CONVERGE: CarbON Valorisation in Energy-efficient Green fuels

Green methanol synthesis for biodiesel production

16-17 th February, Converge Workshop

Objectives: Membrane assisted methanol synthesis

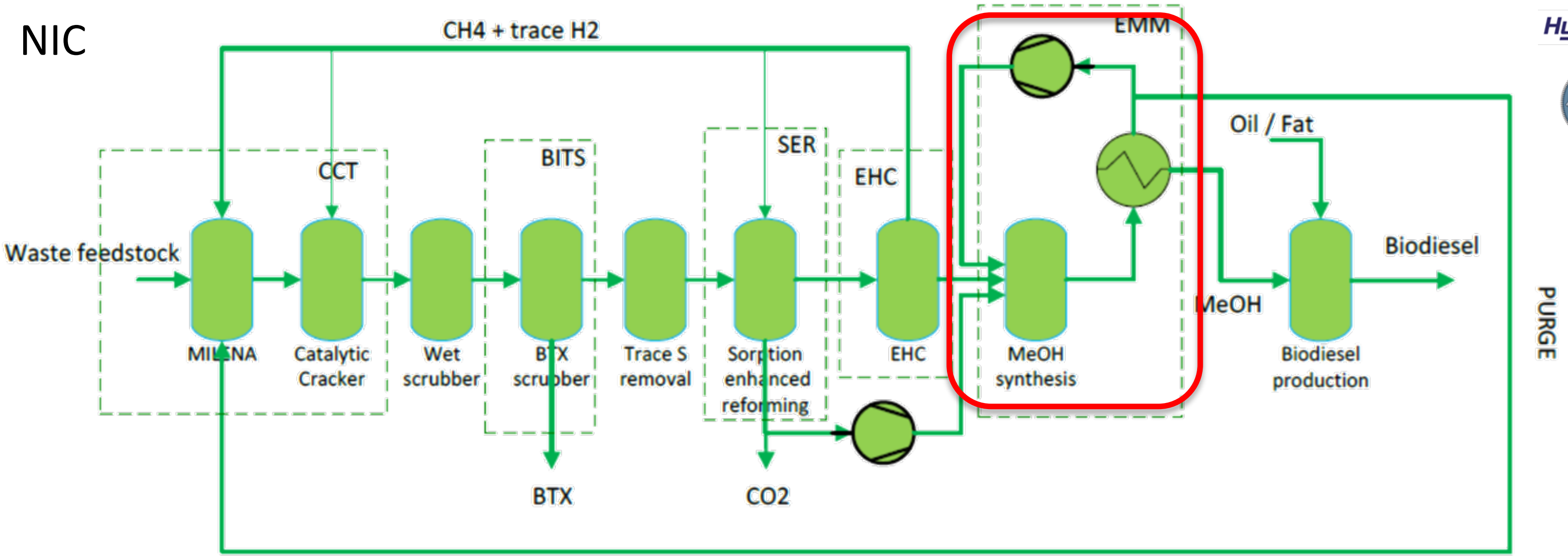
This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 818135

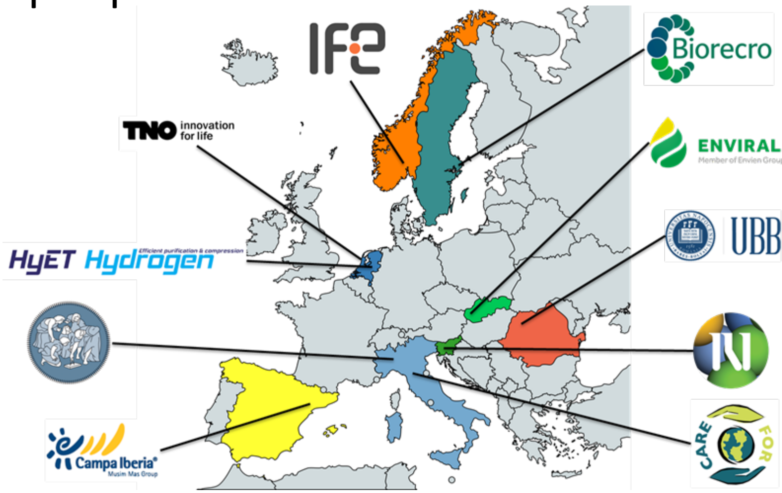
Membrane assisted methanol synthesis.

- 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

Partners involved:

- TNO
- NIC





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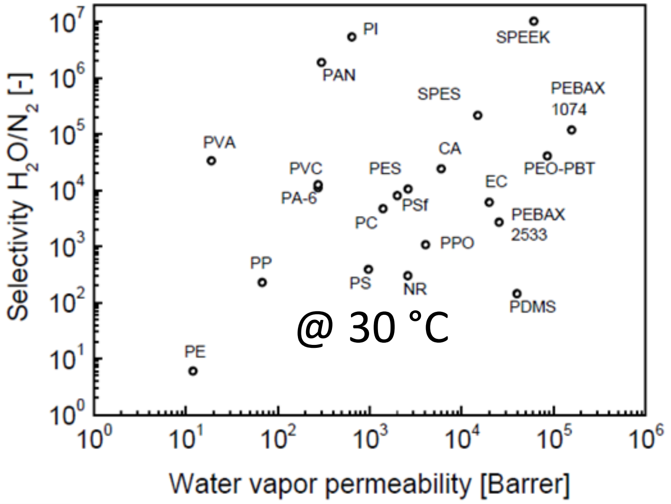
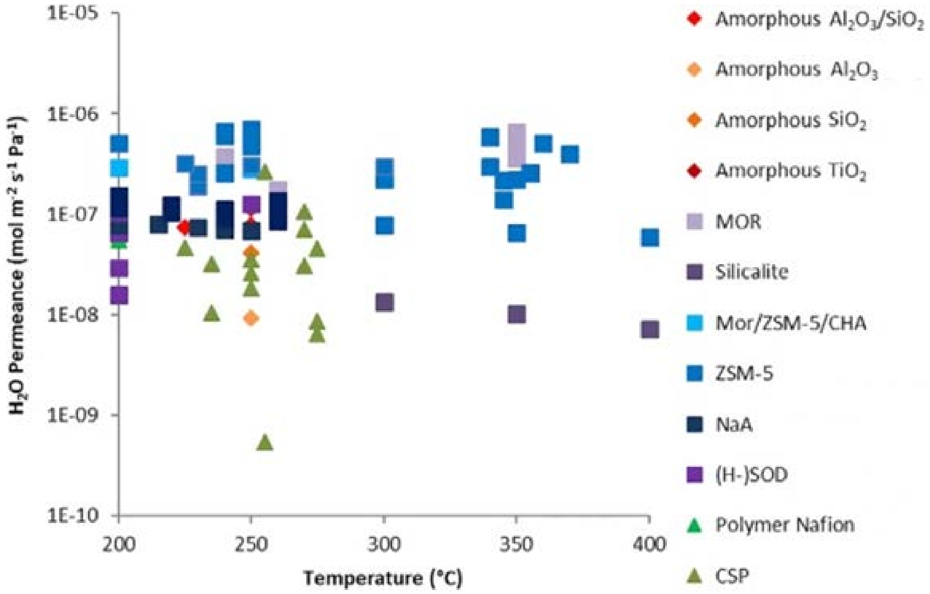
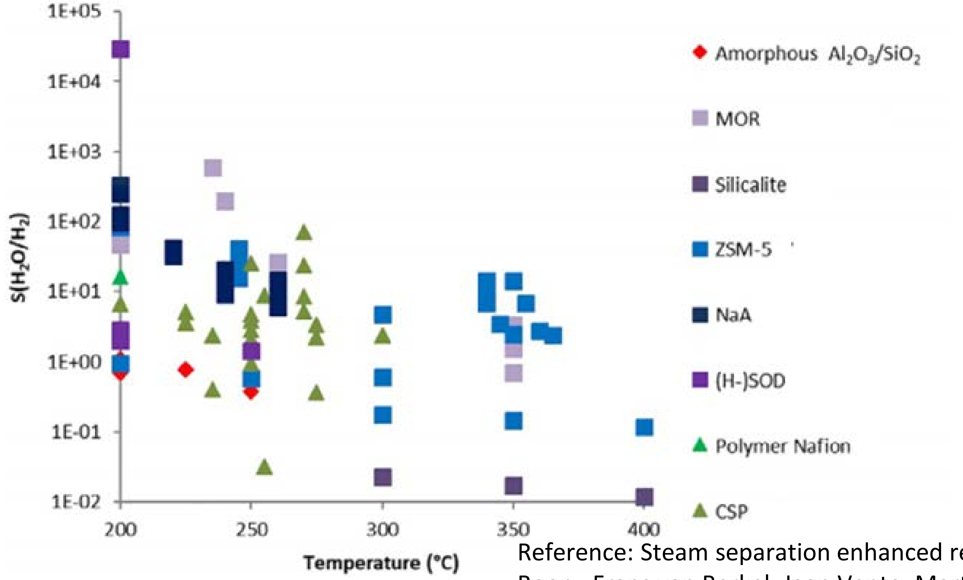
Membrane development targets:

1) Stability at the methanol operating T and p (175-275°C), up to 100bar
2) High selectivity for steam and methanol
3) High steam/methanol permeability ➔ high flux







Reference: Steam separation enhanced reactions: Review and outlook, Jasper van Kampen, Jurriaa Boon , Frans van Berkel, Jaap Vente, Martin van Sint Annaland, Chemical Engineering Journal 374, 21019, 1286-1303

Inventory of suitable membranes

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- Amorphous microporous
  - APTES-PA (Aminopropyl triethoxysilane-Polyamide)
  - BETSE (1, 2-bis (triethoxysilyl) ethane)
- Polymeric
  - SPEEK (sulfonated poly(ether ether ketone))
  - PI (Poly Imides)
  - PBI (Polybenzimidazol)
  - PDMS (Polydimethylsiloxane)
  - Li-Nafion

Membrane synthesis procedure -support

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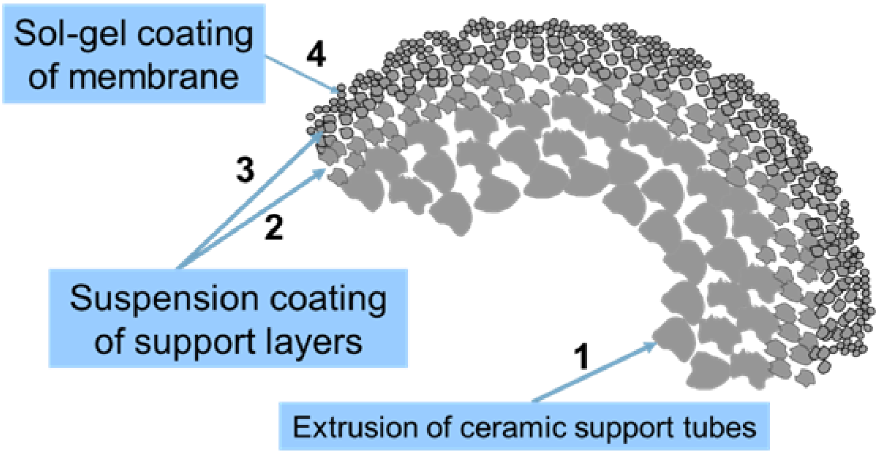
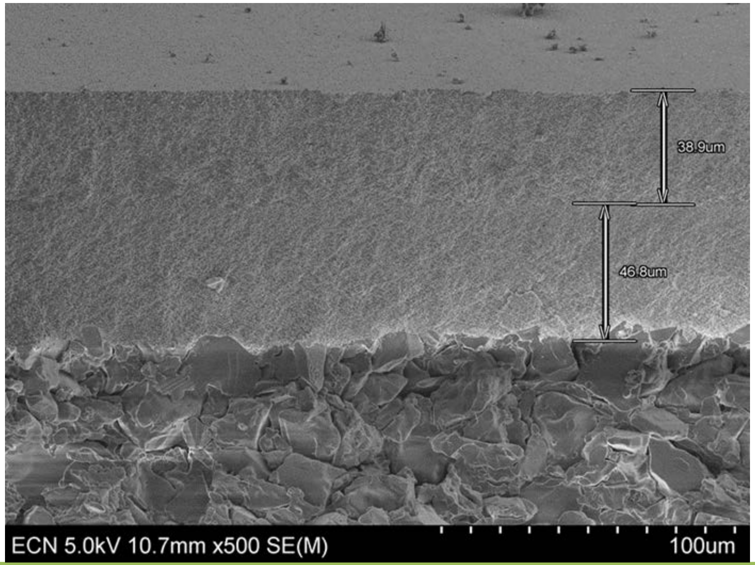
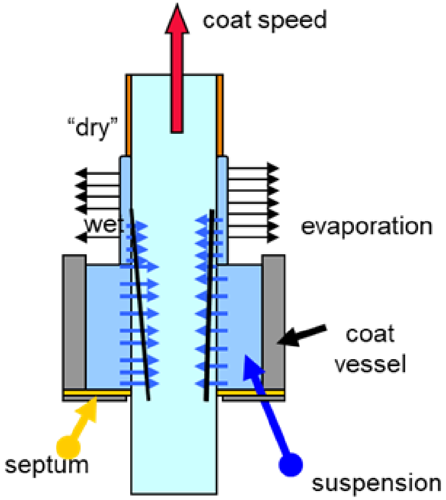
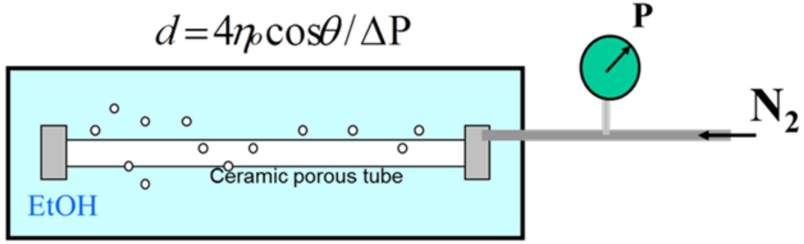


Membrane support layers

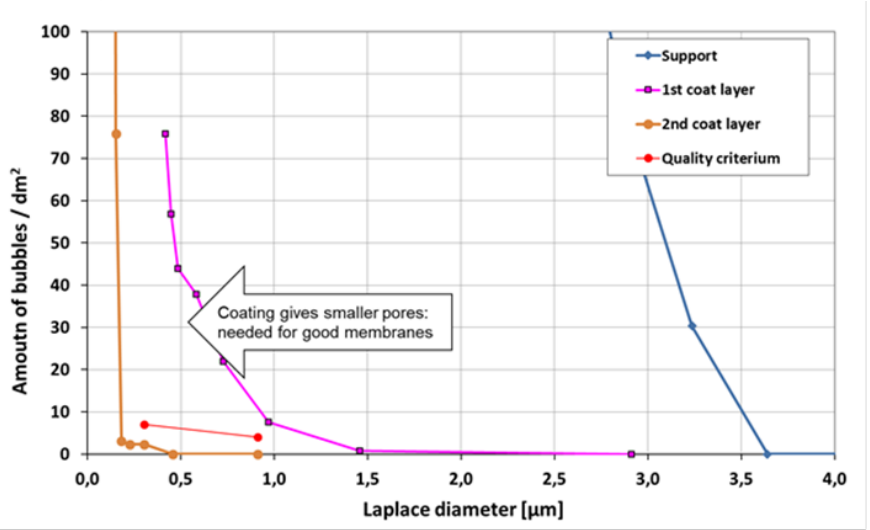




Coating process



Bubble point test



Results membrane separation tests

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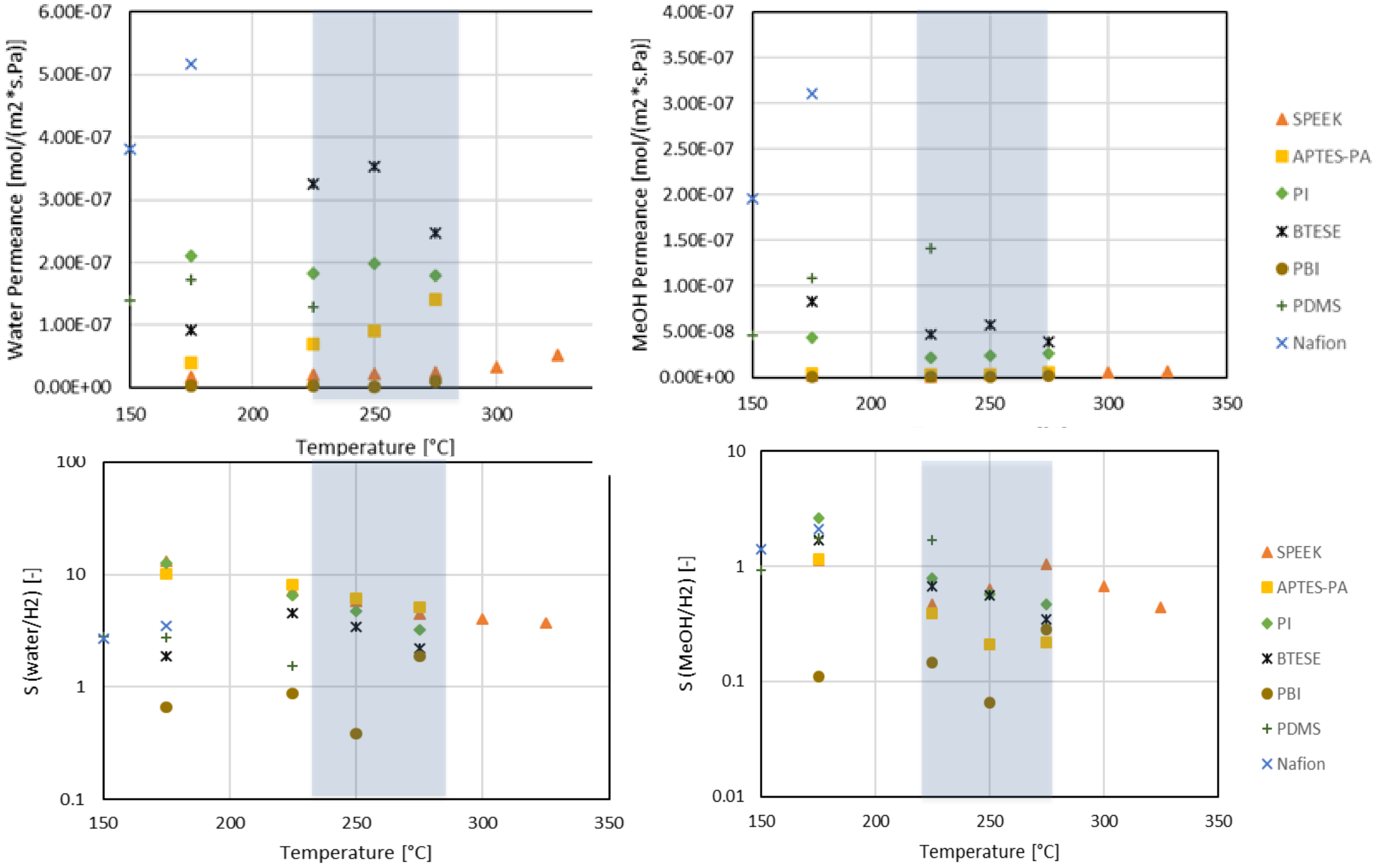

Test conditions:

- 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, BETSE, PI highest steam and MeOH permeance

- BETSE performance decreases at 275°C, Nafion not selective at T>225°
- H_2O/H_2 selectivity highest for APTES-PA, SPEEK and PI
- $MeOH/H_2$ selectivity highest for PDMS 1.7, PI and BETSE ~0.6-0.8

Pre-selection:
1) PI
2) BETSE
3) APTES-PA

PDMS, Nafion ➔ no selectivity > 225 °C
SPEEK➔ low H_2O and MeOH permeance (10X lower than PI)
PBI ➔ low permeance, low selectivity

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Conclusions

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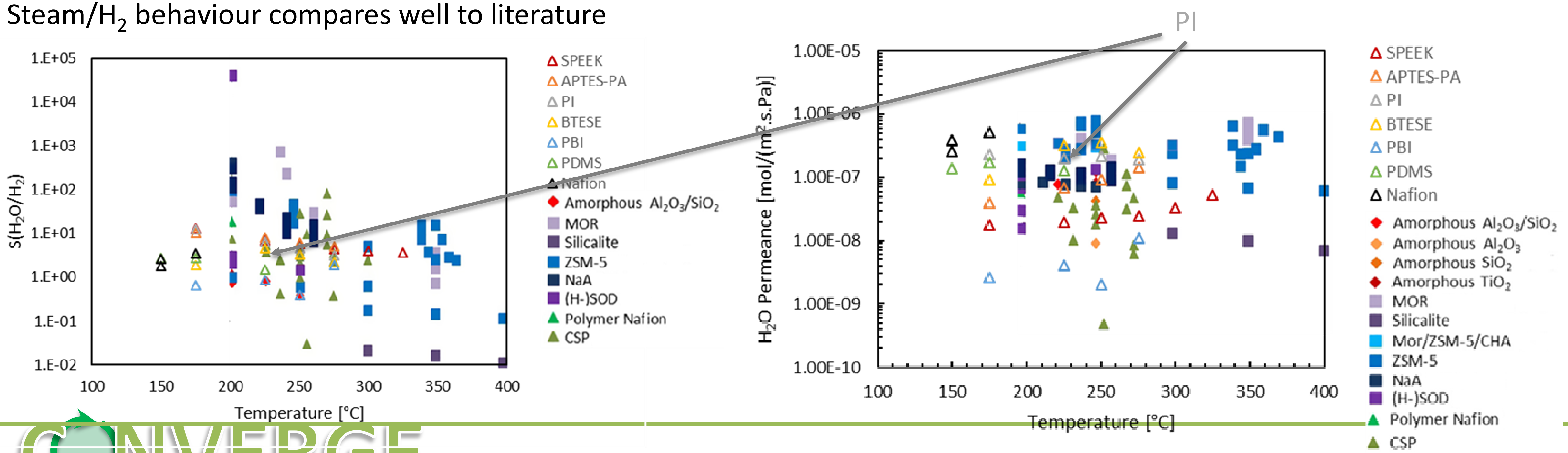
- PI membrane preselected as the most promising to reach conversion targets. Membrane performance comparison steam/MEOH/mix (T_{range} =225-250 °C)

	PI	BETSE	APTES
• 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

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

- Steam/H_2 behaviour compares well to literature



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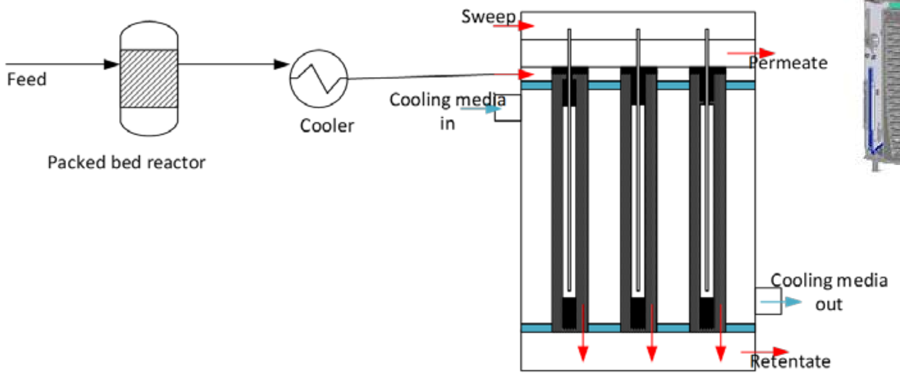
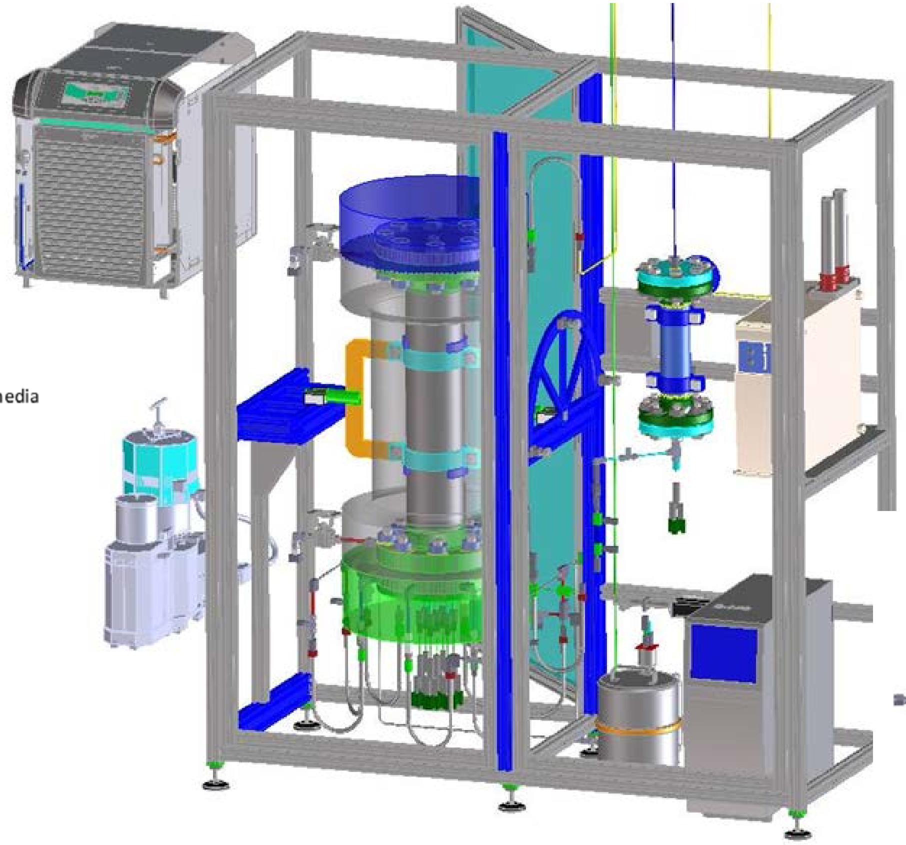
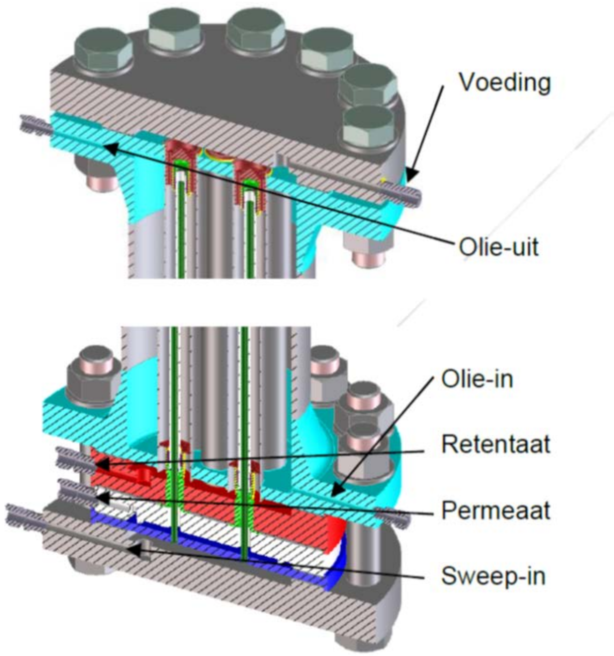
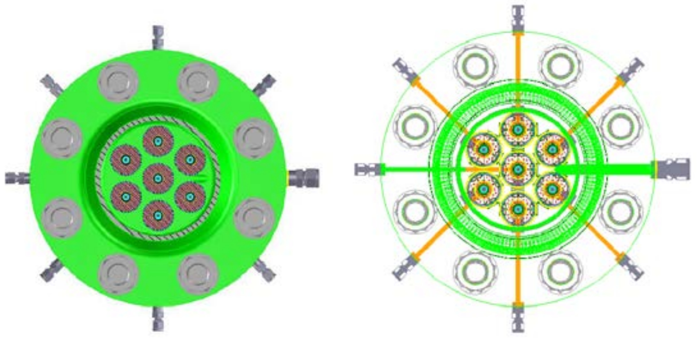
- Testing of preselected membranes in one tube membrane reactor
- Construction and testing of multi-tubular membrane reactor

Feed flow = 45 Nl/min









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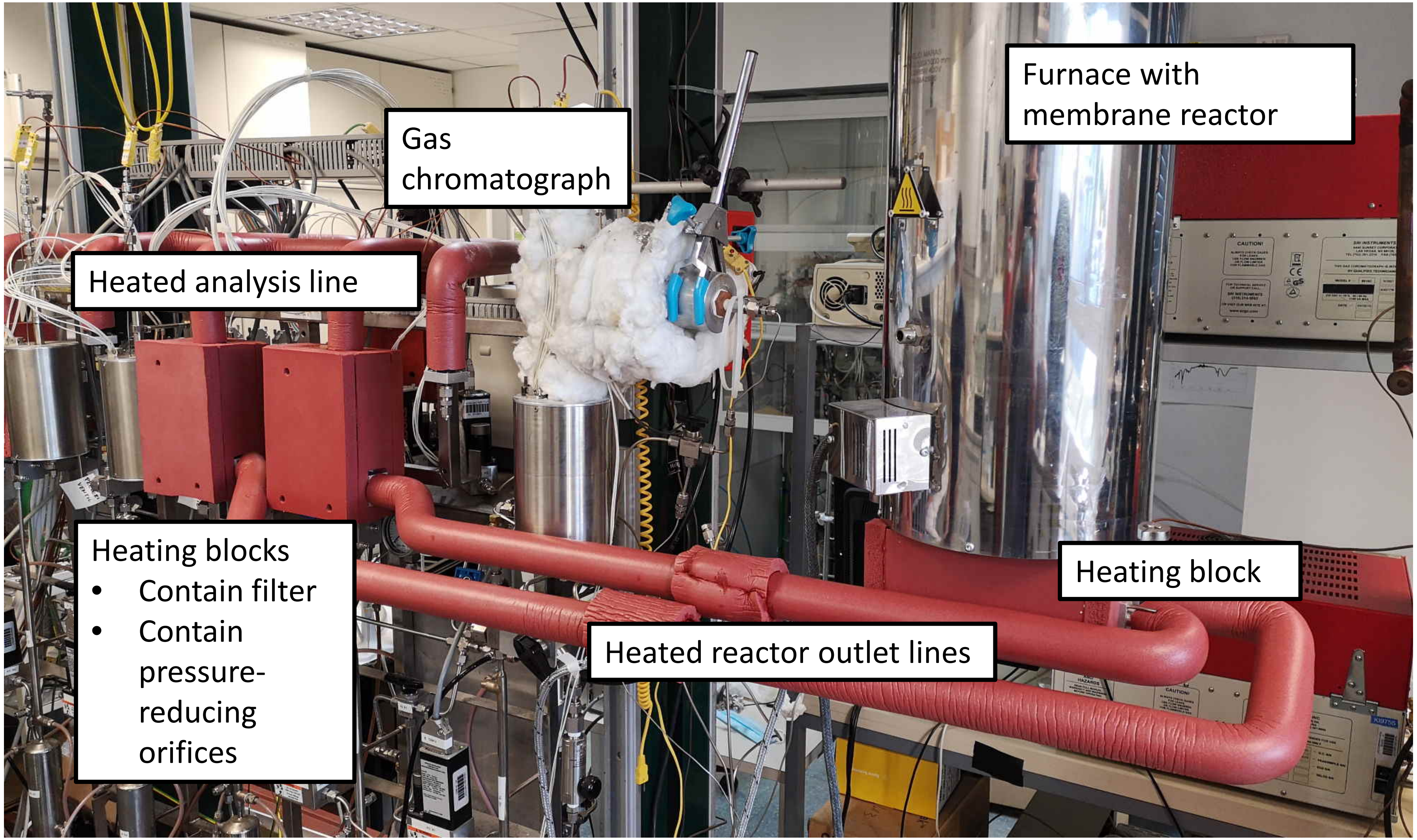
Testing rig upgrade at NIC

- Testing of the prominent membranes supplied by TNO.
- Advantages of NIC system:
  - high pressure op. (80 bar) and
  - high temperature op. (350°C).



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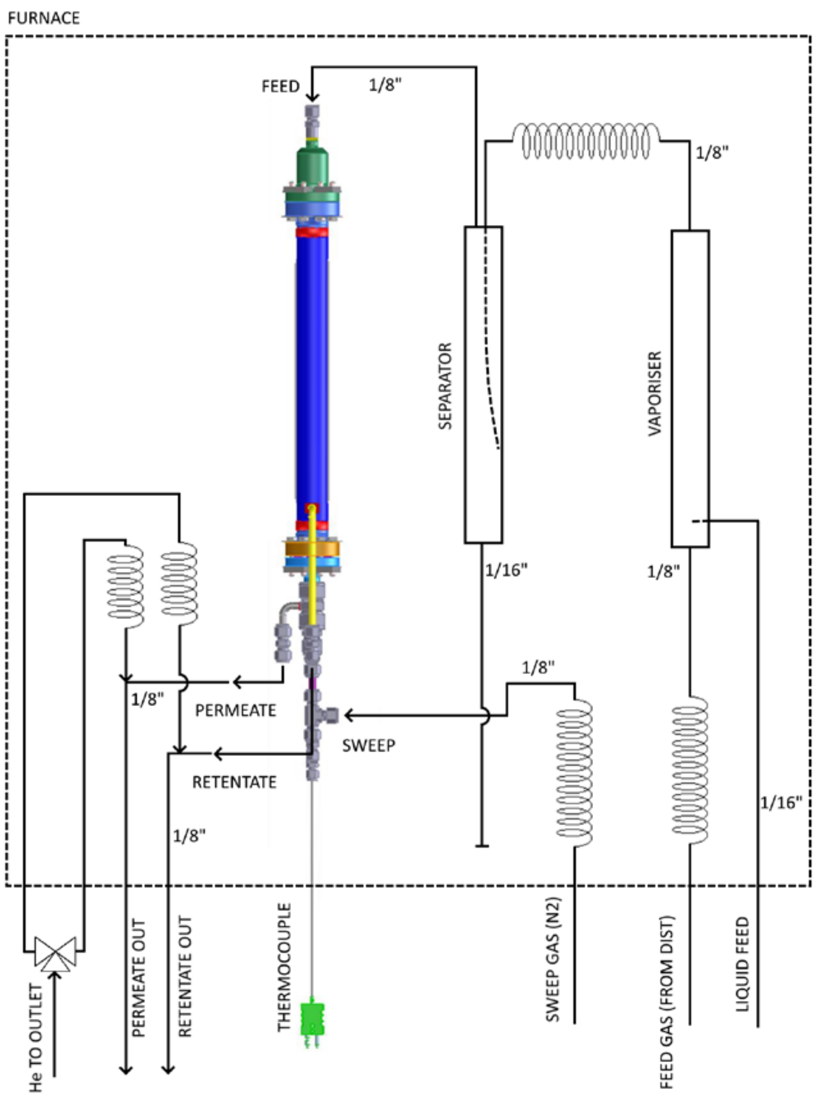
Inside the furnace with the membrane module

- Feed gas saturation with H_2O or MeOH to:
    - determine permeation and
    - simulate thermodynamical equibrium gas mixture.

- He dillution to determine in-situ flow rates of permeate and retentate by gas chromatography.

- CO_2 is pumped into the feed gas using HPLC pump before membrane module.



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Modelling procedure

Selected membrane characteristics
- Permeances for all compounds
- T and P dependence
- Determined empirically

Reaction kinetics for the selected catalyst
- Packed-bed reactor kinetic catalytic tests
- Regression of kinetic data using a PBR model (already developed)

Membrane reactor model

Mass transport phenomena
- Convection
- Diffusion
- Permeation through the membrane

Reaction phenomena
- Catalytic surface microkinetic reactions
- Adsorption/desorption

Model validation
- Catalytic experiments in membrane reactor

Exploration of different operating windows
- Inlet composition
- Temperatures
- Pressures
- Reactor geometry and size

Process optimization

Multi-tube system modelling

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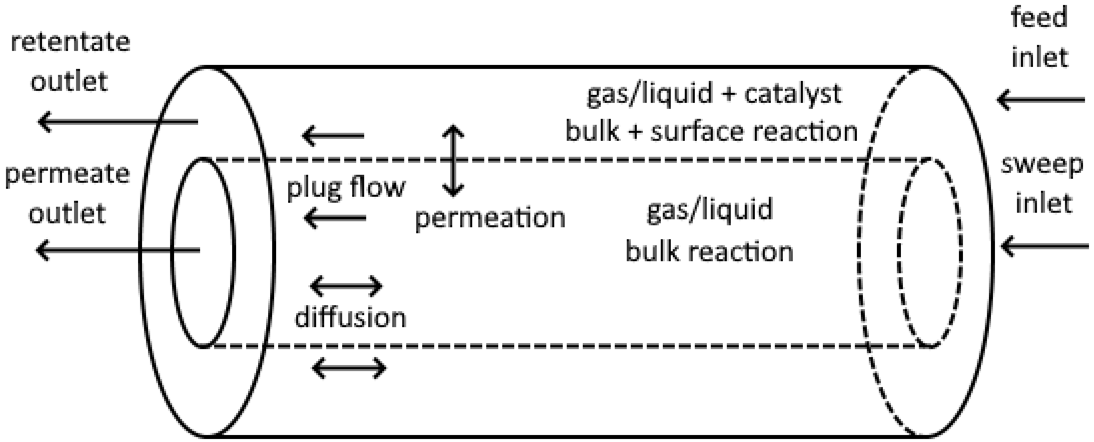
Model development



Retentate MB:

$$\frac{\partial C_i}{\partial t} = -v_{x,ret}\frac{\partial C_i}{\partial x} + \frac{D_i}{\tau}\frac{\partial^2 C_i}{\partial x^2} + C^*\frac{1-\varepsilon}{\varepsilon}R_{i,cat} + R_{i,bulk} - \frac{\dot{N}_{memb.}}{V_{ret}\,\varepsilon}$$

Permeate MB:

$$\frac{\partial C_i}{\partial t} = -v_{x,perm}\frac{\partial C_i}{\partial x} + D_i\frac{\partial^2 C_i}{\partial x^2} + R_{i,bulk} + \frac{\dot{N}_{memb.}}{V_{perm}}$$

Flow through the membrane:

$$\dot{N}_{memb.} = A_{memb.}P_i\left(p_{i,ret} - p_{i,perm}\right)$$
$$= A_{memb.}P_iRT\left(c_{i,ret} - c_{i,perm}\right)$$

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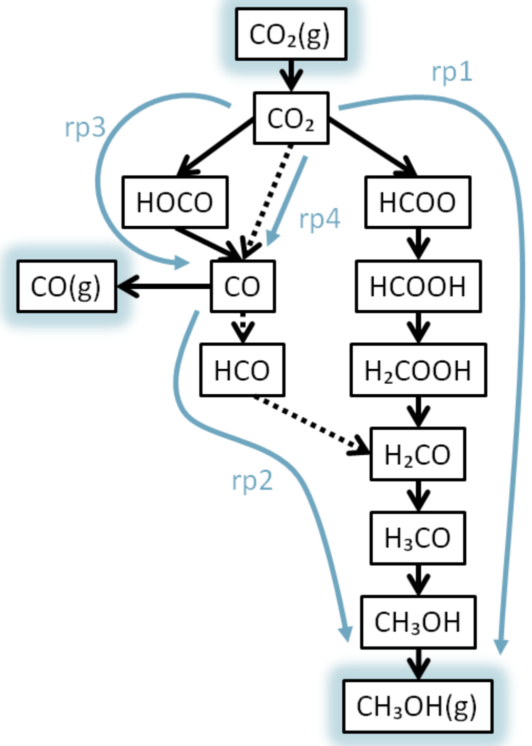
Model development: Kinetics of MeOH synthesis



Overall reaction scheme. Black arrows represent the elementary reaction steps and blue arrows the reaction pathways. Reaction species in black squares without "(g)" are adsorbed on the catalyst's surface.

- Surface reaction mechanism for methanol synthesis on CuZnAl
- Active sites: Cu (&), Zn (*)
- 5 gas phase species, 11 surface species
- 16 reversible surface reactions, 5 of which are adsorption/desorption reactions
- The constants obtained from literature were fitted to experimental data

	optimized				original Zn/Cu(211)			
Reaction	Afor [s-1]	Eafor [kJ/mol]	Aback [s-1]	Eaback [kJ/mol]	Afor [s-1]	Eafor [kJ/mol]	Aback [s-1]	Eaback [kJ/mol]
H2 + & + & ⇌ H& + H&	1.00E+03	51.00	1.77E+12	78.00	1.00E+03	51.00	1.77E+12	78.00
H& + CO2* ⇌ HOCO*&	4.62E+13	83.80	8.23E+13	104.28	3.91E+12	95.53	1.00E+11	123.51
H& + H2CO*& ⇌ H3CO*& + &	3.12E+08	8.47	1.17E+11	88.29	4.66E+12	11.58	1.00E+11	114.82
H& + H3CO*& ⇌ CH3OH*& + &	3.28E+12	112.01	6.98E+12	87.02	1.99E+14	143.77	1.44E+13	116.75
H& + CO2* ⇌ HCOO*&	1.69E+11	58.96	5.97E+14	142.86	3.57E+12	74.30	1.00E+11	188.16
H& + HCOO*& ⇌ HCOOH*& + &	4.69E+09	60.20	2.71E+10	75.73	7.93E+12	114.82	1.77E+11	48.25
H& + HCOOH*& ⇌ H2COOH*& + &	1.13E+12	87.74	6.71E+13	75.98	1.26E+12	58.86	9.57E+13	58.86
H2COOH*& + * ⇌ H2CO*& + OH*	1.82E+13	59.21	4.26E+11	17.08	2.53E+13	50.17	1.86E+11	16.40
H& + OH* ⇌ H2O*+ &	6.43E+09	72.66	2.89E+10	72.73	1.22E+13	77.19	4.83E+11	70.44
CO2* + & ⇌ CO& + O*	3.98E+12	46.16	1.57E+12	52.88	1.04E+13	76.23	8.40E+12	65.61
H& + O* ⇌ OH*+&	5.90E+12	309.13	5.05E+10	226.11	1.88E+13	116.75	1.00E+11	198.77
HOCO*& ⇌ CO& + OH*	3.16E+10	27.99	4.89E+11	65.23	6.60E+13	22.19	1.00E+11	58.86
CO2 + * ⇌ CO2*	7.53E+02	-2.29	2.9E+09	-29.13	7.41E+02	-2.01	1.00E+13	-30.88
CH3OH + * + & ⇌ CH3OH*&	2.59E+01	-0.99	1.34E+13	43.01	8.68E+02	-2.01	1.00E+13	39.56
H2O + * ⇌ H2O*	8.38E+02	-1.69	1.31E+12	39.45	1.16E+03	-2.01	1.00E+13	37.63
CO + & ⇌ CO&	2.86E+02	-0.98	3.25E+13	59.12	9.28E+02	-2.01	1.00E+13	98.42

Reactions and reaction rate constants (original from literature and fitted to experimental data)

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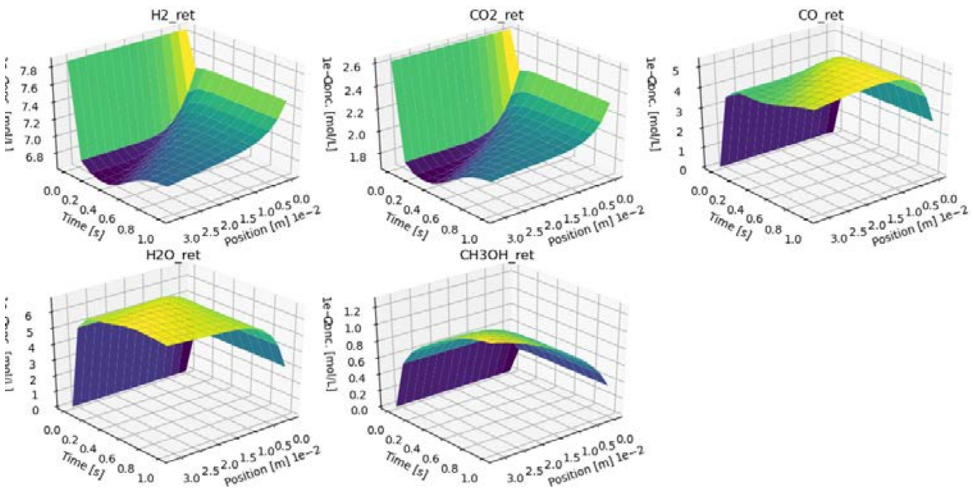
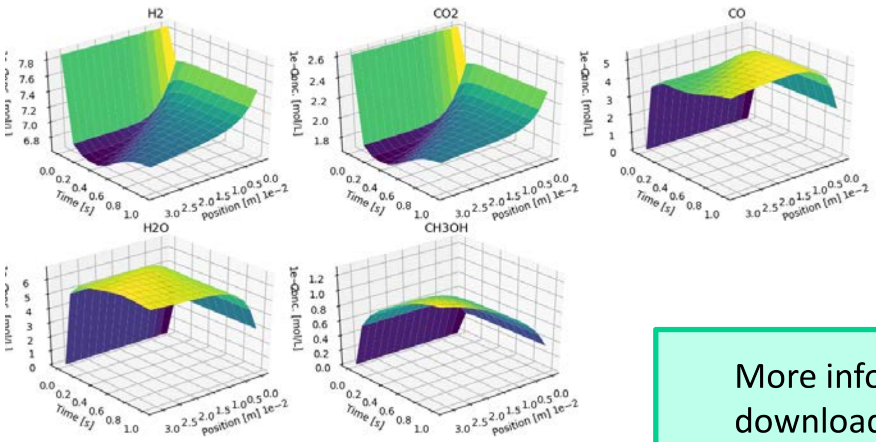
Model development

- Modeling in the programme CERRES developed at NIC

CERRES

- ✔ Simulation of 14 different types of chemical reactors (**including membrane reactor**)
- ✔ Complex user-defined chemical kinetics
- ✔ Model-experiment compare
- ✔ Parameter optimization
- ✔ Sensitivity analysis
- ✔ Efficient computation
- ✔ Plot results and export data
- ✔ Easy to use (graphical user interface)
- ✔ Free for academic/teaching use





More information and download available at:

www.cerres.org

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WP4: Green methanol synthesis for biodiesel production