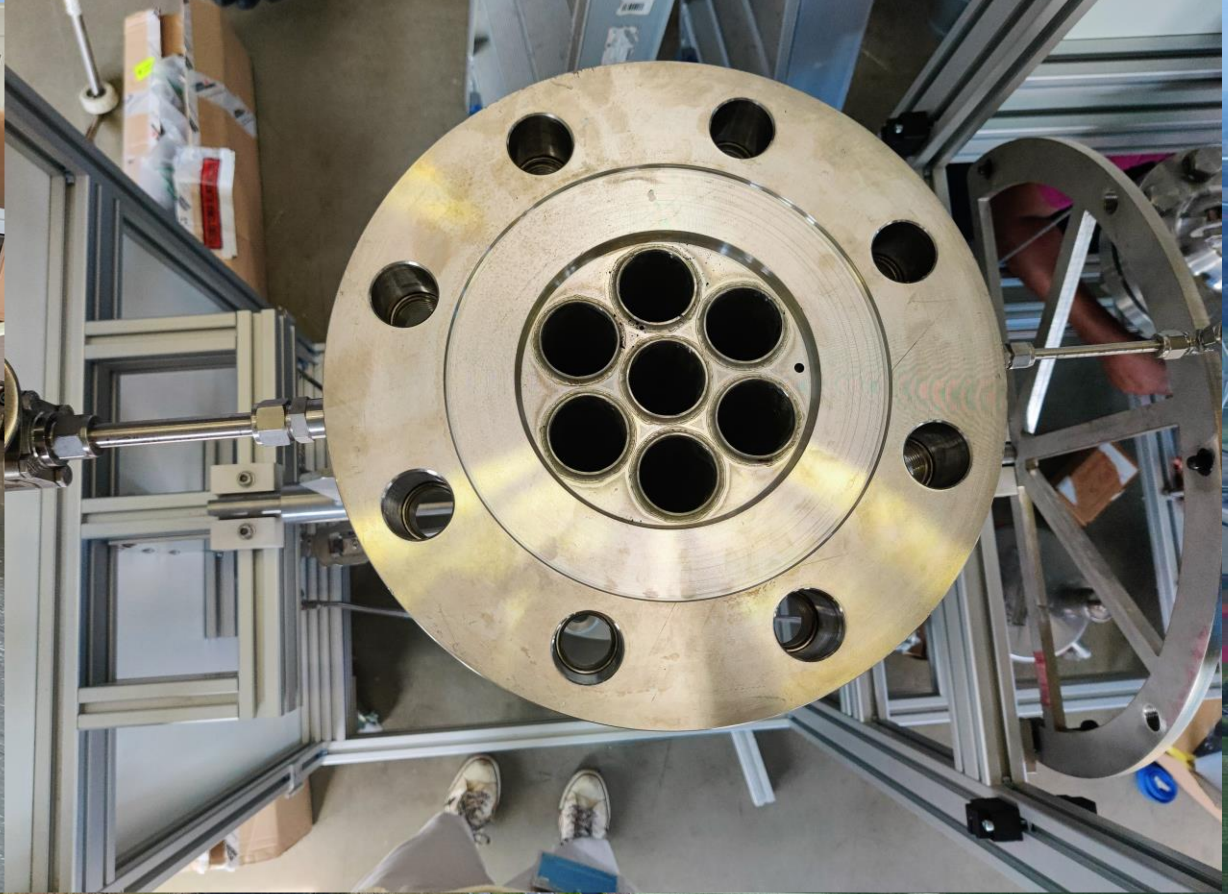




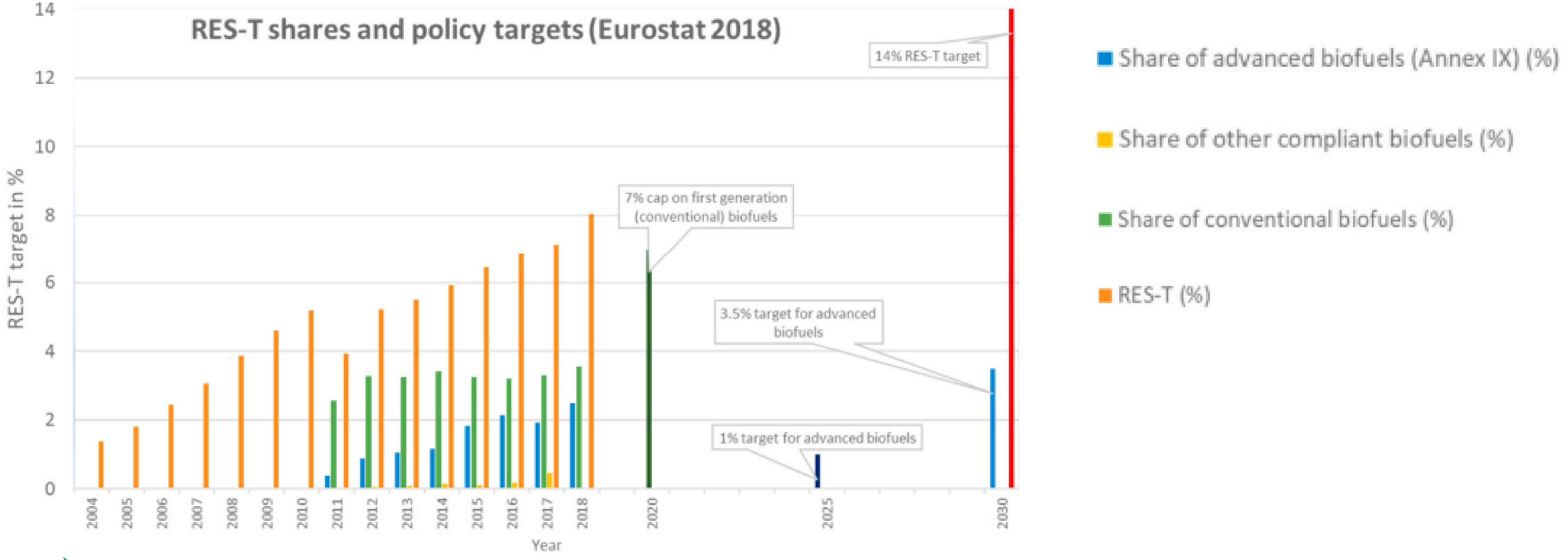
Membrane reactor to enhance a methanol production from CO_2 and H_2 in biomass to biodiesel route

M. Sarić, R. Sumbharaju, M. van Tuel , P. Marcelis

18th May 2022, Innovations in advanced biofuels production, Converge workshop & TNO lab tour

Background

- Advanced biofuels are essential for the transition to zero carbon
- Production costs are higher than their fossil counterparts: *significant innovation*, *technological development* and *scale up needed*



C. Panoutsou et al. , Energy Strategy Reviews 34 (2021) 100633

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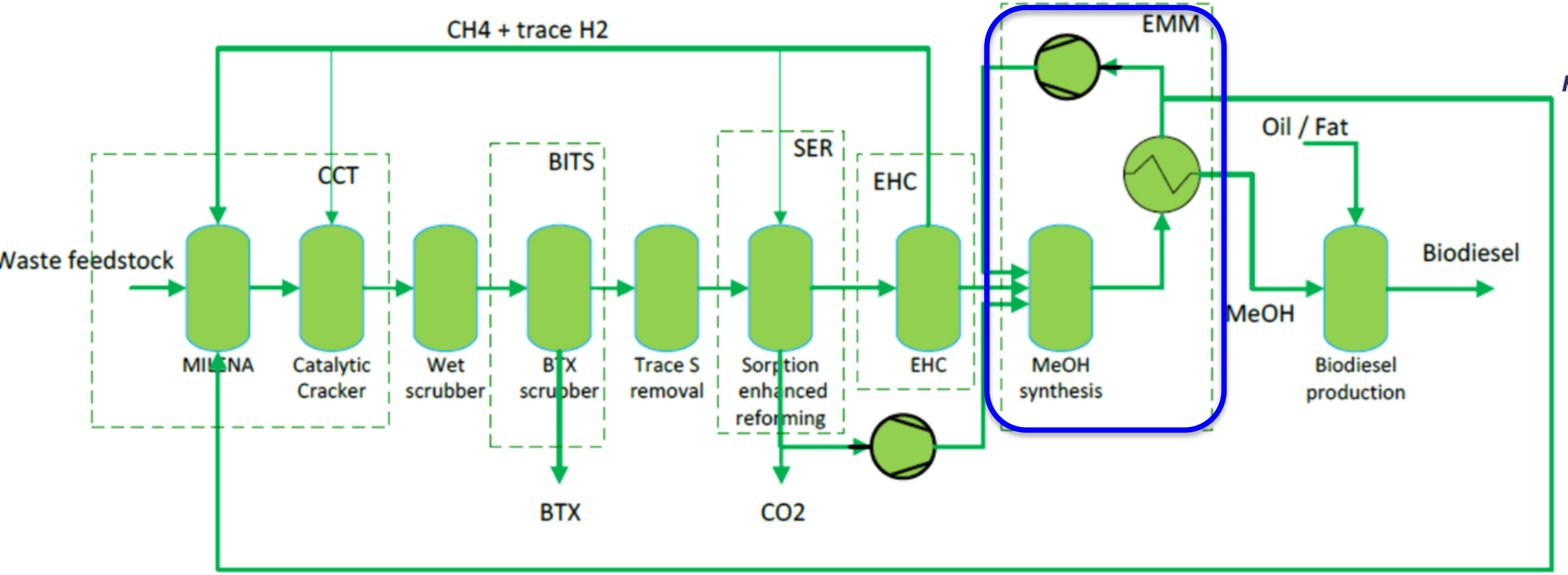
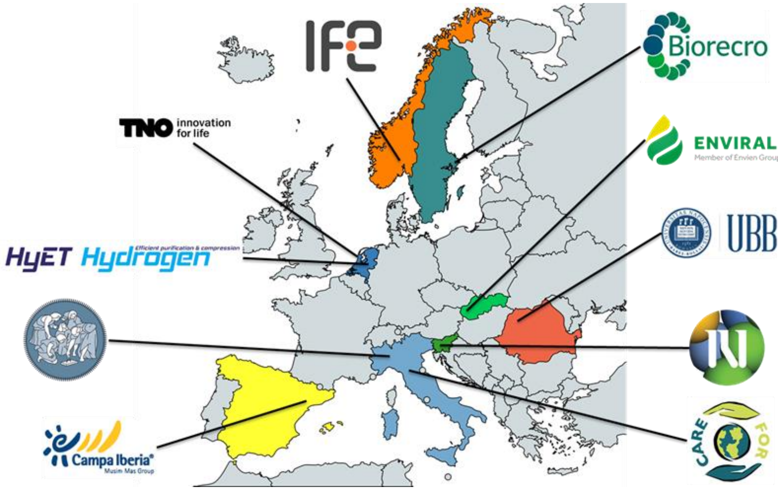
Objectives: Converge project

- The CONVERGE project aims to increase efficiency of the biodiesel production by 12% per secondary biomass unit used, and reduce the CAPEX by 10%
- The CONVERGE technologies will be validated for more than 2000 cumulated hours taking these from the TRL3 to development stage TRL5.





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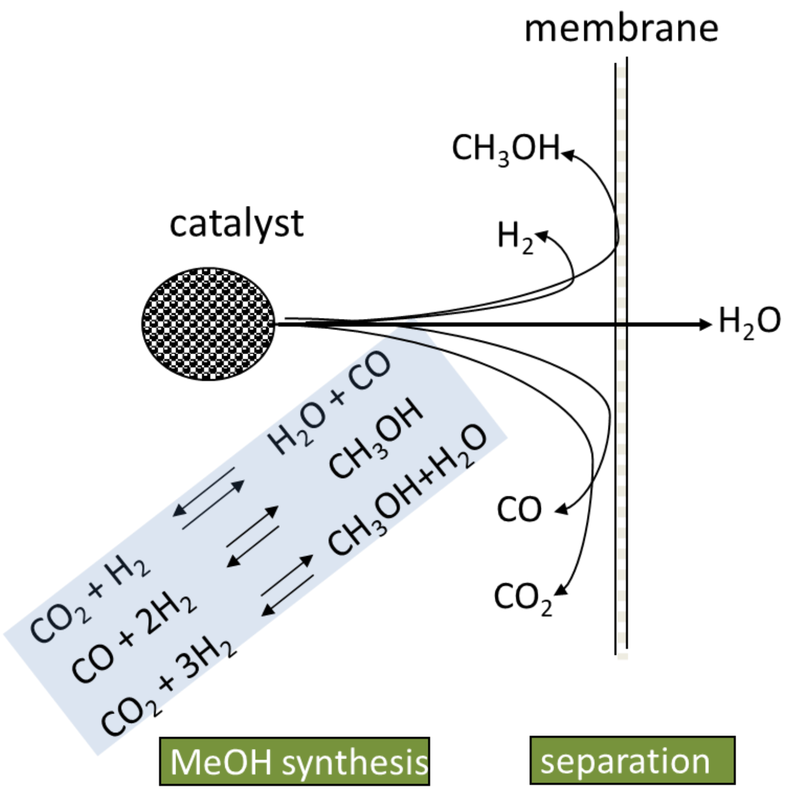
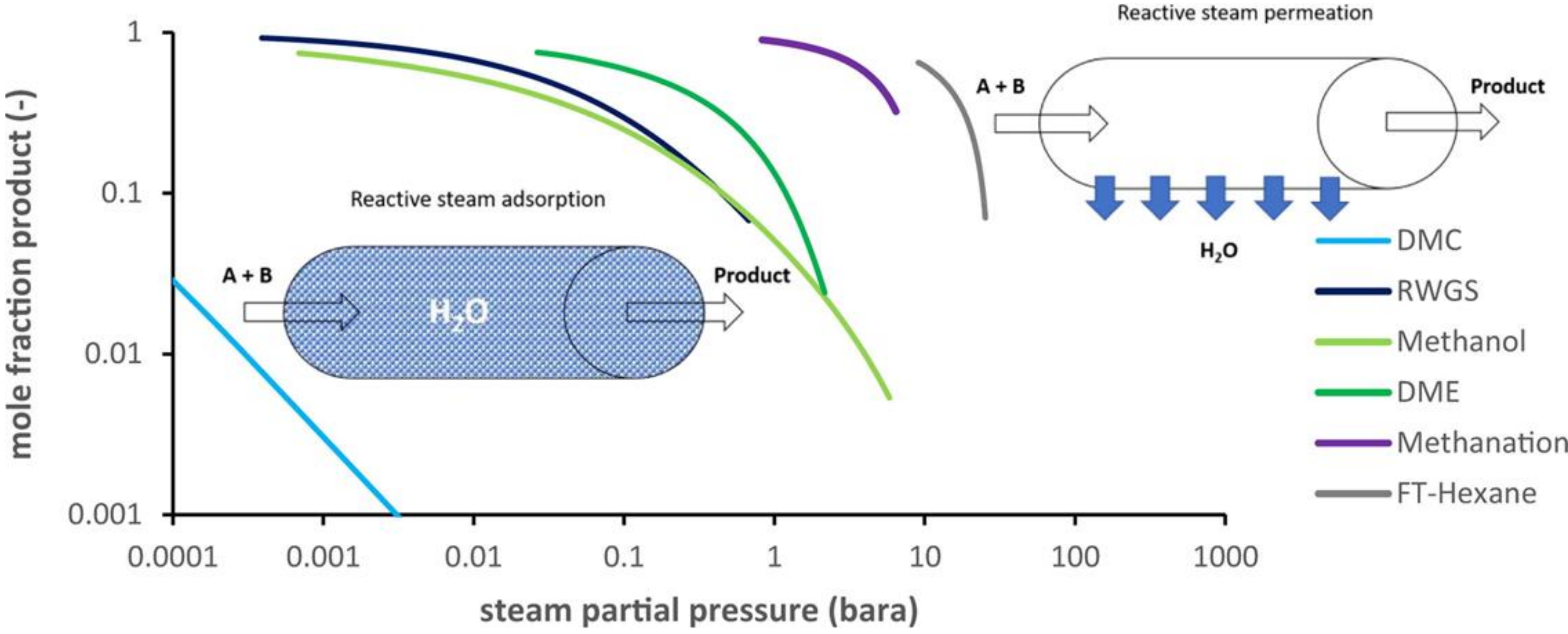
Separation enhanced reactions



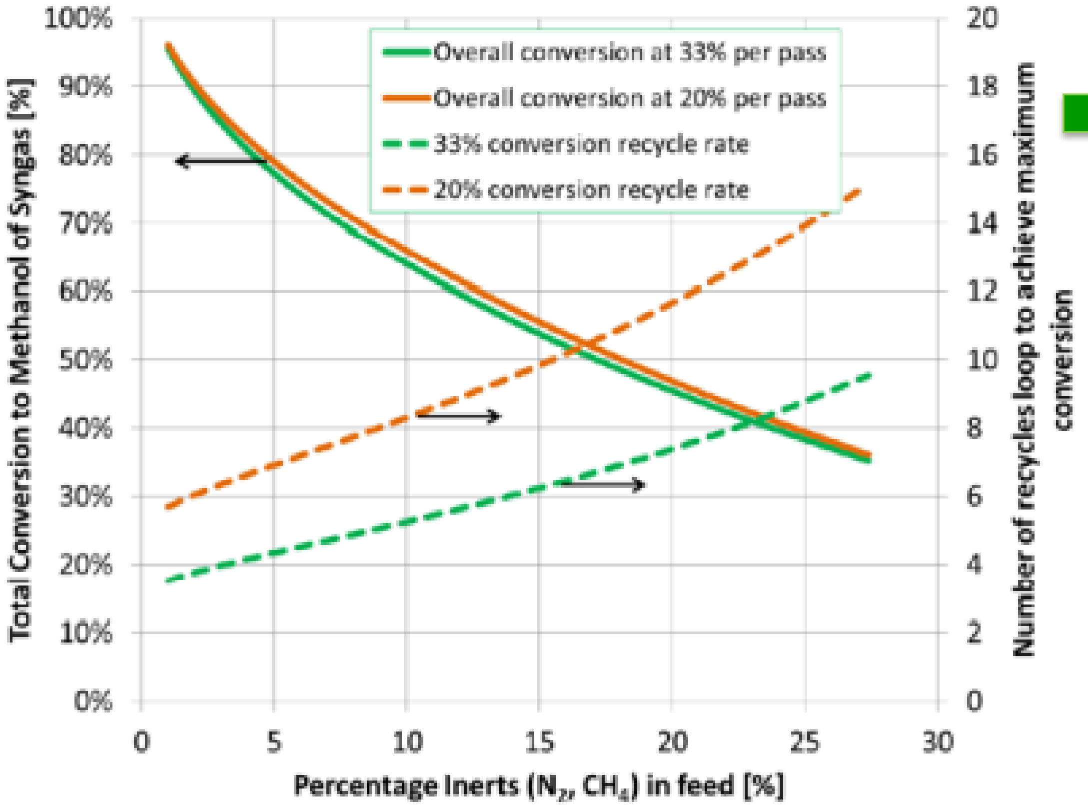


- Significant increase of MeOH yield at moderate steam partial pressures

J. van Kampen et al. (2019) Steam separation enhanced reactions: Review and outlook / Chem. Eng. J. v.374

Objectives: membrane assisted methanol production

- Develop stable membranes at reaction conditions
- Develop multi-tube membrane reactor, targeted conversion for feed CO_2/H_2 33% per pass
- Demonstration of integrated process at TRL 5



Decrease of recycle:

- Decrease of reactor size
- Reduction in energy penalty of the recycle compressors

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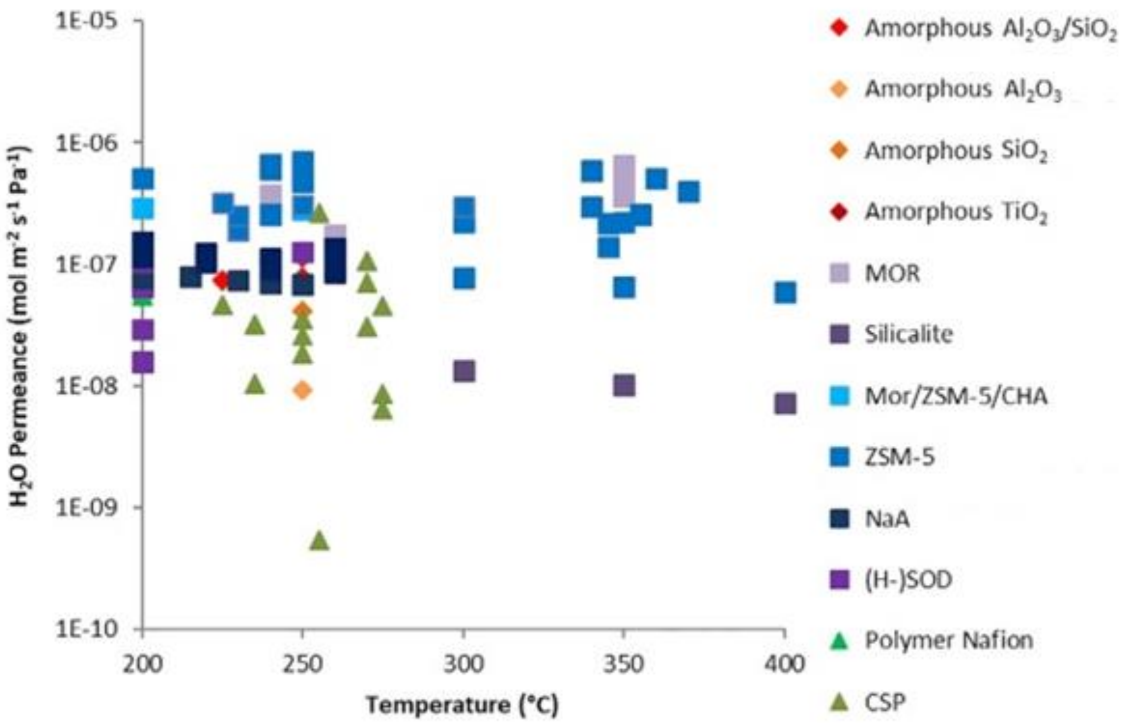
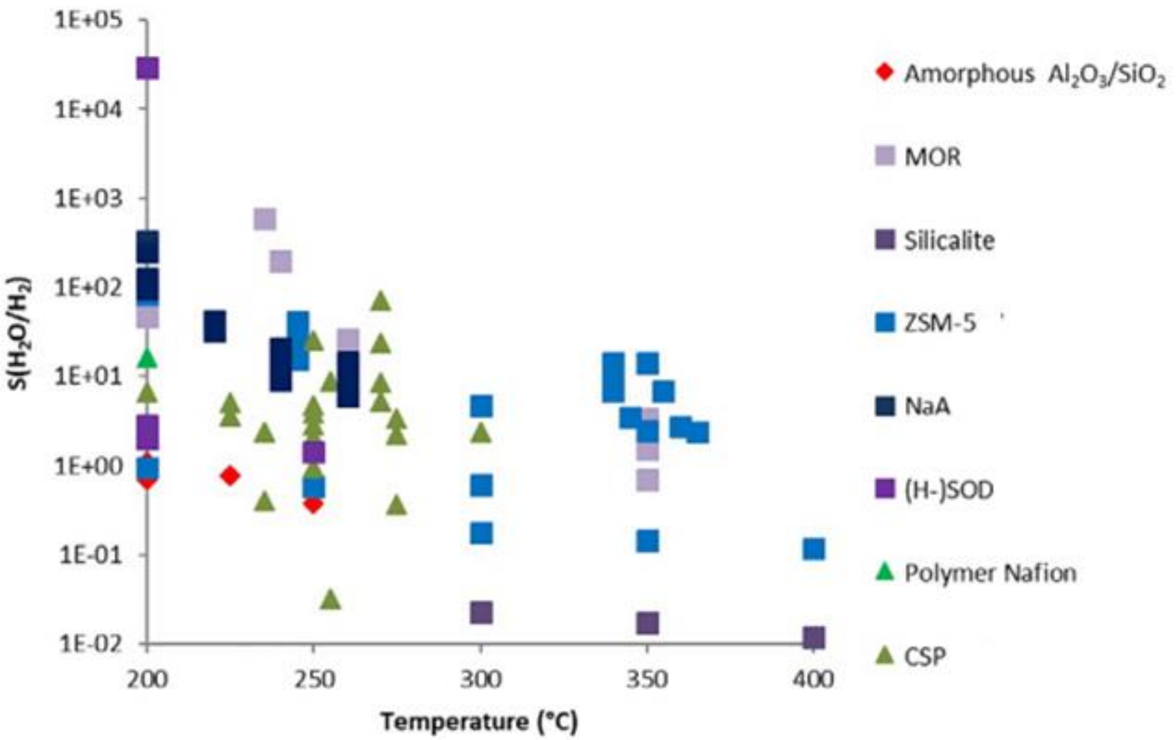
Membrane development -target

Membrane development targets:

1) Stability at the methanol operating T and p (T = 220-275 °C, p up to 100 bar)
2) High selectivity for steam and methanol $CO_2 + 3H_2 = CH_3OH + H_2O$
3) High steam/methanol permeability ➔ high flux





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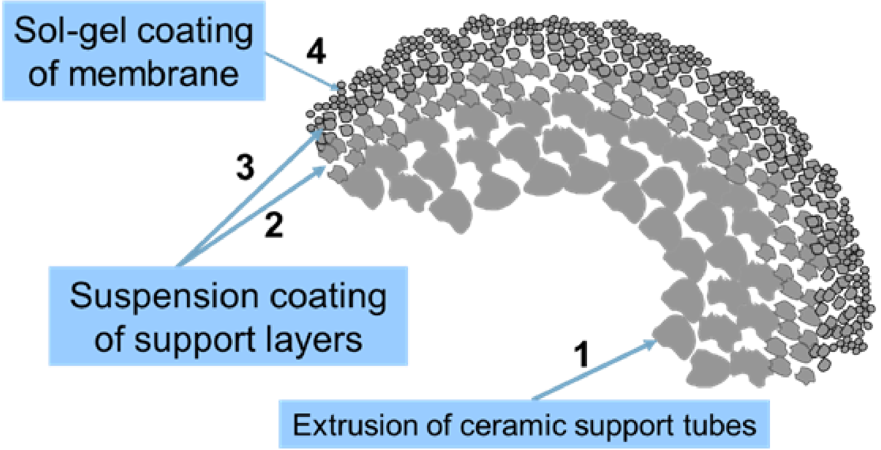
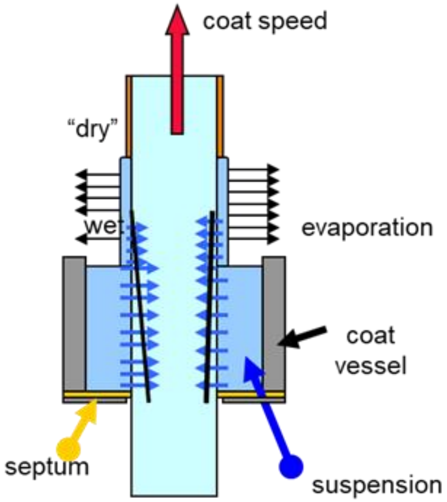
J. van Kampen et al. (2019) Steam separation enhanced reactions: Review and outlook / Chem. Eng. J. v.374

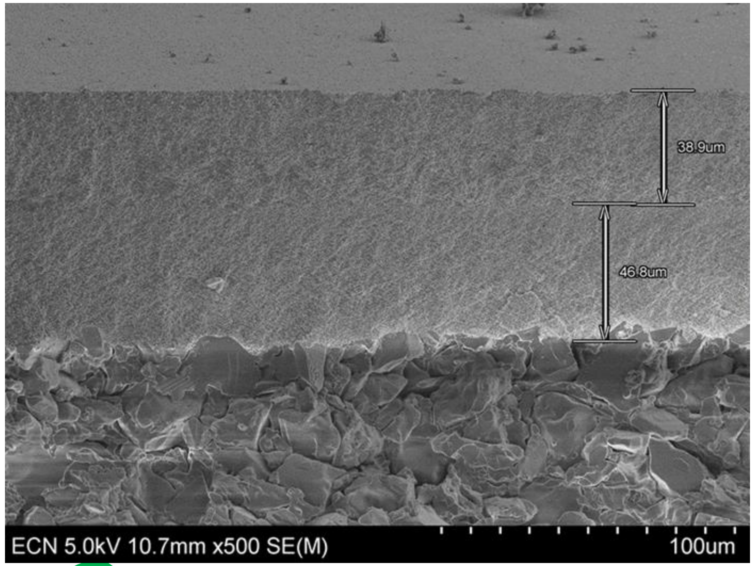
Membrane synthesis procedure

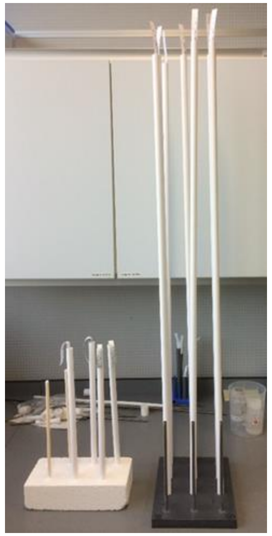




Membrane support layers

Coating process





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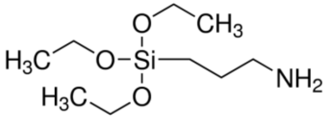
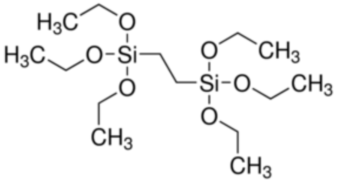
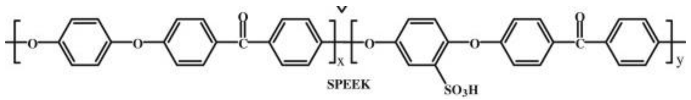
Membrane selection

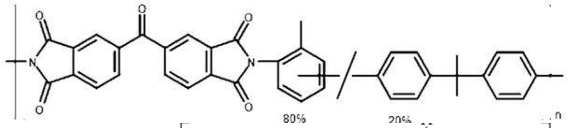
- Amorphous microporous

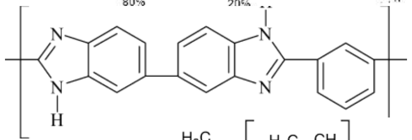
APTES-PA (Aminopropyl triethoxysilane-Polyamide) 

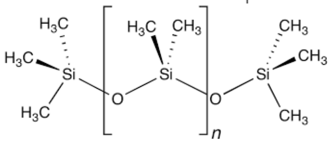
BTESE (1, 2-bis (triethoxysilyl) ethane) 

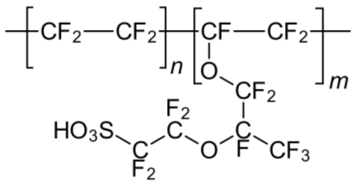
- Polymeric

SPEEK (sulfonated poly(ether ether ketone)) 

PI (Poly Imide) 

PBI (Polybenzimidazol) 

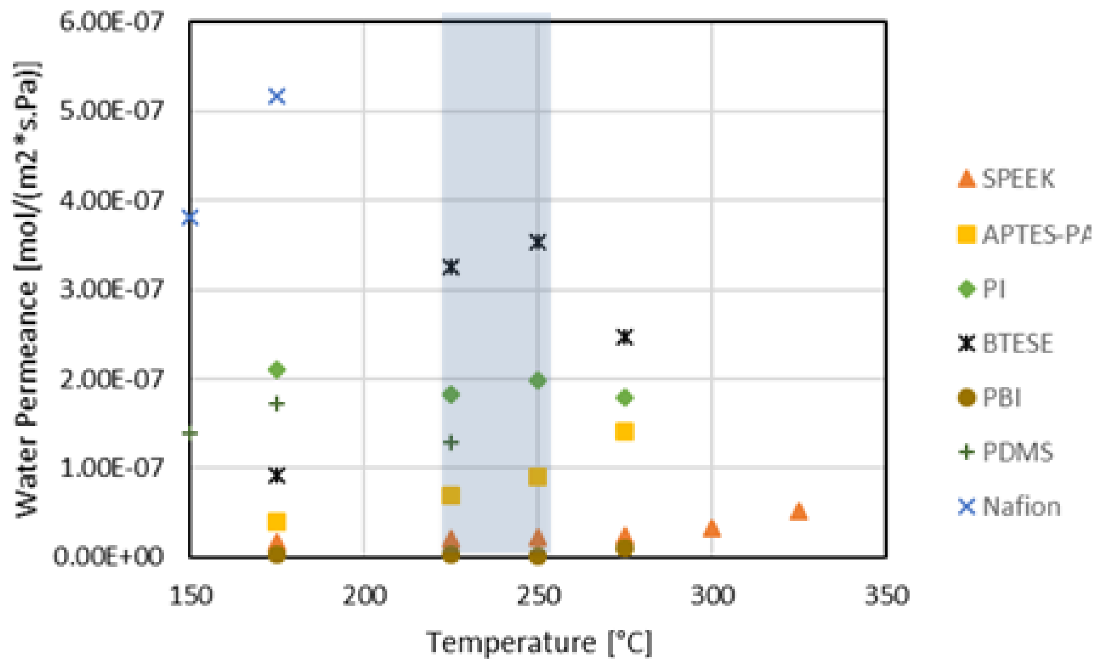
PDMS (Polydimethylsiloxane) 

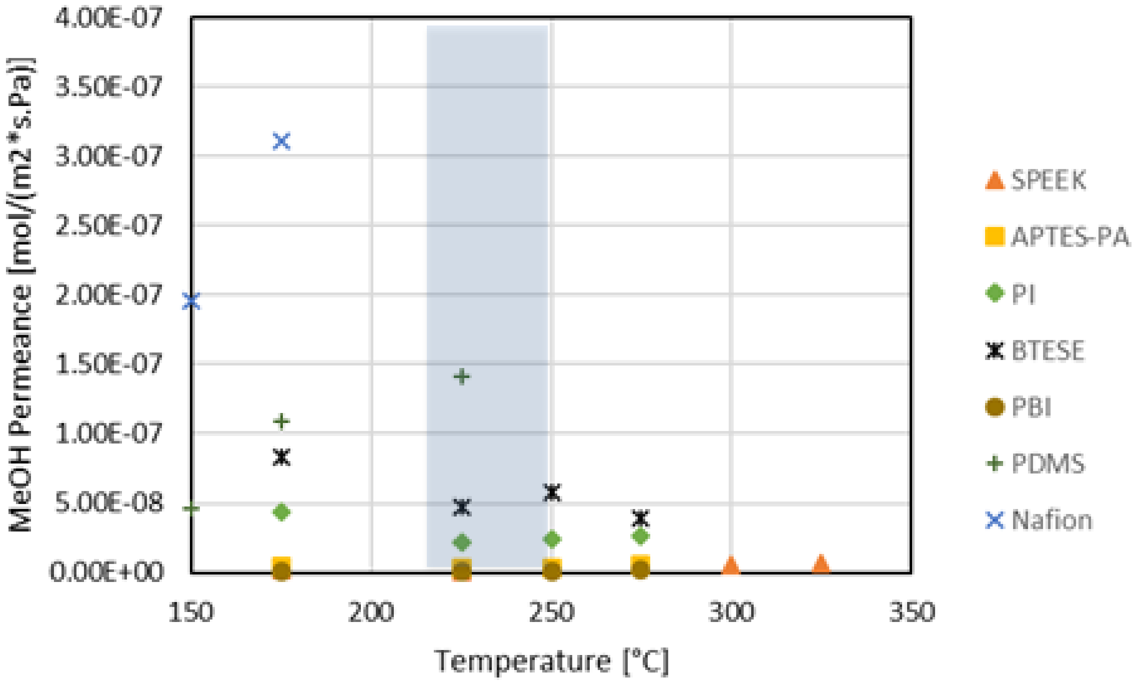
Li-Nafion 

Membrane separation test results

Test conditions:

- p_{feed} =35 bar, p_{perm} =1.5 bar, no sweep
- 60% H_2, 10% (50/50)methanol/steam, 20% CO_2, 1% CO, 9% N_2





- Nafion, BTESE, PI highest steam and MeOH permeance
- BTESE performance decreases at 275°C, Nafion not selective at T>200°C, PDMS not selective T > 225°C
- SPEEK and PBI low H_2O and MeOH permeance

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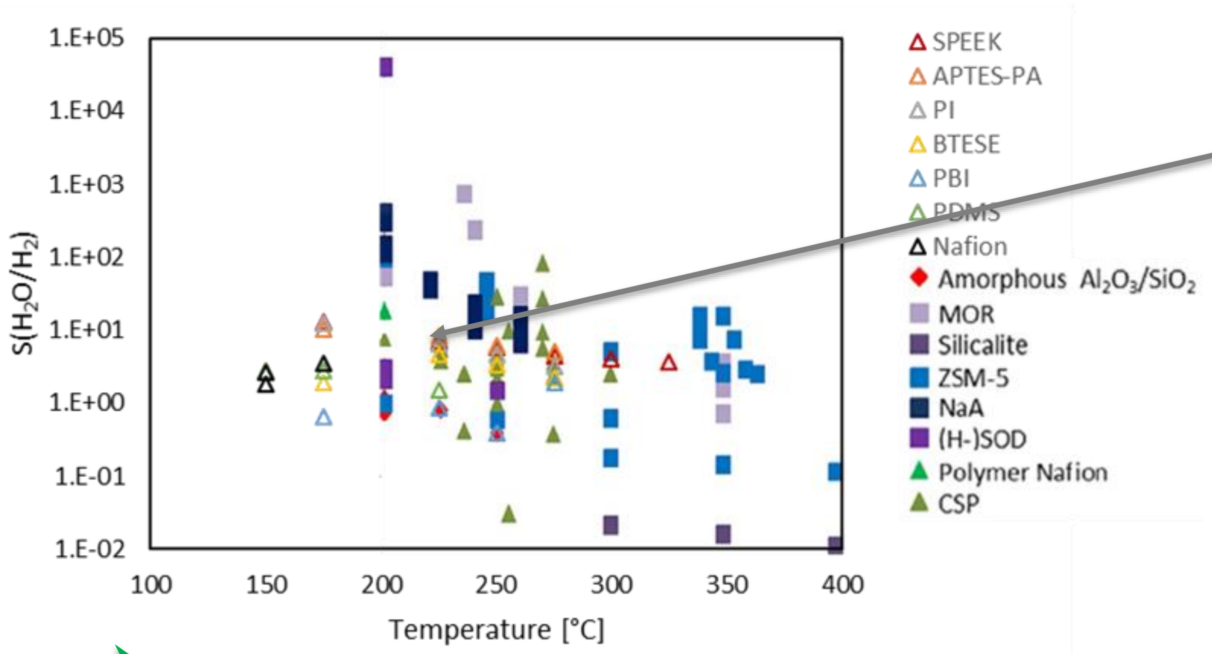
Conclusions: Membrane characterisation

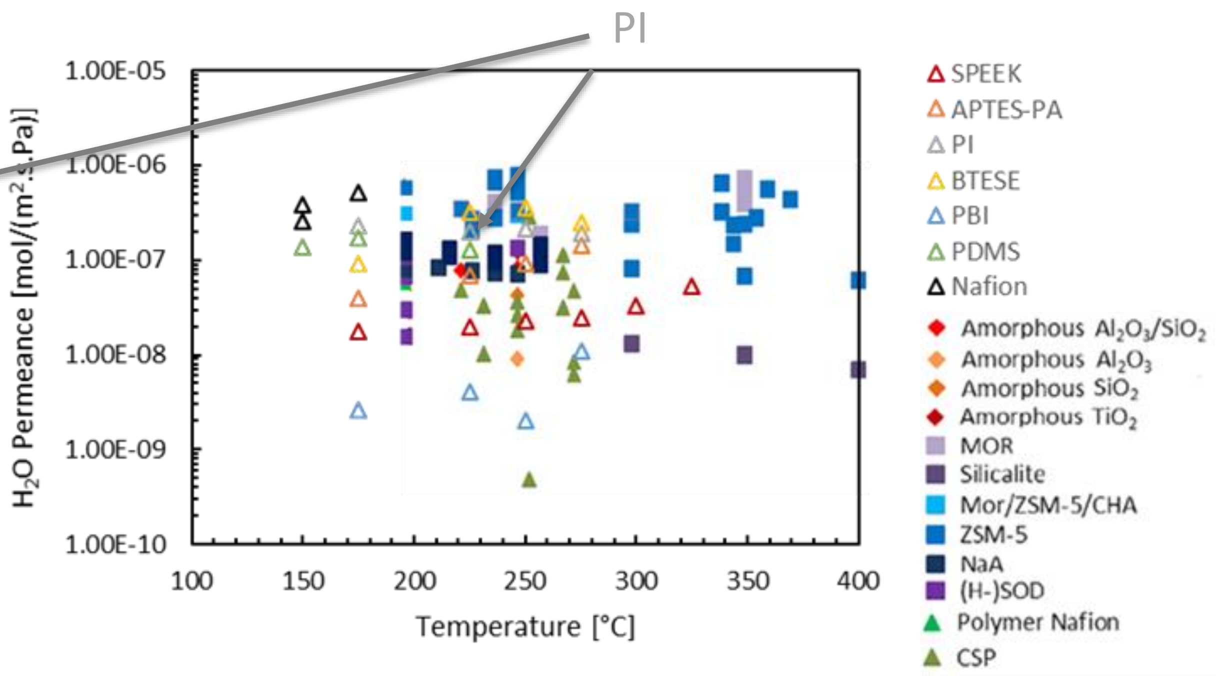
- PI membrane preselected as the most promising to reach conversion targets. (T_{range} =225-250°C)

	PI	BTESE	APTES-PA
• H_2O/H_2 selectivity:	4.7-6.5	3.5-4.3	6-8
• $MEOH/H_2$ selectivity:	0.6-0.8	0.6-0.7	0.2-0.4
• H_2O permeance:	PI	1.6·PI	PI/2.3
• MeOH permeance:	PI	2.2·PI	PI/8.4

$H_2O>H_2>MEOH>CO_2>CO≈N_2$

- Steam/H_2 behaviour compares well to literature





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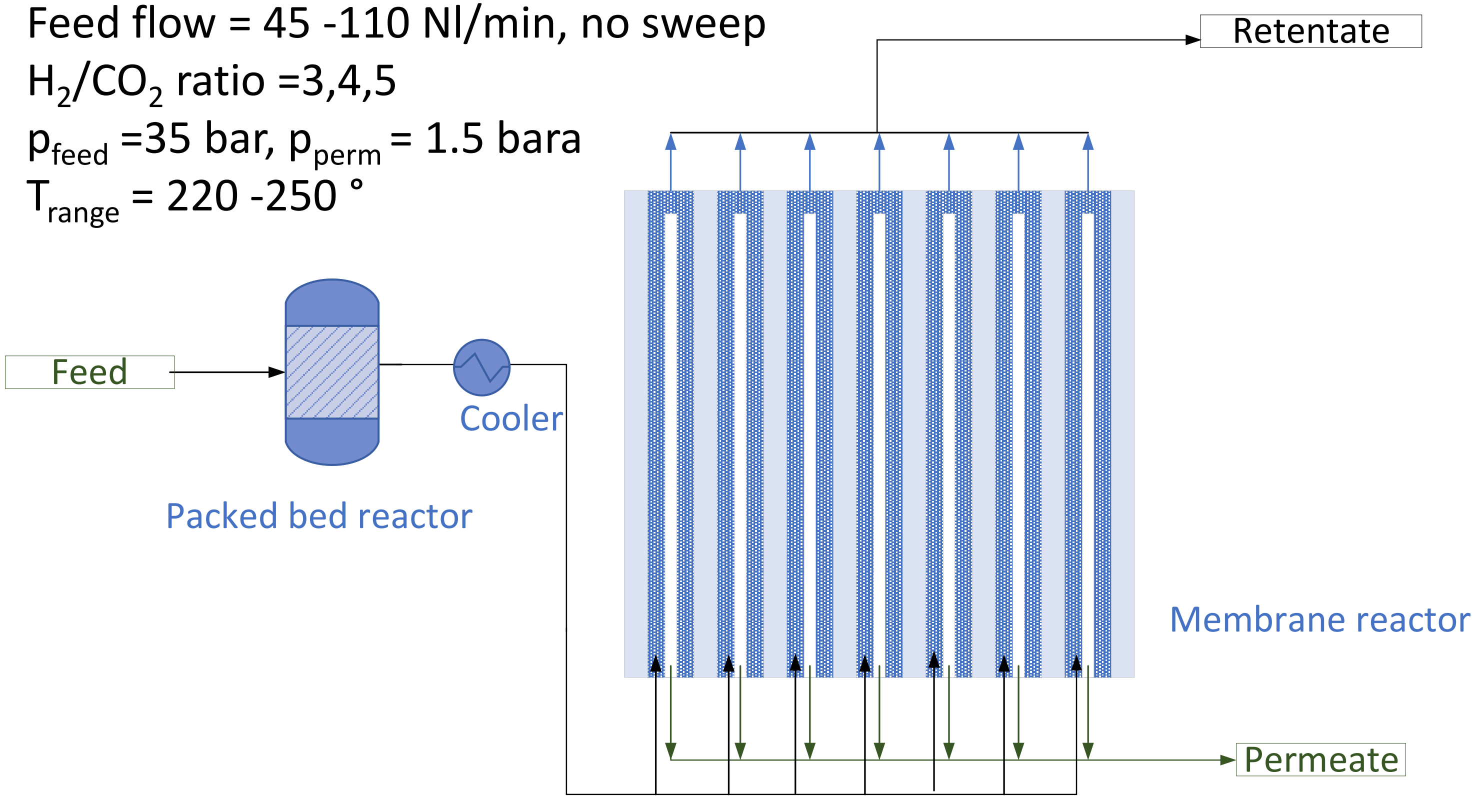
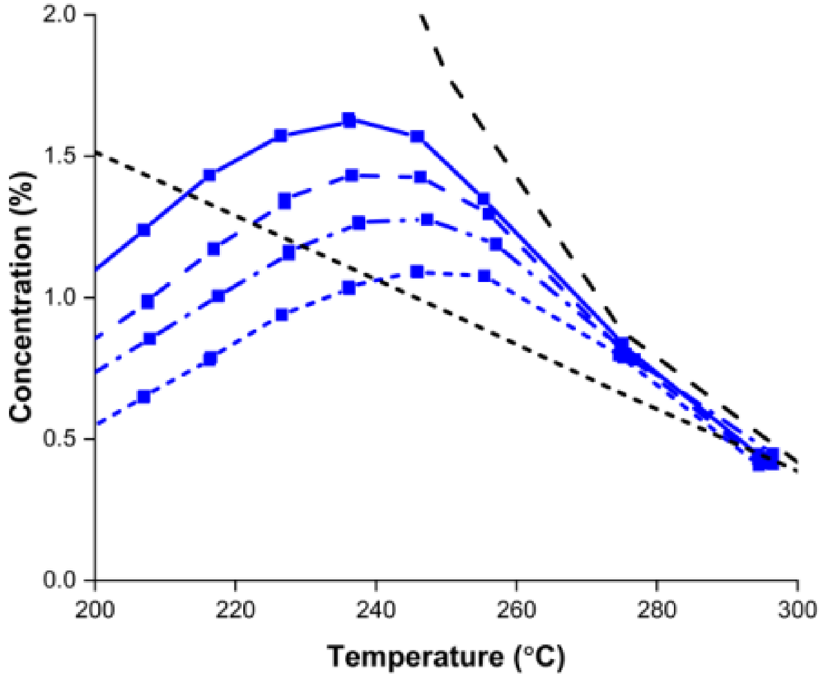
Multi-tubular membrane reactor

- Multi-tubular membrane reactor constructed with 7 PI membranes of 80 cm effective length, $A_{mem} = 0.25 m^2$
- Commercial MeOH catalyst (ALFA AESAR)

Feed flow = 45 -110 Nl/min, no sweep
H_2/CO_2 ratio =3,4,5
p_{feed} =35 bar, p_{perm} = 1.5 bara
T_{range} = 220 -250 °





Catalyst characterisation

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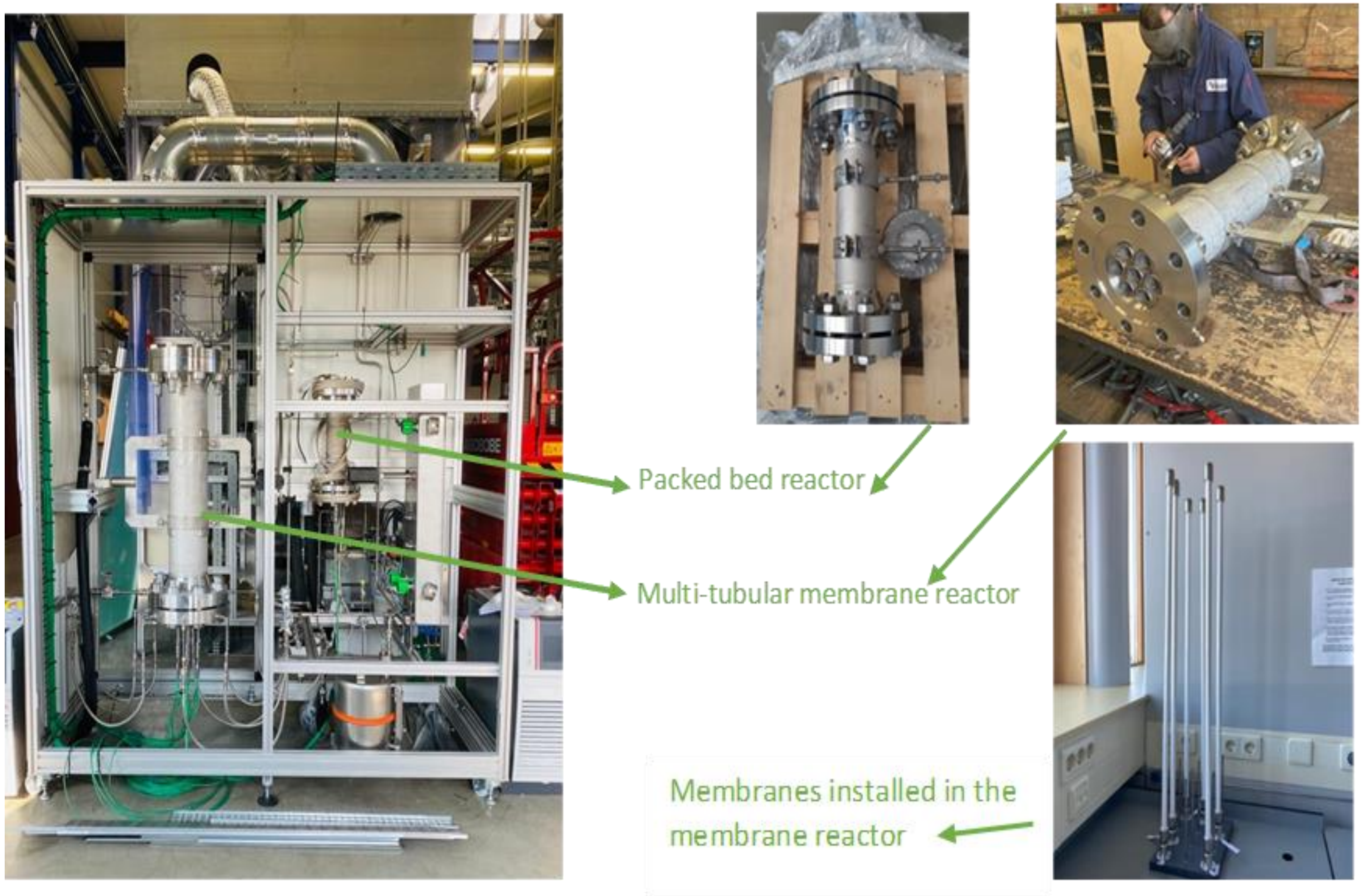
J. Van Kampen, Proof-of-concept for sorption enhanced dimethyl ether synthesis, phD theisis

Multi-tubular membrane reactor construction



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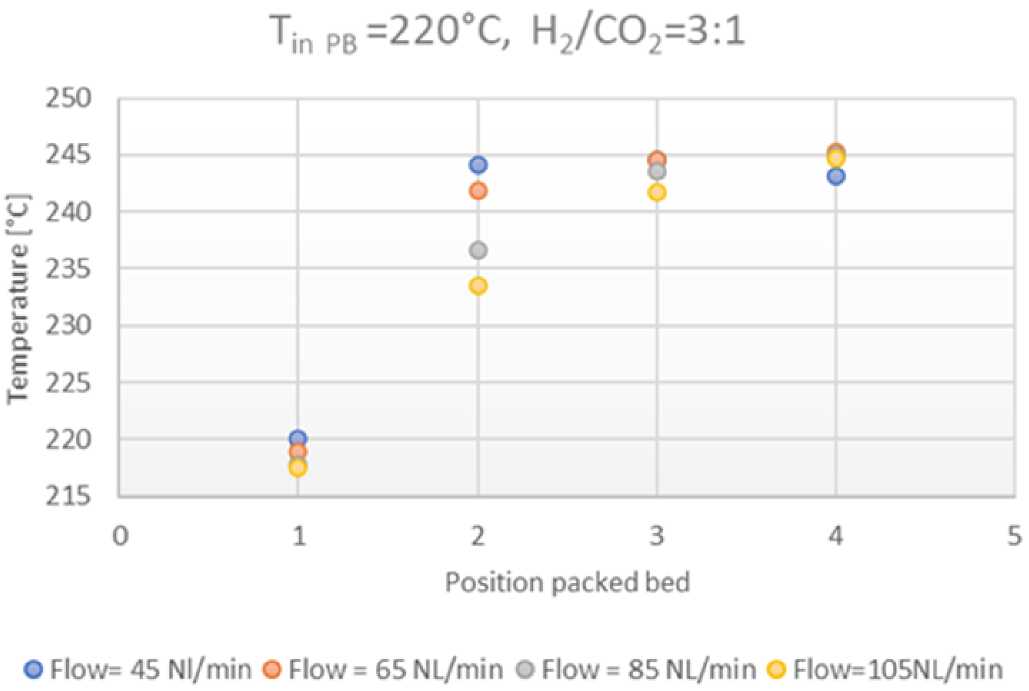
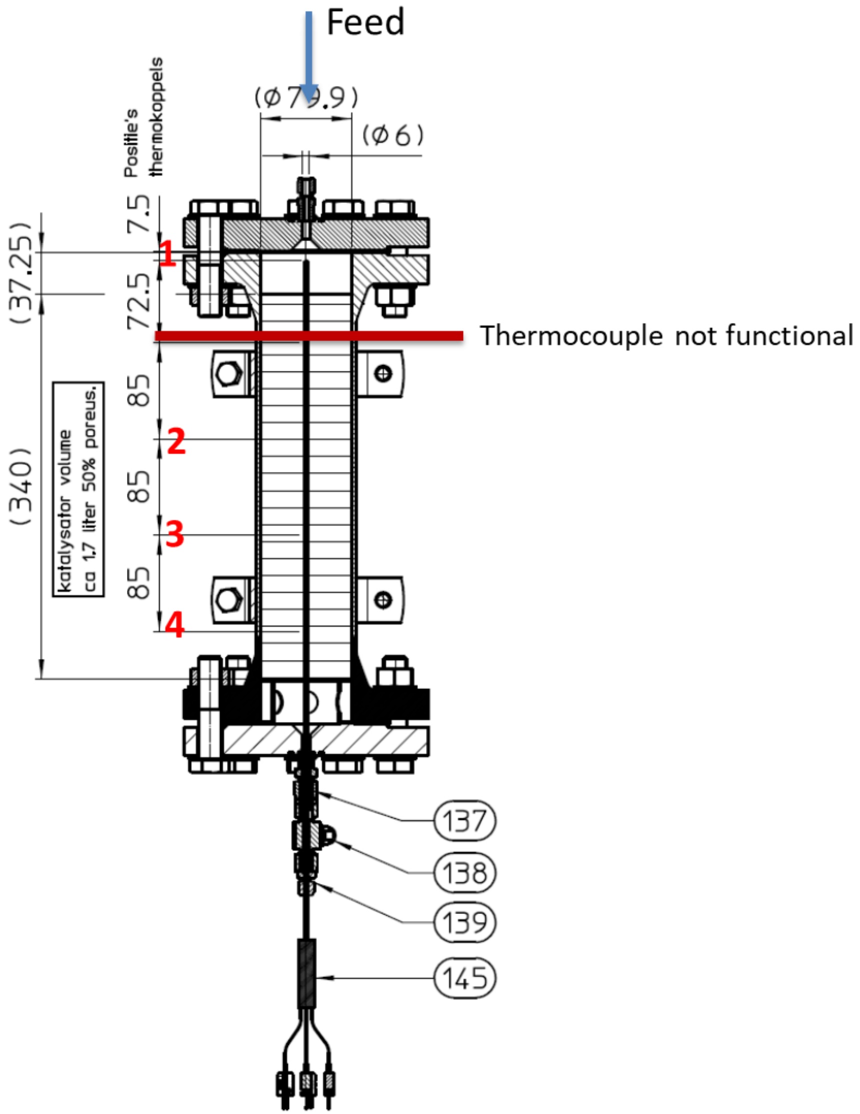
Packed bed reactor results

- WHSV 0.60-1.32 h^{-1}
- 5 thermocouples in the packed bed (one not functional)
- Equilibrium conversion reached for all WHSV, and for all tested T





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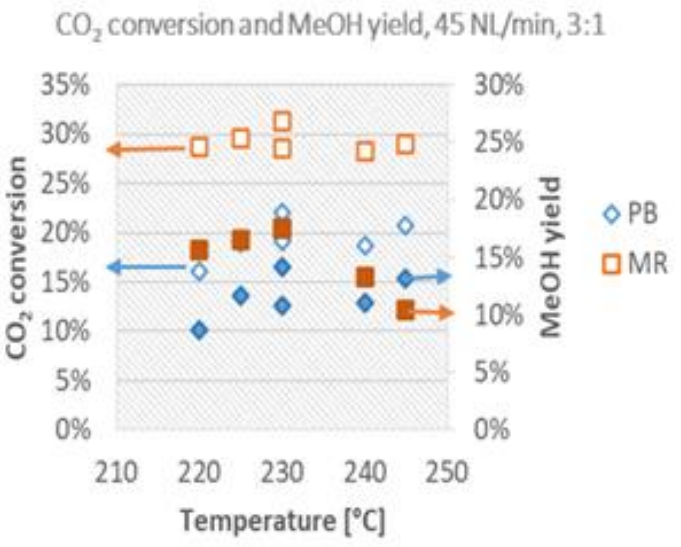
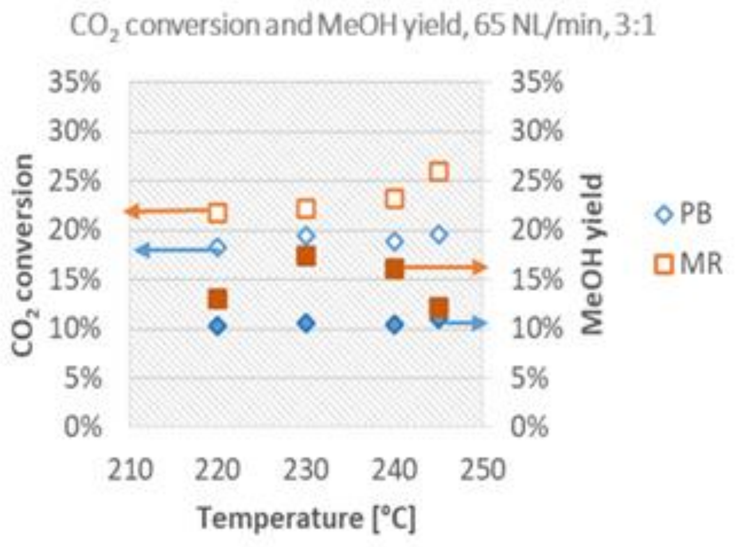
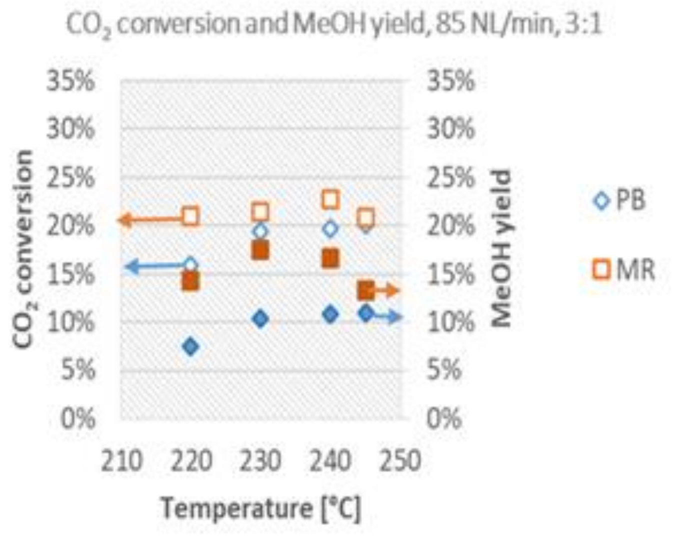
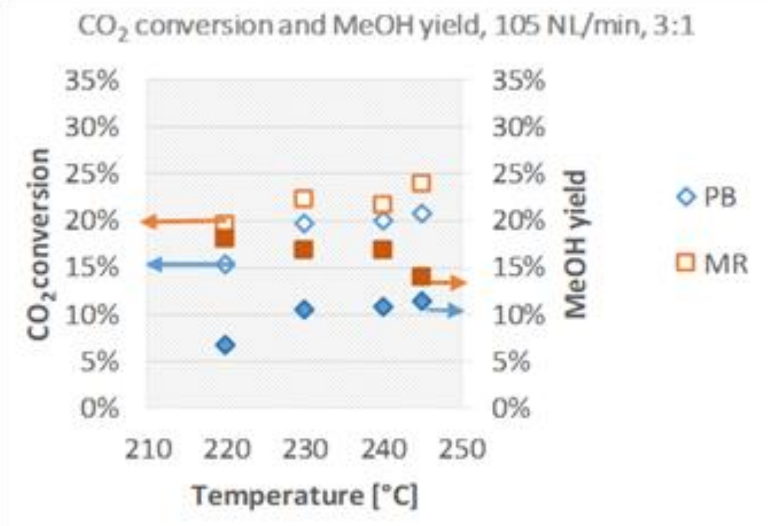
Multi tubular membrane reactor, stochiometric conditions

- WHSV = 0.2- 0.4 h^{-1}
- MR CO_2 and MeOH yield increased compared to packed bed reactor
- Highest increase observed for the lowest feed flow corresponding to WHSV = 0.2 h^{-1} at 230 °C:
  - ➔ 30 % vs 22% MR vs PB CO_2 conversion
  - ➔ 18% vs. 11% MR vs PB MeOH yield









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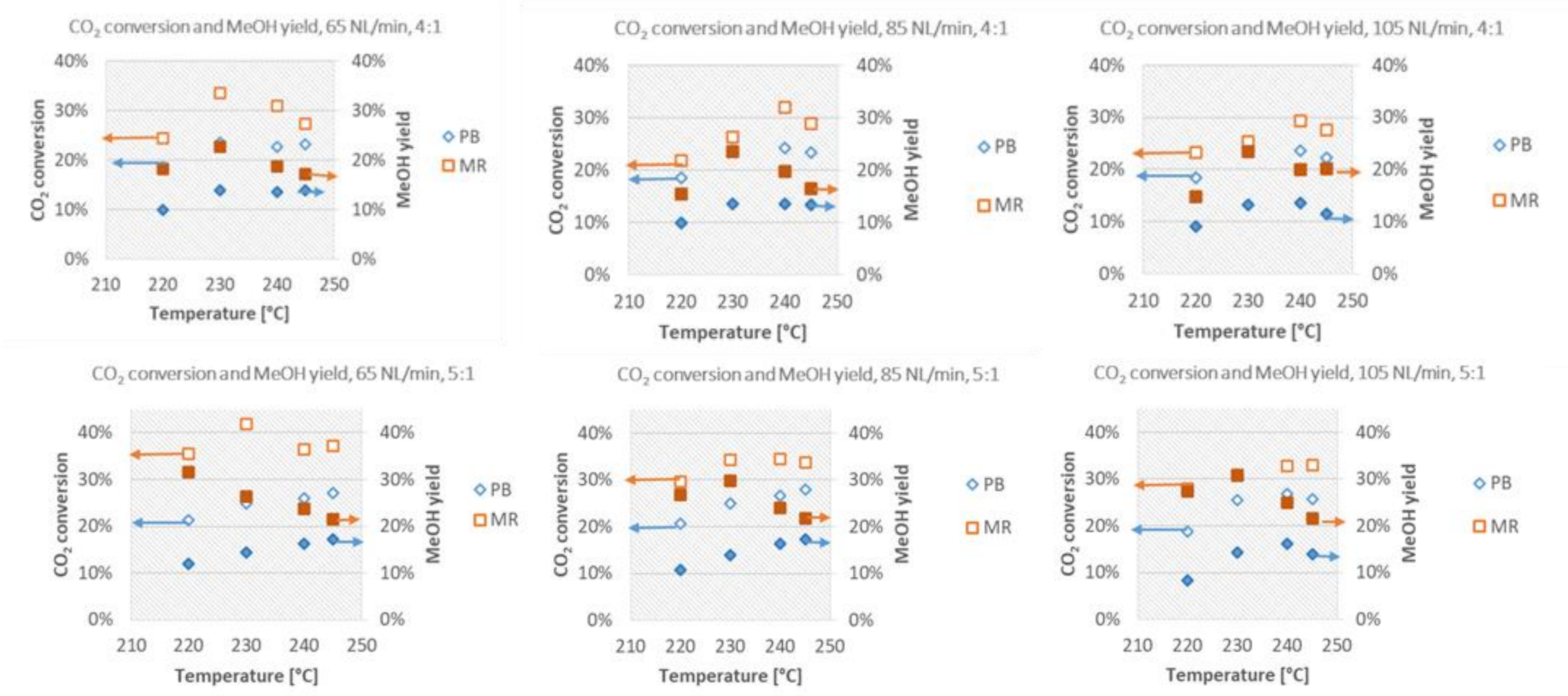
Multi tubular membrane reactor, H_2 excess



- As expected, with increase of H_2 in the feed, overall CO_2 conversion and MeOH yield increase.

Max. achieved 65 NL/min, H_2/CO_2 =5, T = 230°C : ➔ 42 % vs 25% MR vs PB CO_2 conv., 26% vs. 14% MR vs PB MeOH YLD

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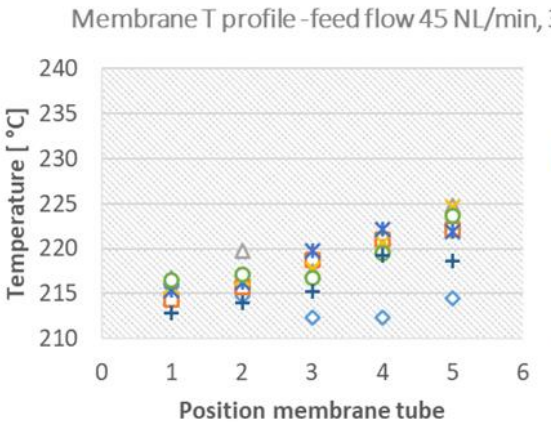
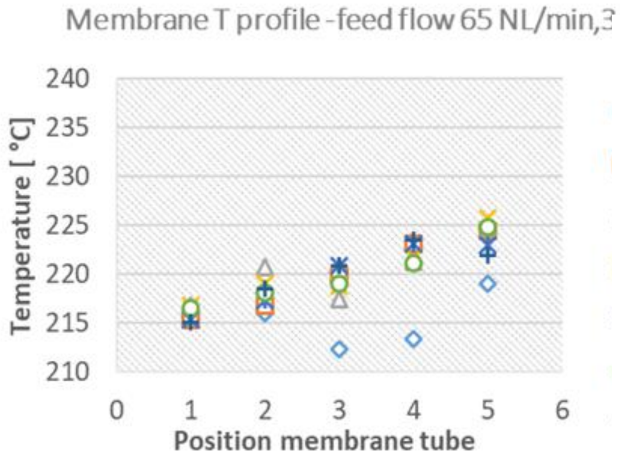
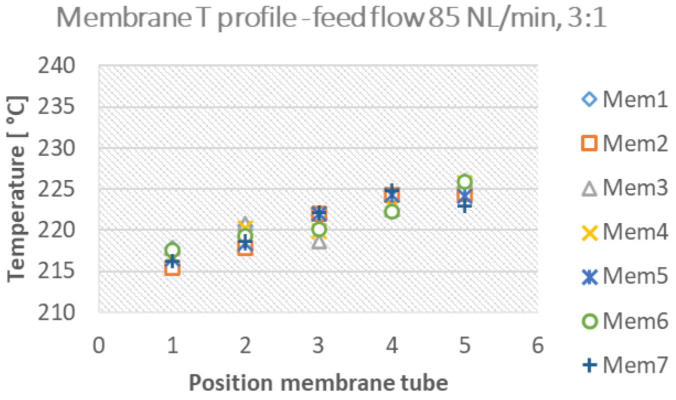
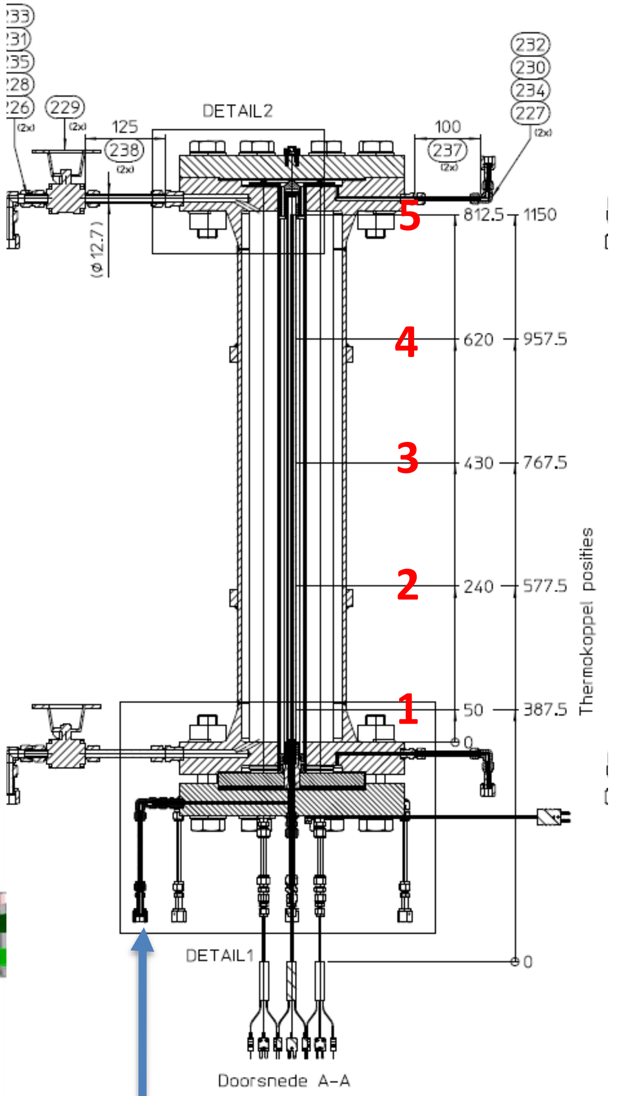
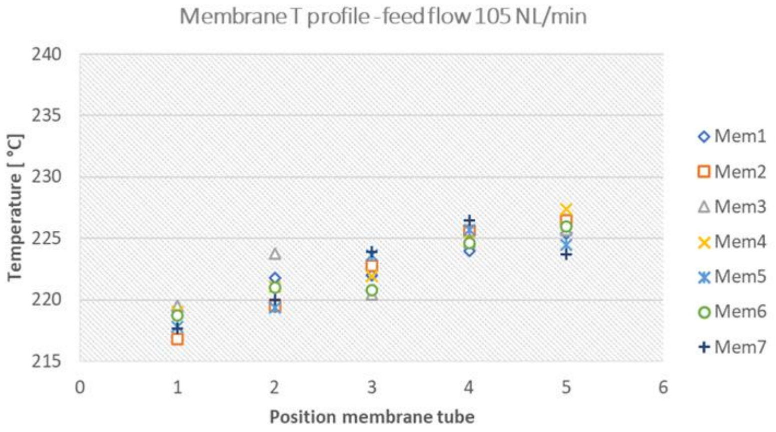
Temperature profiles per membrane at different feed flows



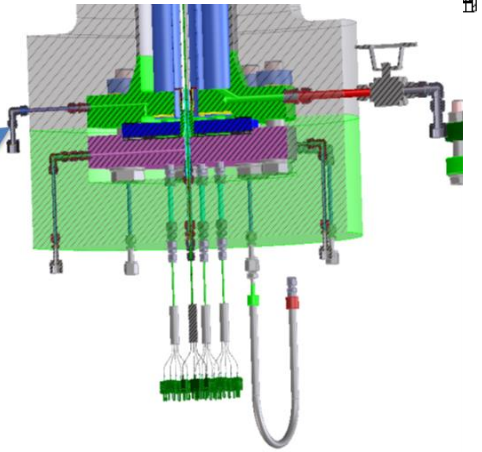








Feed entrance



- Thermocouples are positioned in middle of the membrane tube

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Conclusions

- 5 polymeric and 2 hybrid silica membranes characterized on separation performance
- Membrane performance comparable to reported in the literature
- PI membrane had the best performance ➔ installed in multi-tubular membrane reactor
- Multi-tubular membrane reactor with A_{mem} = 0.25 m^2 constructed, MeOH production capacity 0.5L/h
- MR CO_2 and MeOH yield increased compared to packed bed reactor
- Highest increase for stochiometric composition observed for the lowest feed flow corresponding to WHSV = 0.2 h^{-1} at 230 °C:
  - ➔ 30 % vs 22% MR vs PB CO_2 conversion
  - ➔ 18% vs. 11% MR vs PB MeOH yield
- As expected, in H_2 excess, an overall CO_2 conversion and MeOH yield increase
- Maldistribution of the flow observed in the membrane reactor at low feed flows

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Acknowledgements

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Questions ?

Contact: marija.saric@tno.nl

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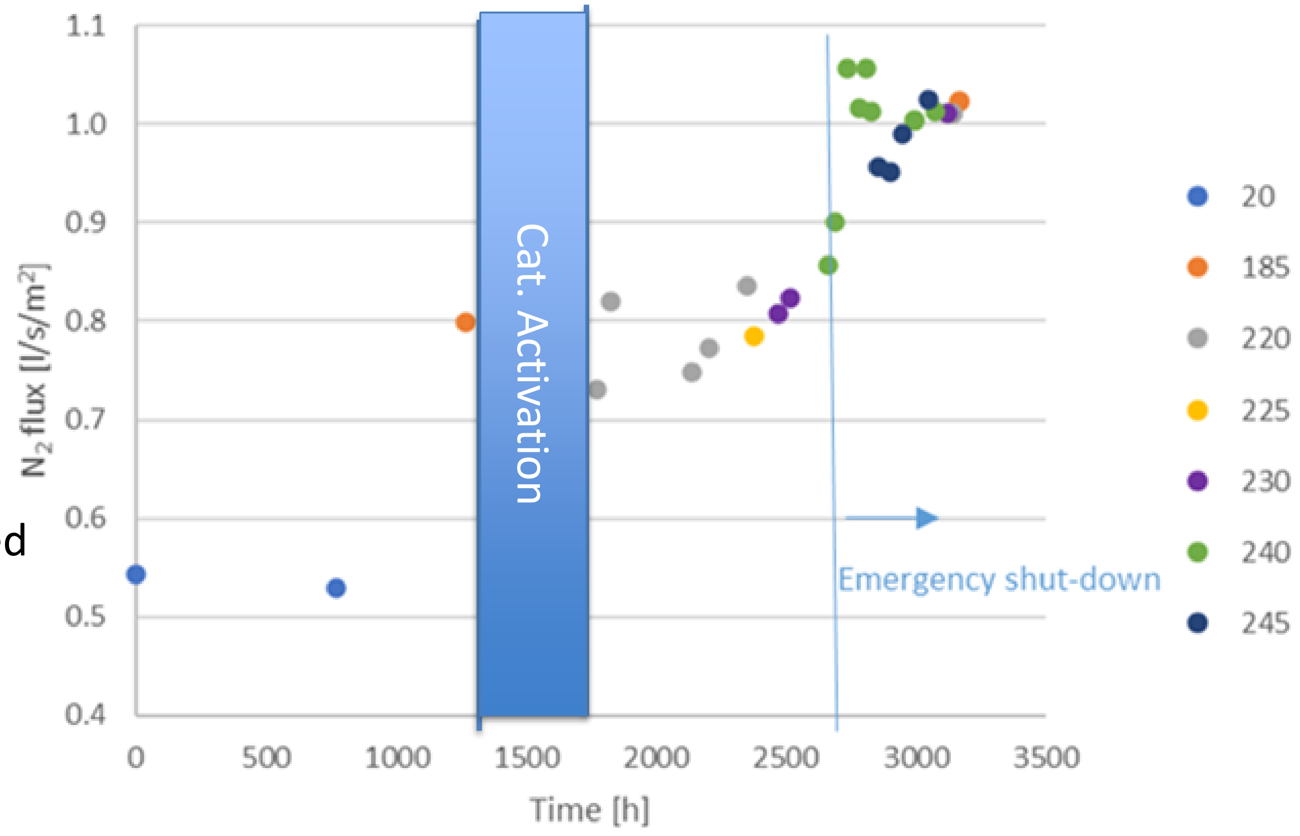
Long term membrane performance

- Experimental campaign lasted 3168 h, with the reactive tests running for 1896 h
- Between 1274-1776 h the activation of the catalyst took place ➔performance of the membranes was not affected by catalyst activation.
- The increase of the N_2 flux was observed at T of 240 °C at 2664h, after emergency shut down in which membrane reactor system cooled down rapidly
- N_2 flux at 185 °C at the end of the experimental campaign was therefore increased for 22% compared to the measured before catalyst activation



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