CO$_2$ as a building for the polyurethane plastics industry

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Pre-read information
CO$_2$ as a building block for polymers

Target product polyurethanes

- Reduced need for fossil resources
- Direct use of CO$_2$ to build polymers
- Avoided CO$_2$ emissions – lower Carbon Footprint
Impact on sustainability
Conservation of resources

- Contributes to resource efficiency by saving petroleum-based raw materials
- New process fundamentally more environmentally compatible than conventional production
- Carbon footprint reduced compared with conventional product
Sleeping on CO$_2$
The new way to flexible foam

- Innovative technology enables production of flexible foam
- Initially conceived for use in mattresses
- Up to 20% CO$_2$ incorporated into foam precursor polyol
- CO$_2$ permanently chemically bound in polyol and polyurethane foam
- Quality at least on par with conventional material based on oil
Scientific breakthrough
Special catalyst found after 40 years

“Open innovation” approach: Collaboration and network as key success factors
Mini-Plant: State-of-the-art reaction engineering

- Construction and operation of a mini-plant
- Upscaling
- Sample production for material trials
- State-of-the-art safety and technology
- Typical development time > 5-7 years
From semi-batch operation to a safe continuous process

SUCCESSFUL REACTION ENGINEERING: ALL OPERATION MODES IMPLEMENTED

*CAOS: continuous addition of starter
**CO₂-based polyurethanes**
Sustainable value materials

Materials with excellent properties – new polyols for industry standard foams

- First end-consumer product: mattresses
- Availability from 2016, 5,000 t/y production capacity
- New industry standard
- Significant improvement in terms of LCA – lower carbon footprint
New CO$_2$-based polyols - targeting the largest market segment: Flexible Foam

**Total PUR market: 13.3 Mio. t**

- **Flexible Foams** ~ 40%
- Rigid Foams ~ 30%
- Coatings ~ ~ 14%
- Elastomers ~ ~ 9%
- Adhesives ~ ~ 4%
- Binders ~ ~ 3%
- Sealants ~ ~ 2%

**Global Flexible Foam Polyol Market (2012)***

* Estimate based on IAL studies
Results of slabstock quality evaluation show excellent foam stability and properties

- No difference in thermal sensitivity
- CO₂ is chemically fixed inside the polyurethane backbone
- Thermal foam stability matches that of conventional polyols

- Machine foam trials show products with properties on the same level or even better than conventional polyurethanes
Impacts on Climate Change

kg CO₂-eq / kg polyol

Conventional polyol

CO₂-based polyol

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

Niklas von der Assen and André Bardow, _Green Chem._, 2014, 16, 3272-3280
Sleeping on CO$_2$

First products on the market

- Industrial production of CO$_2$-based polyols since 2016
- First customers supplied with new product – cardyon™
- Production facility at Dormagen site near Cologne, Germany
- Production capacity: 5,000 metric tons per year
- CO$_2$ sourced as a waste product from adjacent chemical plant
Sleeping on CO₂
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Effect of CO$_2$ in TPU fibers
Carbonate groups contribute to elasticity and fiber quality

- CO$_2$ based TPU fibers available for the first time
- TPU based on cardyon™
- Process uses melt spinning
- No solvents involved, high productivity
- Technical scale established (monofilament & multifilament) Further up-scaling in development
- Filament properties for some specific applications achieved
Effect of CO$_2$ in TPU fibers

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The next development stage - Cross-linkable CO₂ PETs

- Polyols with up to 25 percent of CO₂ incorporated
- Only few % of double bonds needed
- Properties and materials go beyond classical polyurethane applications
- New areas for the use of CO₂ based materials accessible
Concept of unsaturated CO$_2$-polyurethanes
From CO$_2$-polyols via polyurethanes to sustainable elastomers

**Polyols**
- Cross-linkable Polyether carbonate diols
  - Unsaturated CO$_2$-Polyether polyols based on PO
  - 50 kg per batch
  - Conti-process

**Polyurethanes**
- Cross-linkable CO$_2$-based Polyurethanes
  - Chain elongation of with Isocyanates
  - $\rightarrow$ x-linkable ‘PECUs’
  - Scale-up

**Elastomers**
- Elastomers
  - Standard formulation and processing to elastomers
  - Near drop-in for ‘non-PU commodities’
  - Benchmarks
The next development stage -
From CO$_2$-polyols via polyurethanes to sustainable elastomers

Polyols

Cross-linkable Polyether carbonate diols

Polyurethanes

Cross-linkable CO$_2$-based Polyurethanes

Elastomers

- Standard formulation and processing to elastomers
- Near drop-in for ‘non-PU commodities’
- Benchmarks
A new partner for CO$_2$
Bringing ethylene oxide into play

• Covestro successfully developed a process to produce polyols on the basis of propylene oxide (PO) and CO$_2$
• Now a publically funded project is focussing on the reaction of ethylene oxide (EO) and CO$_2$
• By bringing EO and CO$_2$ together, polyols for a broader range of applications can be made
• The aim is to substitute up to 20% of fossil based feedstocks in polyols
• Lab scale process is in development
### Conventional Polyurethane (EO)

<table>
<thead>
<tr>
<th>EO</th>
<th>$\text{R-OH}$</th>
<th>$\text{R}-\text{O} \text{-C} \text{H}_2\text{OH}$</th>
<th>$+$</th>
<th>$\text{O} = \text{C} = \text{N} - \text{R}$</th>
<th>$\rightarrow$</th>
<th>$\text{R}-\text{O} \text{-C} \text{H}_2\text{OH} \text{-N} - \text{R}'$</th>
</tr>
</thead>
</table>

| Polyol | $+$ | Isocyanate | $\rightarrow$ | Polyurethane |

### EO Based Polyurethane

| EO | $+$ | CO$_2$ | R-OH | $\rightarrow$ | $\text{R} - \text{O} \text{-C} \text{H}_2\text{OH}$ | $+$ | $\text{OC} = \text{N} - \text{R}$ | $\rightarrow$ | $\text{R} - \text{O} \text{-C} \text{H}_2\text{OH} \text{-N} - \text{R}'$ |

| EO Based Polyurethane | $+$ | CO$_2$ | R-OH | $\rightarrow$ | $\text{R} - \text{O} \text{-C} \text{H}_2\text{OH}$ | $+$ | $\text{OC} = \text{N} - \text{R}$ | $\rightarrow$ | $\text{R} - \text{O} \text{-C} \text{H}_2\text{OH} \text{-N} - \text{R}'$ |
Driving, cooling, cleaning with CO₂
Different applications are conceivable

- Combination of the novel EO/CO₂ polyols with isocyanates yield polyurethanes for rigid or molded foams
  - Application in car seats and insulation boards possible
- Furthermore the EO/CO₂ materials are promising candidates for non-ionic surfactants
  - These can be found in laundry detergents or shampoo
  - EO/CO₂ material show enhanced sustainability
Building blocks available from CO$_2$

pFA - A sustainable building block

- Paraformaldehyde has a lower carbon footprint than conventional polyol building blocks like ethylene oxide or propylene oxide
- Paraformaldehyde is based on the precursor methanol – becoming a resource independent feedstock
- Traditionally, methanol is gained from natural gas
- And there are also alternative routes: either from CO$_2$ and hydrogen or from biomass
A sustainable alternative
Paraformaldehyde – a new building block for polyols

- CO₂ or biomass can already be used as new components for polyurethanes
- Now Covestro and partners are expanding the portfolio: paraformaldehyde (pFA) is under investigation as new building block in polyols
- Paraformaldehyde is based on resource independent methanol – always lower carbon footprint than conventional polyol building blocks
- Successful lab scale process, technical implementation is underway
CONVENTIONAL POLYURETHANE (PO)

PO → R-OH

Polyol + Isocyanate → Polyurethane

pFA BASED POLYURETHANES

PO + pFA → Polyol + Isocyanate → Polyurethane
Direct and indirect use of CO₂
Close cooperation between academia and industry

pFA production
Polyol synthesis
Material tests

Ecological evaluation
Process support & evaluation
Turning the right screws
Process design for a new class of polyols

- Refined reaction conditions to use the intact pFA building block as reactant in polyol synthesis
- Up to 40% of the conventional oil-based feedstocks are substituted by pFA
- Reduction of global warming impact by at least 10% compared to conventional polyols
- Novel pFA-based polyols are thermally stable and show similar behavior as conventional polyols
Turning the right screws
Process design for a new class of polyols

- Refined reaction conditions to use the intact pFA building block as reactant in polyol synthesis
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Preliminary results for climate change:
Data for polyol with 22.5% FA; molecular weight 2000 g/mol; starter pFA 450 g/mol; functionality F=2
Doing sports with pFA
A wide range of possible applications

- Thermoplastic polyurethanes (TPU) are in the focus as applications of pFA based polyols
- TPUs can be found in sporting goods such as skiing boots or sneakers
- First application tests have been accomplished
- In addition, rigid foam applications are targeted e.g. insulation boards
Selected reading

Low-Carbon Process Industries Through Energy Efficiency and Carbon Dioxide Utilisation

A study in support of a DG Research & Innovation Projects for Policy (P4P) report


Pages 9 ff.
Dream projects for higher carbon productivity

A timeline for R&D and investments

- **CO₂ Foam**
  - 2010 Lab plant
  - 2011 Miniplant

- **CO₂ Rubber**
  - 2016 Industrial plant

- **CO₂ Fiber**
  - 2016 Industrial plant

- **CO₂ Detergent**
  - 2016 Industrial plant

- **CO₂ Rigid foam**
  - 2016 Industrial plant
  - 202X World scale plant

**Timeline**

- **2007**
  - Dream Reactions
  - CO₂ Chemistry
  - CO₂/pFA/CO

- **2012**
  - Dream Production
  - Dream Products
  - Dream Polymers

- **2017**
  - Dream Resource
  - Production Dreams
  - Dream Polyols

- **2022**
  - Carbon4PUR

**Projects**

- Dream Resource
- Production Dreams
- Carbon4PUR
- Dream Polyols
- Dream Polymers
- Dream Products
- Dream Production
- CO₂ Chemistry
- CO₂/pFA/CO
- Dream Reactions
- CO₂ Chemistry
- CO₂/pFA/CO

**Expertise**

- Building up research
  - Competence phase

- Expertise and process
  - Know how

- CO₂ and CO₂ Chemistry
  - Industrial experience

**Further C₁ projects to come**

- Upscaling
- Expertise and process
  - Know how
- CO₂ and CO₂ Chemistry
  - Industrial experience

**Additional Information**

- NSF Presentation
- Building up research
  - Competence phase
- Expertise and process
  - Know how
The dream goes on …
… more products to come

- A series of consecutive projects helped and needed to get one topic going
- Typical development time around 7 years
- The dream turned into reality

Our vision

- Make polyurethanes more sustainable – with very good product properties
- A broad range of applications with CO₂ based PU materials will be available

Summary
Thank you

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1. Evaluate the major technical challenges associated with increasing the commercial viability of carbon utilization (CU) technologies
   a. What are the primary limitations to the specific CU technologies? Consider technical issues separately from social and political factors.
   b. What is the potential scale of this CU technology?
   c. What boundary conditions are you considering when determining the scale of a given CU tech?
   d. How “ready” do you see CU technology and at what scale, i.e., kilotonnes (kt) vs megatonnes (Mt) of CO2 per year?
   e. What other considerations that play a role?
2. Identify the research and development questions that will address those challenges
   a. What are the current unknowns in the field that may be preventing CU from being adopted on larger scale?
   b. What might a research agenda look like to answer these unknowns?
   c. Where would you place the research needs on a scale of 1-10, in terms of basic research (lab-scale), pilot-scale (kt/yr), and demonstration/commercial-scale (Mt/yr)?
3. Assess current research efforts, including basic, applied, engineering and computational, that are addressing these challenges a...
Questionnaire (II)

a. Where would you place current research efforts on a scale of 1-10, in terms of basic research (lab-scale), pilot-scale (kt/yr), and demonstration/commercial-scale (Mt/yr)?

b. Identify gaps in the current research portfolio

4. Analyze the factors associated with making technologies viable at a commercial scale

a. What is the technically feasible scale of this CU technology? considering material resources, land, water, and energy requirements, siting of plants, sources of waste streams, etc. Do these demands present challenges to CU moving forward, if so, to what extent?

b. What should the energy resources be for running a CU plant and what net negative emissions are achieved?

c. How do you foresee costs for CU changing? Current vs nth of a plant?

d. Are there environmental risk considerations of CU that one has to consider?

5. Discuss a set of criteria to assess the factors identified in (4)

a. What milestones should be achieved in technological, research, pilot scale deployment, demonstration scale deployment?

b. What is the time frame for these milestones considering a 2 °C target?