and Bayer Technology Services with pillow-plate apparatuses. Heat transfer areas were in the range of 8 to 10 m^2, thus at least one order of magnitude larger than at lab scale.

Fig. 2 presents a top view of the Linde setup together with condensation data for the binary system n-pentane/i-octane at 1.5 bar and 20 kW/m^2. A good agreement between single tube and bundle data is obvious as well as a significant reduction in heat transfer performance of the mixture compared to the pure components.

Finally, lab scale and pilot plant data were complemented with real plant data of a large scale pillow-plate condenser operated at a production facility of project partner Evonik. Although operated at conditions not covered by the previous experiments, its fluid dynamic and thermal performance could be described satisfactory using the simula-tion tools developed within the research project.

Modeling and simulation

Experimental data together with qualitative information on the operational performance of the innovative equipment technologies were used to establish methods and tools to assess the efficiency potentials connected to

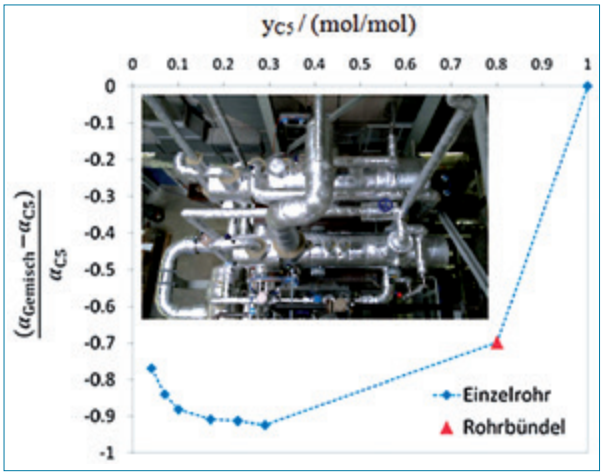


Fig. 2: Top view of Linde pilot plant with condensation data for n-pentane/i-octane at 1.5 bar and 20 kW/m2 (© Linde AG)

their use, allow a shortcut design as well as an economic and ecological evaluation of its advantages. The short-cut design aims at enabling engineering service providers and potential applicants to get a first idea about the applicability, design and competi-tiveness of structured tubes or pillow-plates as an alternative to the reference solution using plain tubes. This introduces these new technologies into the portfolio of equipment alternatives design engineers are considering in the process and equipment selection and design phase.

A novel approach was developed to quantify the ecological impact of new equipment technologies. The Three-Level-Model is used to break down a production process and its infrastructural environment into a modular structure based on the concept of unit operations, see Fig. 3. Level 1 represents the individual unit operation, consist-ing of equipment units, such as pumps, vessels, heat exchanger, and operations, such as filling, cleaning, heating. On Level 2, unit operations are combined to the actual manufacturing process which is embedded and integrated into its site infrastructure represented in Level 3. This approach has been applied to a multi-product batch process of Merck KGaA and to a continuous single product plant suggested by LANXESS GmbH. Alternations at the equipment level, i.e. replacing standard equipment with the new technologies in Level 1, may result in new process opportunities in Level 2 and thus a reduced energy demand for heating or cooling in Level 3.

The approach and results of InnovA^2 have been communicated at various national and internatio-nal occasions. More than 30 poster and oral presentations have

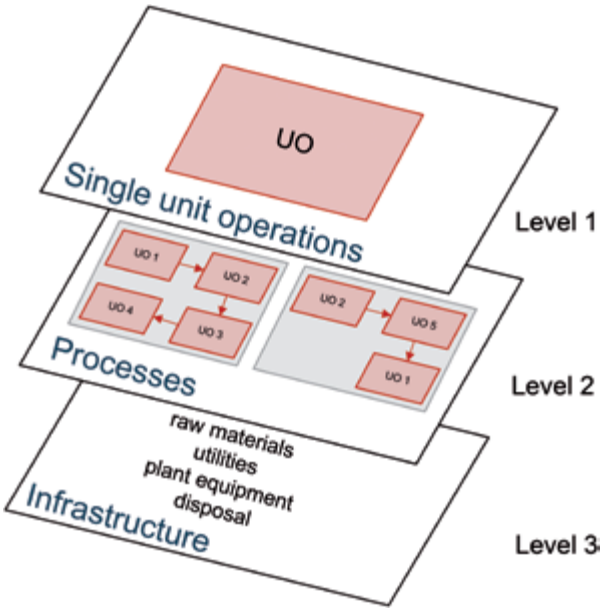


Fig. 3: 3-Level-model for ecological assessments
Dissemination and leverage effect

been given at the ProcessNet working groups on "Heat and mass transfer", "Fluid process engineering", "Process, equipment and plant technology" as well as the annual meeting of ProcessNet. A Discussion Corner as well as a separate conference session were dedicated to InnovA^2 at the ACHEMA 2012 fair, and an equivalent session will be held at the ACHEMA 2015 on June 15.

In March 2015 a dedicated issue of Chemie Ingenieur Technik compiled ten reviewed journal papers based on InnovA^2 research projects on innovative equipment for energy efficiency.

Within the InnovA^2 project nine young researchers were involved as doctoral candidates at the different universities together with four young professionals at industrial partners. Twice a year general meetings were held at the different partner locations. These general meetings were followed by a one-day working meeting of the doctoral candidates supporting a working-level exchange of ideas, best practices, methodology as well as stimulating networking among this group. It can be expected that this will strengthen sustainability of the achieved technical results as well as the spirit and approach towards future innovative products and concepts among this next generation engineers.

The collaborative research project InnovA^2 started on Jan. 1, 2011 and finished after a six and nine month extension, resp. on Sept. 30, 2014. More technical details on the InnovA^2 project may be found in Chemie Ingenieur Technik 86 (2015) 3 and at the website www.innova2.de.

Project partners:

- Technische Universität Braunschweig
- Universität Kassel
- Helmut-Schmidt-Universität – Universität der Bundeswehr Hamburg
- Technische Universität München
- Universität Paderborn
- Bayer Technology Services GmbH
- DEG Engineering GmbH
- Evonik Industries AG
- LANXESS Deutschland GmbH
- Linde Aktiengesellschaft
- Merck Kommanditgesellschaft auf Aktien
- Wieland-Werke Aktiengesellschaft

Contact:

Prof. Dr.-Ing. Stephan Scholl
Technische Universität Braunschweig
Institut für Chemische und Thermische Verfahrenstechnik ICTV
E-mail: s.scholl@tu-braunschweig.de
Homepage: www.ictv.tu-bs.de
www.innova2.de

HY-SILP – Development of new Resource-Efficient Hydroformylation Technologies using Supported Ionic Liquid Phase (SILP) Catalysts

The goal of the HY-SILP project is to develop a new, resource-efficient hydroformylation technology using SILP catalysts. SILP catalyst technology (Fig. 1) is an innovative approach to immobilization of homogeneous catalysts, combining the advantages of homogeneous and heterogeneous catalysis.

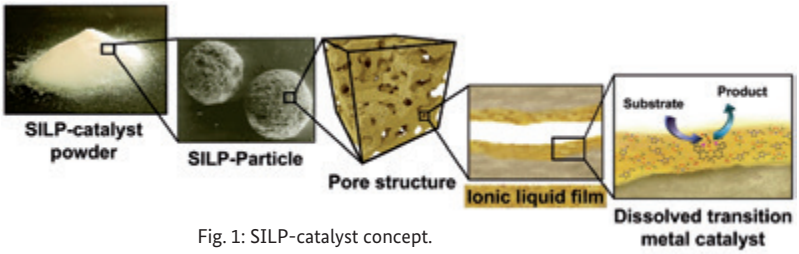


Fig. 1: SILP-catalyst concept.

Here, the homogeneous transition metal complex is solved in a solvent with negligible vapor pressure, a ionic liquid. This solution will supported onto a porous catalyst carrier, and thus, be immobilized.

A SILP process, for example, eliminates all of the steps which demand a solvent for the catalyst system. Specific solubility in ionic liquids (ILs) creates pathways for selective processing of complex raw material mixtures. This can significantly reduce the hydroformylation carbon footprint and process design modifications can reduce energy consumption compared to current technology.

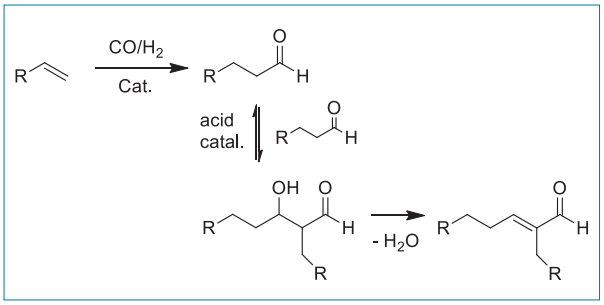


Fig. 2: Catalytic hydroformylation of olefines and possible acid catalysied consecutive reaction pathways to aldol addition and condensation products.

Researchers at universities TU Darmstadt and FAU Erlangen-Nuremberg are working closely with Evonik Industries AG on 10 work packages. The results of WP3 should give the researchers a better understanding of how the different components of a SILP catalyst influence the behavior of the catalyst in continuous gas-phase hydroformylation. The results so far clearly show that interaction between the precursor, ligand and ionic liquid (IL) in the substrate's pore network is highly complex. The complexation behavior of the precursor and ligand as well as the type of IL or substrate have a pivotal influence on the activity, stability and selectivity of the catalysts.

Fig. 3: SILP-Hydroformulation plant, Technical center Evonik Industries AG.

When different IL's were used, a correlation was found to exist between catalyst activity and the solubility of the substrate in the IL. Equally, the character of the carrier has high influence on the activity, stability and selectivity of the reaction. Acide surface groups catalyze the unwanted aldol reaction (figure 2). [1, 2]

Based on the factors which limit the performance of SILP catalysts, investigations are made in WP4-6 to define the best formulations for production of SILP catalysts. IL wetting and fluid distribution on and in the substrate is crucial for precise characterization of SILP catalysts (WP4). Using substrate/IL systems, the researchers

[1] Schönweiz et al. Ligand-modified rhodium catalysts on porous silica in continuous gas phase hydroformylation of short-chain alkenes – catalytic reaction in liquid supported aldol product, *ChemCatChem* 2013, 5*(10)*, 2955–296.

[2] A. Schönweiz, Optimierung von Supported Ionic Liquid Phase (SILP) Katalysatoren für die kontinuierliche Gasphasen-Hydroformylierung, Dissertation, Erlangen-Nürnberg, 2014.

investigated the effect which the IL has on texture. Systems with different mass fractions were produced and the BET surface area and pore size were measured using N2 sorption. The investigations confirmed that linear correlation exists between the mass fraction and the surface area. The researchers carried out TEM, HREM and HREM-EDX measurements on the substrate and on unused and used SILP catalysts. On the basis of these results, the model of a homogeneous distributed film of ionic liquids must be revised within the work package.

A test equipment with Berty reactor was built and launched to carry out kinetic investigations (WP5 and 6). Using a defined SILP catalyst with benzopinacol ligands, kinetic measurements were taken with variable partial pressure, absolute pressure, residence time as well as temperature.

Modeling using a simple formal kinetics model (exponential) shows an acceptable level of agreement with the experimental results, producing reaction orders and activation energies for the formation of *n*-aldehyde and *iso*-aldehyde.

Besides optimizing the variables which have a crucial effect on the reactions, researchers in WP6 are working to gain a better understanding of the interplay between material transport and the chemical reaction. Experiments are being carried out to determine the diffusion coefficients of the pure educts and the products in selected ILs. The team developed a suitable method (Transient Thin Liquid Film Method) [3] and they then installed and validated the necessary instrumentation. In the course of the project, the global kinetic of the hydroformulation succeeded as well as the parallel executed isomerisation and hydration by adapt a suitable kinetic model with excellent approximation (WP 7). By means of the model it is possible to determine a stable and efficient operation of a SILP catalyst within the parameters in dependency of the raw material concentration.

Traces of water or 1,3 butadiene caused deactivation of the SILP catalyst. Thermogravimetric analysis showed that the ligand is the most temperature-instabile component. The WP8 research team was able to reactivate a thermally deactivated SILP catalyst by adding fresh ligand. Furthermore, the precious metal components, rhodium, was recovered with help of an exploration method and, used for SILP-materials once more. These successful experiments show the prospect to recycle expensive precious metal from a deactivated SILP catalyst.

The long-term stability of selected SILP systems developed in WP3 was evaluated in WP9. The test plant is illustrated in figure 3. The long-term stability of the SILP-material with a notable run time > 2,000 hours and a n/isoselectivity of an average bigger than 85 % to the linear aldehyd demonstrates the potential of the hydroformylation technology.

The used ligand system, a homogenous catalysts system, which contains an antracentriol fragment, was synthesized at Evonik industries AG (WP2). The chemical lead structure shows already at the virtual screeing [4] via COSMO-RS as particularly well soluble within the ionic liquid

In parallel with the experimental work and based on the long-term stability results obtained in WP9, a potential emissions reduction has been identified for a process with a SILP-reactor in comparison to the conventional hydroformulation, as in operation at Evonik Industries AG. The most promising scenario in regards to the process technology displays a reduction of CO_2 emissions by 2.3 %.

Looking at the societal leverage effects of the HY-SILP project, up to this point work on four doctoral dissertations has started and four Bachelor's and Master's theses have been completed.

Project partners:

- Evonik Industries AG
- Friedrich-Alexander-Universität Erlangen-Nürnberg
- Technische Universität Darmstadt

Contact:

Dr. Hanna Hahn
Evonik Industries AG
E-mail: hanna.hahn@evonik.com

[3] Y. Hou; R. E. Baltus, Experimental Measurement of the Solubility and Diffusivity of CO_2 in Room-Temperature Ionic Liquids Using a Transient Thin-Liquid-Film Method. *Industrial & Engineering Chemistry Research* 2007, 46, 24, 8166-8175.

[4] Franke et al. Accurate pre-calculation of limiting activity coefficients by COSMO-RS with molecular-class based parameterization, *Fluid Phase Equilibria* 2013, 340, 11-14.

CO_2 Compressor – Development of a Miniaturized Oil-Free CO_2 Compressor with Built-In CO_2-Cooled Electric Motor Drive for Large CO_2 Heat Pumps

Project goals and content

The goal of the project is to develop a miniaturized oil-free CO_2 compressor with built-in CO_2-cooled electric motor drive for high-capacity CO_2 heat pumps and chillers.

The project deliverable is a functional demonstration showing the feasibility of using CO_2 in a turbo machine as the working medium in the compressor, the lubricant in the gas bearings and the coolant in an electric motor drive unit. The technology will be based on an innovative design, and the defined operating environment is a high-capacity heat pump with 4.0 COP. Various simulation-based methodologies are being developed in the Fluid Mechanics and Hydraulic Machinery Dept. at the University of Applied Sciences in Kaiserslautern to quantify the power losses caused by shear forces between the rotor and the stator and determine the correct dimensioning of the gas bearings. The models are verified on test beds installed at a subcontractor's site (KSB) and in the Department of Thermo and Fluid Dynamics at Mannheim University. The results are used during development of functional prototypes for the compressor stages, the rotor, the stator and the electric motor drive unit.

Project status

The methods used to make the design calculations for the hydraulic stages have progressed to the point where an initial compressor stage consisting of an impeller and diffuser has been evaluated in the simulator. Rotordynamic analysis has been performed for the shaft, and the results obtained through iterative simulation have been verified during trials. At speeds up to around 180,000 RPM, vibration resulting from the rotor's rigid and deformable body modes made it necessary to redesign the rotor and stator in the electric motor drive unit. A drive unit with oil-lubricated rolling bearings has run at speeds up to 170,000 RPM during trials. The speed was kept below 180,000 RPM due to the characteristics of the rolling bearings. The compressor will have gas bearings, so that aspect is of no practical consequence. The fluid mechanics characteristics of the CO_2-lubricated gas bearings are being modeled. The current models have not yet been verified in trials, primarily because it has not been possible to create a consistent model for the axial bearings and axial thrust compensation. It is also not yet clear what material should be used for the gas bearing shells. The researchers have succeeded in developing a satisfactory model of the losses in the stator cavity caused by shear forces in the CO_2 induced by the rotation of the rotor. The current models have not yet been consistently verified in trials due to the complex manner of dilution of the CO_2 medium. It is important to know the magnitude of these losses in order to ensure that the high capacity heat pump delivers 4.0 COP.

Economic, environmental and societal leverage effect

In the short term, the oil-free CO_2 compressor will make it possible to design cost-effective high-capacity heat pumps (50 – 1000 kW thermal capacity) which use CO_2 as the working medium. Large manufacturers in the heating equipment industry have entered the market for high-capacity heat pumps. The high-capacity CO_2 heat pump will make a significant contribution to energy-efficient space and water heating in existing residential and commercial buildings, because CO_2 has very good specific heating characteristics along with low space requirements due to the high energy density of the medium. Compared to current working media, CO_2 places fewer demands on system safety design. There is market demand for high-capacity heat pumps which deliver reliable cooling power (e.g. for food) with working media which are less dangerous than those which are currently used.

In the medium term, it may be possible to use the electric motor drive in vehicles which have higher power density (e.g. e-boost for combustion engines in the automobile industry).

The long-term vision includes product features on drives with very high power density in transportation and CO_2 utilization applications.

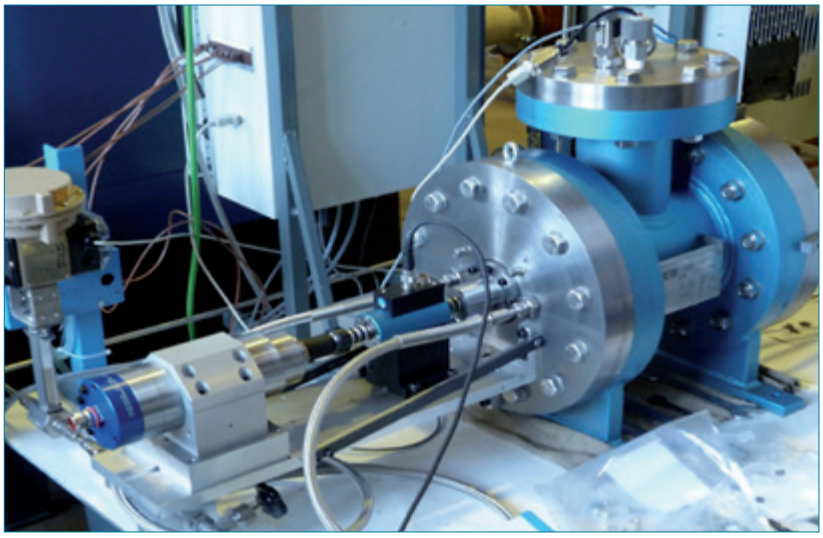


Fig. 1: Test bed shear force losses University of Mannheim

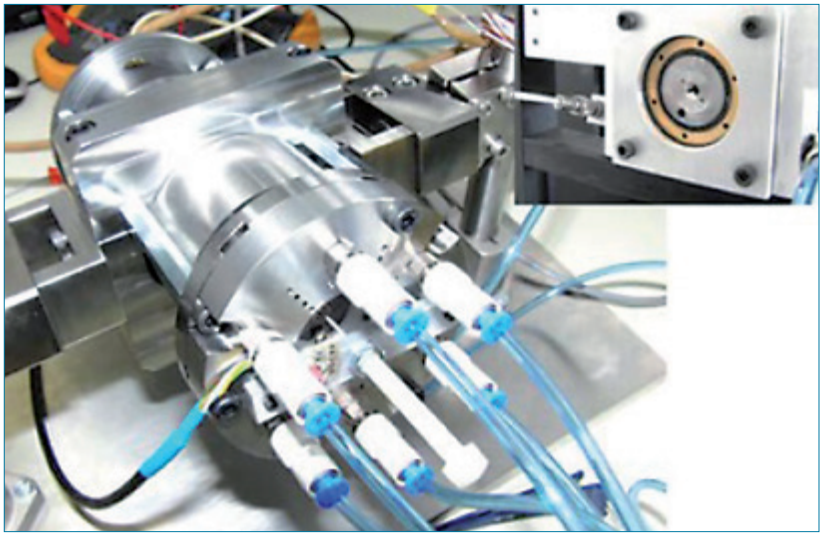


Fig. 2: Test bed single-stage CO_2 compressor KSB/awtec

Development of the oil-free CO_2 compressor is also significant from the environmental standpoint because the potential greenhouse effect of the halogenated working media currently in use is up to 6,000 times greater than CO_2. The use of CO_2 as the working medium in high-capacity heat pumps/chillers can play an important role in climate protection. In addition, high-capacity heat pumps/chillers are able to use or store electricity produced from renewable resources.

For society in general, development of a CO_2 compressor which can help heat existing residential homes and buildings at a relatively affordable cost and provide security of supply to meet the basic human need for heat is a very significant step forward. Involvement by the universities in Stuttgart, Kaiserslautern and Mannheim in the project provides opportunities for students to complete degree course requirements, which is another important social contribution made by the project.

Project partners:

- KSB Aktiengesellschaft
- Universität Stuttgart
- Hochschule Mannheim
- Technische Universität Kaiserslautern

Contact:

Dr.-Ing. Gerd Janson
KSB Aktiengesellschaft
E-mail: gerd.janson@ksb.com
Homepage: www.ksb.com

Mixed-Matrix-Membranes for Gas Separation

Project goals and content

Progressive climate change creates the need for greater resource and energy efficiency. Optimization of industrial production can make an important contribution. Gas separation is used in many industrial applications. Conventional techniques are complex and very energy-intensive. Gas permeation membrane technology is an energy-efficient alternative. To make the technology economically competitive with conventional techniques, the membrane material must have sufficiently large trans-membrane flow and selectivity. There is growing demand for separation of higher hydrocarbons, e.g. in natural gas upgrading. The goal of the project is to develop high-performance membrane materials for the separation of higher hydrocarbons from permanent gases as nitrogen or methane. The new material should reduce the size of gas purification membrane systems, hence reducing its energy consumption and CO_2 emissions. The project is based on the development of mixed matrix membranes made of a polymer matrix with embedded activated carbon particles which have higher hydrocarbon selectivity compared to polymer-only membranes. When production advances to pilot scale, it will be possible to validate the results in a bypass configuration to an industrial installation after the ende of the project. A material transport model based on the experimental data is being developed to support process simulations. The objective is to demonstrate the economic viability of the process which uses the new membranes and to provide a basis for lifecycle analysis.

Project status

The polymer matrix is made of rubbery, silicon-based polymers which facilitate the transport of long-chain hydrocarbons. In order to support solubility controlled transport in the polymer matrix, modified hydrocarbon-selective activated carbon is being employed in the project as an active filler. A number of factors influence the separation performance of the hybrid material. The materials must have good compatibility to avoid non-selective defects at the interfacial surface and have to be well distributed in the polymer matrix. Determining the right combination of filler content and particle size presented a major challenge. Besides the morphological parameters, operating conditions such as pressure, temperature and composition have a crucial influence on the separation performance of the membrane. During material development, the researchers investigated the influence which various factors have on the separation performance of mixed matrix membranes. They discovered a material combination which delivers better selectivity for long-chain hydrocarbons compared to polymer-only membranes as well as the operating conditions in terms of temperature, pressure and higher hydrocarbon content where the benefits of the novel membrane material can be exploited to the full. Extended trials lasting about 5 weeks provided evidence that the improved separation performance remains stable as shown in Fig. 1.

Production is now possible on an industrial scale. More than 100 m^2 of mixed matrix membrane is already available (see Fig. 2). A pilot plant for testing the membrane in a bypass configuration in an industrial plant was designed and built. A rigorous mechanistic transport model has been developed for the mixed matrix membrane. It describes the solubility of the permeating components in the polymer material, the diffusion process in the polymer, transition between the polymer and activated carbon phase and transport in the activated carbon's pore sys- tem. The latter is further broken down into transport processes during the gas phase and the adsorbed phase. The model provides a

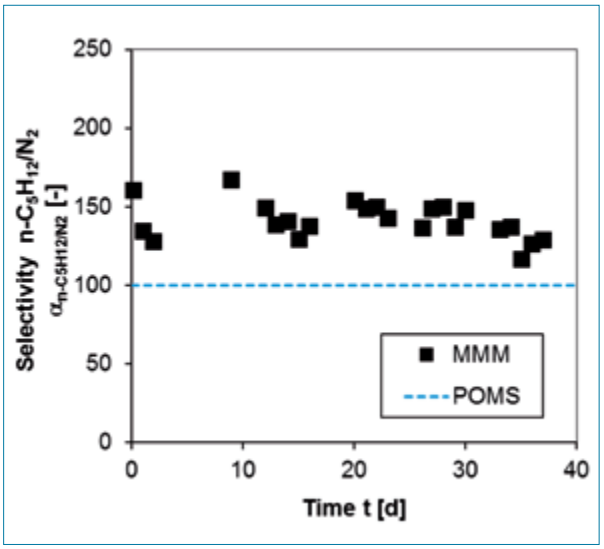


Fig. 1: Stability of the mixed matrix membrane for a period of five weeks using n-pentane/nitrogen as the test system (1.5 Vol.-%/98.5 Vol.-% on the high pressure/feed side) at 20°C, a feed pressure of 30 bar and a permeate pressure of 1.1 bar

very good description of the permeation process for the individual components and it is currently being enhanced for multi-material systems.

Economic, environmental and societal leverage effect

The assumption is that the membrane technology will become even more competitive and that new market opportunities can be exploited. A rough estimate of the market potential shows that demand for the new mixed matrix technology could be as high as 1,000 systems between now and 2030. Based on current results, energy consumption would be 16.8% lower compared to systems with conventional membranes. That equates to a reduction of 16 $ktCO_2$/yr. A lifecycle assessment consideration for a gasoline vapour recovery unit equipped with the newly developed membrane was carried out. It showed that the developed membrane technology is ecologically beneficial for almost all considered categories, if today's boundary conditions in Germany are assumed. The benefits could be diminished by other boundary conditions. One example being an electrical energy mix containing a higher contribution of renewables. However, it has to be pointed out that the LCA was conducted for only one possible process. The results might be different for other processes as e.g. natural gas processing.

If the benefits of the technology were to be proven, the result would be greater job security in membrane production and system manufacturing, and it would further stimulate innovation in Germany. To our knowledge, mixed matrix membranes have never been used up to this point for gas permeation in industrial applications. Three doctoral candidates on the project are working toward completion of their theses.
13 Bachelor's theses and four master theses have also been completed.

Fig. 2: Mixed matrix membrane production on technical scale

Project partners:

- Helmholtz-Zentrum Geesthacht Zentrum für Material- und Küstenforschung GmbH
- Technische Universität Berlin
- Blücher GmbH
- Sterling Industry Consult GmbH

Contact:

Dipl.-Ing. Torsten Brinkmann Ph. D.
Helmholtz-Zentrum Geesthacht Zentrum
für Material- und Küstenforschung GmbH
Institut für Polymerforschung
E-mail: torsten.brinkmann@hzg.de

Waste Heat Recovery by Absorption Cycles for Refrigeration and Heat Transformation – Application of New Working Pairs

Many branches of industry, like chemical or food industry and metallurgy discharge huge amounts of waste heat in a temperature range of 100 to 120°C. This up to now unused waste heat offers an enormous potential of primary energy savings and CO_2 emission reduction.

The goal of the project funded by the German Ministry of Education and Research (BMBF) was to develop absorption cycles with capacities > 10 MW for transformation of the heat to a higher and useable temperature level or for chilling. The use of new working pairs incorporating ionic liquids creates opportunities to increase operating reliability and efficiency. The researchers took on the task of identifying suitable working pairs, collecting material data and conducting lab trials. The material data can be used to simulate the absorption cycles and study the operating parameters.

Higher solvent viscosity is one issue which needs to be addressed. Also, the researchers want to increase the heat capacity. As a result, they are working on the development of new heat exchangers to increase efficiency without the need of wetting enhancing additives.

During the project duration of three years, the consortium members have identified ionic liquids which look very promising. Thermophysical data and simulation tools were used to design absorption cycles and compare different working pairs. By implementing internal heat and mass transfer models, the absorber was simulated in more detail to estimate its dimensions.

A fully operational pilot-scale (4 kW nominal useful heat output) absorption heat transformer was built at the Karlsruhe Institute of Technology (KIT) – see Figure 1. A water – ionic liquid working pair has been evaluated on the system under various operating conditions. The experimental results are used to evaluate predictions generated by a simulation program and interpret the differences. New equipment design features with promising operating characteristics have been built

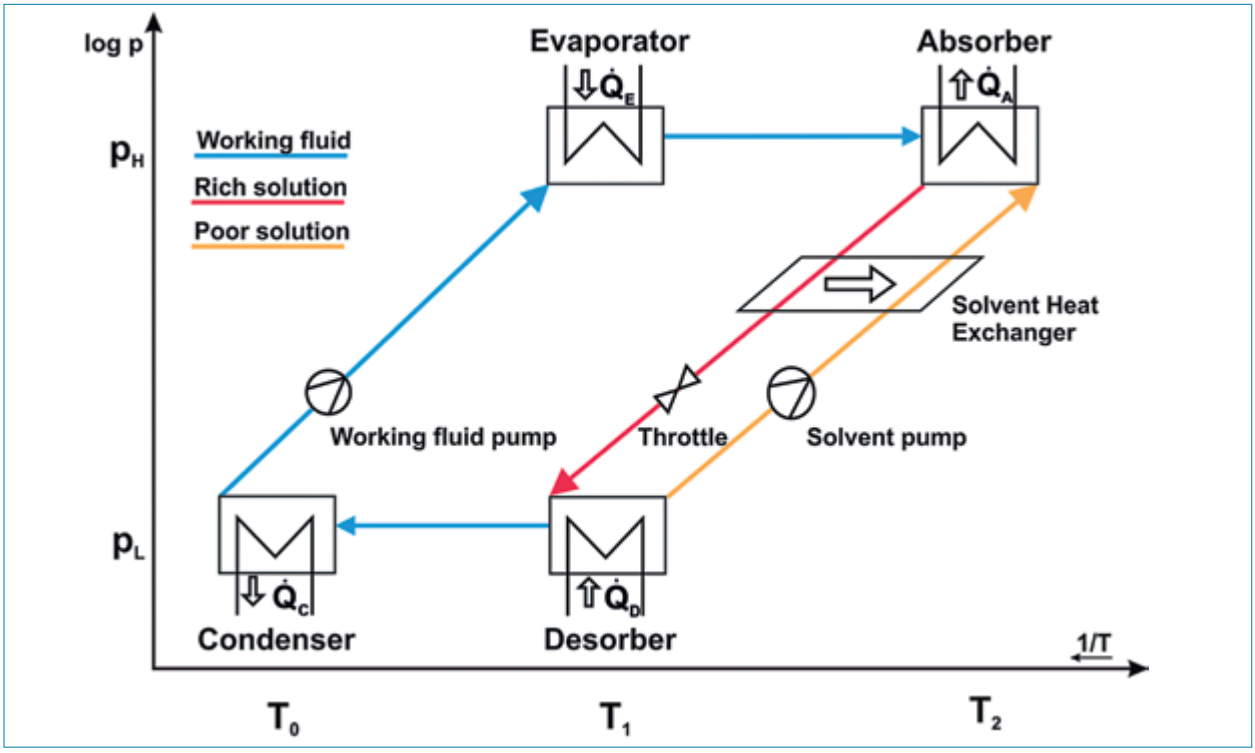


Fig. 1: Schematic absorption heat transformer displayed in a Dühring-diagram.

into the lab system. A patent application has been prepared in partnership with API Schmidt-Bretten for the fluid distribution system of the new absorber.

In parallel, the suitability of a different absorber design was under evaluation at BASF SE, and the suitability of the new working pair has also been assessed under various operating conditions. The researchers have identified additional heat sources and evaluated the process at its integrated site in Ludwigshafen as well as at other sites.

The results achieved at KIT and by BASF SE suggest that the economic advantages are more likely to be significant if operating conditions are favorable (Systems > 10 MW and waste heat temperature level around 120°C). Figure 2 displays the Net Present Value for a 10 year period assuming variable waste heat duty and temperature, heat rejection to central European river water and production of externally superheated 4 bar steam by the high temperature heat. As energy costs continue to rise and CO_2 emission-regulations become more stringent, absorption cycles and heat flow integration could become more attractive.

The ionic liquids can be regenerated and reused. Recycling would further reduce costs and enhance the sustainability of the sorption system lifecycle. Manufacturers of sorption systems would not be the only ones to benefit from the use of sorption technology to recover waste heat. The technology could also create new market opportunities for the recycling industry. Given the magnitude of the potential opportunities, demand for the materials would probably be measured in tons.

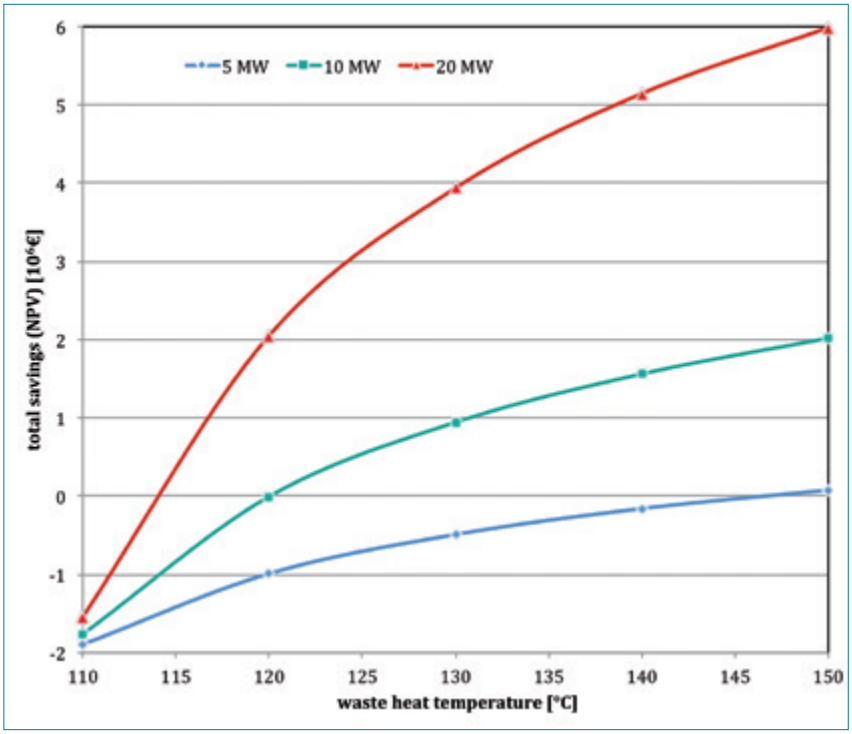


Fig. 2: Total savings (including investment) for a 10 year period.

Four Bachelor's theses, two Master's theses and three Diploma's theses were completed during the course of the project, and the research has generated greater interest in this approach to energy recovery. A doctoral dissertation on absorption heat transformation using the water – ionic working pair is in progress.

Information on the research results was shared with the scientific community on posters and during presentations at various conferences.

Project partners:

- Karlsruher Institut für Technologie (KIT)
- API Schmidt-Bretten GmbH & Co. KG
- IoLiTec Ionic Liquids Technologies GmbH
- BASF SE

Contact:

Nina Merkel
Karlsruher Institut für Technologie (KIT)
Institut für Technische Thermodynamik und Kältetechnik (ITTK)
E-mail: nina.merkel@kit.edu

InReff – Integrated Resource Efficiency for Reducing Climate Impacts in the Chemical Industry

Project goals and content

The goal of the InReff consortium project is to develop an IT-based modeling and analysis environment which can provide answers for a wide range of resource efficiency and climate protection issues in the chemical industry. Integrated analysis and optimization of complex production systems including raw material and energy consumption and informed management of the associated costs and environmental/climate impact are needed to reduce greenhouse gas emissions of chemical plants.

Various tools and techniques including life cycle analysis, thermodynamic simulation, heat integration studies, costing models and optimization methodologies are used to quantify the climate impact and resource efficiency of production systems in the chemical industry (Fig 1). This holistic approach requires but also facilitates methodological and technological innovation in system modeling and analysis as well as in real-world production at project partner chemical sites.
The project consortium consists of three industrial and two academic partners: ifu Hamburg GmbH (software development), the Institute for Industrial Ecology (INEC, Pforzheim University) and the Chemical and Thermal Process Engineering Institute (ICTV, Technical University Braunschweig), H.C. Starck GmbH and Sachtleben Chemie / Huntsman Pigments (both chemical industry). Wacker Chemie, BASF SE and Worlée Chemie (as an additional SME) are also involved in the project as associate members. Funding for the three-year project is being provided by the Federal Ministry of Education and Research (BMBF).

Project status

Corresponding to the advanced state of the project, the project team has achieved important conceptual and technical results already. Based on the practical experience gained in the project they developed a methodology for integrated resource efficiency analysis which describes the interaction between the different analytical methods in the application domain. While doing so, they also defined specific IT support requirements and developed the initial prototypes. Material flow modeling plays a key role as the unifying overall model. Complementary methodologies such as flow sheet simulation and heat integration analysis (e.g. pinch method) serve to refine the model or to analyze certain perspectives (e.g. heat flow) in detail. Material flow modeling also provides a basis for standardized visualization, evaluation and optimization of partial results using a variety of analytical tools.

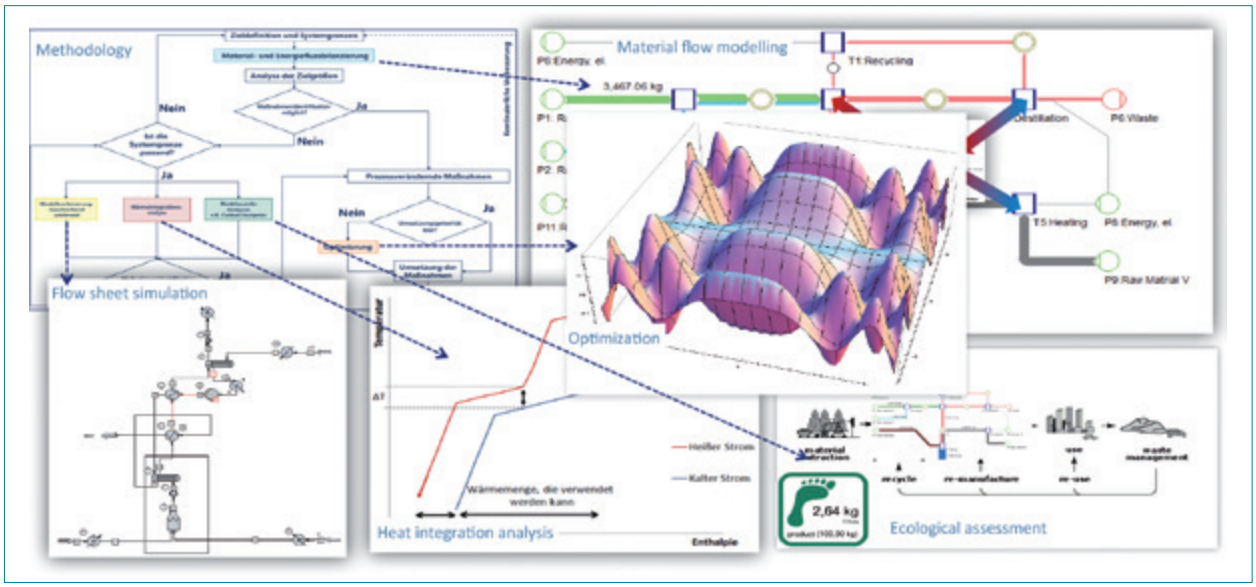


Fig. 1: Elements included in the integrated resource efficiency analysis

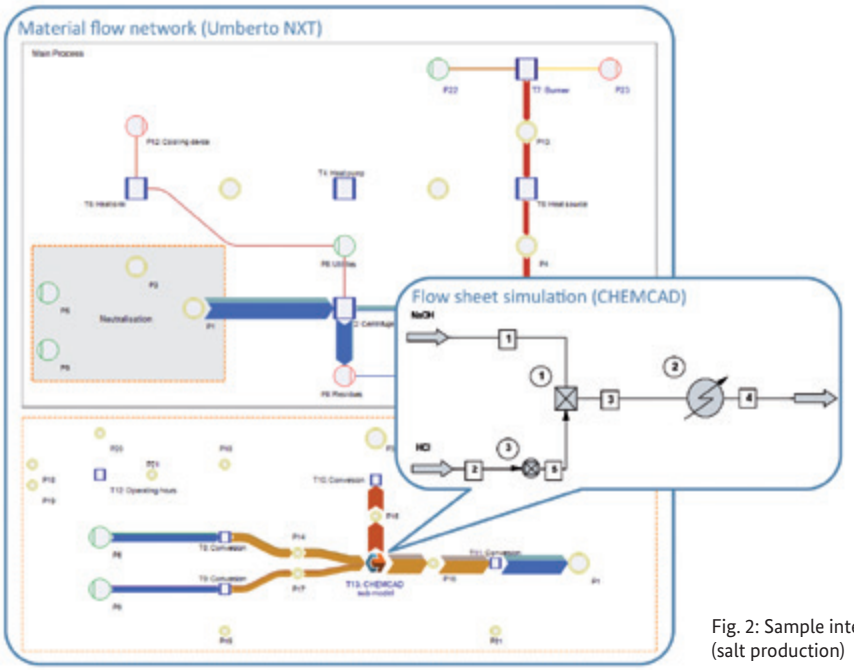


Fig. 2: Sample integrated model of a neutralisation process (salt production)

In that context, the team developed a prototype interface which creates a link between a material flow modeling tool and a flow sheet simulator (Fig. 2). They also created prototypical interfaces between material flow modeling and heat integration analysis tools. Furthermore, they added software components to optimize material flow networks using simulation-based as well as analytical optimization algorithms. Using this approach, the researchers were able to provide initial demonstrations showing the feasibility of integrated analysis, both in interactive and largely automated processes.

Detailed research work continued on the methodological and practical aspects of model-based resource efficiency optimization. Further progress was also made on modeling of typical processes at industry partner sites as pilot studies for the integrated modeling platform.

Economic, environmental and societal leverage effects

Up until this point, a holistic approach to technical, ecological, and economic analysis and optimization of production systems has been lacking in the chemical industry. This is particularly the case in the SME sector. Based on a limited information base, it seems reasonable to assume that opportunities for reducing the environmental impact are of a similar magnitude as opportunities to reduce cost. A holistic approach which includes quantitative analysis of the economic and environmental optimization potential enhances the likelihood that companies will accept the need to take action to protect the climate and increase resource efficiency and by doing so promote their own long-term business development. The InReff project is providing new insights and delivering practicable solutions. After completion of the project these results will provide a solid foundation to develop a market-ready software product that supports integrated resource efficiency analysis in the chemical industry.

Project partners:

- ifu Institut für Umweltinformatik Hamburg GmbH
- Sachtleben Chemie GmbH
- Technische Universität Braunschweig
- Hochschule Pforzheim - Gestaltung, Technik, Wirtschaft und Recht
- H.C. Starck GmbH

Contact:

Dr. Nicolas Denz
ifu Hamburg GmbH
E-mail: info@ifu.com

EP-Wüt – Energy Efficient Polymer Film Heat Exchangers

Project goals and content

The goal of the project is to develop an energy efficient heat exchanger for the chemical industry, for example to condense organic solvents. The heat exchanger is intended as an alternative to current equipment made of glass or ceramics, and it will be made entirely of plastic.

The unit is basically a plate heat exchanger in which thin sheets of plastic film (75 – 150 µm) act as the heat exchange surfaces. Fig. 1 shows a simplified diagram. The base plates (red) have rectangular pimples on the condensation side to stabilize the highly flexible sheets of film (brown). The heat exchanger features a modular design, and more elements can be added as needed.

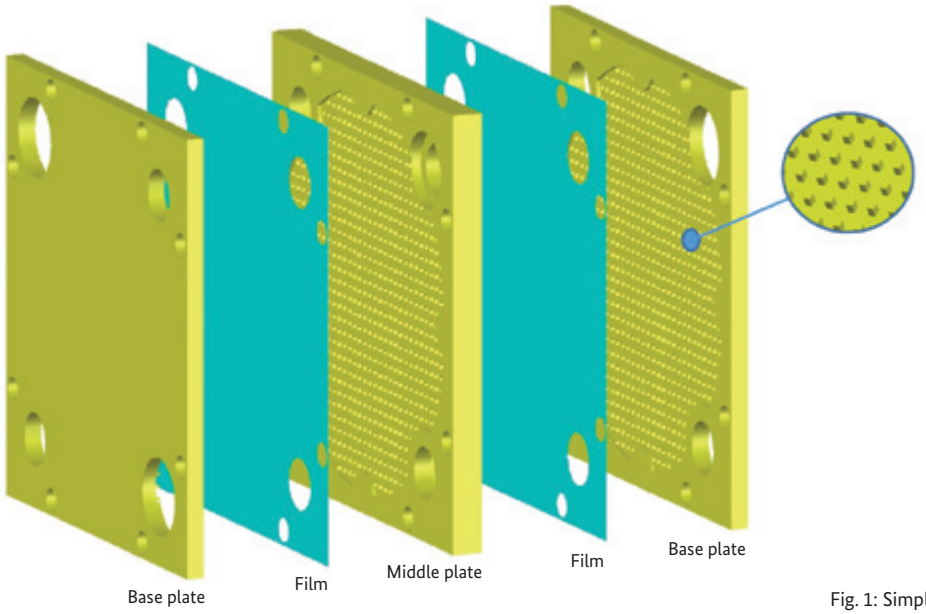


Fig. 1: Simplified diagram of a heat exchanger

The heat exchanger must meet very demanding requirements (pressure up to 6 bar, temperatures up to 90°C, aggressive organic media such as toluene, hexane/heptane and tetrahydrofuran). During the entire project, researchers were studying the chemical, mechanical and thermal resistance of polymer materials, such as polyimide (PI), polyethylene terephthalate (PET) and glass fiber enforced polytetrafluoroethylene (PTFE). Besides investigating the creep resistance of the film under the specified operating conditions, they also looked at how the foil behaves when exposed to vibration stress. Tests showed that film made of polytetrafluoroethylene and partially polyimide meets the resistance requirements if it is properly supported. Heat transfer performance was determined by experiment and numerical analysis. A simple model heat exchanger was set up in the department to run experiments on different configurations (cross-flow, counter-flow, parallel flow). Data collected during the experiments was used to validate numerical models which were then applied to the final geometry. The final experimental work consisted of heat transfer investigations on the full-scale demonstrators built by Calorplast GmbH.

Project results

During experiments with the full-scale demonstrators (see Fig. 2) overall heat transfer coefficients of up to 1000 W/m² K were achieved for the condensation process of hexane. Hence, a heat exchanger with a competitive performance was designed. Furthermore, the chemical resistance and durability of the PTFE films at operating conditions could be proven. No damages could be observed on the material after more than 1000 hours of permanent operating.

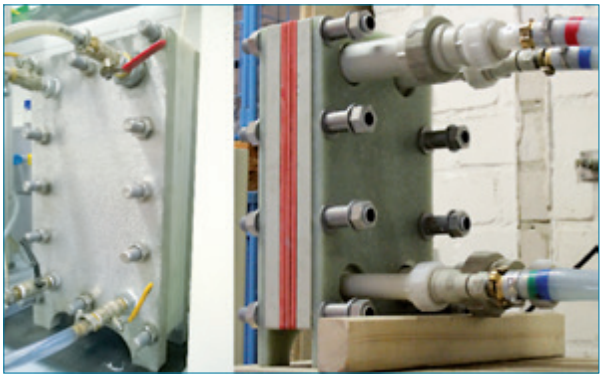


Fig. 2: Demonstrators during testing

The sealing of the heat exchanger, however, remains an unsolved challenge. For the test runs, proper sealing could only be fulfilled with the combination of PET-films and fluorinated rubber seal. A sufficient sealing could be achieved with the PTFE-film, which is the only film to match all requirements to chemical resistance.

Since the film is highly susceptible to pressure caused deformation, FSI (fluid structure interaction) was used for the numerical simulation of heat transfer. Thanks to this approach, it is possible to model the geometric changes, which take place during ongoing operation and to understand the effect, which these changes have on flow and heat. This model was successfully applied to small parts of the heat exchanger. Enormous hardware requirements of the used software, however, made it impossible to apply the model to the entire apparatus, as the very thin film and its small deformations required a non-workable amount of elements.

Seventeen student papers were completed during the project including five final degree theses. A final dissertation is expected to be completed in 2015. Information on the economic findings during the project in the area of material science, heat transfer and fluid mechanics is being shared with the public at conferences and congresses and through publications.

There is constant demand in the chemical industry for small heat exchangers, many of which are used at test centers. Polymer film heat exchangers have the advantage of lower CO_2 consumption during equipment manufacturing (theoretically up to 30 t CO_2 e/yr compared to glass heat exchangers). Other advantages include lighter weight and significantly lower material costs due to the low thickness of the heat transfer surfaces.

The defined targets (also the CO_2 reduction goals) could not be fulfilled entirely due to the unsolved sealing problem. For minor pressures (below two bar) and simple aliphatic solvents, however, the designed heat exchanger can be used. The new technology can give manufacturers a competitive edge and contribute to job security. The lower costs can also help manufacturers to reduce their equipment production costs.

Project partners:

- Technische Universität Kaiserslautern
- MERCK KGaA
- Calorplast Wärmetechnik GmbH

Contact:

Prof. Dr. Hans-Jörg Bart
Lehrstuhl für Thermische Verfahrenstechnik
Technische Universität Kaiserslautern
E-mail: bart@mv.uni-kl.de
Homepage: www.uni-kl.de/tvt

Multi-Phase – Increased Energy Efficiency and Reduced Greenhouse Gas Emissions Based on Multi-Scale Modelling of Multi-Phase Reactors

A gas and/or liquid or solid phase is dispersed in a continuous phase fluid during the production and downstream processing of many chemicals and biochemicals. Designing multi-phase reactors is a highly complex undertaking due to the complex interplay between the hydrodynamics, kinetics, substance transfer and heat transfer. It has not been possible up to this point to provide a complete numerical description of an industrial-scale scenario. Besides the amount of computing power needed to handle the large mathematical models, another limiting factor is the availability of validated models for simulating the different phenomena involved.

Most of the literature is limited to modeling of aqueous multi-phase systems with air as the dispersed phase. The derived model equations are not applicable to typical industrial substance systems in organic media at elevated temperature and pressure. To address this issue, three main goals were defined for the project.

- Develop **models and methods** for designing, or enhancing the design of, multi-phase equipment.
- Suitable **measurement techniques** are needed to provide the underlying experimental data. Development of these techniques is another aspect of the project.
- A **pilot-scale test reactor** at Evonik is used to evaluate the measurement techniques and obtain measurement data (Fig. 1).

The measurement techniques have now been developed and thoroughly tested on the pilot reactor at Evonik Industries (Fig. 2). The researchers are using the results to identify, validate and enhance suitable calculation models. The experimental data and calculation models are being archived in a web-accessible database. Other project work packages will be looking at the potential for CO_2 mitigation in an industrial process. The

Fig. 1: Pressurized bubble column at the Evonik Industries Test Center.

improved techniques for multi-phase reactor design are being implemented in CFD code.

More efficient multi-phase reactor designs can reduce greenhouse gas emissions and conserve resources, and these two factors are key economic aspects of the project. In parallel, the acquisition of new expertise can give German companies a competitive advantage in the global marketplace and help ensure job security at home. Networking between universities and industrial partners promotes intensive information sharing in both directions. The results are communicated at conferences and in trade journals on an ongoing basis. Student internships and the provision of a suitable context for Bachelor's and Master's theses and doctoral dissertations promote the development of young professionals, which is another positive aspect of the project.

Fig. 2: Testing a laser endoscope to measure bubble size

Project partners:

- Evonik Industries AG
- BRUKER OPTIK GMBH
- Eurotechnica GmbH
- ILA Intelligent Laser Applications GmbH
- PreSens Precision Sensing GmbH
- Helmholtz-Zentrum Dresden-Rossendorf e.V.
- Ruhr-Universität Bochum
- TU Hamburg-Harburg

Contact:

Dr. Marc Becker
Evonik Industries AG
E-mail: marc.becker@evonik.com

LICIL – A new Method for the Extraction of Lignin, Cellulose and Hemicellulose from Biogenic Material using Novel Ionic Liquids

The newly developed method enables the targeted isolation of cellulose, lignin and hemicellulose from hardwood and softwood and wastes from crops such as corn stalks, straw, hay, etc. in pure form. Lignin was extracted by so-called RIBIL`s (Reactive Iminium salt based Ionic Liquids), whereupon alkoxymethylene iminium salts delivered the best results. First, the pulpings were carried out in the pure IL, but in further optimization work the used amount of RIBIL (ratio of pulping material to IL in a range from 1:2 to 1:5) could be reduced to about 13% (based on the weight of the pulping material) by addition of a suitable co-solvent.

The main advantages of the novel pulping process are the reduced energy consumption compared to conventional wood pulping process and the ease of separation of the components by means of two filtration steps. The digestions are carried out at atmospheric pressure in a temperature range of 60 to 160 ° C, after which the cellulose simply is filtered off and the lignin is precipitated from the filtrate and also separated by filtration. The hemicellulose fraction is gained by concentration of the obtained filtrate.

The current state of technology allows the separation of 200-250 g lignin (low molecular weight, soluble in organic solvents), 500-600 g fibrous cellulose (containing only small amounts of lignin), 200-250 g syrupy hemicellulose and 30-50 g resins from 1 kg of spruce chips. The obtained lignin is investigated by the industrial partner Rampf Eco Solutions GmbH & Co. KG with respect to its utilization in the production of PU materials and polyesters. In addition, this partner transfers the pulping process from laboratory to industrial scale and optimizes the process and plant engineering for a large-scale industrial utilization. The second industrial partner, the JELU-WERK Josef Ehrler GmbH & Co. KG, deals with the exploitation and commercialization of the gained cellulose and hemicellulose in the polymer sector. Furthermore, some special applications in the WPC sector will be explored. Basic research investigations are performed at the HTW Aalen (synthesis and characterization of the required ionic liquids, optimization of the extraction process in laboratory scale, further work concerning the utilization of the wood fractions and a value creation thereof) and at the University of Hamburg (biotechnological issues, analysis of the starting materials and the gained wood fractions).

As part of the project three bachelor and one master thesis were performed. At the beginning of the project also a Ph.D. thesis was started, which is expected to be completed mid-2015.

Project partners:

- Hochschule Aalen
- Universität Hamburg
- Rampf Eco Solutions GmbH & Co. KG
- JELU-WERK Josef Ehrler GmbH & Co. KG

Contact:

Prof. Dr. Willi Kantlehner
Hochschule Aalen
E-mail: willi.kantlehner@htw-aalen.de

Valery – Energy-Efficient Synthesis of Aliphatic Aldehydes from Alkanes and Carbon Dioxide: Valeraldehyde from Butane and CO_2

Utilization of CO_2 in the production of high value-add products cycles the greenhouse gas back into the value-add chain and creates access to an alternative non fossil fuel based C1 carbon source. Carbon dioxide is an attractive building block for chemical syntheses. It is available at low cost and supplies are virtually unlimited.

However, CO_2 is relatively inert, and conversion to high value-add products presents a big challenge. There are, however, some examples which demonstrate the feasibility of utilizing CO_2 on an industrial scale.

The vision of the Valery project is to develop new feedstock sources for the chemical industry. The researchers are looking in particular at CO_2 and alkanes as alternative carbon sources for industrial-scale production of high value-add products. The specific objective is to find an alternative process to replace conversion of olefins and carbon monoxide (CO) into aldehydes by hydroformylation. Carbon dioxide (CO_2) will be substituted for toxic carbon monoxide, and energy-efficient dehydrogenation of alkanes will provide the source of olefins. The researchers have chosen synthesis of valeraldehyde from n-butane as an example.

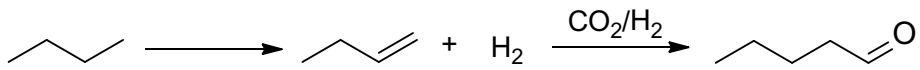


Fig. 1: Energy-efficient syntheses of valeraldehyede from butane and CO_2.

During the course of the project, the researchers have been able to reproduce results described in the literature, and they have also been able to improve on those results through specific optimization. In the case of hydroformylation using CO_2, introduction of a new ligand class has increased throughput and improved selectivity. In the case of energy-efficient dehydrogenation, selectivity performance was greatly improved. In addition, a suitable combination of two ionic fluids and a substrate material was used to stabilize the

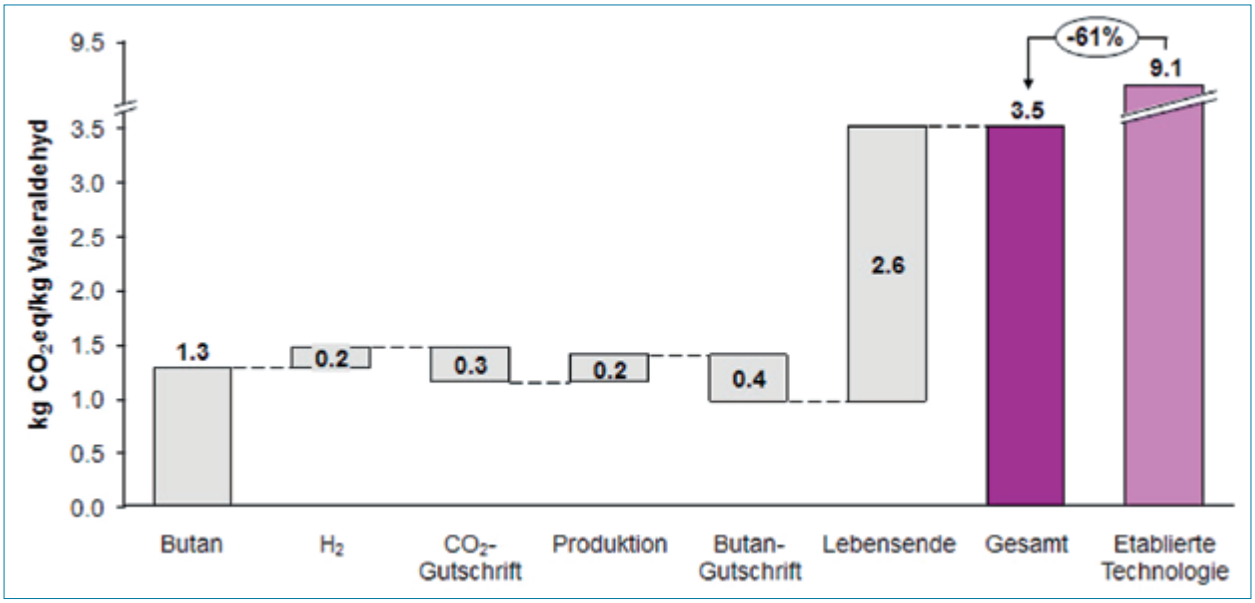


Fig. 2: CO_2 footprint of the new process compared to established technology.

hydroformylation catalyst system. Besides carrying out a detailed investigation of both reactions, the researchers were able to run energy-efficient dehydrogenation in a semi-continuous reactor setup. In the case of hydroformylation using CO_2, the reaction could be run continuously with the immobilized catalyst system.

In parallel with the chemical investigations, an economic and environmental evaluation was carried out on energy-efficient synthesis of valeraldehyde from butane and CO_2. Economic analysis shows that the use of CO_2 and butane as alternative feedstock for aldehyde production can reduce feedstock cost by up to 47%. Utilization of CO_2 and butane increases feedstock flexibility and provides a secure source of aldehydes which are a key intermediate in plasticizer synthesis. Looking at the environmental impact, the CO_2 footprint was estimated and compared with the established technology. Cradle-to-grave analysis of CO_2 emissions shows that energy-efficient synthesis of olefins and subsequent hydroformylation using CO_2 can reduce the carbon footprint of valeraldehyde by up to 61% compared to established technology.

Project partners:

- Evonik Industries AG
- Universität Bayreuth
- Leibniz-Institut für Katalyse e.V. an der Universität Rostock

Contact:

Dr. Daniela Kruse
Evonik Degussa GmbH
Creavis Technologies & Innovation
E-mail: daniela.kruse@evonik.com

HyCats: New Catalysts and Technologies for Solar Chemical Hydrogen Production

The goal of the HyCats project was to develop photocatalytic water splitting technology to harness solar power for climate-neutral production of hydrogen. As photocatalysts, the team used semiconductors in suspension or in layered systems which produce hydrogen from water when they are exposed to sunlight in suitable solar reactors. Because existing photocatalytic systems were not economically viable, the team set out to provide scalable technology as a basis for development of marketable solar chemical systems for the production of hydrogen. The project delivered a toolbox which supports rapid development of economically viable photo-electrochemical hydrogen production systems. The toolbox consists of the following.

- Quantum chemistry simulation tools for calculating band gaps, doping effects and surface reactions
- Spectroscopic techniques to achieve an
- understanding of the mechanisms involved
- High throughput synthesis and activity measurements using a rapid screening system integrated into a synthesis robot
- Production techniques for upscaling
- photocatalyst synthesis
- Photocatalyst activity tests for photocatalyst suspensions and electrodes in different types of reactors
- SoCRatus (Solar Concentrator with a rectangular Flat Focus) test bed
- Economic viability evaluation

The thermodynamic stability, electronic structure and effect of substituents on the light absorption shift into the visible spectrum were calculated for different photocatalysts using quantum chemistry modelling based on density functional theory (DFT). The team investigated doping effects and water adsorption on the surface of the solid-state bodies and developed a semi-empirical method for calculating optical excitation spectrums of solid-state bodies. In some cases, disassociation of the adsorbed water was observed, which is the first step in the water splitting reaction. The researchers applied spectroscopic techniques to investigate the photocatalytic water splitting mechanism in the presence of sacrificial agents. They were able to identify the best catalysis to promote the formation of molecular hydrogen and molecular oxygen. Time-resolved laser pulse photolysis studies enabled the team for the first time to identify intermediary oxygen radicals during water oxidation and study their subsequent reaction kinetics in detail. They developed a synthesis robot with integrated rapid screening system (photo reactor with a gas chromatograph attached) for high throughput production and rapid testing of photocatalysts. The team prepared and tested approximately 620 tantalate and niobate based samples using a variety of synthesis techniques. The most promising photocatalysis were optimised under for conditions analogous to those in a production environment. The researchers analyzed the influence which different scalable production methods and parameters have on the physical properties, and hence the hydrogen formation rate, of the photocatalysts. A number of different co-catalysts were also tested. Successful test results for hydrogen production using particulate systems and electrodes were obtained with three different types of reactors. The solar efficiency and economic viability of various catalysts were evaluated. A solar concentrator test bed (SoCRatus=Solar Concentrator with a Rectangular Flat Focus) was set up and a suspension reactor with two separate reaction chambers along with the appropriate instrumentation was placed into operation. For parallel testing, the suspension reactor was mounted next to a photoelectrochemical cell in the focal plane of the SoCRatus.

Hydrogen produced using renewable resources can make a major contribution to climate protection in a wide range of applications such as conversion of CO_2 to hydrocarbons, fuel for domestic energy supply or vehicle fuel cells. Compared to other known renewable-based techniques, solar chemical production of hydrogen has the advantage of much simpler process technology, because water is split in a single low-temperature reactor. This can be an advantage in distributed applications. Hydrogen for domestic heating systems or fuel cells could be supplied under ideal conditions with simplified infrastructure. Hydrogen produced on a large scale at industrial solar parks could

be stored and distributed as an alternative to natural gas. Another objective of the HyCats project was to provide career development opportunities for young scientists. 3 Bachelor's Theses, 2 Master's Theses and 3 doctoral dissertations directly related to the project work were completed, two other doctoral dissertations were started which are expected to be completed next year and work done on a Bachelor's Thesis supported the commissioning of a reactor.

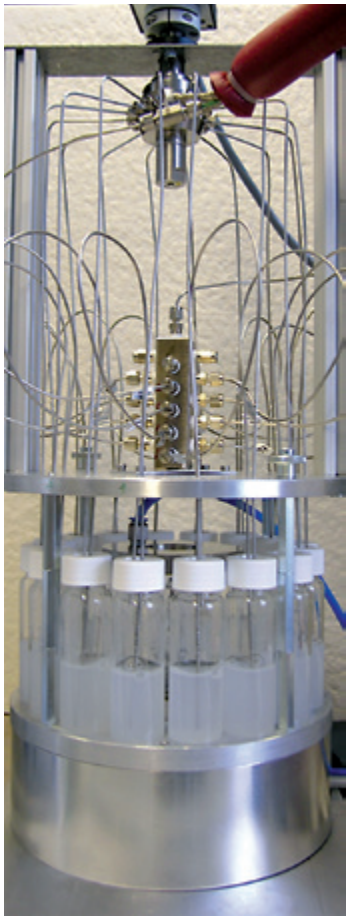


Fig. 1: Rapid screening system for parallel testing of photocatalysts

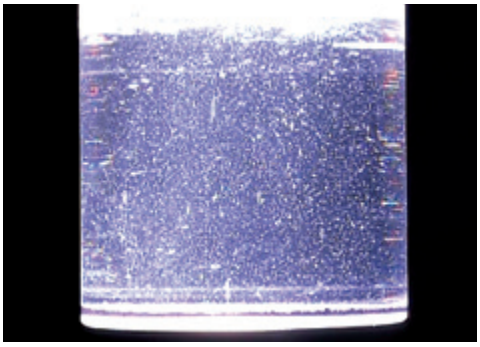


Fig. 2: Hydrogen bubbles rise during a photocatalyst lab test

Fig. 3: Solar reactor at DLR in Cologne

Project partners:

- H.C. Starck GmbH
- Leibniz Universität Hannover
- Leibniz-Institut für Katalyse e.V.
- Deutsches Zentrum für Luft- und Raumfahrt e.V.
- Universität Bonn
- ODB-Tec GmbH & Co. KG
- Zinsser Analytic GmbH

Contact:

Dr. Sven Albrecht
H.C. Starck GmbH
E-mail: sven.albrecht@hcstarck.com
Homepage: www.hcstarck.com

EffiCO_2 – New Absorbents for More Efficient CO_2 Separation

Worldwide anthropogenic CO_2 emissions resulting from the use of fossil resources were estimated at 34 Gt in 2011 (German Ministry of Economics and Technology, 2013). Fossil fuel will continue to be our major source of energy in the future (BP, 2013). In order to reduce CO_2 emissions despite rising energy demand, technologies are needed for efficient CO_2 capture from industrial and other waste gas streams. CO_2 capture from flue gas can make an important contribution. However, efficiency losses during CO_2 capture from power station flue gas can currently be as high as 12%. The goal of the consortium project was to conduct research on new and improved absorbents for carbon capture to reduce energy and resource consumption. The project deliverables also included a demonstration of the efficiency gains through simulation of the entire power station and CO_2 capture process and lifecycle assessments to evaluate the sustainability of the new processes. All substance classes in the Evonik product portfolio were included during development of chemically stable absorbents which require less energy for regeneration. The researchers used synthesis techniques to modify the absorbents at the molecular level. They then conducted lab studies to analyze the CO_2 absorption behavior and thermodynamics. A test system connected to the flue gas stream at the coal-fired CHP

Fig. 1: Test system following detailed engineering

Fig. 2: Test system in the chimney base at the power plant in Herne

plant in Herne gave the researchers the opportunity to study the absorbents under real-world conditions. Only the most promising absorbents were included in the test system trials. The team collected thermodynamic and process engineering data and analyzed and evaluated the ability of the absorbents to withstand secondary constituents in the flue gas.

Based on the results of lab and test system trials, a simulation was run to see how the absorbents would perform in a large-scale power station process and to assess the economic viability. The simulation showed that energy consumption could be reduced by around 40% compared to existing CO_2 absorption using monoethanolamine. This equates to a reduction in CO_2 emissions of approximately 120 kg CO_2/t CO_2. At the reference power plant, the emissions reduction potential exceeds 240,000 t CO_2e/a.

The technology is not limited to flue gas applications. It could also be used, for example, in natural gas upgrading, chemical production, cement and lime manufacturing and the iron and steel industry. Besides efficient CO_2 capture, it also provides access to high-purity CO_2 which can be used for high value-add products. The consortium project ended on September 30th, 2013.

Project partners:

- Evonik Industries AG
- Universität Erlangen-Nürnberg
- Universität Duisburg-Essen

Contact:

Dr. Jens Busse
Evonik Industries AG
E-mail: jens.busse@evonik.com

OPHINA – Organophilic Nanofiltration for Energy-Efficient Processes

Avoidance of CO_2 emissions is a key element in a broad-based strategy to reduce greenhouse gases. Finding substitutes for fossil fuel is one option. Reducing consumption of energy which is largely fossil-based can be another major factor in CO_2 mitigation. Optimization of process energy efficiency can make an important contribution to CO_2 avoidance.

Solvents are often used in the chemical industry. It can take a lot of energy to recover the solvents at the end of the process. Energy-efficient recovery can significantly reduce process CO_2 emissions. Organophilic nanofiltration is one such technology, because in contrast to thermal separation it works without heat. The goal of this project was to develop technology for producing OSN (organophilic solvent nanofiltration) membrane modules. Reproducibility and consistent high quality were two of the key deliverables for the new module production process. The solvent stability, permeate flux, rejection (selectivity) and long-term mechanical stability of the modules have to meet industrial-grade standards. To improve on commercially available membranes, the project team developed membranes which have a high-selectivity silicon-based filtration layer on a cross-linked polymer backing. The membranes were optimized to meet the requirements profile of industrial users (Evonik Industries, Bayer Technology Services and BASF Personal Care & Nutrition). The researchers were also able to develop a range of membranes with different cut-off values. Two module generations were developed. Project partners carried out feasibility studies on flat sheets and additionally spiral-wound modules were also produced and made available to the partners.

The chemical resistance of the material composite in the spiral-wound modules was evaluated using process solvents. The results showed that the resistance of the membrane material guarantees good resistance of the module. The measurement results obtained by the project partners were forwarded to RWTH Aachen for modelling of mass transport through the membrane and in a spiral-wound module.

Following the module development phase, the product carbon footprint of the membrane module was calculated. This data can be very helpful to customers who use the modules in their production operations and want to carry out a complete lifecycle assessment for their products.

A number of different OSN applications were identified during trials which were conducted by the project partners.

Fig. 1: Photo of a spiral-wound module

The cost-effectiveness of the OSN applications was carefully scrutinized, because low membrane flux performance can result in high investment costs for large membrane surfaces. However, the use of OSN in the process can also have other advantages besides a reduction in recycling costs and CO_2 emissions. Recovery with OSN membranes can enhance product purity and product quality and reduce thermal stress on the products. The consortium project ended on April 30th, 2013.

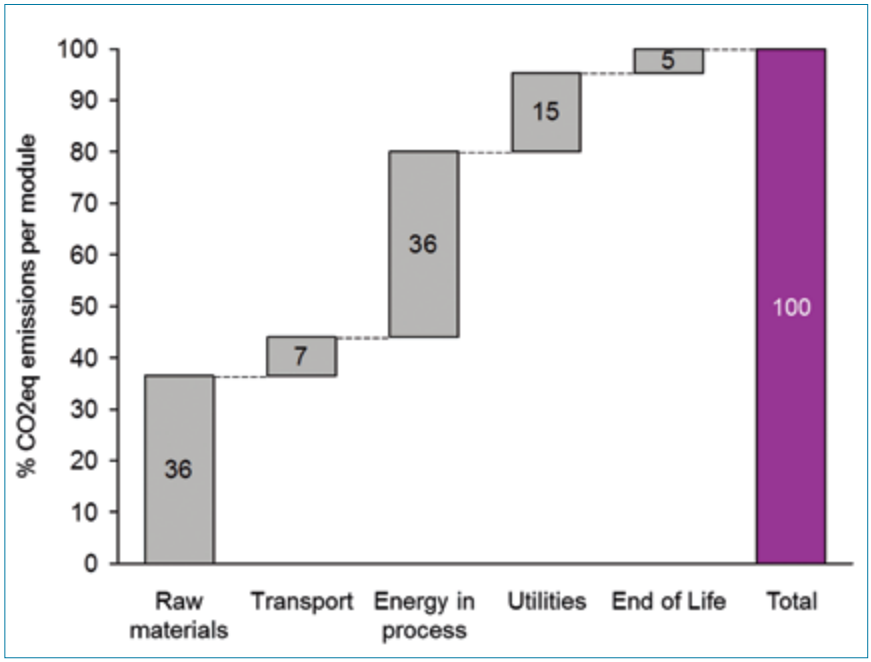


Fig. 2: Contribution of a spiral-wound module to the product carbon footprint broken down by class.

Project partners:

- Evonik Industries AG
- Bayer Technology Services GmbH
- BASF Personal Care and Nutrition GmbH
- RWTH Aachen

Contact:

Dr. Daniela Kruse
Creavis Technologies & Innovation
Evonik Industries AG
E-mail: daniela.kruse@evonik.com

IL WIND – Development of IL-Based Lubricants for Wind Turbines

Project goal

As the rated capacity of wind turbines continues to increase, the designs place greater specific stress on all of the subsystems. The rolling bearings are particularly susceptible to failure which is often caused by inadequate lubrication. The primary failure mechanism damages the microstructure, resulting in early failure. This significantly reduces the availability of the wind turbines. The economic and environmental benefits decrease, and there is a negative impact on the overall CO2 cycle.

The goal of the IL Wind project is to develop high-efficiency IL-based lubricants which are capable of neutralizing the damage mechanism. Higher system availability decreases the cost and increases the environmental benefits of wind power generation, particularly on multi-megawatt turbines.

The consortium partners took responsibility for different aspects of the overall development effort. The University of Erlangen-Nürnberg provided basic scientific support. Responsibility for engineering feasibility was placed in the hands of industry partners Merck and Schaeffler Technologies, with consultancy provided by the end user Senvion SE (formerly REpower Systems).

Project status

The research team on the IL WIND project developed halogen-free ionic liquids (ILs) with a target solubility of 5 wt% in petroleum-based oil and evaluated their thermal properties. COSMO-RS was used to help identify the required structural elements of the ILs. The tribologic properties (friction and wear surfaces) of the ILs in contact with 100Cr6 steel in air, argon and CO2 atmospheres were assessed and compared with standard oils. The corrosion behavior of the ILs was also evaluated using six different metals and alloys.

The researchers conducted screening trials to demonstrate the tribologic suitability of the structures for subsequent rolling bearing trials. A basic test bed was set up which uses IR spectroscopy for in situ investigation of the damage mechanism.

Fig. 1: Rolling bearing (© Schaeffler Technologies GmbH & Co. KG)

Fig. 2: Wind turbine (© Senvion SE)

The IL additive was shown to be effective in preventing damage during rolling bearing trials at Schaeffler. Adding just 1% of the IL substance to a reference oil resulted in a four-fold increase in runtime to failure. Lubrication trials were run to further demonstrate the basic tribologic properties of the new lubrication formulation prior to release for scale-up of the formulation to 1,000 liters by Merck. This quantity was sufficient to run extended testing with large bearings, which was completed after 3,000 hours without damage. The trials demonstrated the basic suitability and damage prevention potential of the bearing lubricant.

Economic, environmental and societal leverage effect

Early bearing failure on wind turbines reduces the supply of CO2-free power and the expected environmental and economic benefits. The excellent tribologic properties and intrinsic conductivity of the lubricant with IL additive which was developed on the IL WIND project inhibits the bearing failure mechanism and prevents turbine downtime.

Less conventional fossil-based fuel is needed to compensate for the loss of generation capacity.

The intention is to run field verification trials and continue development of the lubricant right up through market introduction

The project outcome would of course not have been possible without productive collaboration between industry and the university. 10 Bachelor's theses, 4 Master's theses and four doctoral dissertations were completed during the project.

Project partners:

- Merck KGaA
- Schaeffler Technologies GmbH & Co. KG
- Friedrich-Alexander-Universität Erlangen-Nürnberg

Associated Partner:

- Senvion SE

Contact:

Prof. Dr. P. Wasserscheid
Friedrich-Alexander-Universität Erlangen-Nürnberg
Lehrstuhl für Chemische Reaktionstechnik
E-mail: wasserscheid@crt.cbi.uni-erlangen.de

SIT – Utilization of Low-Calorific Industrial Heat by Means of Sorption Heat Pump Systems using Ionic Liquids and Thermochemical Accumulators (SIT)

Project goals and content

Large volumes of heat are constantly being released by German industry into the surroundings without being used, either because the heat temperature is too low or there is no need for the heat at the time when it is available. In recent years particularly in the chemical industry, the deployment of heat integration technology at integrated sites has increased production energy efficiency to the point where further improvement will not be possible without the introduction of innovative technology.

Additional heat flows can only be utilized by bringing them up to a useable temperature with the aid of a heat pump. High-density chemical heat storage can be used to store the higher-temperature heat and make it available on demand in the form of thermal energy, significantly reducing primary energy consumption and greenhouse gas emissions.

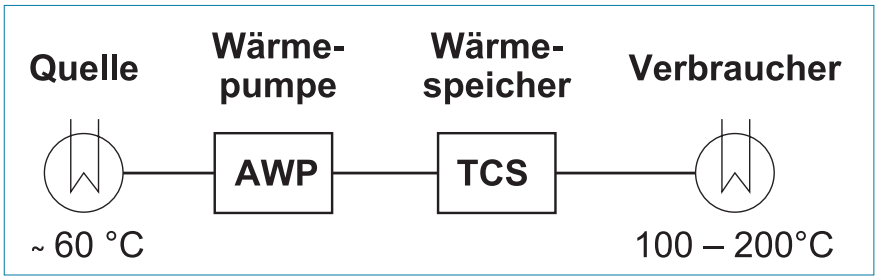


Fig. 1: Scenario for utilizing low-calorie industrial waste heat.

New working fluid pairs based on ionic liquids are being developed for absorption heat pumps. By tailoring suitable ternary working fluid pairings, it is possible to enhance overall performance and create advantages compared to conventional working fluid pairings. Process engineering assessment and validation are carried out using pilot-scale heat pumps as well as commercially available heat pumps.

In order to develop a thermo-chemical heat storage system with high energy storage density, the researchers are working to identify and evaluate suitable reaction systems. A reactor design is being developed which is optimized for these materials and is suitable for this heat pump – heat storage combination. Development of a pilot-scale heat storage system will provide the basis for commercial upscaling at a later date.

Project status

The project came to an end on October 31st, 2013. Two different working fluid pairings were identified for use in absorption heat pump systems. These pairings are suitable for different temperature ranges. The systems have been used successfully on a demonstration-scale and in commercially available absorption heat pump systems. Lifecycle analysis was carried out for production of an ionic liquid based working fluid pairing which reduces resource and energy consumption compared to conventional working fluid pairings. Possible storage materials were evaluated for use in chemical heat storage systems, and lab-scale testing was carried out on a material which the researchers identified. They also identified and tested various reactor designs for a chemical heat storage system. Important knowledge was gained during the project, which provides a foundation for further development of full-scale chemical heat storage systems. A carbon footprint estimate derived from the research results provides a basis for gauging the possible reduction in CO_2 emissions and resource consumption.

Economic, environmental and societal leverage effect

As of 2007, 406 TWh of waste heat potential was available each year at industrial sites in Germany alone. If this potential were exploited, it would be possible to reduce primary energy consumption and greenhouse gas emissions and also save money. That would give Germany a competitive advantage as a business location

and generate long-term growth in the country. Development of thermochemical heat storage systems is still at an early stage and it is not yet possible to operate an absorption heat pump and heat storage system in combination at full scale. The work done during the project did however demonstrate that this technology could create opportunities to reduce CO_2 emissions.

Close collaboration between university research organizations and industrial partners created opportunities to align innovative research with application-related needs. Young scientists involved in the project completed 4 doctoral dissertations and a number of Bachelor's and Master's theses.

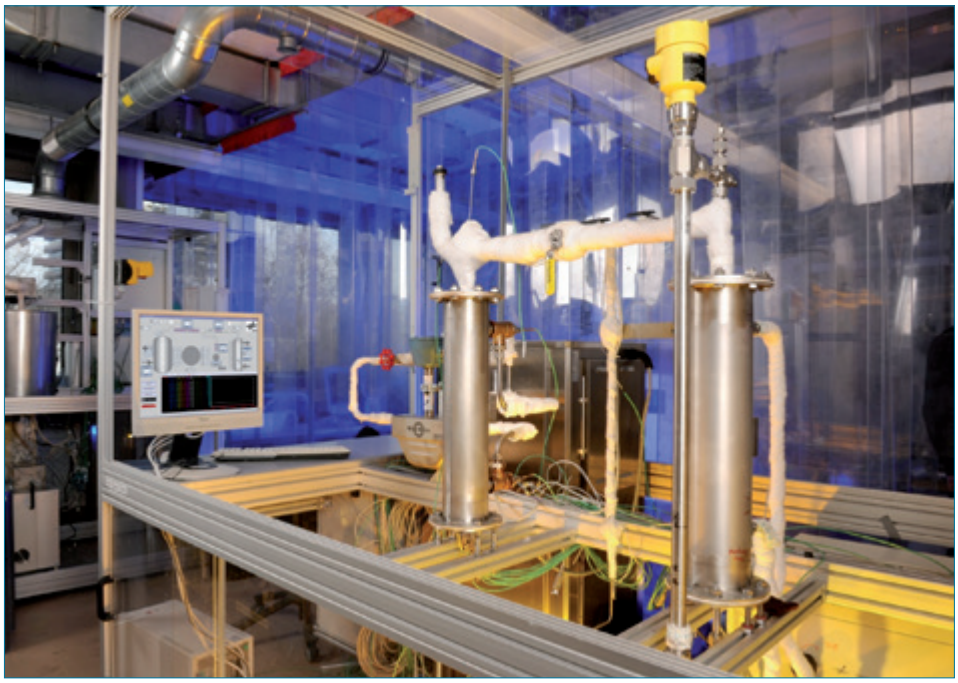


Fig. 2: Chemical heat storage test system (Source: DLR e.V.)

Project partners:

- Evonik Industries AG
- Friedrich-Alexander-Universität Erlangen-Nürnberg
- Deutsches Zentrum für Luft- und Raumfahrt e.V. (DLR)
- GasKlima GmbH

Contact:

Dr. Jens Busse
Senior Project Manager
CREAVIS – Science to Business
Evonik Industries AG
E-mail: jens.busse@evonik.com

EE Management – Energy Efficiency Management and Benchmarking for the Process Industry

The ability to improve energy efficiency has long been a major competitive factor in the chemical industry. In addition, a reduction in greenhouse gas emissions is becoming an increasingly important aspect of sustainable climate protection policy. Besides finding ways of improving energy efficiency, one of today's major challenges is to minimize energy consumption and greenhouse gas emissions as soon as possible using technologies which are sustainable over the long term. Power generation and distribution obviously need to be optimized. Beyond that, often the most effective strategy is to maximize energy efficiency in production. Possible pathways for achieving that include operating parameter enhancements, equipment optimization, interconnection of heat flows and process engineering improvements.

More and more companies are using energy management systems to track and control energy consumption, set energy goals and identify opportunities to save energy. The diversity of process technologies and energy sources, the lack of benchmarks and quite simply the definition and measurability of energy efficiency often create unsurmountable obstacles which reduce the utility of these systems.

The *STRUCTese*® energy management system developed by Bayer to facilitate continuous, sustained maximization of energy efficiency forms the basis of the project. In contrast to conventional energy management systems, *STRUCTese*® not only reports and tracks (specific) energy consumption over time, it also compares specific primary energy consumption to various theoretical optima. The losses (actual vs. optimum) caused by suboptimal equipment, partial load, the product mix, external factors and suboptimal operation are presented in a clear and transparent manner. Using this approach, energy efficiency becomes measurable. *STRUCTese*® provides an optimization pathway and removes the obstacles mentioned above.

Advanced development work is being done on the project to transform the method into a standardized energy efficiency management and benchmarking tool which many companies can use for different process scenarios. The method was implemented in a number of real-world processes and enhanced so that it can model a very broad spectrum of process scenarios, e.g. parallel production lines, production of multiple products and batch-continuous transitions. The researchers worked closely with universities to define the theoretical optima. They did this to ensure that the bench-

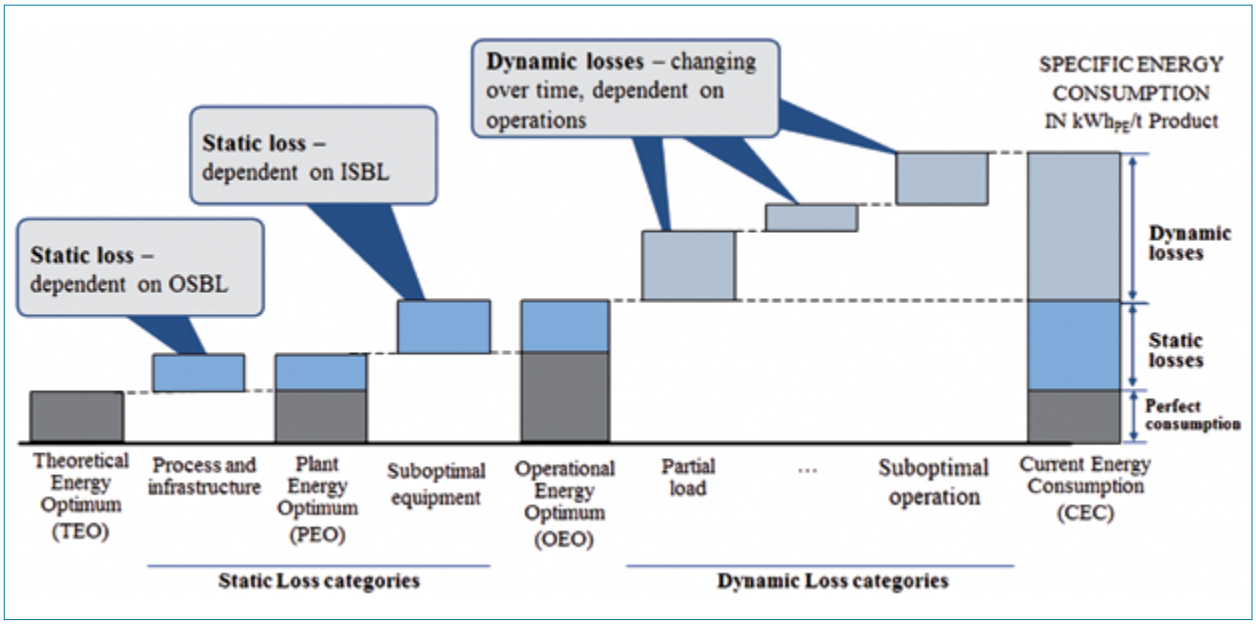


Fig. 1: Energy loss cascade

marks have been objectively defined and that they are based on the most advanced techniques from the world of science and technology. The project demonstrated that the method can be applied across an entire site. Case studies have shown that an intelligent management system can reduce energy consumption by more than 20%. The system has already helped Bayer save more than 1 million MWh of primary energy and reduce CO_2 emissions by a good 300,000t /yr.

Project partners:

- Bayer Technology Services GmbH
- Bayer MaterialScience AG
- BASF Personal Care and Nutrition GmbH
- Inosim Consulting GmbH
- instrAction GmbH
- bitop Aktiengesellschaft (bitop AG)
- RWTH Aachen
- Technische Universität Dortmund
- Clariant Produkte (Deutschland) GmbH

Contact:

Dr. Christian Drumm
Bayer Technology Services GmbH
E-mail: christian.drumm@bayer.com

Published by
Bundesministerium für Bildung und Forschung/
Federal Ministry of Education and Research (BMBF)
Division Resources and Sustainability
53170 Bonn
Germany

Orders
In writing to
Publikationsversand der Bundesregierung
P.O. Box 48 10 09
18132 Rostock
Germany
E-mail: publikationen@bundesregierung.de
Internet: http://www.bmbf.de
or by
Phone.: +49 30 18 272 272 1
Fax: +49 30 18 10 272 272 1

April 2015

Printed by
Seltersdruck GmbH, Selters

Layout
PM-GrafikDesign, Peter Mück, Wächtersbach

Photo credits
Front cover: Thinkstock; Page 3: Bundesregierung/Denzel

Page 5: Porträt Prof. Dr. Johanna Wanka,
Presse und Informationsamt der Bundesregierung, Steffen Kugler

Edited by
Dipl.-Ing. Dennis Krämer, DECHEMA
Dr. Stefanie Roth, Project Management Jülich | Forschungszentrum Jülich

www.bmbf.de