CARENA WP3: Valorization of CO_2 to MeOH and DMC

Gerhard Remmers - AkzoNobel

Introduction

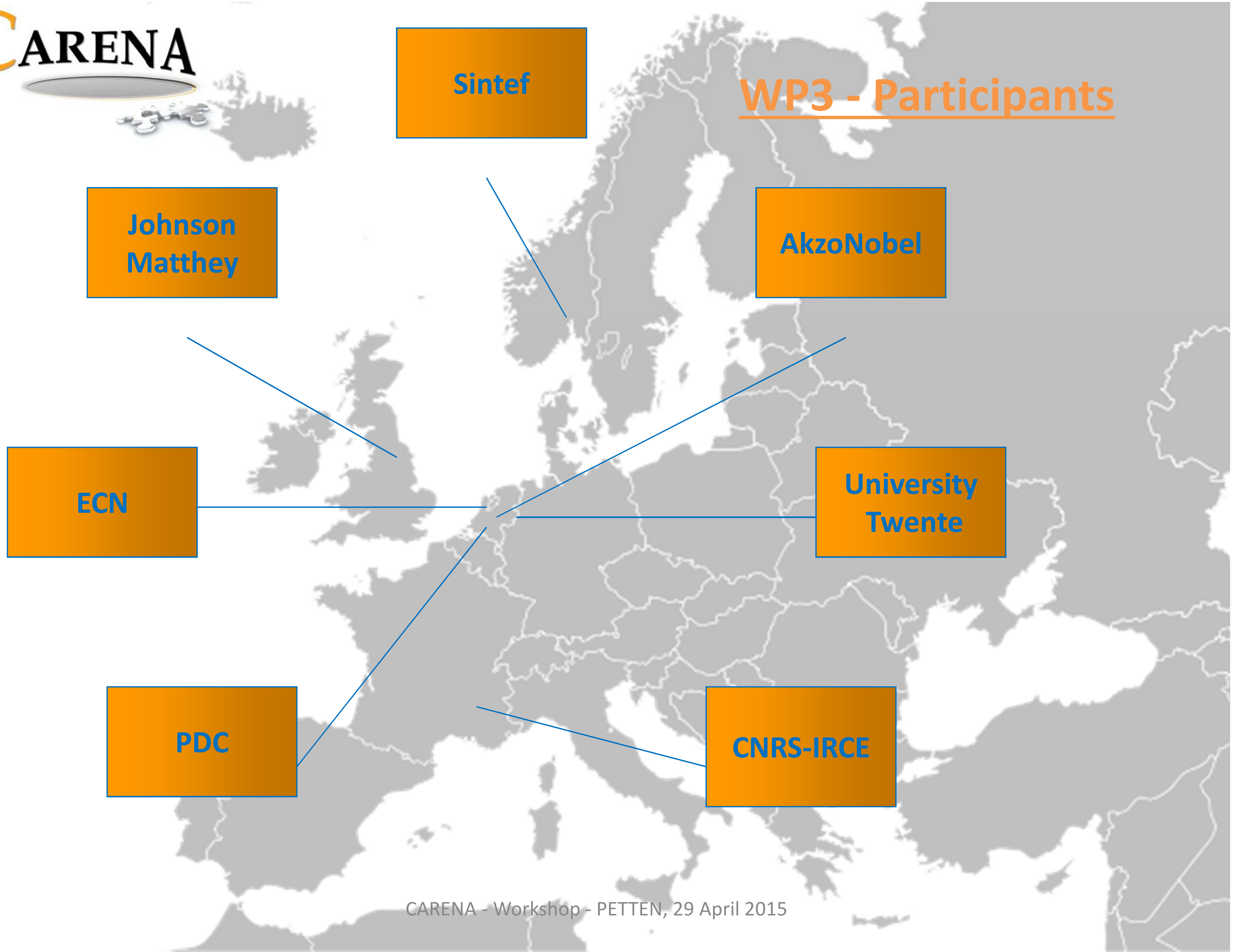
AkzoNobel incentive for CARENA:

- Interest in new affordable processes for green Methanol and green Di Methyl Carbonate (DMC)
- Open innovation driver
- Catalytic membrane reactors identified as high risk high reward option

EU FP7 programme:

- Working with excellent EU expertise on catalysts, membranes and process design
- Substantial technical and financial leverage realized
- Expected low Probability of Success acceptable

WP3 - Participants

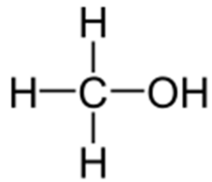


Incentives WP 3

<u>Valorization of CO_2:</u>

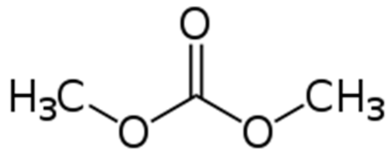
- **Methanol synthesis:**

  $CO_{2(g)} + 3H_{2(g)} \leftrightarrows CH_3OH + H_2O$



- **DMC synthesis:**

  $CO_{2(g)} + 2MeOH \leftrightarrows DMC + H_2O$



- **Selective removal of H_2O/products through a membrane reactor**

Incentives WP 3

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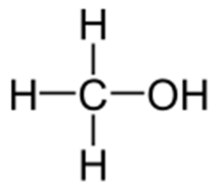
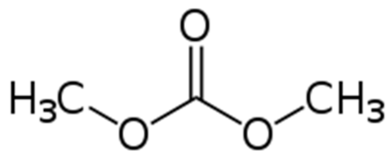


- **DMC synthesis:**

  $CO_{2(g)} + 2MeOH \leftrightarrows DMC + H_2O$



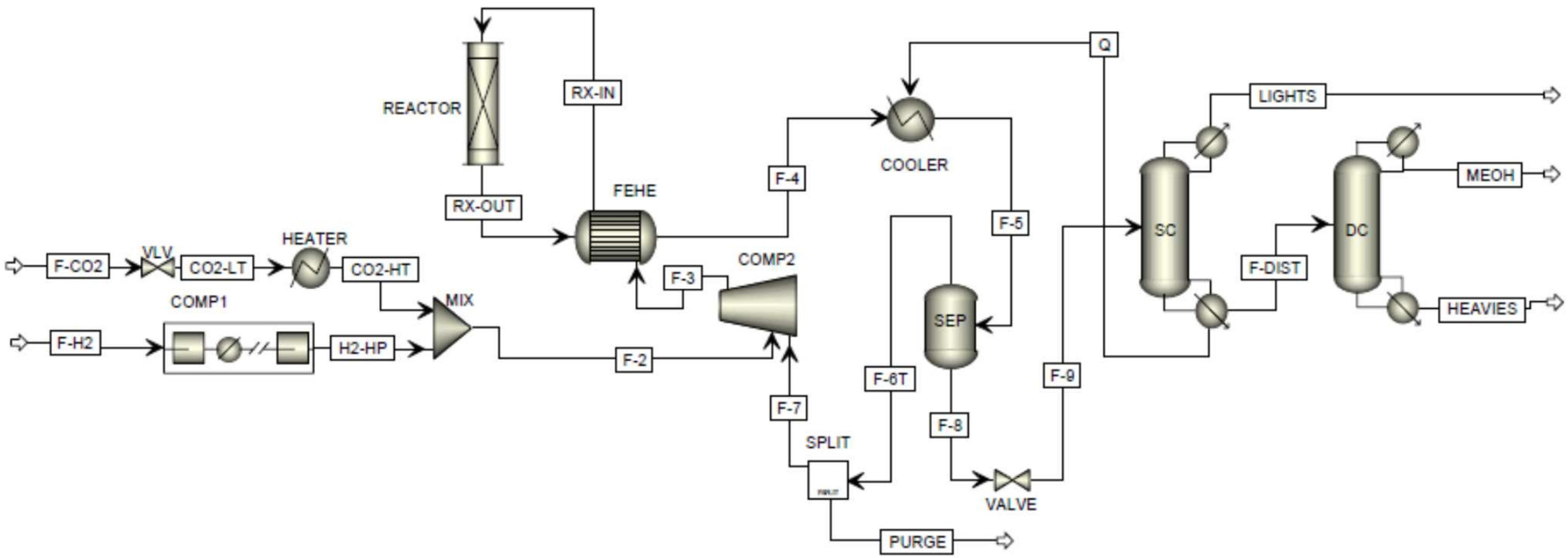
- **Selective removal of H_2O/products through a membrane reactor**

Commonalities:

- Equilibrium reactions
  → need for high pressure
- Need for catalysts
- Water produced as co-product
- Reaction T:
  120 – 300 °C

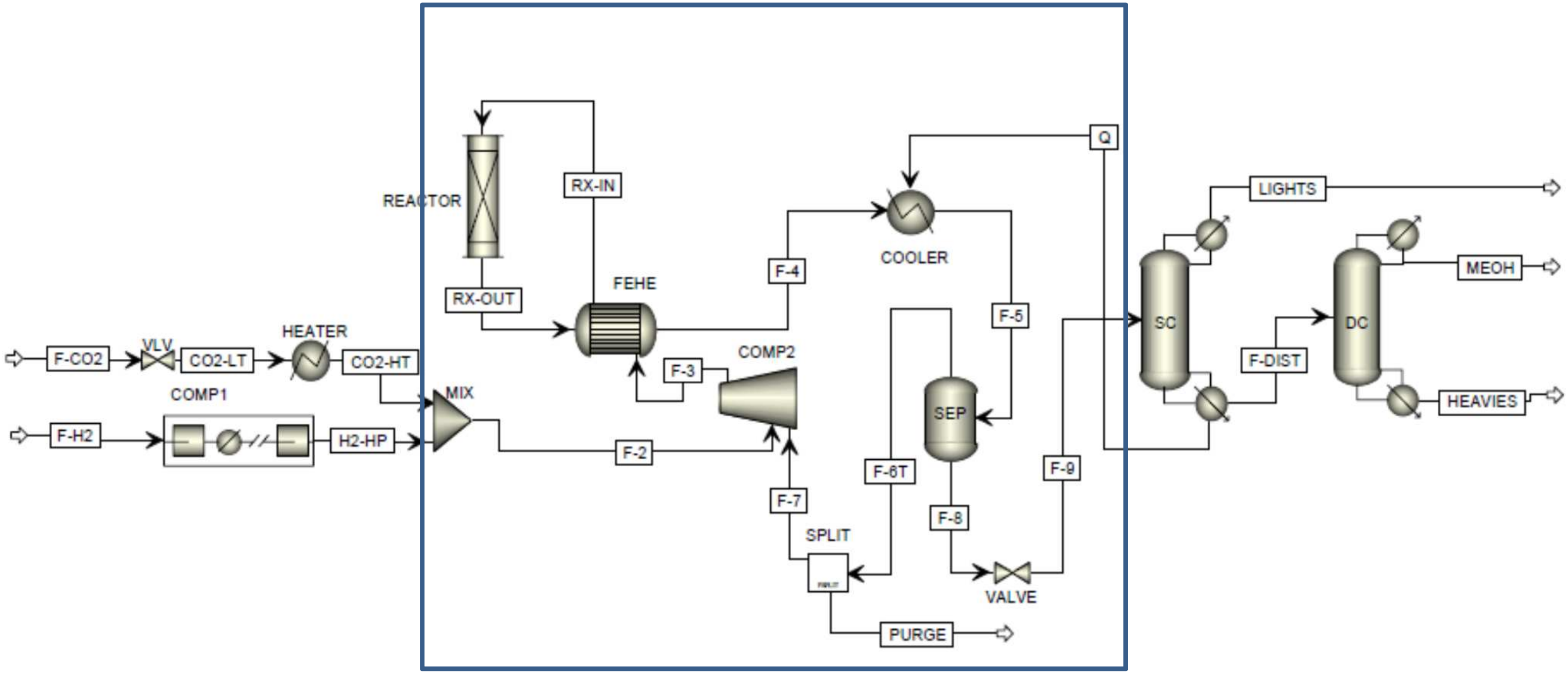
Challenges for Methanol process

Methanol synthesis: non-membrane process



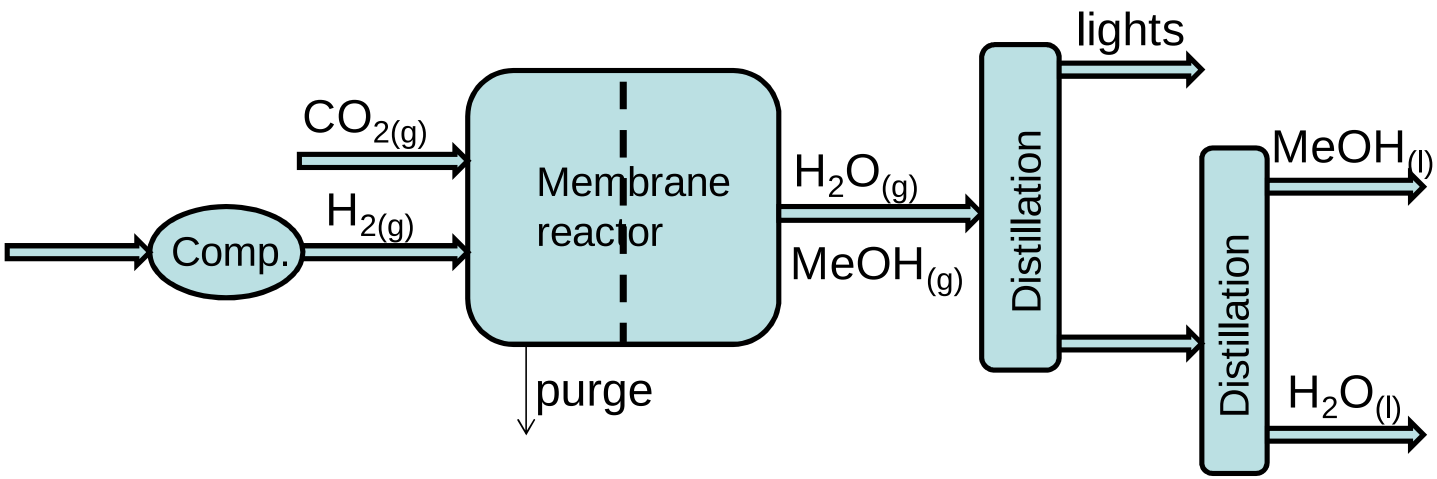
- Total electricity usage: 700 kWh/t MeOH
- Total steam consumption: 2 -3 t steam/t MeOH

Methanol synthesis: non-membrane process



- Total electricity usage: 700 kWh/t MeOH
- Total steam consumption: 2 -3 t steam/t MeOH

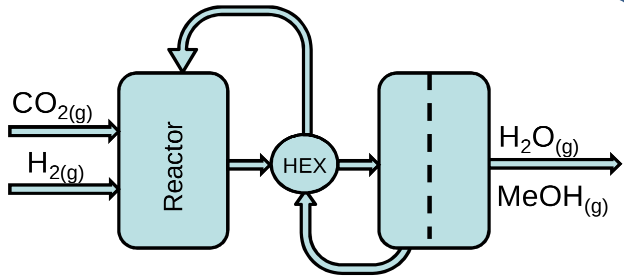
Potential economic gain of membrane process



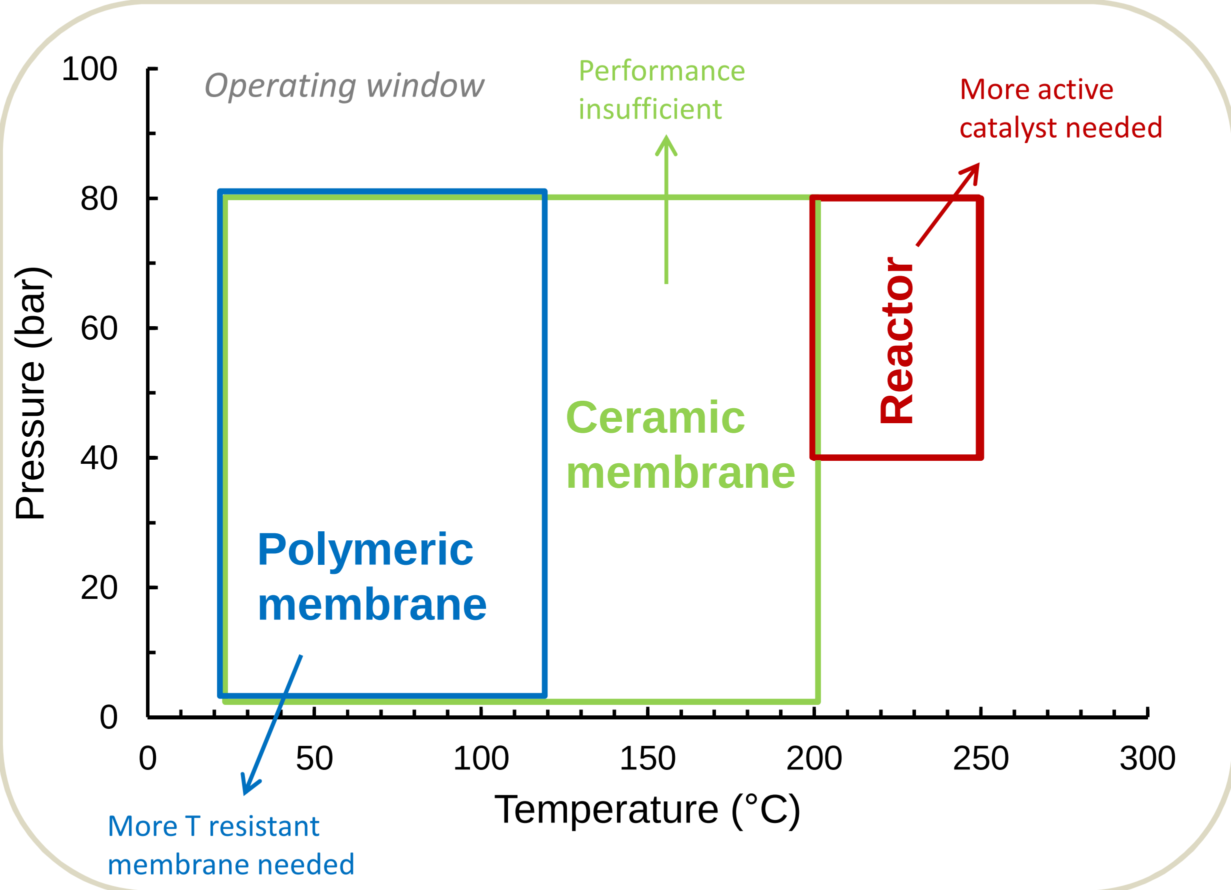
- Reduction in investment costs due to removal of recycle loop: one compressor and one heat exchanger
- Reduction in energy consumption of compressor(s)

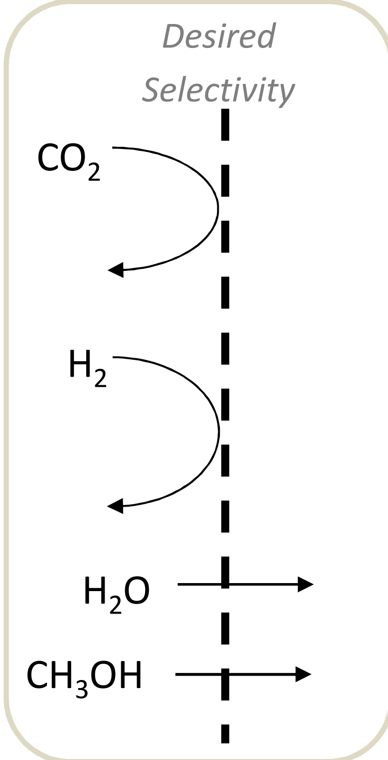
Incompatibility of reaction conditions (250 °C, 50 bar) and membrane limitations will require need for recycle

⇨ Reduces cost advantage



Methanol



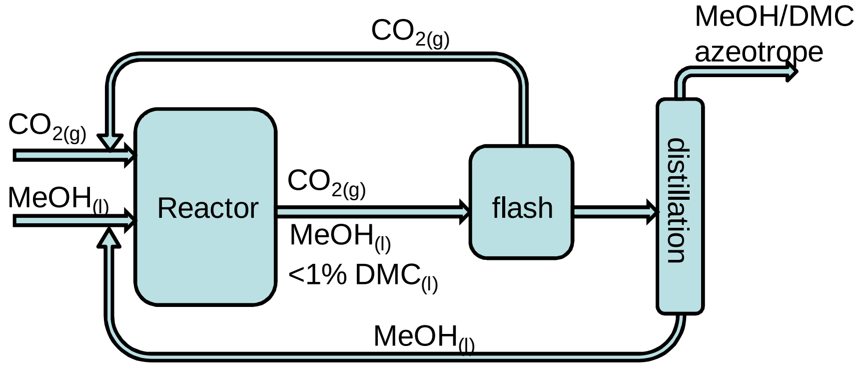


- **<u>Methanol:</u>** **Mismatch between operating window of membrane and reaction**

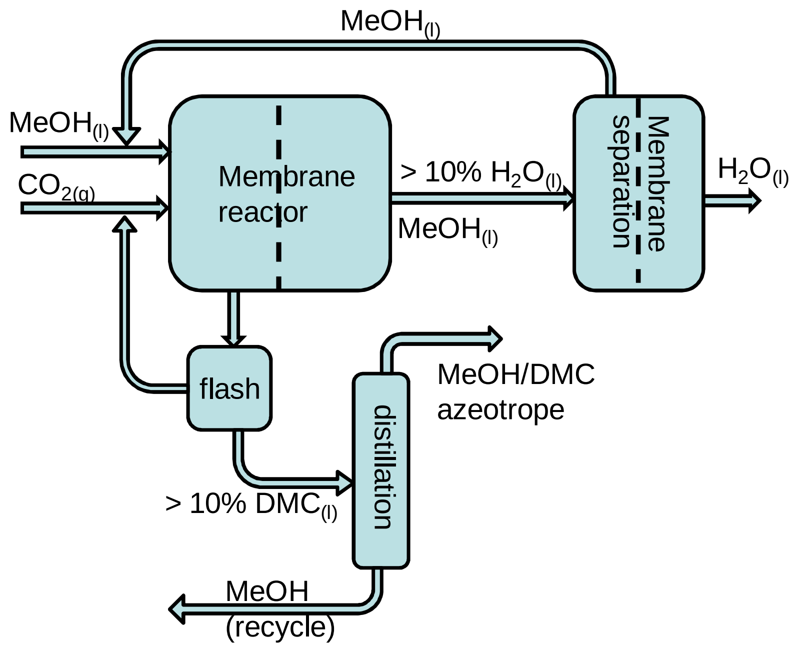
Challenges for DMC process

DMC synthesis

Non-membrane process

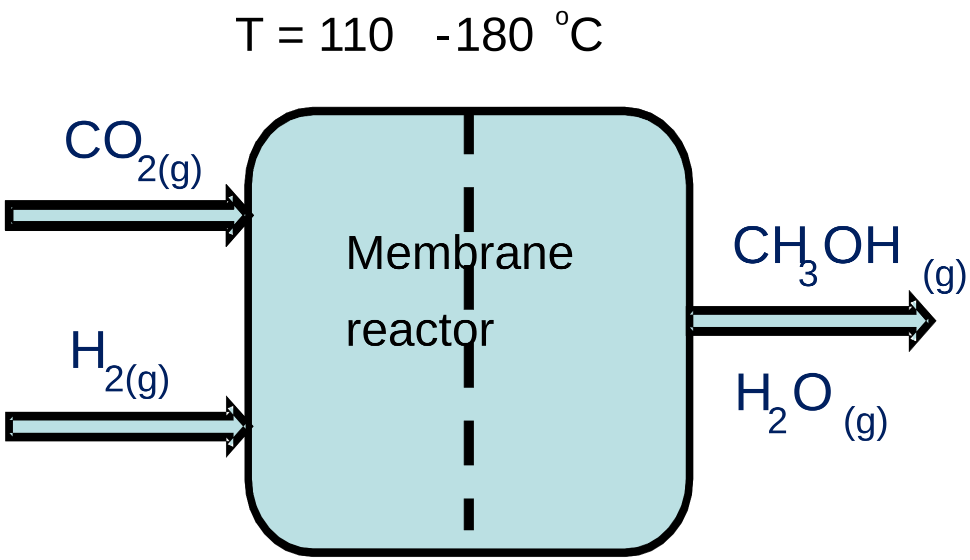


Membrane process



- Non-membrane process for DMC synthesis not feasible due to large recycles
- Membrane process requires a membrane with a large selectivity of H_2O over methanol: >50

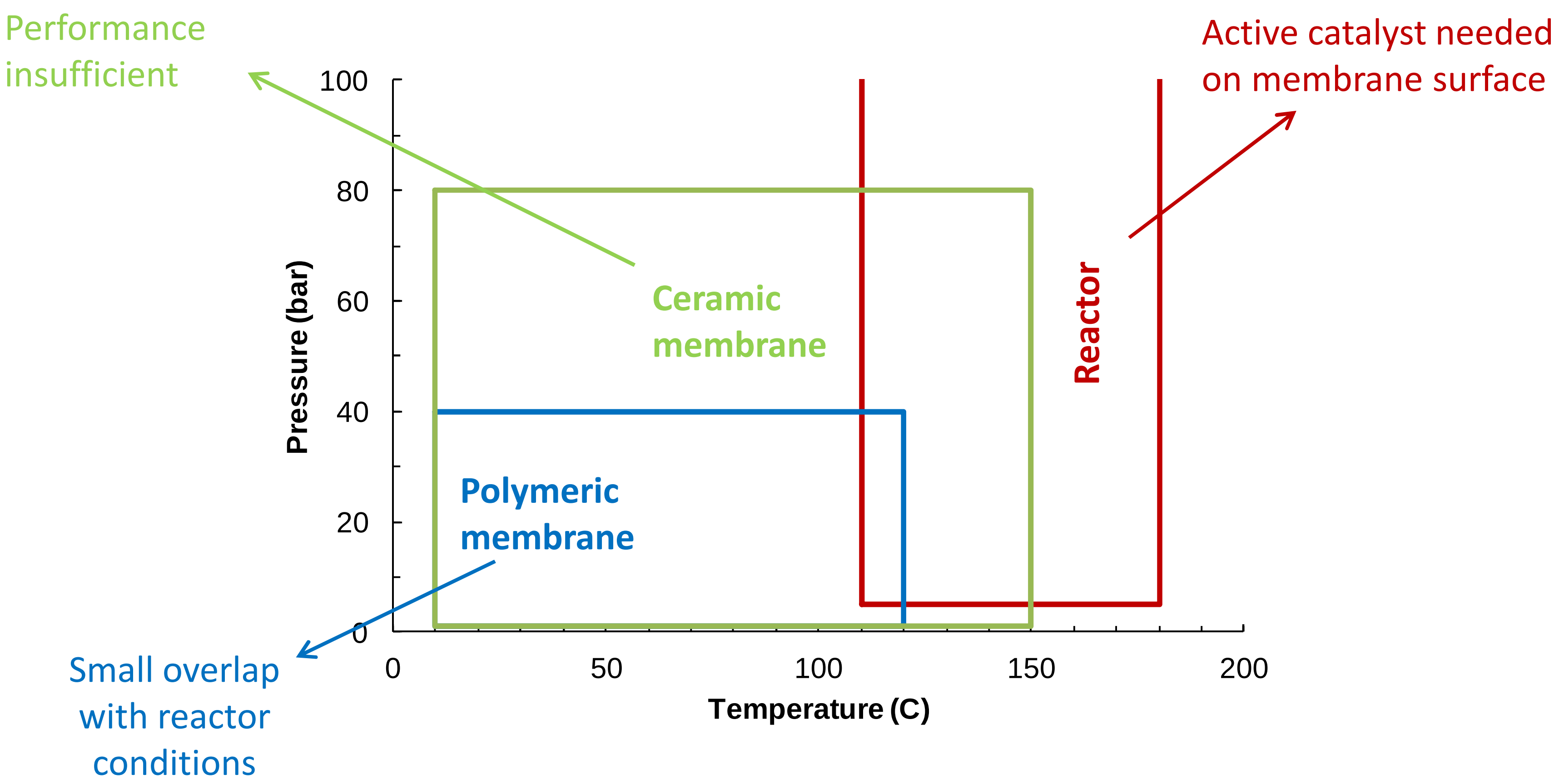
Processing options for DMC production



Options:

- **R&S in same unit**
- **R&S in same unit and cat on membrane (most likely)**

Required operating window for DMC production



Issue:

- **DMC equilibrium conversion is only around 1% !**

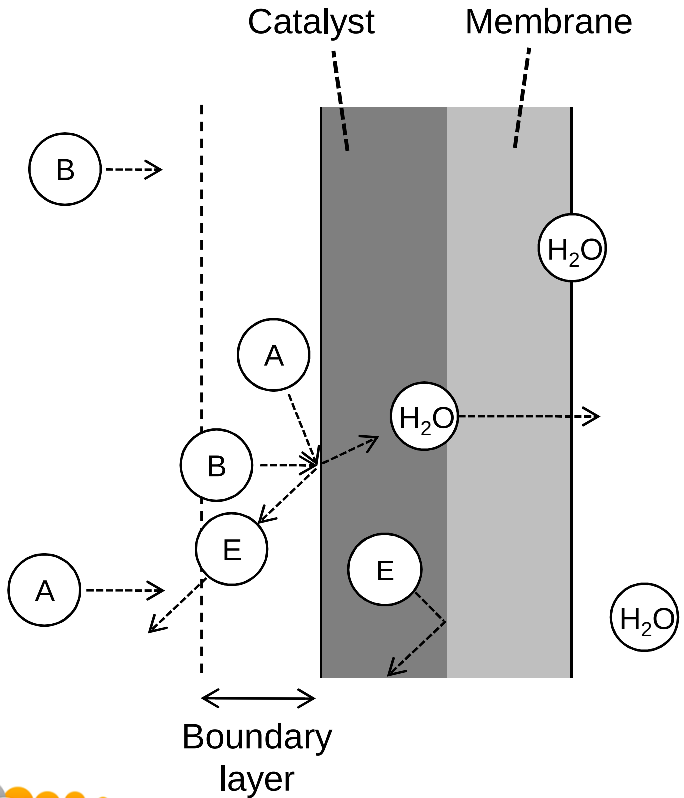
Workpackage 3

Objectives

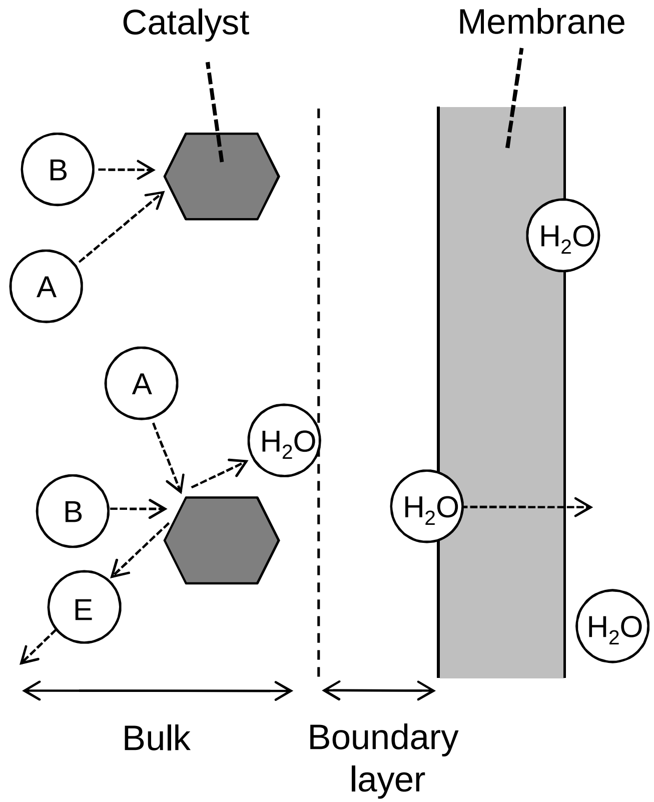
- **Catalyst for hydrogenation of CO_2 to MeOH**
- **More active DMC catalyst**
- **Hydrothermally stable membranes for selective removal of water/ products and retention of gases**
- **Labscale demo unit MeOH/DMC membrane process**
- **First economic evaluation**

Model

Catalytic membrane reactor (CMR)



Inert membrane reactor (IMR)



H.J. Mengers et al., Multi-component mass transfer behavior in catalytic membrane reactors, Chem. Eng. Sci. 117 (2014) 45-54.

Theory

Model

- Reaction $2A + B \rightleftharpoons E + H_2O$

- Bulk membrane reactor: CSTR

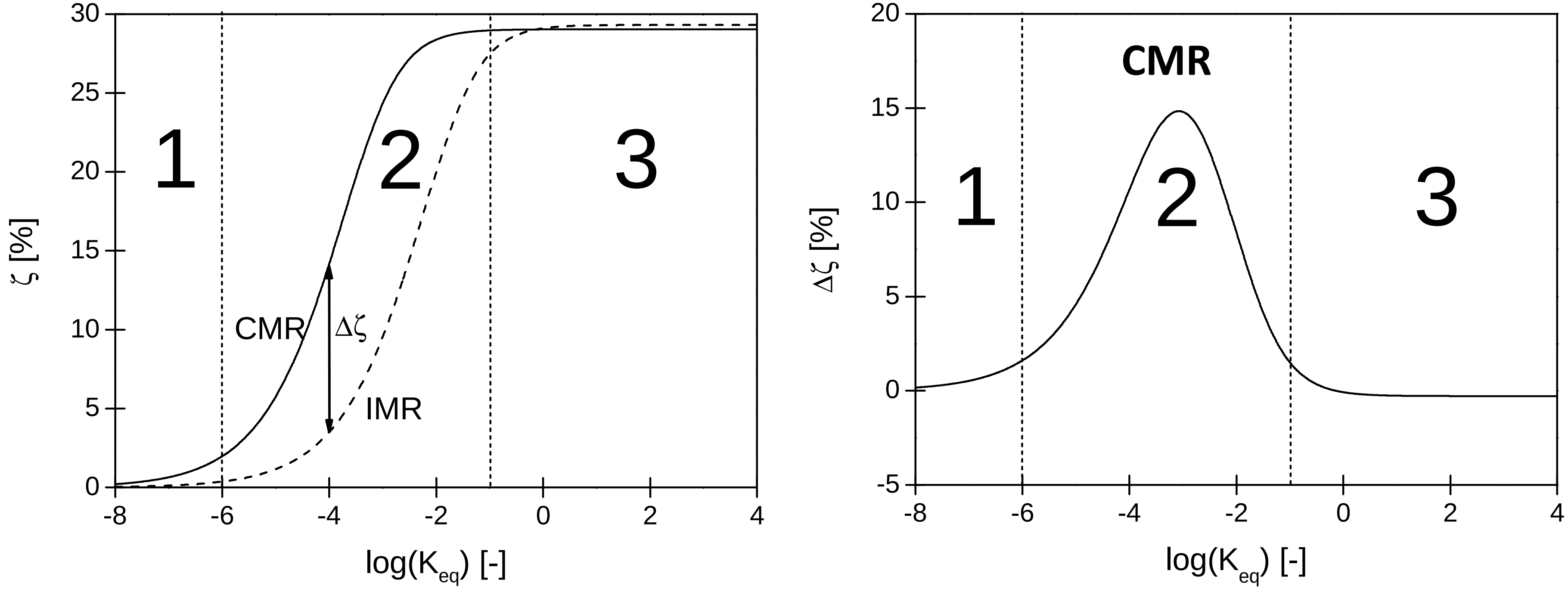
- Mass transport: Maxwell Stefan $$\Delta x_i = \sum_{i \neq j} \frac{\left(\bar{x}_j N_i - \bar{x}_i N_j \right)}{k_{bl} \bar{c}}$$

- Only H_2O permeates through the membrane

- Only mass transfer limitations in boundary layer and membrane

H.J. Mengers et al., Multi-component mass transfer behavior in catalytic membrane reactors, Chem. Eng. Sci. 117 (2014) 45-54.

Results



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Conclusions

- Process and material parameters have a strong influence on results

- Selection membrane reactor depends on equilibrium
  - Low K_{eq} CMR
  - Intermediate K_{eq} CMR
  - High K_{eq} IMR

- Exact position of maximum depends on
  - k_{bl}
  - k_f
  - P_{H2O}
  - τ
  - A/V

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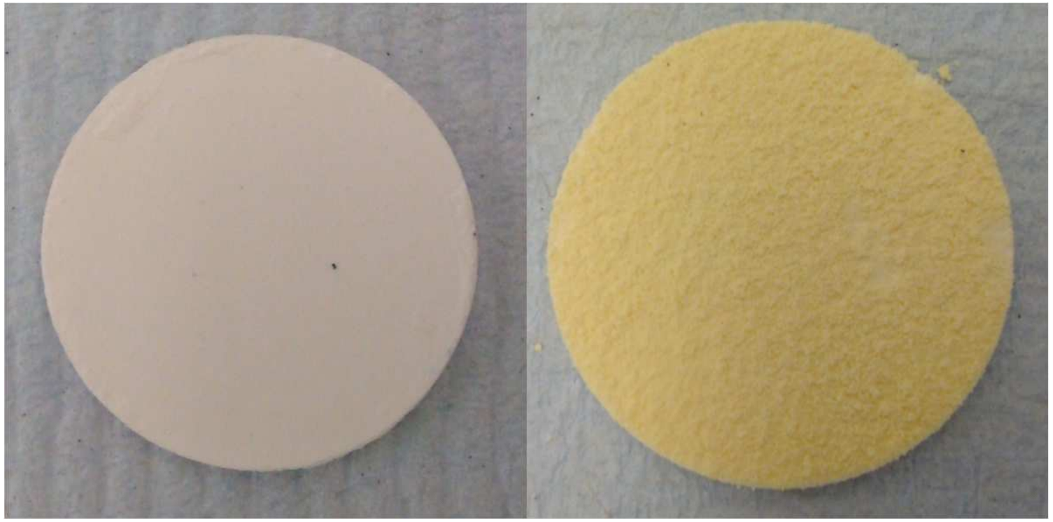
Membranes

Clean Membrane Coated Membrane



Pictures courtesy of Johnson Matthey, 2015

State of the art test setup at the UT

Picture courtesy of the UT

IPR + PhD’s

- **3 patent applications**
- **8 publications**

- **PhD. Cécile Daniel, CNRS-IRCE Lyon**
- **PhD. Harro Mengers, University of Twente**
- **PhD. Michiel Raaijmakers, UT → AkzoNobel**
- **PhD. Nanyi Wang, Leibnitz University Hannover**

Highlight summary

- **New catalysts produced and tested for hydrogenation of CO_2 to MeOH**
- **New DMC catalyst developed and tested**
- **Development of hydrothermally stable membranes for selective removal of water/products and retention of gases at high temperature made good progress**
- **Two new state of art testing facilities for membranes realized and in operation**
- **Economic evaluation almost finalized**

Many thanks for your attention !