

# Green hydrogen for CO<sub>2</sub> conversion to valuable chemicals

Development of a combined process for CO<sub>2</sub> scrubbing and hydrogenation to methanol

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## Expanding production and demand (p.a., world)

- 2005: 35.8 million t <sup>[1]</sup>
- 2010: 45.2 million t <sup>[1]</sup>
- 2015: 75.0 million t <sup>[2]</sup>

## Broad usage

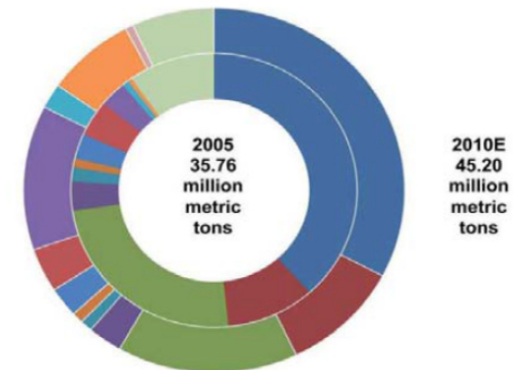
### Chemical industry

- Formaldehyde – further treated to resins, glues and plastics
- Acetic acid – polyester fibres and PET plastics
- Olefins – via MTO process, new fast growing market (PRC)

### Transportation

- Blend (M15) or direct/indirect use (MTBE)
- High octane number (106)
- Reduction of emissions (NO<sub>x</sub>, HC, CO)

Methanol Use - World  
By Derivative  
[www.methanolmsa.com](http://www.methanolmsa.com)



[www.methanolmsa.com](http://www.methanolmsa.com) / 2012



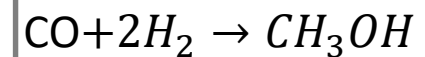
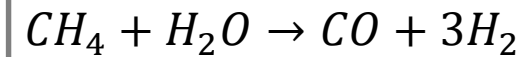
[www.bluefuelenergy.com](http://www.bluefuelenergy.com) / 2018

[3] [www.methanol.org](http://www.methanol.org) / 2018

[1,2] Bolle, F.-W., RWTH Aachen, 2012

## ■ Conventional production

- Feed: Natural gas/coal
- Conventional methanol synthesis
- Primary energy demand (world): appr. 700 TWh [3]
- CO<sub>2</sub> emissions: about 175 million t



## ■ Usage of carbon dioxide and hydrogen

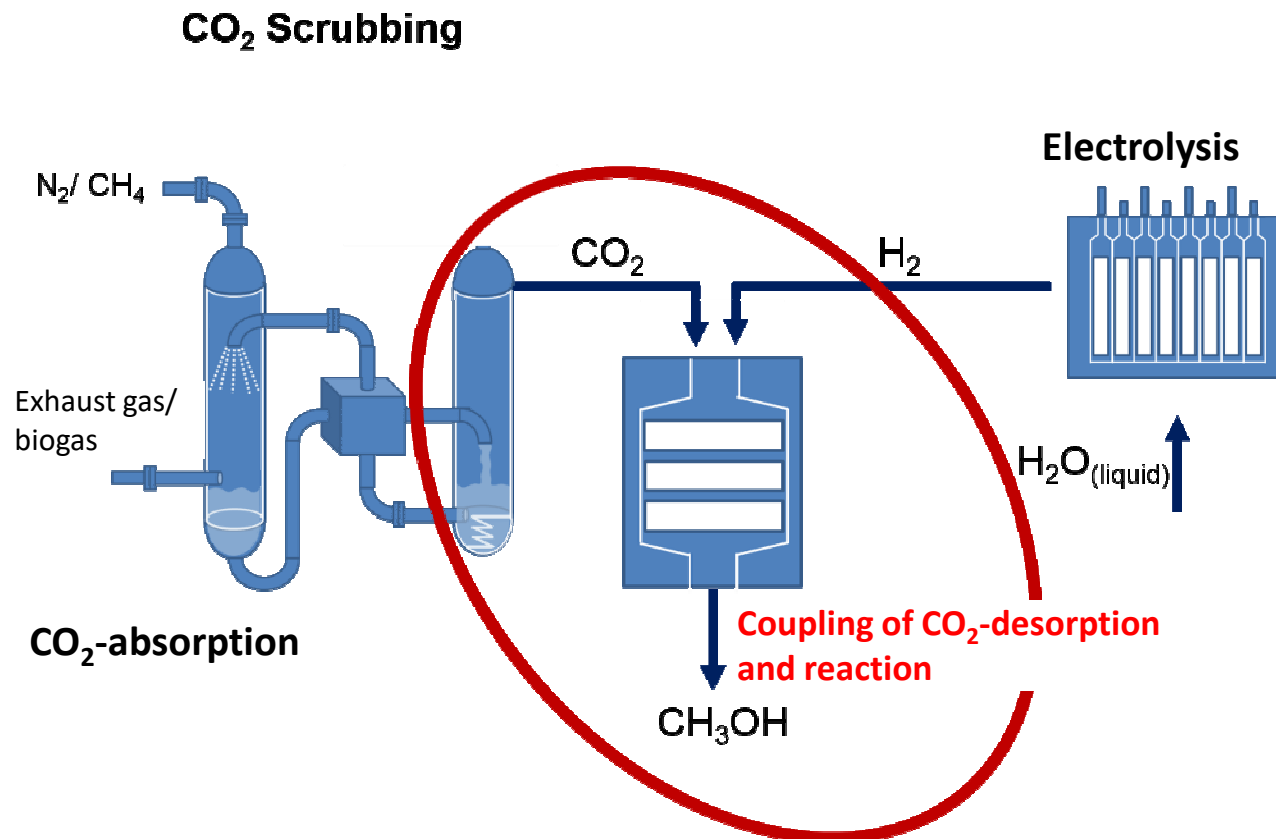
- Carbon dioxide demand: 100 million t
- Hydrogen demand: 14.2 million t  
→ 18.5 million m<sup>3</sup>/h (8500 h/a)



Ely Technology Level	Conventional	Advanced
Ely efficiency ( $\eta_{ely}$ )	65 %	85 %
Ely plant size	10 MW	100 MW
Required electrical power	85.4 GW	65.3 GW
Number of electrolyzers	> 8000	650

- Convert greenhouse gas CO<sub>2</sub> in usable substance
  - Methanol as an energy source, fuel and basic chemical
  
- State of the art:
  - Washing of CO<sub>2</sub>-containing exhaust gases and biogases with alcohol-amines → CO<sub>2</sub> absorbed in amines
  - Separation of CO<sub>2</sub> and alcohol-amines
  - Hydrogenation of CO<sub>2</sub> to methanol
  
- Idea: conversion of the absorbed CO<sub>2</sub> to methanol in an one-step process at lower temperatures

## Schematic view of the COOMet idea



### Technical process

- 50...100 bar
- 240...260 °C
- Cu-ZnO/Al<sub>2</sub>O<sub>3</sub>
- Recycle unreacted educt

### New COOMet process

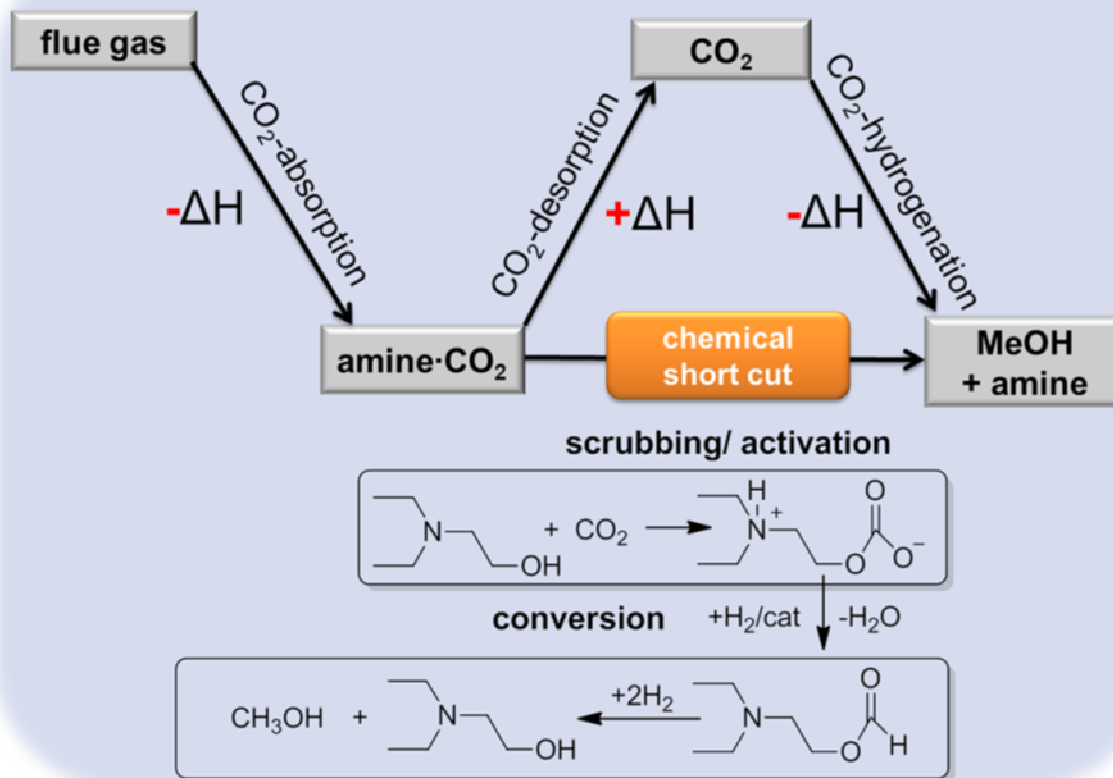
- 20...30 bar
- 130...170 °C
- Cu-ZnO/Al<sub>2</sub>O<sub>3</sub>-Amin

# CO<sub>2</sub>-ABSORPTION AND HYDROGENATION IN ONE STEP



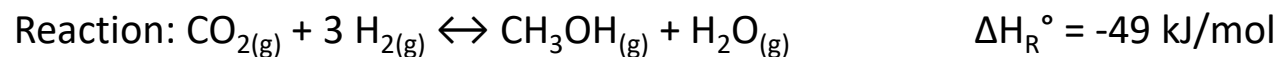
## Aim

- Development of a coupled process of CO<sub>2</sub> collecting and methanol-synthesis
- High efficiency of integrated heat transfer



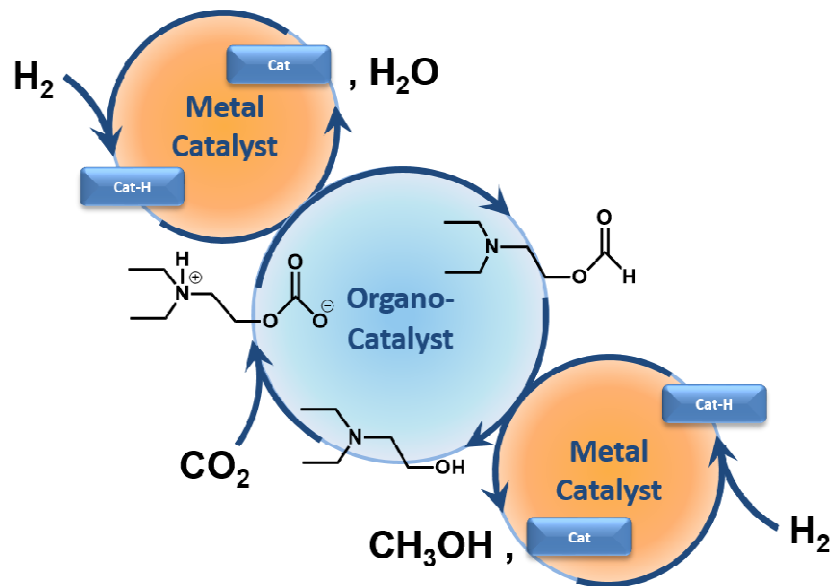
! Partly compensation of  $\Delta H_{\text{des}}$  and  $\Delta H_{\text{hydr}}$

TU Freiberg (IPC)

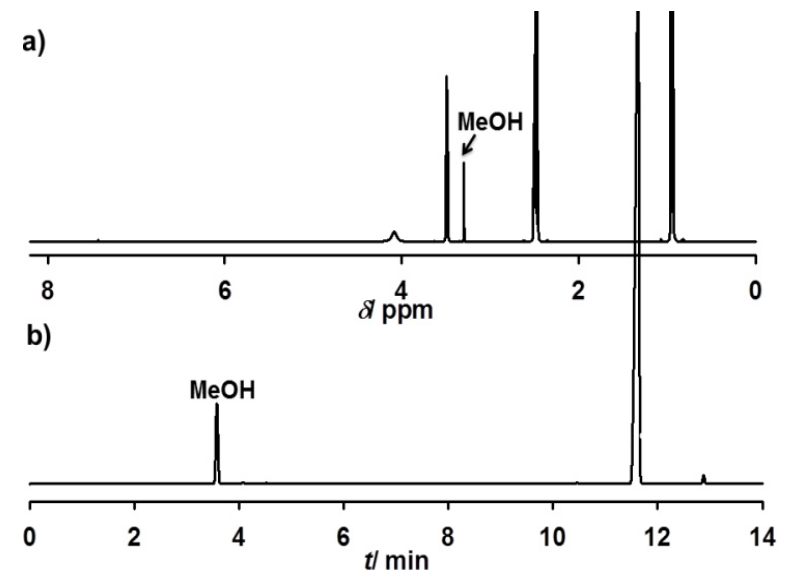


- Metal catalyst + amine (function as an organo-catalyst)

- Methanol is the only product
- The other peaks are the amine



Scheme of the catalyst system © TU Freiberg (IPC)



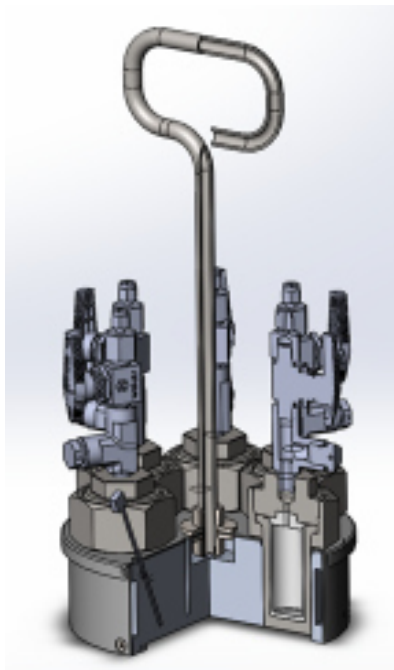
Analysis of NMR-spectroscopy © TU Freiberg (IPC)



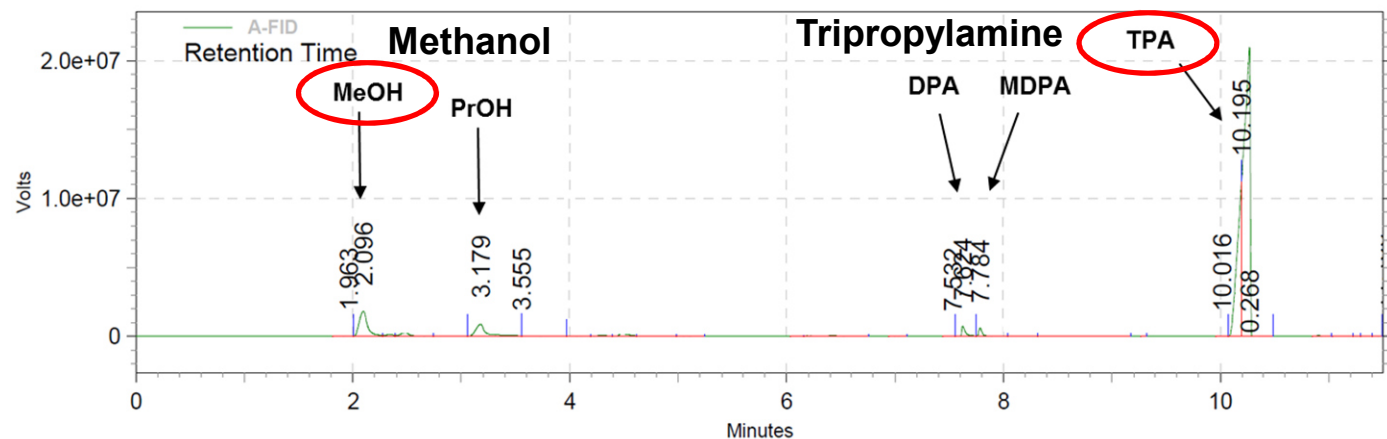
- First results are created in a batch reactor of TUBAF in 2013 (patented process no.: DE2013201246A1)
- Currently use of a multiplex-reactor-system and a headspace gas chromatograph to get fast in-situ analysis of the product

## Scientific aims

- Understanding the reaction mechanism
- Determination of the reaction kinetics

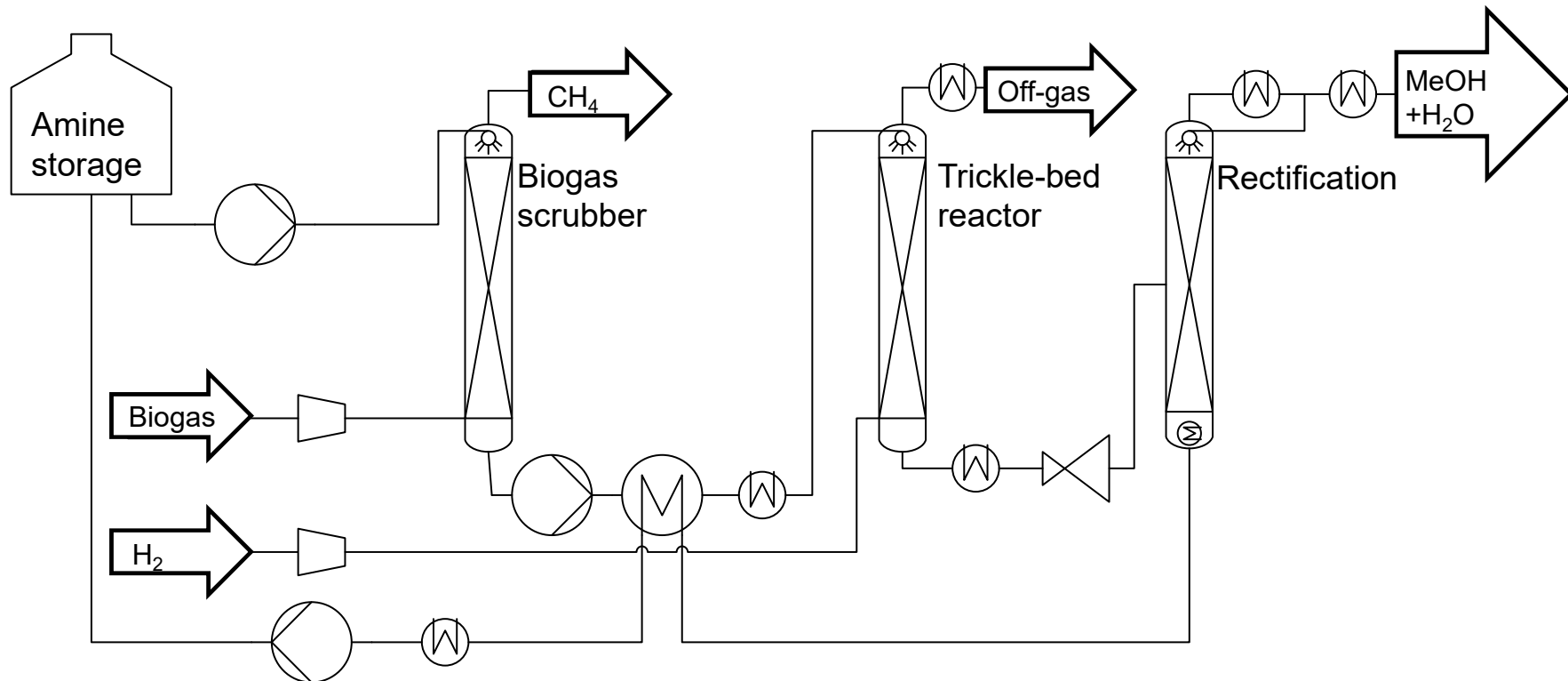


Multiplex-reactor-system © TU Freiberg (IPC)



Headspace gas chromatograph © TU Freiberg (IPC)



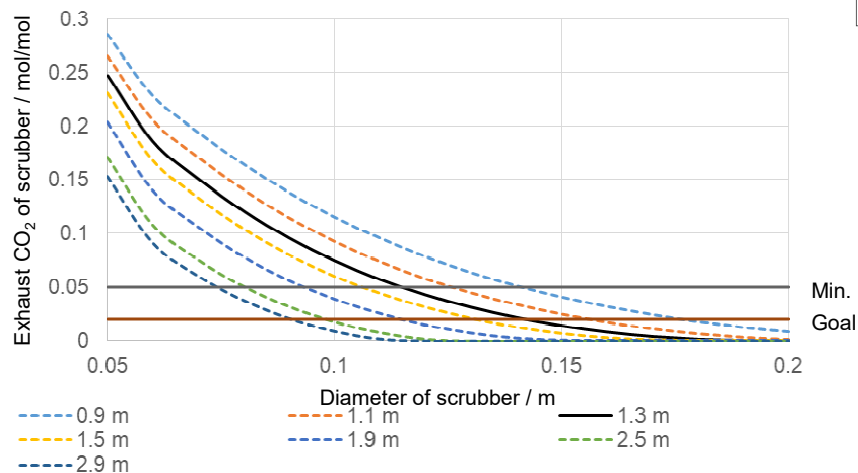


### ■ Process parameters:

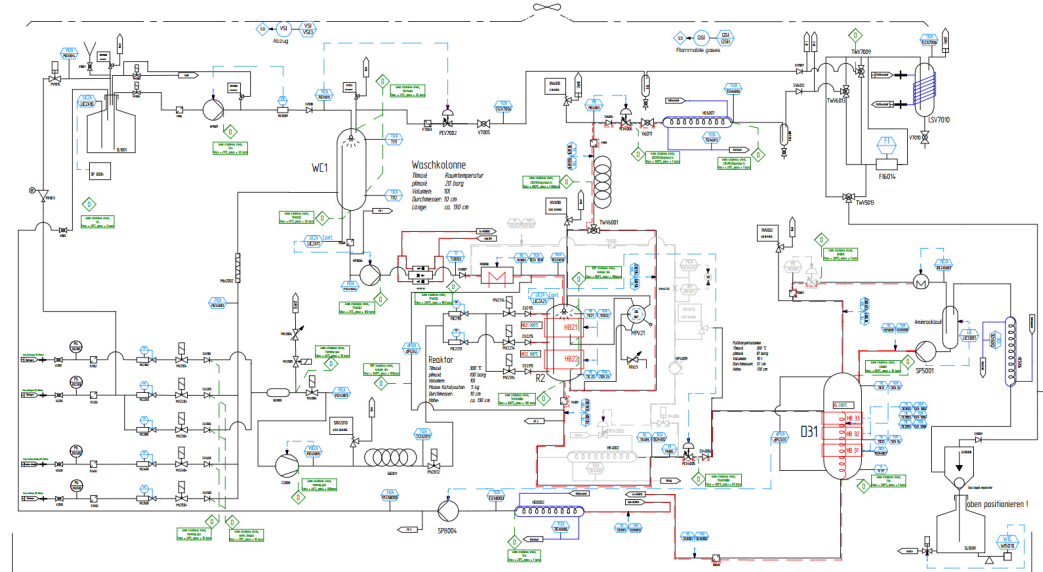
- Up to 100 bar (20 bar expected)
- Up to 300 °C (160 °C expected)
- Max. product capacity 0.2 l/h methanol (1 l/h expected)

## Challenges

- Complex process for lab scale
- Amines have low CO<sub>2</sub> capacity  
→ high recycling rate
- Amine stability
- Activity and stability of catalyst
- Low amine loss
- High methanol selectivity



Simulation of scrubber



P&ID © Amtech

- Size of the lab
- Handling of reactor
- Process handling

### Summary

- Process is running in lab scale
- For faster results multiplex-reactor-system and a headspace GC necessary
- Planning of the technical scale was difficult but is nearly finished
- Downscale of technical plant necessary for well handling



First layout construction © Amtech

### Next steps

- First experiments will be conducted after final planning and construction of the technical plant in the beginning of 2019
- First results are expected in Q2 2019

## PROJECT-PARTNER AND SUPPORT



- Technische Universität Bergakademie Freiberg (Institut für Physikalische Chemie)
- DBI Gas- und Umwelttechnik GmbH
- John Brown Voest GmbH
- Advanced Machinery & Technology Chemnitz GmbH
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THANK YOU FOR YOUR ATTENTION!

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