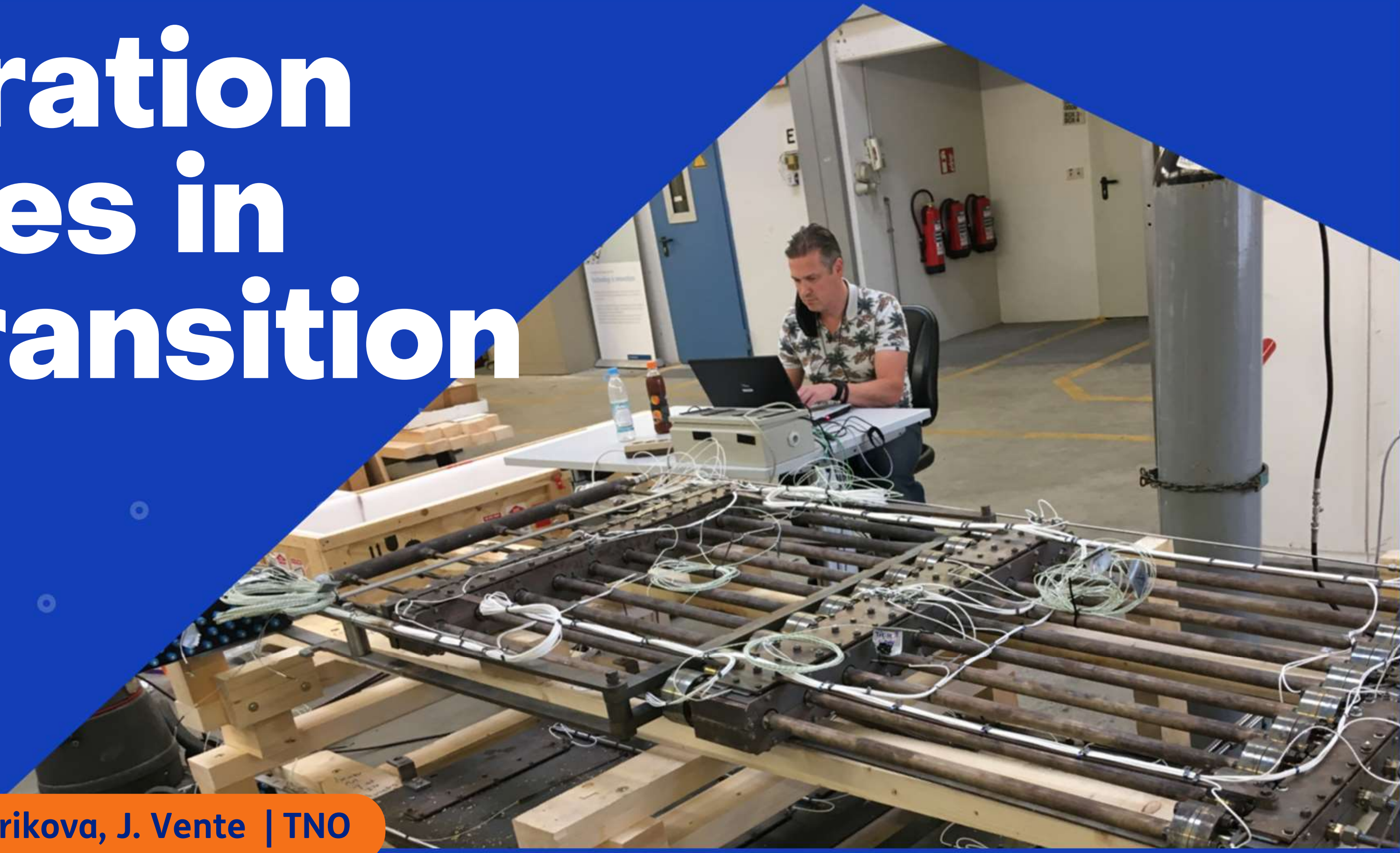
Gas separation membranes in Energy Transition

16.10. 2023, ICCMR 16 Conference



M. Sarić, J. Overbeek, V. Dikić, G. Skorikova, J. Vente | TNO

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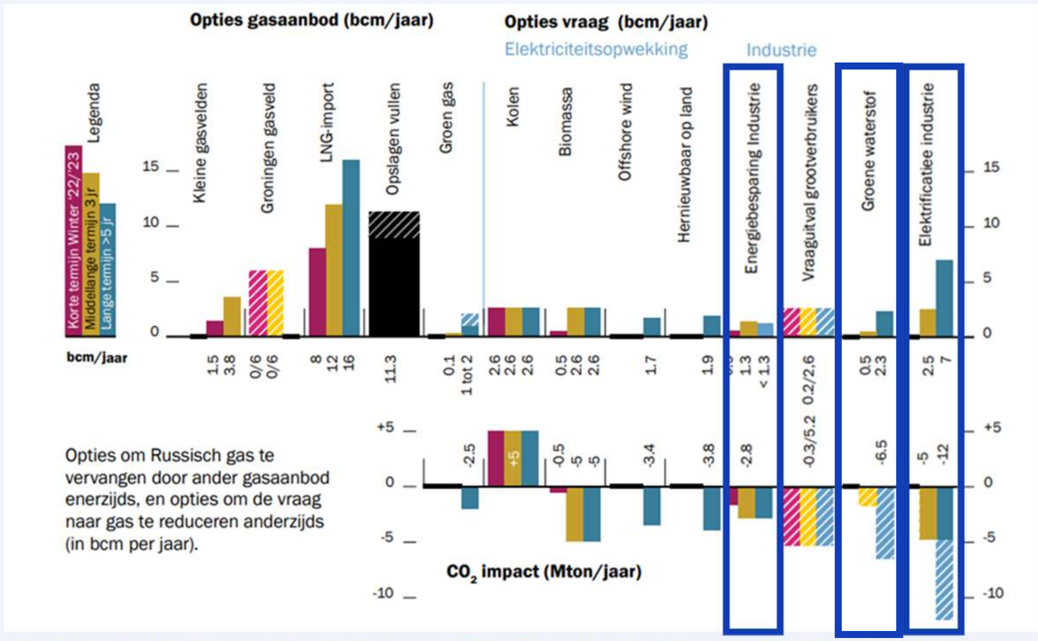
Introduction

- Reducing energy-related carbon emissions and shift from fossil towards circular carbon feedstock is critical to limit damaging climate change
- The competing challenges of energy security and affordability together with global supply chain issues are creating headwinds for further growth and innovation
- Next to hydrogen, important role for Energy Efficiency and Electrification to reduce dependency of industry on (Russian) gas

SHORT, MID and LONG TERM SOLUTIONS



Nederland Onafhankelijk Van Russisch Gas - Opties Voor Korte En Lange Termijn , TNO (2022)

Membranes in energy transition

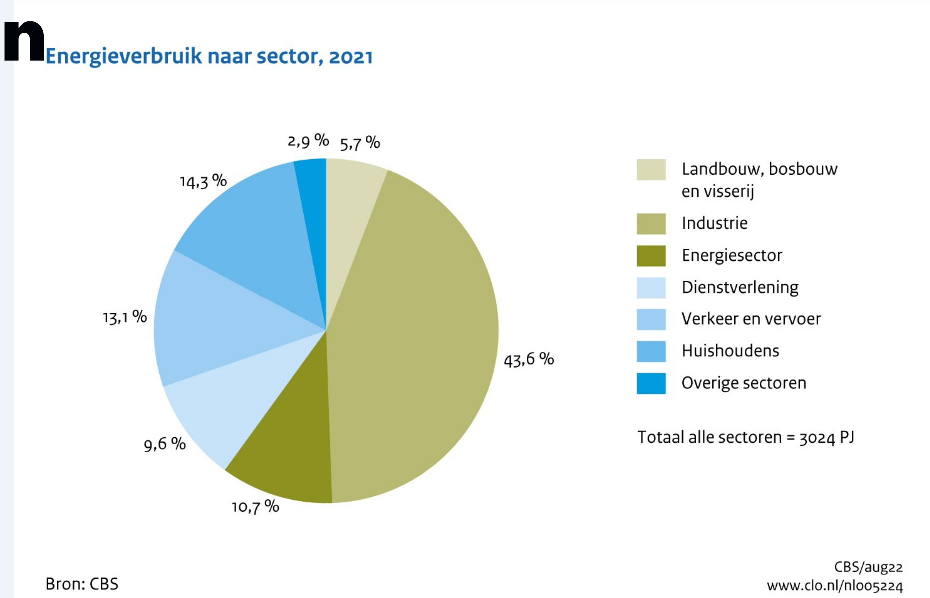
40-45% of energy used in industry is used for separation, of which 80% for thermal separation:

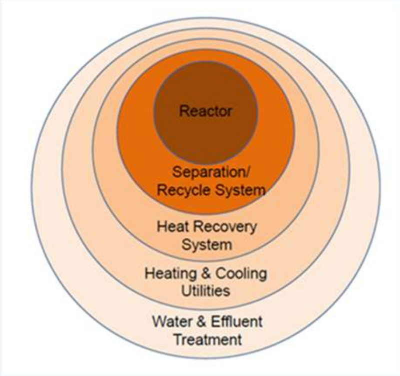
- Distillation
- Drying & Dewatering
- Evaporation

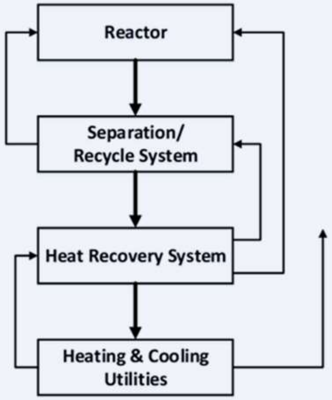
Membranes can have a large role in important environmental and energy-related processes: energy efficiency increase and electrification solution.

Membrane reactors to reduce material use, energy requirements and save costs for thermodynamic equilibrium limited processes

- Membrane reactors for:
  - Blue hydrogen production
  - CO_2 utilization to MeOH







Hierarchy

Interactions

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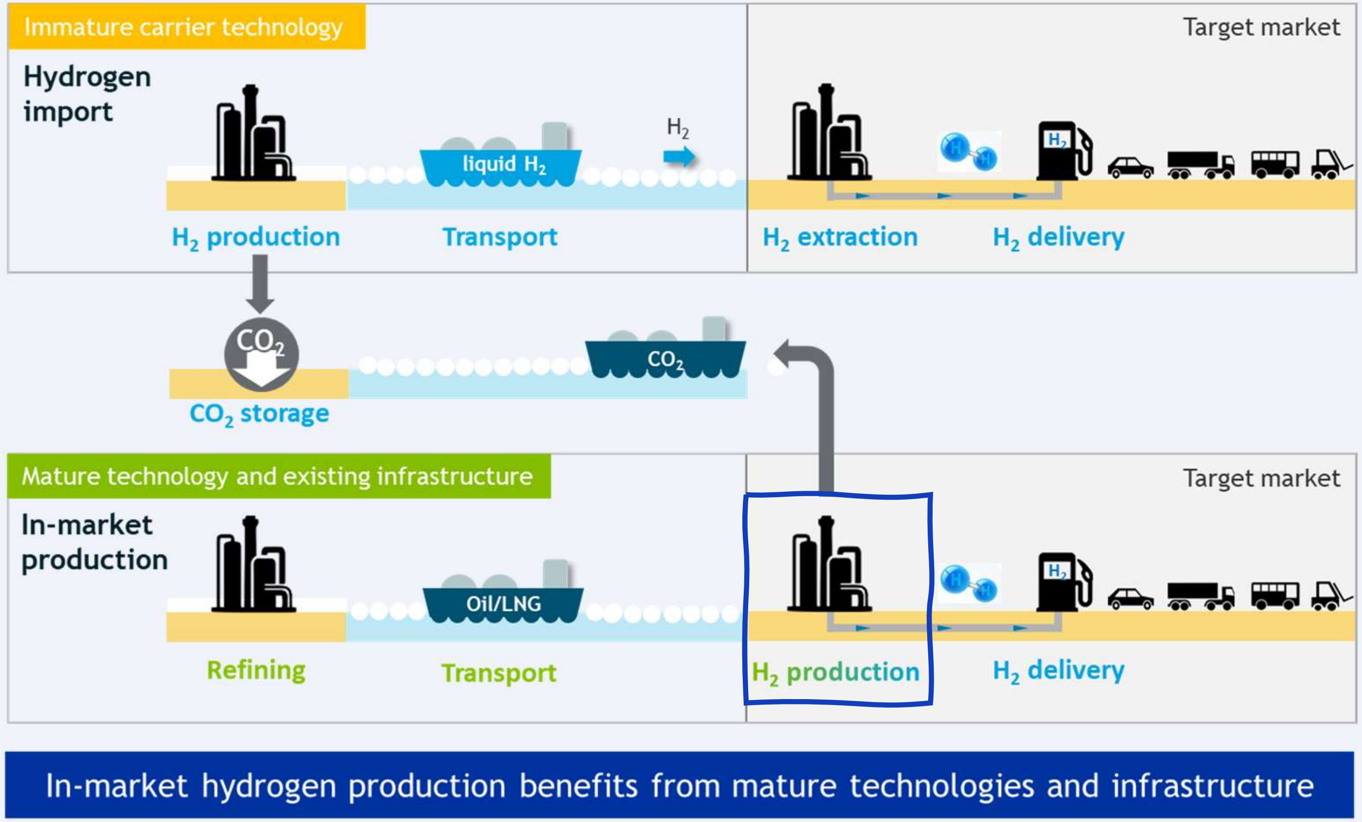
Onyx project : Blue hydrogen production

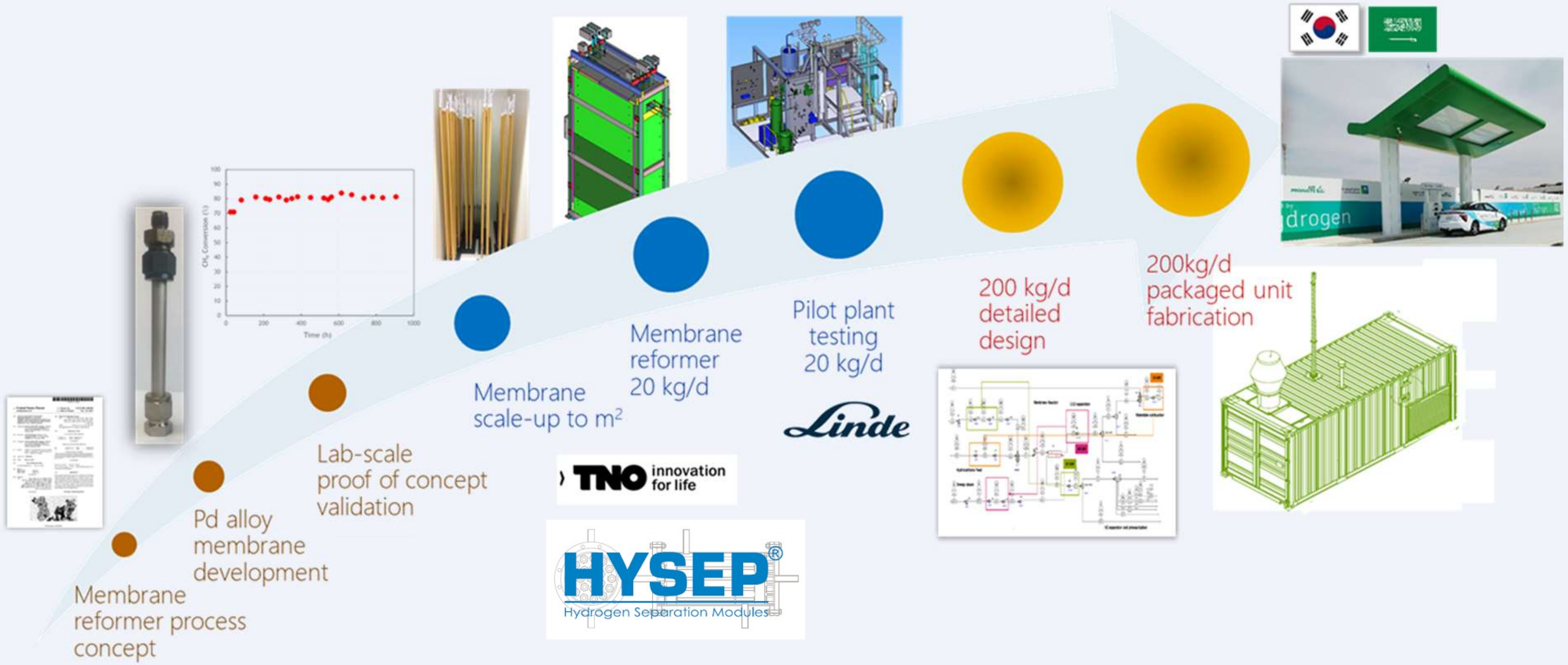


Project focus

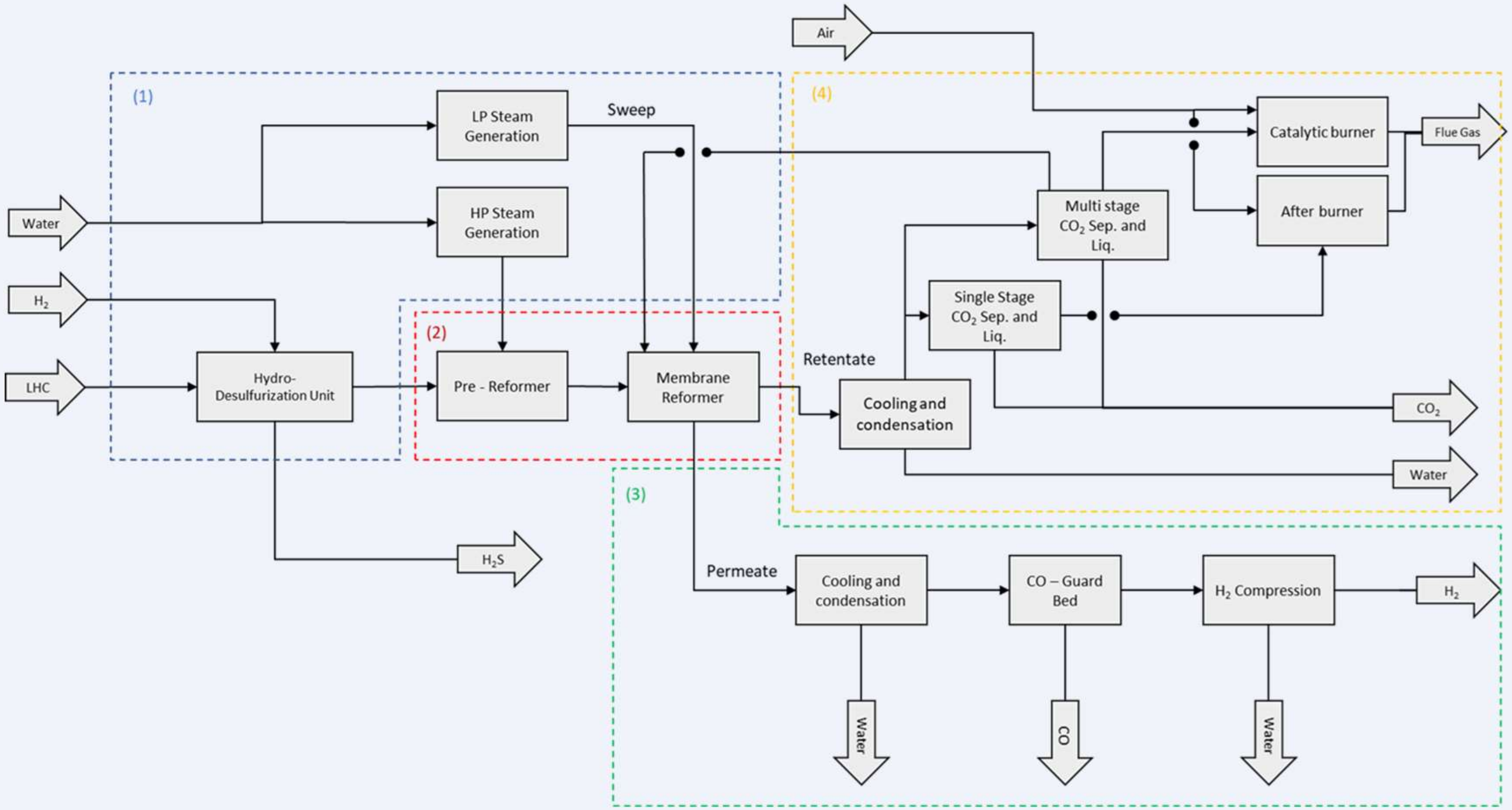
Membrane reforming piloting at 10 Nm^3/hr H_2 production rate

Project objective

- Prove & validate functionalities for membrane reactor that produces 10 Nm^3/hr (20 kg/h) H_2 targeted, HRF > 90% and stable continuos operation for 1500 h to de-risk scale-up to 200 kg/h



System evaluation



Target productivity > 16 kg H_2/m^2/day

HRF > 90%

MR operating T = 550 °C

S/C ratio = 3

naphtha feed pressure = 40 bar

$P(H_2)$ = 950 bar

Electricity price = 60 $/MWh

Naphtha price = 300 $/t

CO_2 emission penalty = 65 $/t

CO_2 grid intensity = 517 g CO_2/kWh

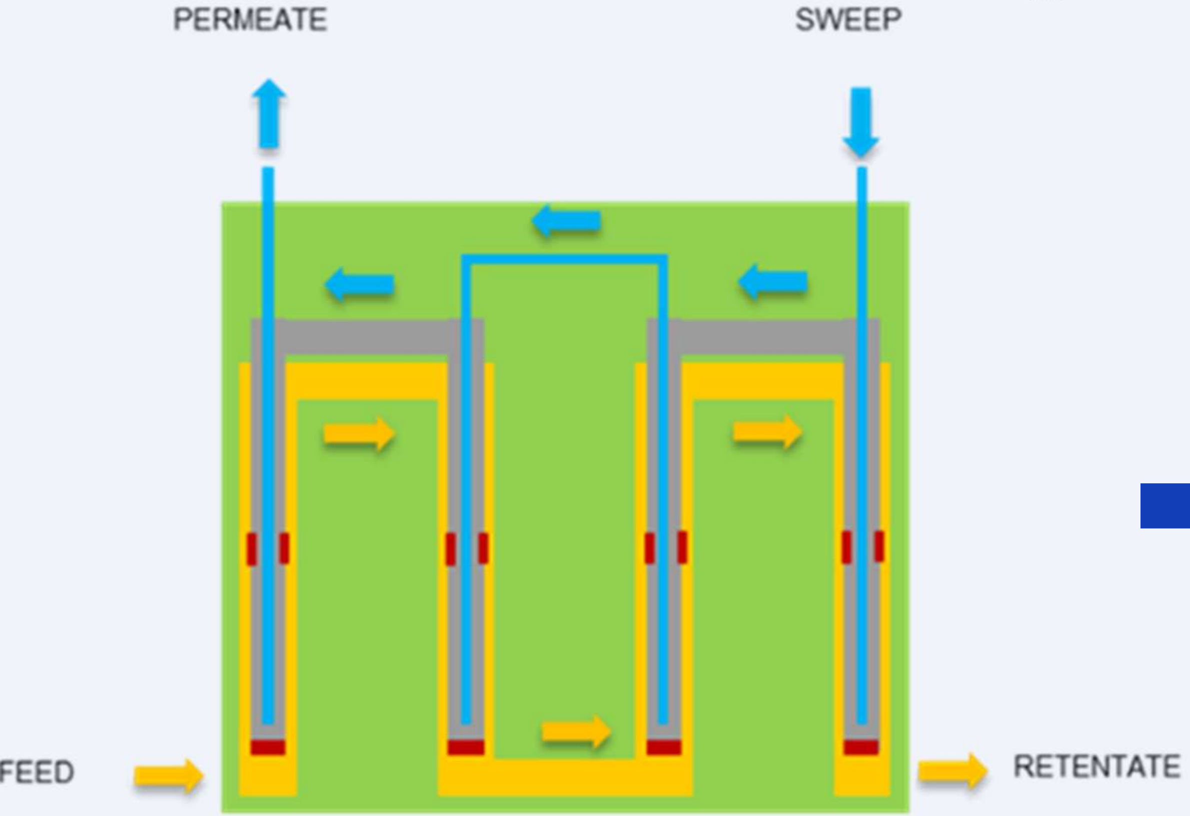
100 Nm^3/hr and 5000 Nm^3/h of H_2 for use in mobility sector

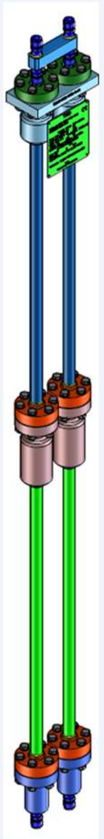
System evaluation results: 5000 Nm^3/h H_2

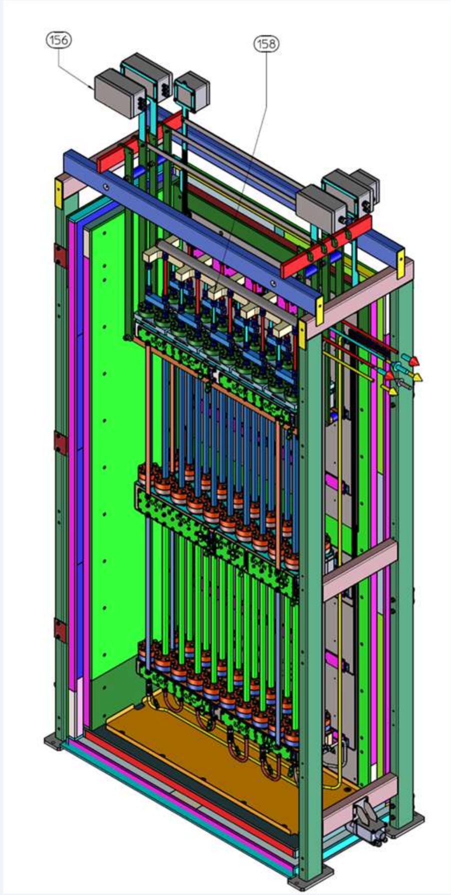
	Reference (Naphtha)	Electric MR+ naphtha heating	Electric MR & heating	Electric MR+ H_2 heating	Naphtha MR & heating	H_2MR & heating
Energy need [MJ/Nm^3 H_2]	16.2	14.5	14.5	19.4	14.5	20.2
CO_2 emissions [kg/kg H_2]	11.8	6.3	8.6	5.7	4.5	2.9
LOHC (no CO_2 tax) [$/kg H2]	1.5	1.6	1.9	2.1	1.4	2.1
LOHC(CO_2 tax 65 $/t) [$/kg H2]	2.3	2.5	2.5	2.5	1.7	2.3

- Electricity as utility more attractive for a grid emission intensity < 250 gCO_2/kWh and electricity price < 25 $/MWh
- H_2 as process utility ➔ lower energy efficiency and higher capital costs.
- CO_2 tax > 65$/t can make H_2 as process utility attractive in mid/long term

Membrane reactor Design

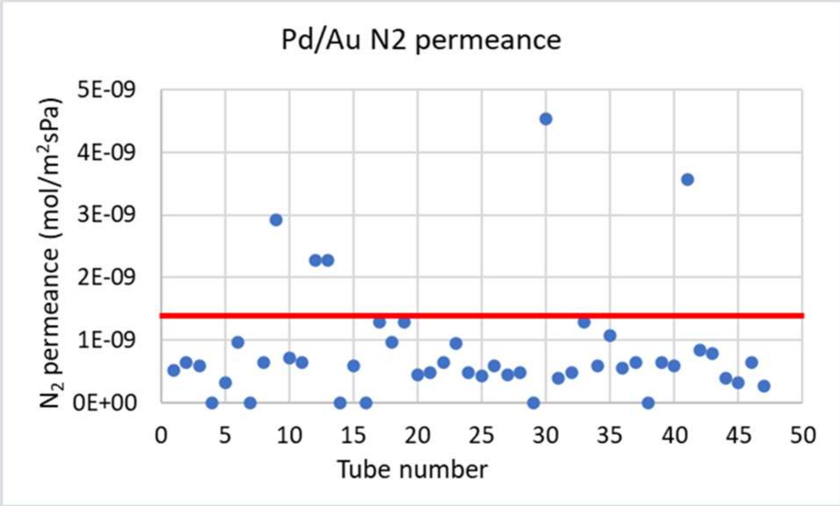






- Total membrane area 1.4 m^2
- Fixed bed catalyst pocket, with a total of 30 catalyst-membrane steps

Membranes production

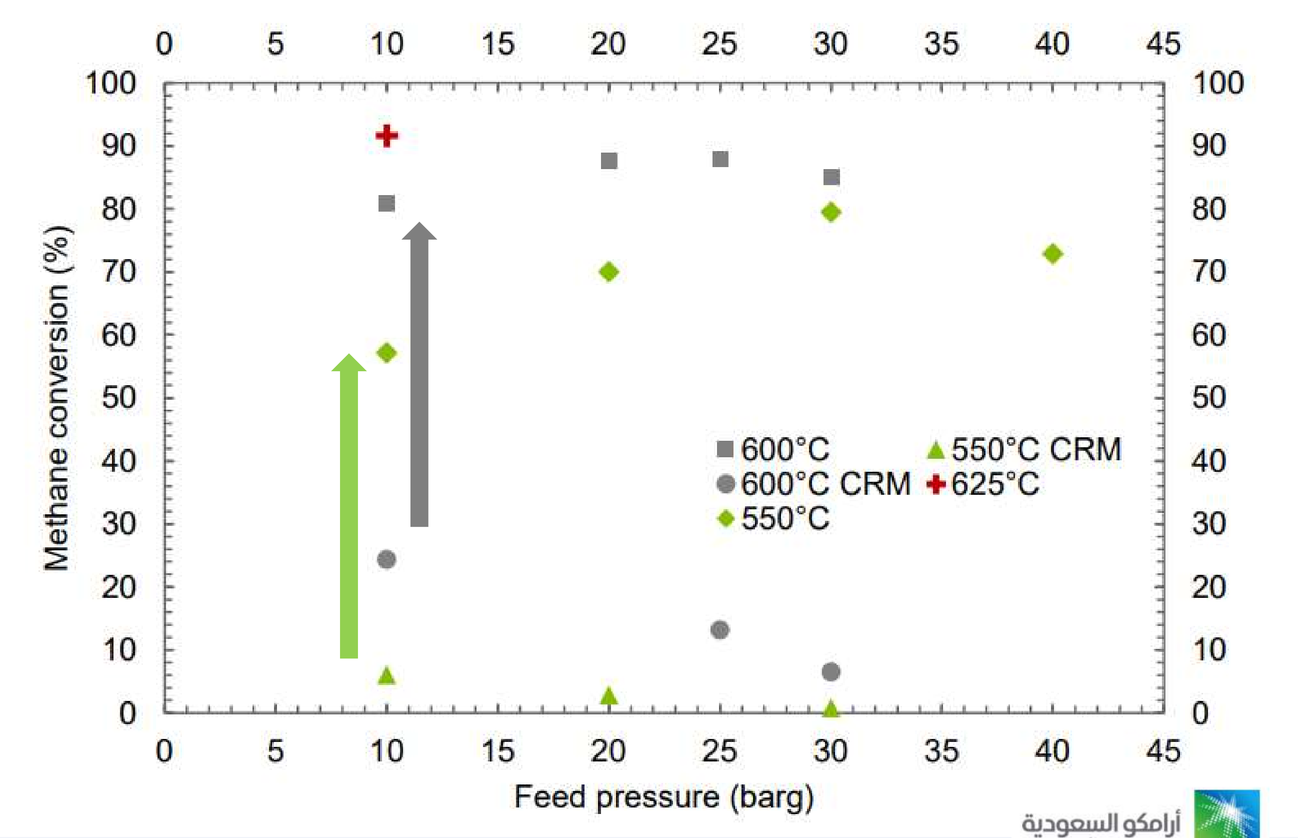


- Pd layer directly on 200nm support
- 1 m membrane length (80 cm effective length) connected to 2m with intermediated welded caps

Membrane characterization

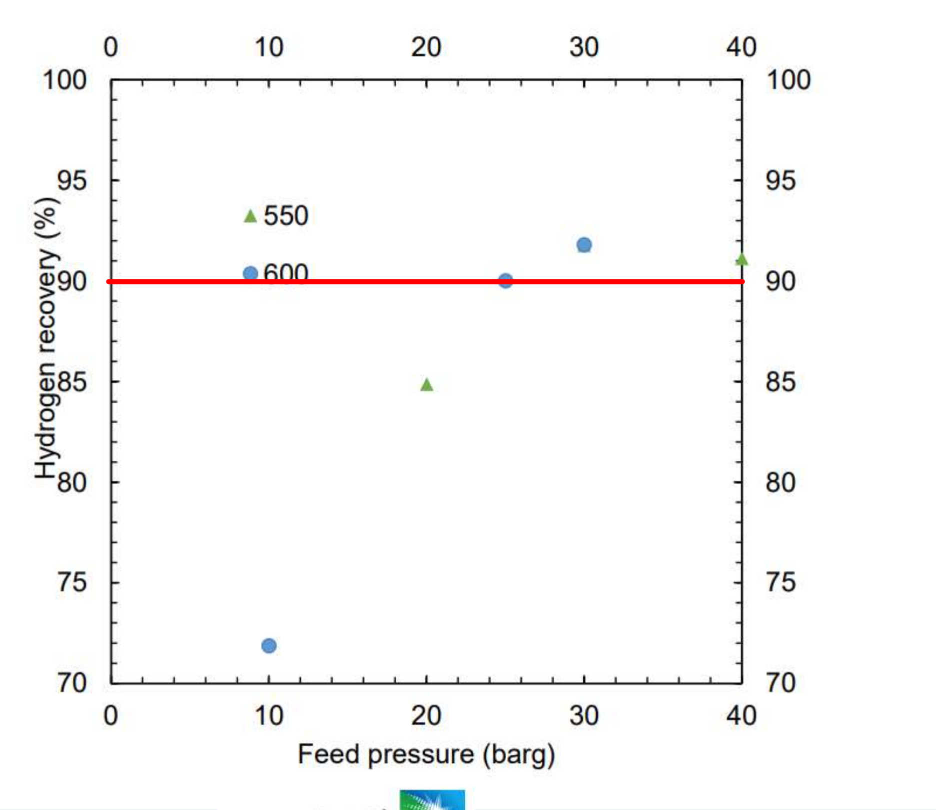
	Simulated pre-reformed naphtha (PRN)
CH_4	34.6%
H_2	37.8%
CO_2	22.8%
CO	1.7%
N_2	3.4%
SCR	3, 3.5, 4

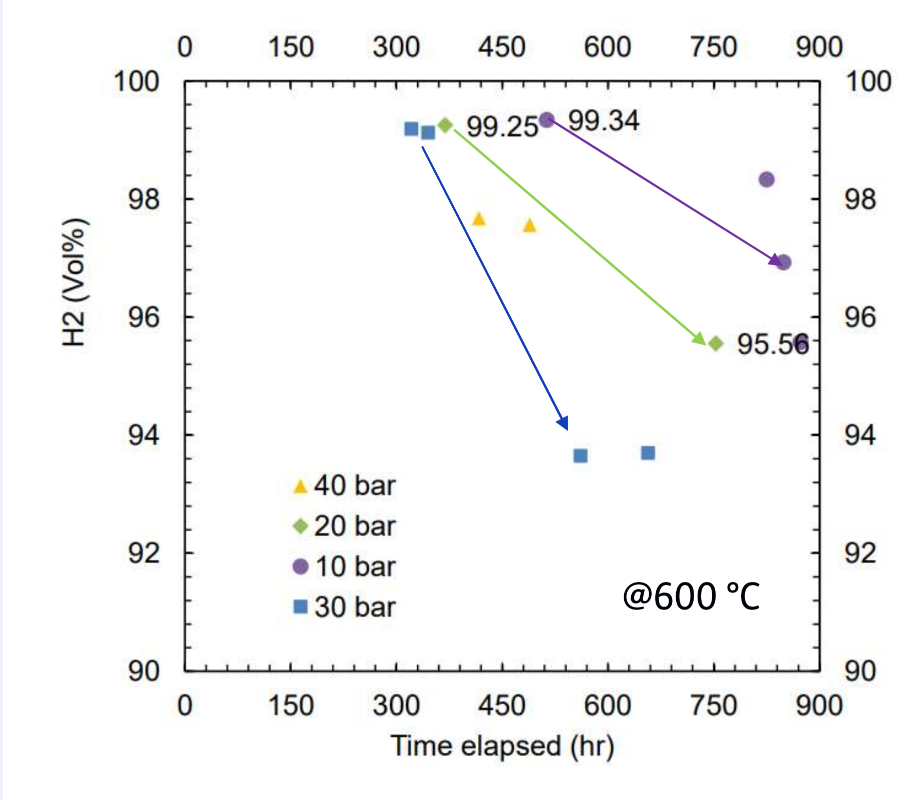
PdAu membrane after annealing under 31 bar pure H_2 at 550°C for a total of 8.7 h.



Tested at saudi aramco TNO innovation for life

Membrane characterization : simulated pre-reformed naphtha feed





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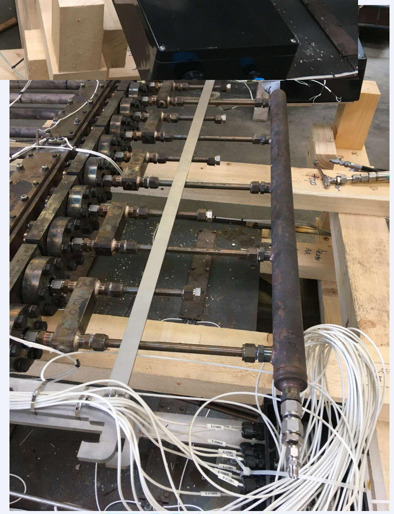
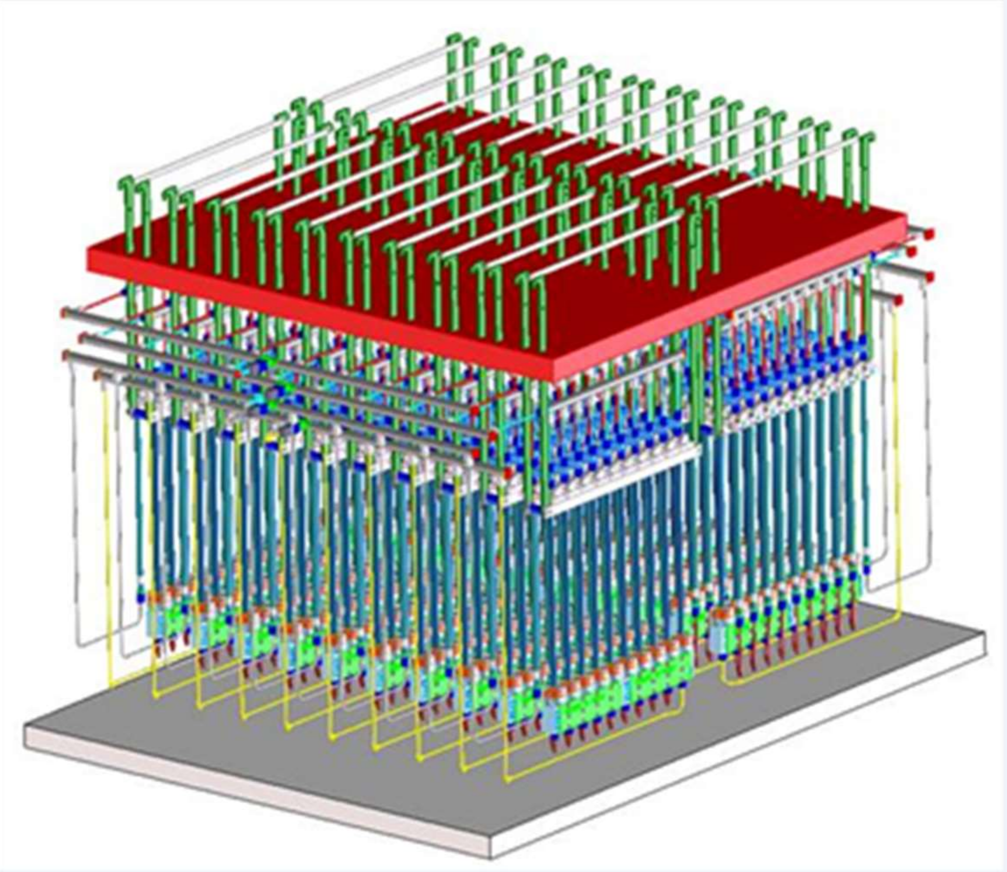
Membrane reactor construction

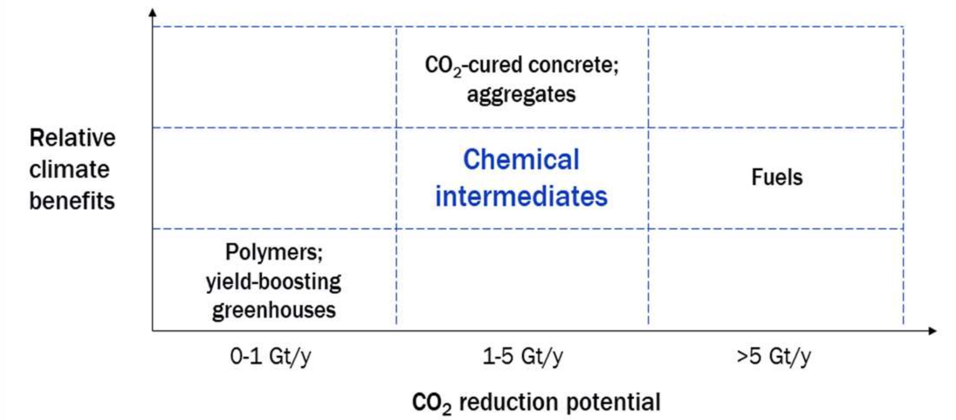


Conclusions

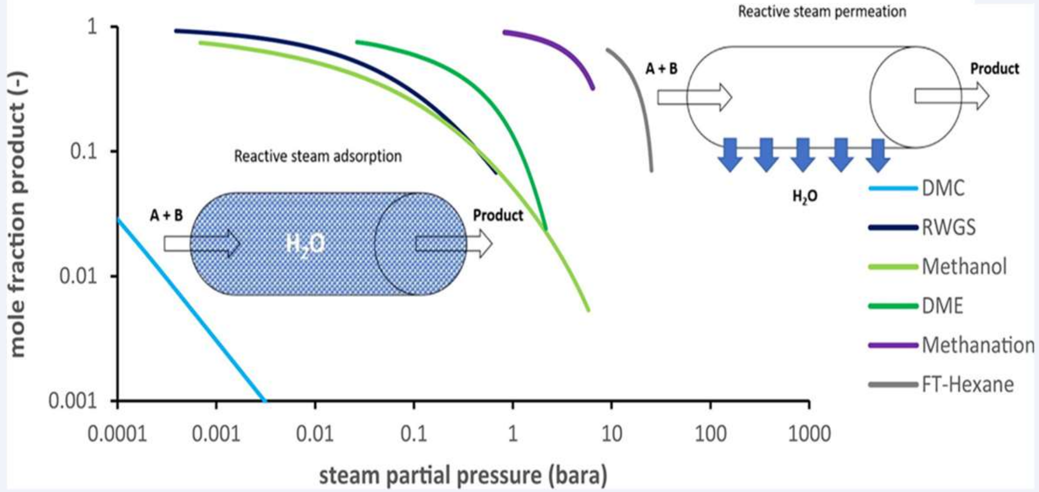
- The naphtha based MR process has the potential to reduce 10% energy consumption and 62% CO_2 emissions compared to conventional naphtha reforming
- Electricity as utility still not competitive, but can become more attractive for grid emission intensity < 250 gCO_2/kWh and electricity price < 25 $/MWh
- A membrane reactor based on integrated PdAu membranes with total membrane are of 1.4 m^2 with electrical heating and fixed bed reactor technology was built, constructed
- The highest degree of integration ever built by TNO compared to previous membrane reactor concepts

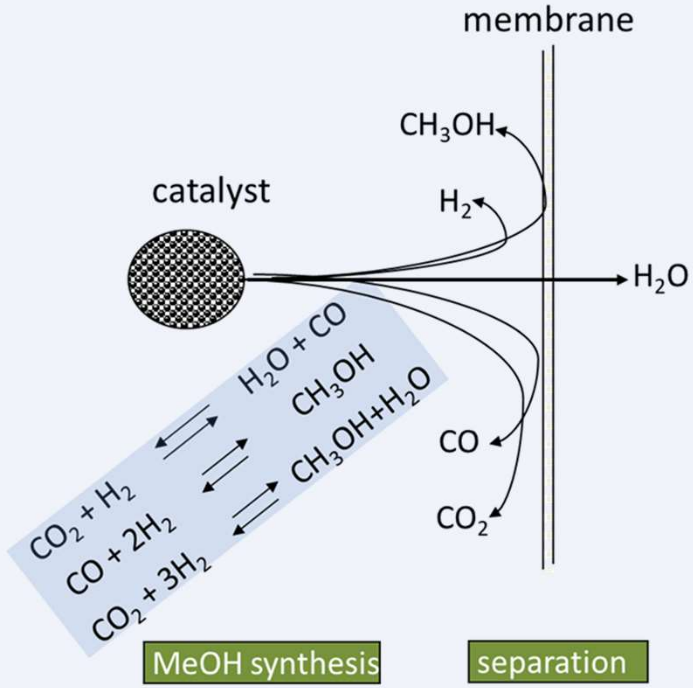


Membrane reactors for CO_2 utilization



2019 IEA: Putting CO_2 to Use

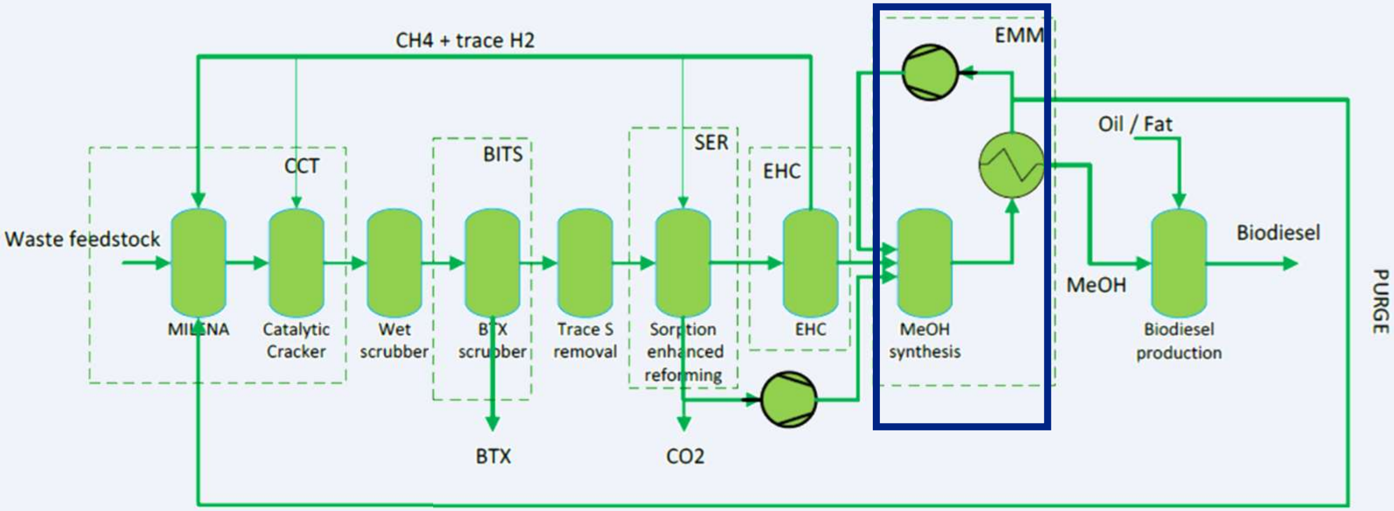


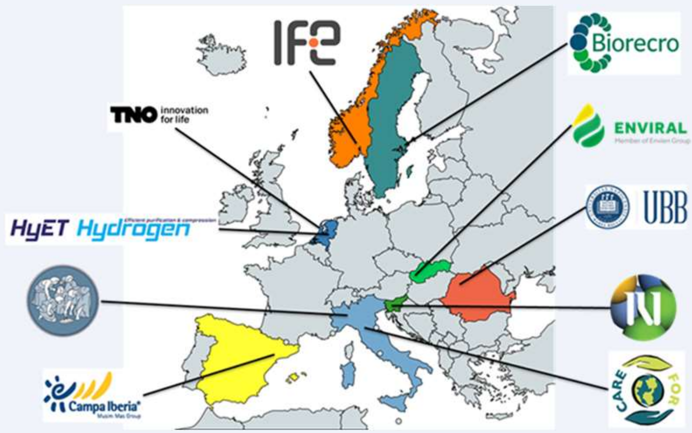


J. van Kampen et al. (2019) Steam separation enhanced reactions: Review and outlook / Chem. Eng. J. v.374

CONVERGE project: Membrane enhanced MeOH production

- The CONVERGE project aimed 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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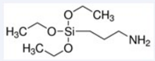
Membrane development targets & membrane selection

Development targets:

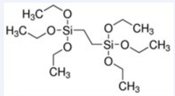
- Stability at the methanol operating T and p (T = 220-275 °C, p up to 100 bar)
- High selectivity for steam and methanol
- High steam/methanol permeability ➔ high flux

Membrane selection:

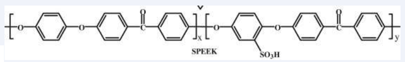
- Amorphous microporous
  - APTES-PA (Aminopropyl triethoxysilane-Polyamide)



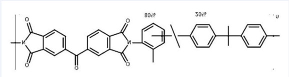
  - BTESE (1, 2-bis (triethoxysilyl) ethane)



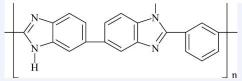
- Polymeric
  - SPEEK (sulfonated poly(ether ether ketone))



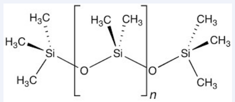
  - PI (Poly Imide)



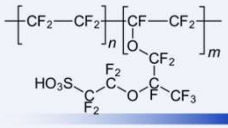
  - PBI (Polybenzimidazol)



  - PDMS (Polydimethylsiloxane)



  - Li-Nafion



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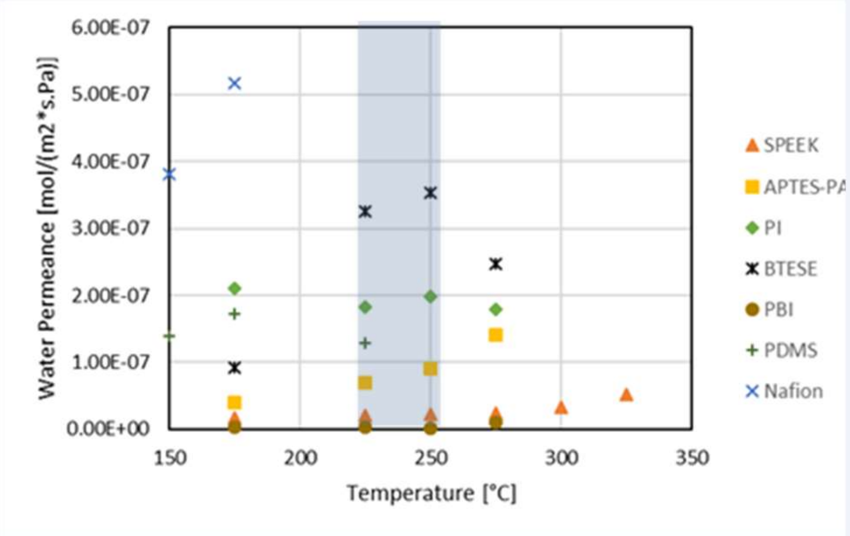
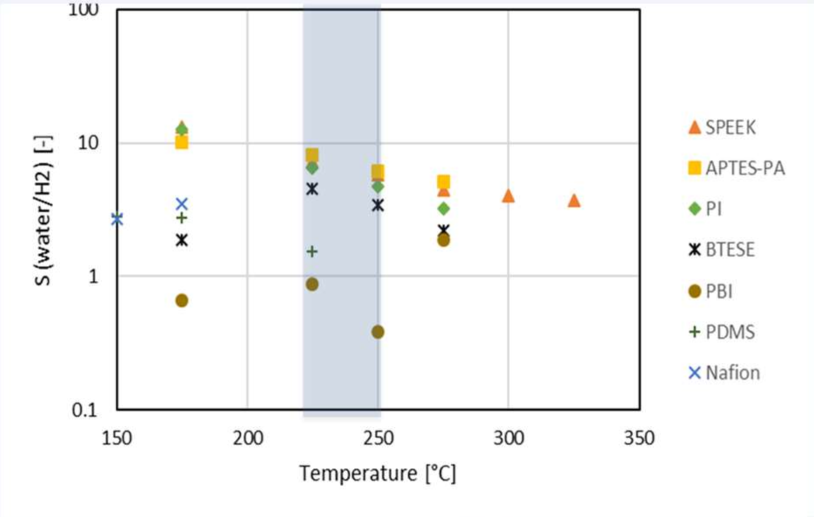
Membrane characterization results

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

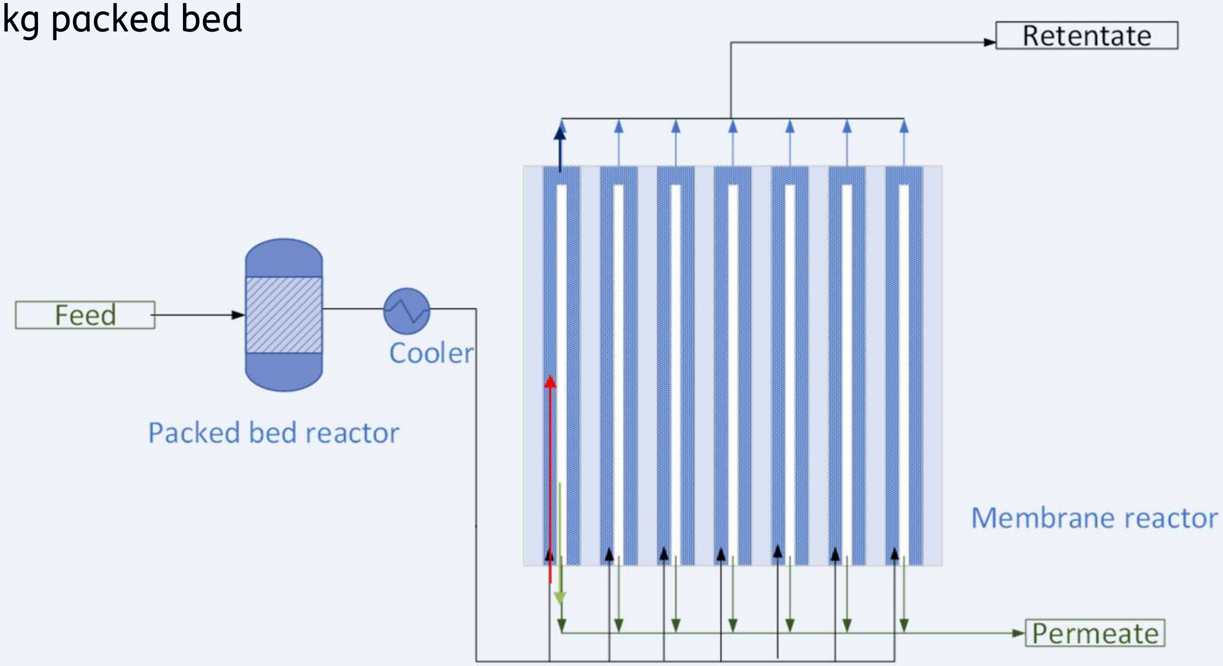
$H_2O > H_2 > MEOH > CO_2 > CO \approx N_2$





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) , 2.7 kg packed bed and 9 kg membrane reactor
- Operating conditions:
  Feed flow = 45 - 110 Nl/min, no sweep
  H_2/CO_2 ratio = 3, 4, 5
  p_{feed} = 35 bara, p_{perm} = 1.5 bara
  T_{range} = 220 - 250 °C



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Reactor construction

Packed bed reactor

Multi-tubular membrane reactor

Membranes installed in the membrane reactor

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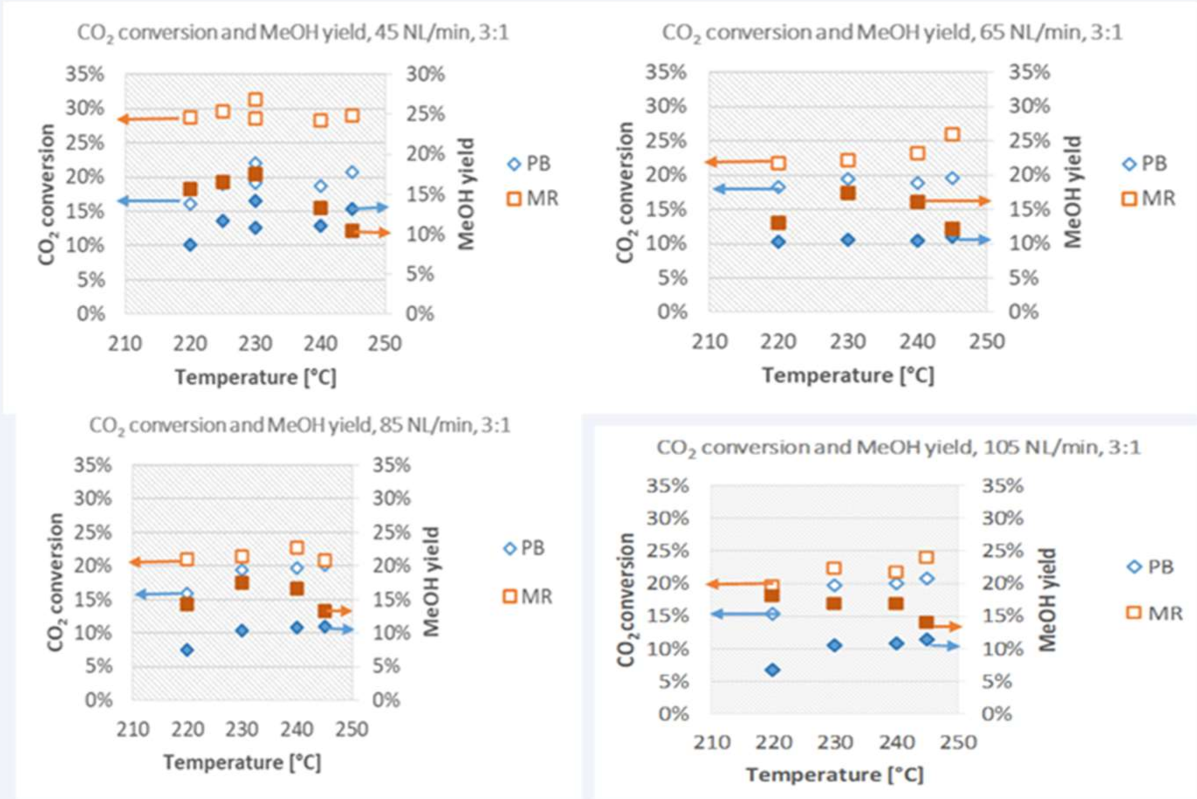
MR test results

- 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:
  - ➔ 36% increase in CO_2 conversion
  - ➔ 63% increase in MeOH yield

➔20% reduction of energy used due to lower operating pressure



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Conclusions

- Membrane reactors can bring energy savings in thermodynamically equilibrium limited reactions : 10% energy consumption reduction for blue hydrogen production, and 20% for membrane enhanced methanol ➔ CO_2 emission reduction
- Electrification of heat would need lower electricity costs and CO_2 grid intensity to become attractive option for blue hydrogen production
- TRL5-6 membrane reactors successfully constructed

Questions

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Sensitivity studies