CyclicCO$_2$R

Production of Cyclic Carbonates from CO_2 using Renewable Feedstocks

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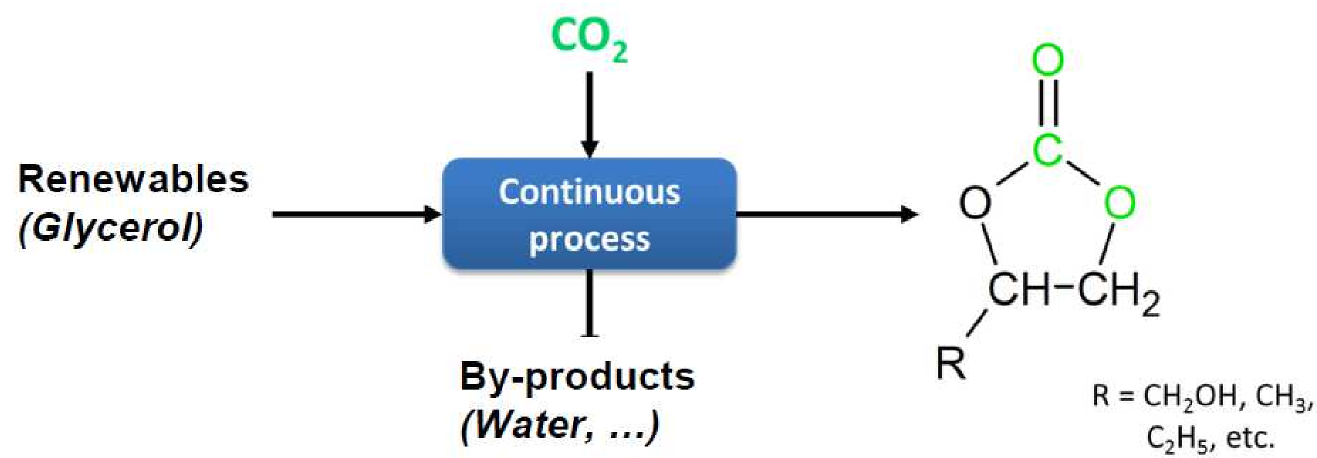
Project objectives



The consortium behind CyclicCO_2R wants to kick-start the implementation of CO_2 utilization technologies by converting CO_2 into a high value-added product, thus providing a showcase that inspires industry to further develop technologies utilizing CO_2 as a sustainable raw material and valorizing CO_2 in such a way that drives the market for CO_2 capture and utilization.

Several challenges for use of glycerol carbonate

Challenge for the use of glycerol carbonate (GC)

- Cyclic carbonates are niche products only
- Glycerol carbonate is only used as an intermediate in the synthesis of special surfactants and fine chemicals
- Current market for GC is a few kt per year

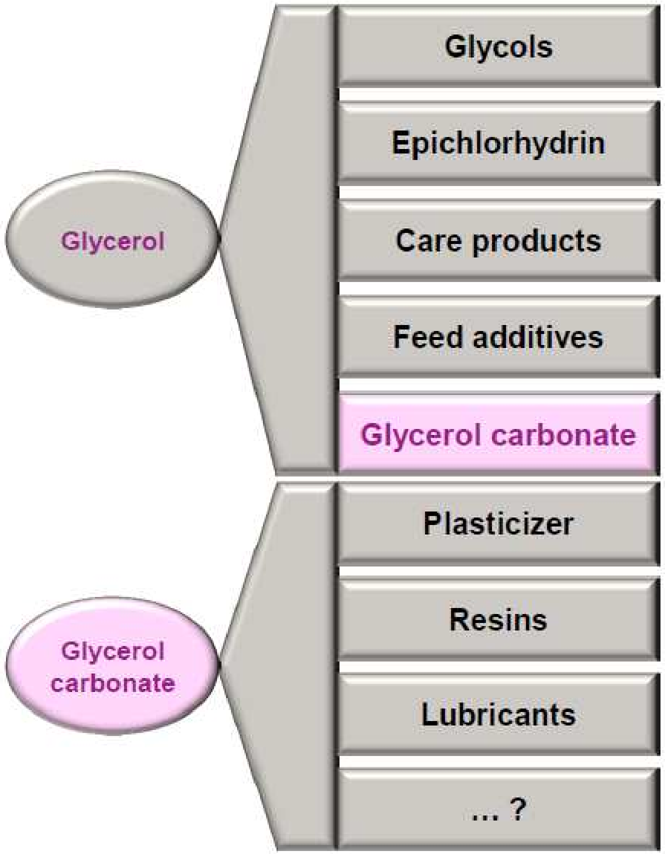
Major limitations for the use of GC today

- High price > 6 € / kg
- Purity is maximum 98% with impurities of glycerol
- Limited knowledge of subsequent chemistry with GC (e.g. esterification, etherification, alcohol exchange)
- Limited access to GC for researchers / academia (e.g. due to high catalogue prices)

Biodiesel → glycerol → glycerol carbonate

Opportunities for the use of glycerol carbonate

- **Crude glycerol** is available on very large scale from biodiesel (Europe approx. 800 – 1000 kt 2013)
- **Price of crude glycerol is significantly lower** (~ 300 € / t) than purified glycerol (~ 600 €/ t)[1]
- **Limited use for crude glycerol** due to impurities with H_2O (15 –20 %), salts (7 – 15 wt.%) and organics
- **Some shares of glycerol from biodiesel are purified** to serve the demand of chemical industry (~ 20%)



How will CyclicCO$_2$R improve the situation?

- Develop **robust catalysts** to use crude or pre-purified glycerol
- **Lower the impurities of glycerol** in the final product (< 0.5%)
- Realize an efficient process with **competing production costs** for glycerol carbonate (< 6 €/ kg)

1) Glycerol prices for Europe Oct 2012; ICIS pricing (www.icispricing.com);

CO_2 in abundance

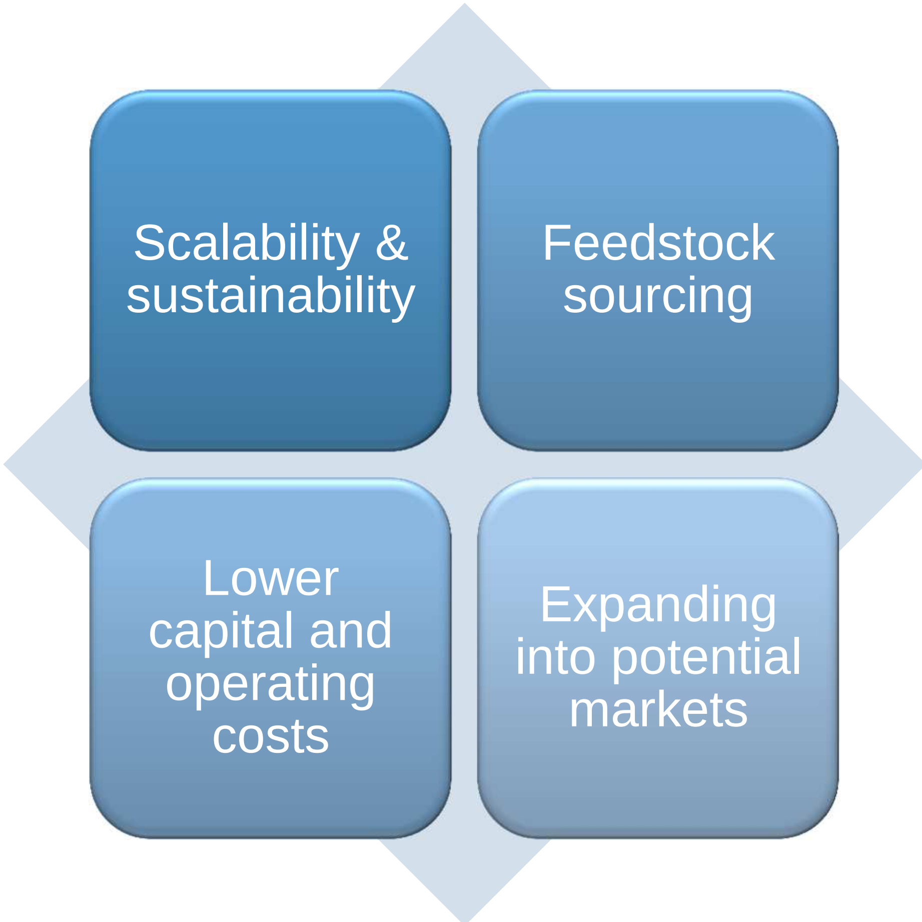
- From one power plant about **3 Mton** CO_2 produced per year

- Global anthropogenic emissions are **33.4 Gton** CO_2 per year
  - 91% from fossil fuel usage and cement production
    Source: http://co2now.org/Current-CO2/CO2-Now/global-carbon-emissions.html

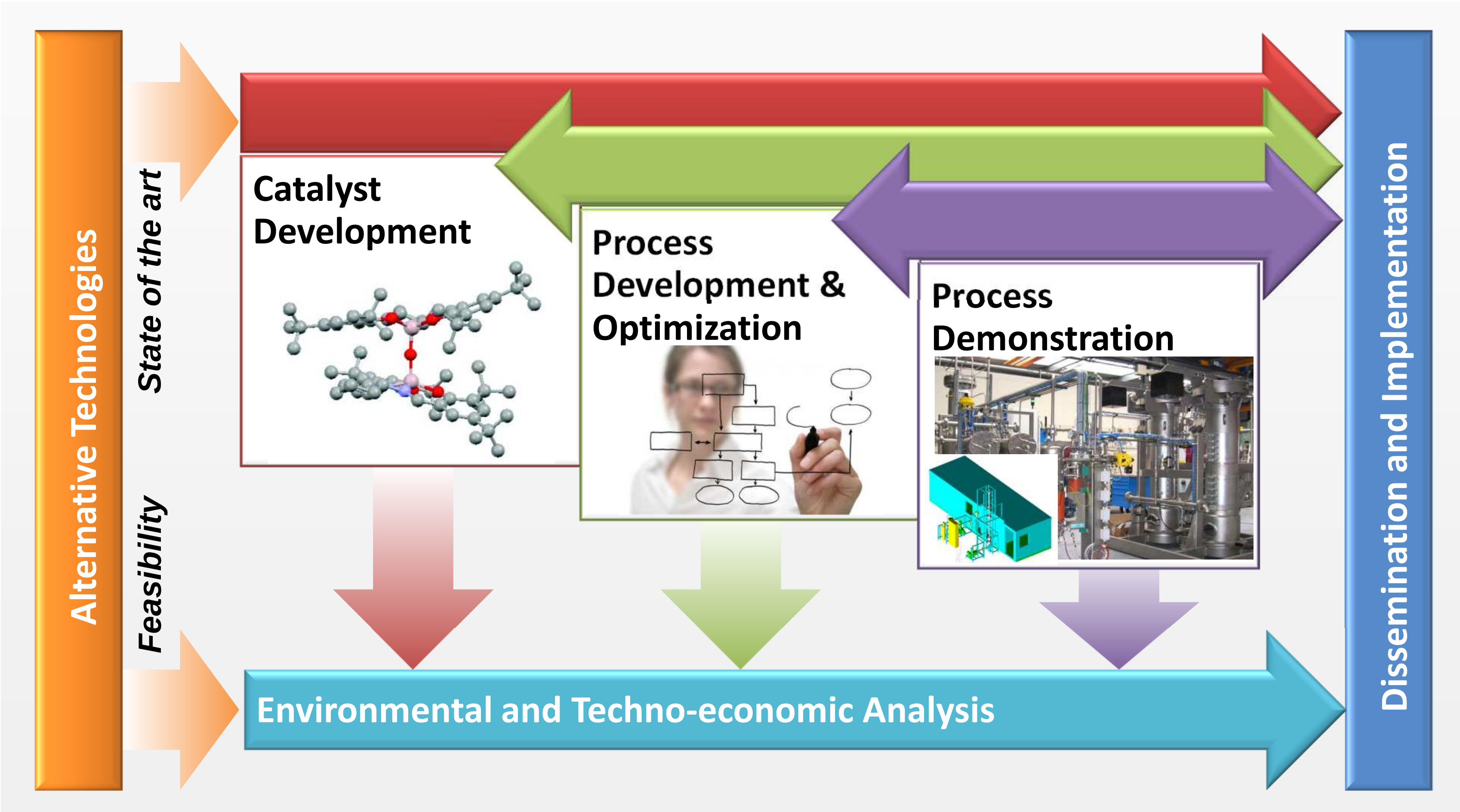
- EU targets for sustainable growth include:
  - Reducing GHG emissions by **20%** w.r.t. 1990 levels
  - Increasing share of renewable energy in total consumption to **20%**
  - Moving towards **20%** increase in energy efficiency
    Source: http://ec.europa.eu/europe2020/europe-2020-in-a-nutshell/targets/index_en.htm

- Cost of CO_2 capture from power plants is **40 – 60 €**
- Cost of CO_2 storage is **3 – 14 €/ton** CO_2
  Source: "The Costs of CO_2 Storage," ZEP report, 2011
  - Political and public issues also a major factor

Key industrial drivers



Main activities of the project



Project partners

Industrial partners

EVONIK INDUSTRIES

FeyeCon

CARBON RECYCLING INTERNATIONAL

Academic partners

Newcastle University

MESA+ Institute for Nanotechnology
University of Twente
The Netherlands

CAT Catalytic Center

RWTH AACHEN UNIVERSITY

Knowledge organization partners

SINTEF

TNO innovation for life

Project coordinator

Three routes to be investigated

Direct route

Glycerol carbonate directly from glycerol and CO_2

- Extensive catalyst development using high throughput testing and molecular modelling with novel reactor designs for *in-situ* water removal

Indirect route

Glycerol carbonate and other cyclic carbonates from glycidol or other epoxides and CO_2

- Ability to produce enantiomerically pure cyclic carbonates and use CO_2 directly from a flue gas source

Alternative technologies route

Photo- and electro-chemical routes to produce cyclic carbonates and intermediates from CO_2 and water

- Feeds state-of-the-art information from alternative technologies back into the rest of the project while assessing feasibility

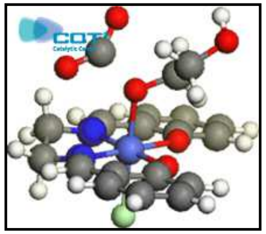
Direct route catalyst development

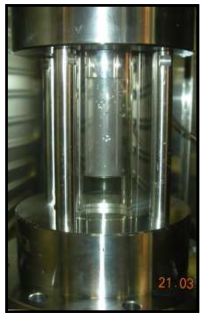
Crack the code for equilibrium reactions involving CO_2 and alcohols or diols

Tangible, long-term benefits for the development of commercially competitive industrial processes involving CO_2
(i.e. DMC, EC, PC, carbamates)

Key tools include

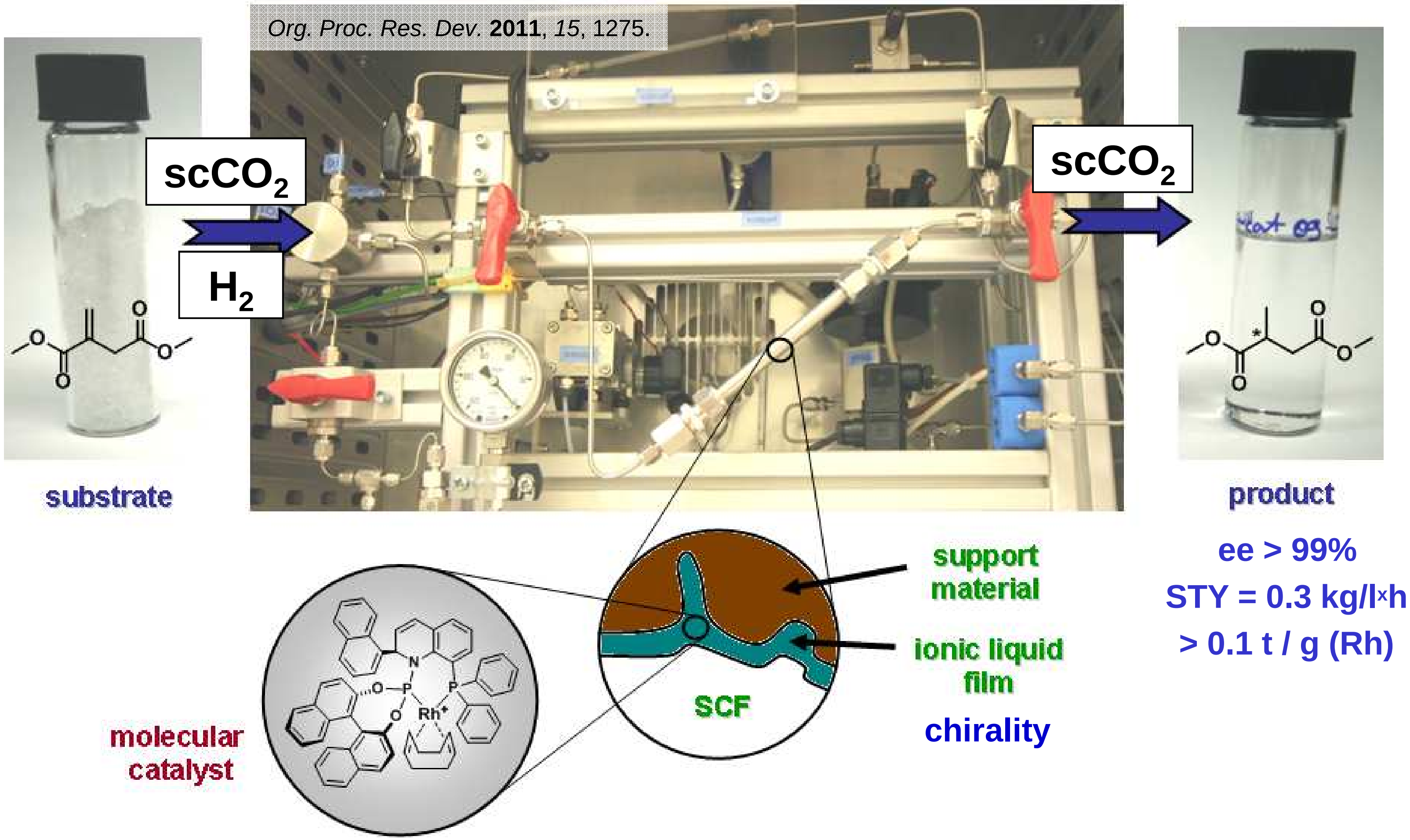
- High throughput, high pressure screening
- High pressure view cells
- State-of-the-art molecular modeling





Supported Ionic Liquid Phase catalysis

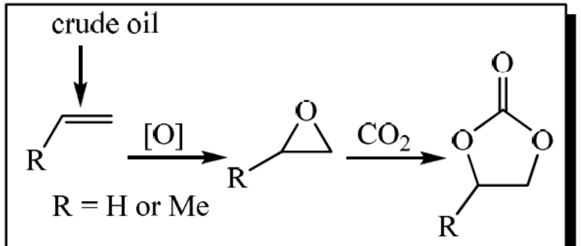
continuous flow process *ChemCatChem*, **2010**, *2*, 150.



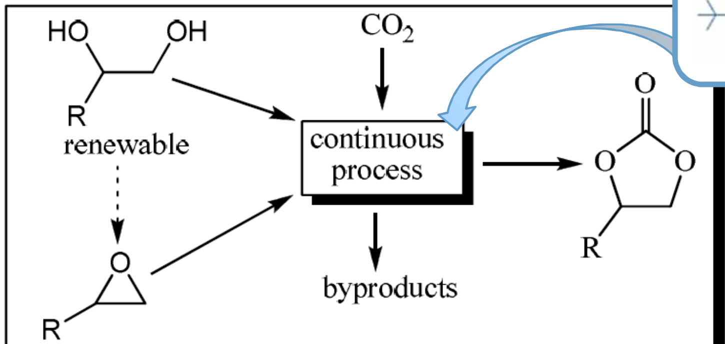
Indirect route catalyst development

Glycerol → Allyl alcohol → Glycidol → Glycerol carbonate

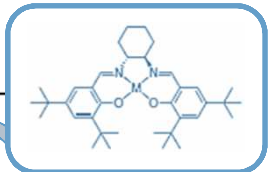
Project focus



Scheme 1: Current commercial process for cyclic carbonate synthesis



Scheme 2: Sustainable cyclic carbonate production

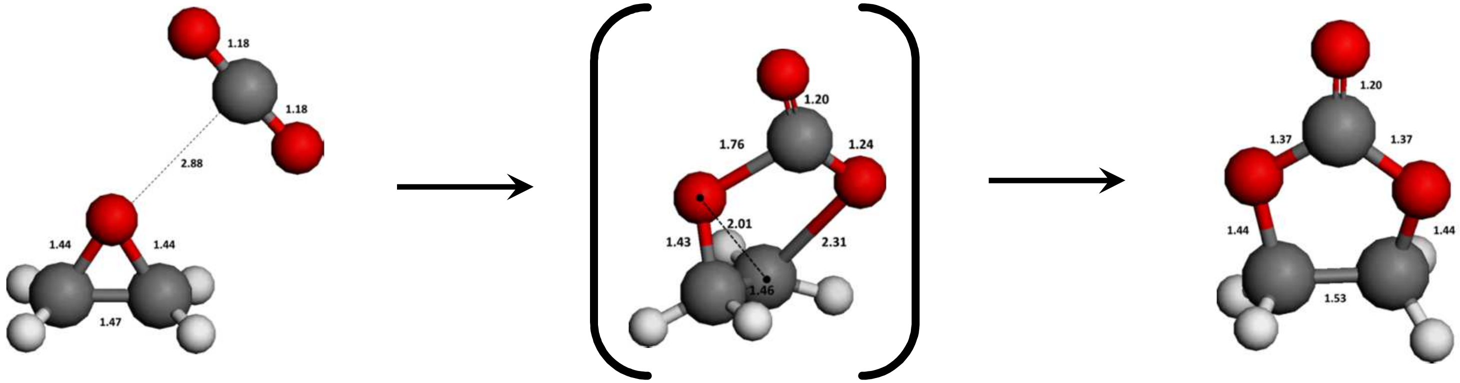


Patented catalyst

Challenges:

- Continuous process with immobilized catalyst
- Use of impure CO_2 (i.e. from flue gas)
- Production of enantiomerically pure glycerol carbonate and other cyclic carbonates

Cycloaddition of epoxide and CO_2: A detailed molecular picture of an elementary reaction step



Adduct

Transition state

Ethylene carbonate

Adduct

$\Delta H° = -6\ kJ\cdot mol^{-1}$
$\Delta S° = -65\ J\cdot mol^{-1}\cdot K^{-1}$
$\Delta G° = 13\ kJ\cdot mol^{-1}$

Transition state

$\Delta H° = 211\ kJ\cdot mol^{-1}$
$\Delta S° = -111\ J\cdot mol^{-1}\cdot K^{-1}$
$\Delta G° = 244\ kJ\cdot mol^{-1}$

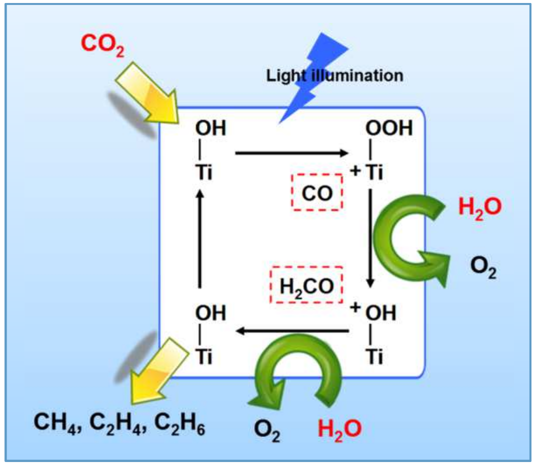
Ethylene carbonate

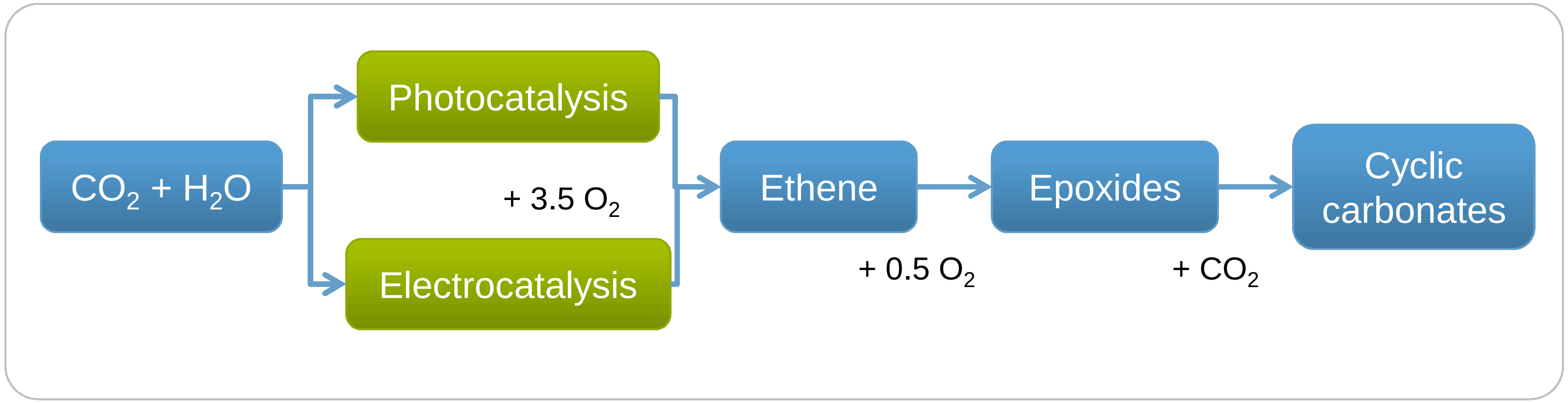
$\Delta H° = -58\ kJ\cdot mol^{-1}$
$\Delta S° = -127\ J\cdot mol^{-1}\cdot K^{-1}$
$\Delta G° = -21\ kJ\cdot mol^{-1}$

Alternative technologies route

Main activities

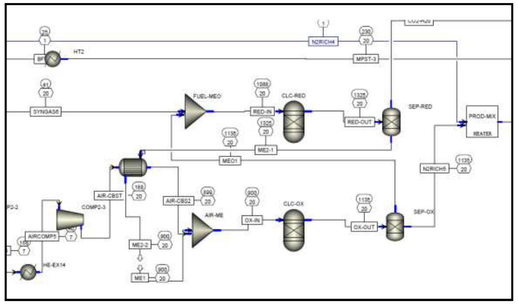
- Exploration into electro- and photo-chemical production of inter-mediates (alkenes, epoxides) for cyclic carbon-ates with only CO_2 and water as raw materials.
- Evaluation of feasibility feeds into the environmental and techno-economic analysis

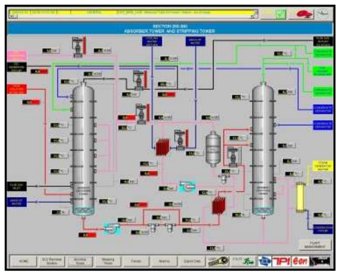




Process development



Reactor development

Process optimization

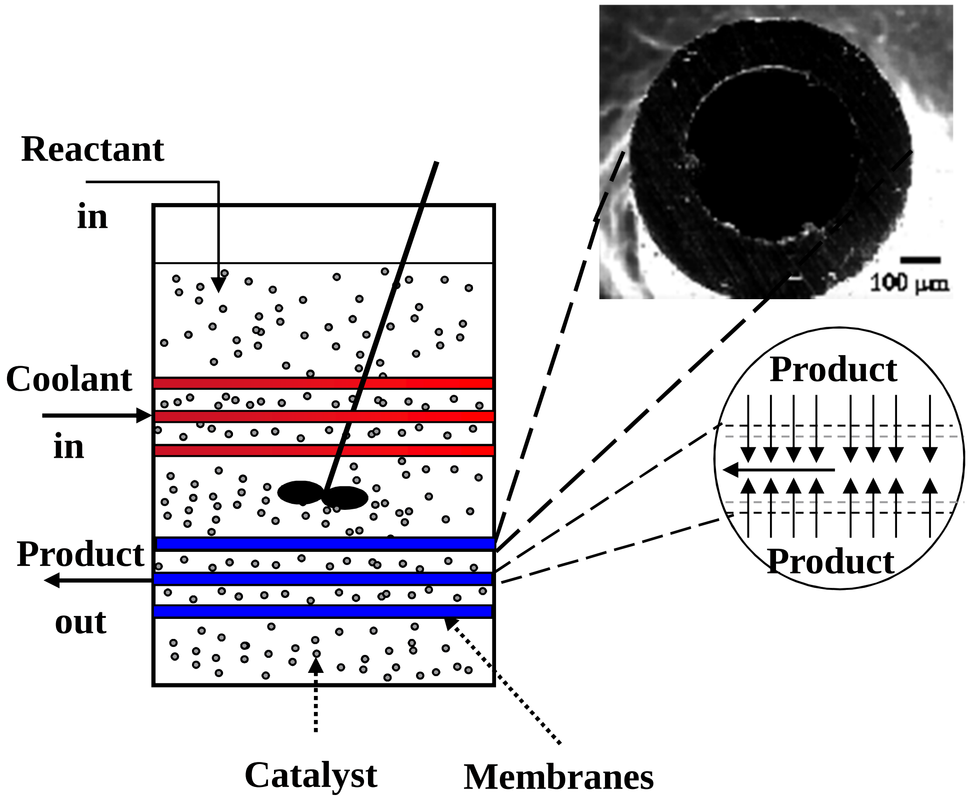
Process demonstration

Novel reactor concept to be tested for the direct route: Membrane Slurry Reactor

Principle: Product can pass membrane while catalyst particles are retained in reactor

Advantages

- Increased activity of catalysts
- Mild mechanical treatment of catalyst
- Continuous operation
- Low hold up of catalyst in system



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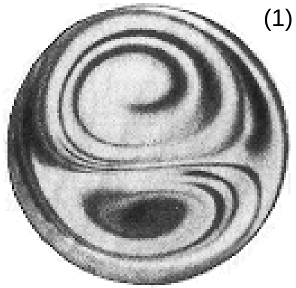
Novel reactor concept to be tested for the indirect route: Helix reactor

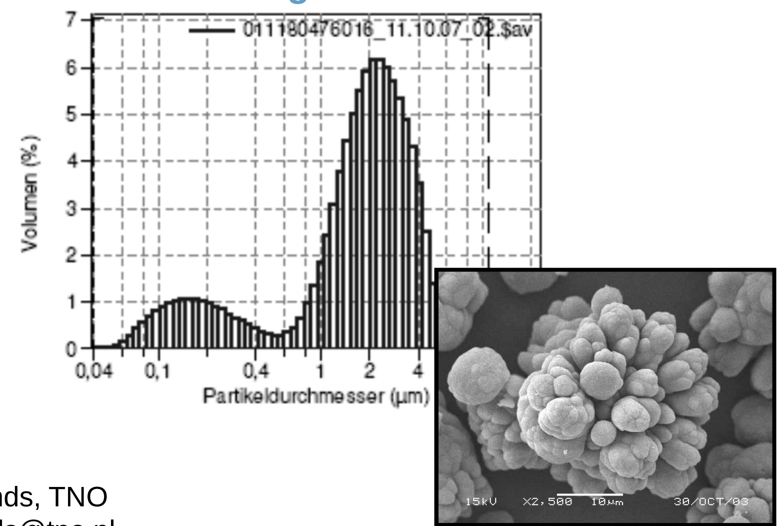
- Mixing behavior and plug flow: demonstration of production of mono disperse nano-particles
- Reaction time reduced from 4 hours in batch reactor to 15 minutes in Helix Reactor



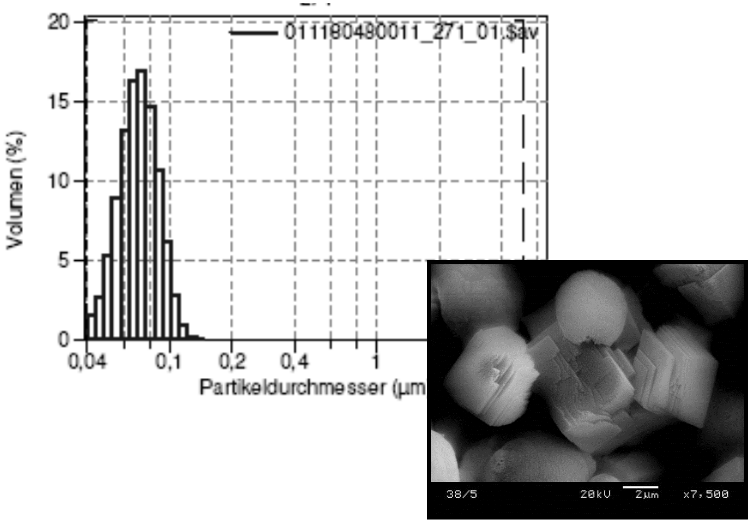
(1)

(1) T.J. Hüttl,. and R. Friedrich, *Int. J. of Heat and fluid flow.*, 21(2000) 345-353.

Straight tube



Helix reactor



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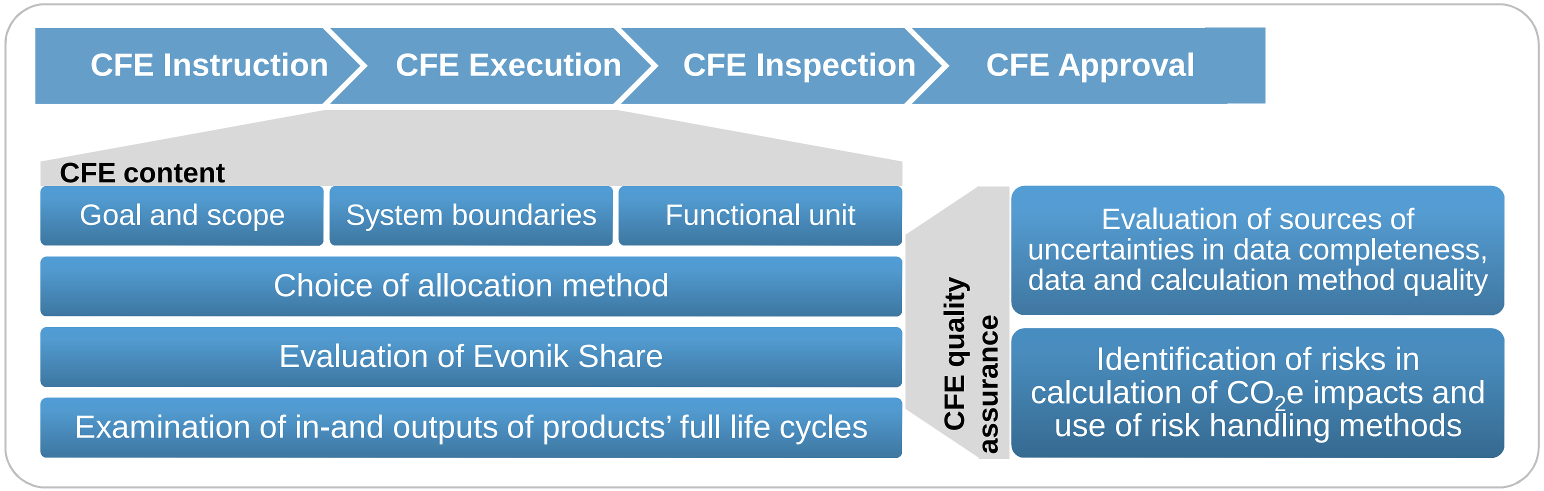
Environmental & Techno-economic analysis

Approach

- Use Aspen simulations of the process in development to feed into the Carbon Footprint Estimation (CFE)
- Use experimental data to validate calculations and allow for more complexity

Goals

- Ensure process meets project objectives
- Guide key decisions (i.e. between direct and indirect routes)
- Keep the project connected with the market



Summary

- 4 year project started in January 2013
- Overall goal is to provide a showcase continuous, highly-efficient process for the conversion of CO_2 into fine chemicals
- Both the direct and indirect routes will be investigated until one proves to be more promising to take forward to the process demonstration
- Alternative technologies will be explored throughout the entire project
- An environmental and techno-economic analysis will ensure the project objectives are met
- The website to be up and running soon! http://www.cyclicco2r.eu/

Acknowledgements

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Thanks for your attention!