Modeling of methanol synthesis using novel carbon-based membranes in a packed bed membrane reactor

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BioMeGaFuel MEMCAT ISCRE29 TU/e EINDHOVEN UNIVERSITY OF TECHNOLOGY

Overview

- *The rising demand for biofuels*
- *Why methanol?*
- *Bio-MeGaFuel Project*
- *Methodology*
- *Results*
- *Conclusions and Outlook*

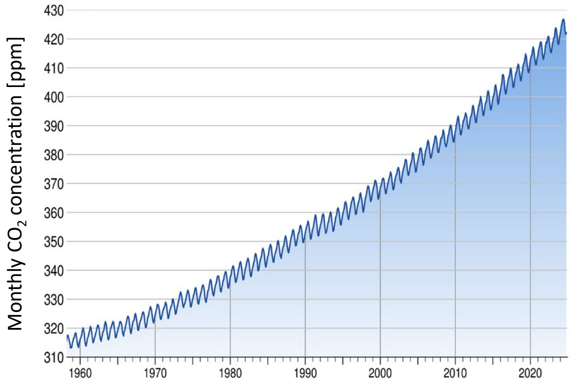
Figure 1. World's first commercial-scale CO_2-to-CH_3OH plant in Anyang, Henan Province, China[01].

[01] Carbon Recycling International, Press release, **2022** October 26th.

Introduction

The rising demand for biofuels

- ***Global biofuel demand** hit a record high of 170 billion liters in 2022* [03].
- *By 2030, biofuel production needs to increase by 11% per year to meet **Net Zero Emissions** goals; up to 400 billion liters* [03].
- *High-emission sectors (aviation, shipping, heavy-duty transport) are key drivers of growth* [04].
- *Shift in feedstocks: By 2030, over 40% of biofuels should come from bio-waste, bio-residues, and non-food crops (up from 9% in 2021)* [03].



[02] Keeling and Graven, *Annu. Re. Eniron. Resour.* **2021**, 46, 85-110.
[03] IEA (2024), *Renewables* **2023**, IEA, Paris https://www.iea.org/reports/renewables-2023
[04] IEA (2022), *World Energy Outlook* **2022**, IEA, Paris https://www.iea.org/reports/world-energy-outlook-2022

Introduction

Why methanol?

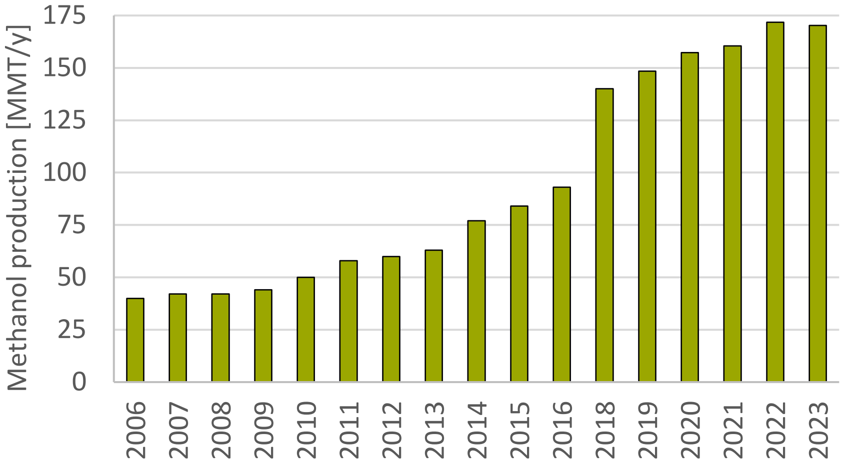
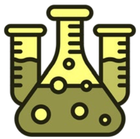
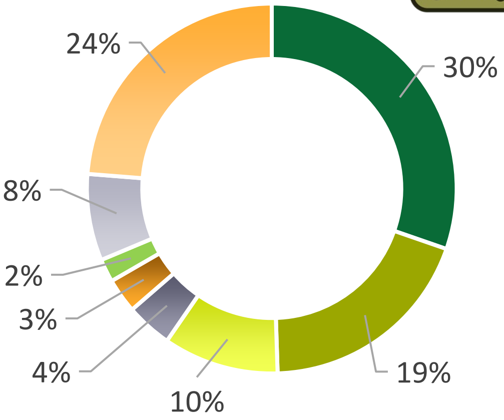


Figure 4. Methanol production from 2006 to 2023 [05],[06].

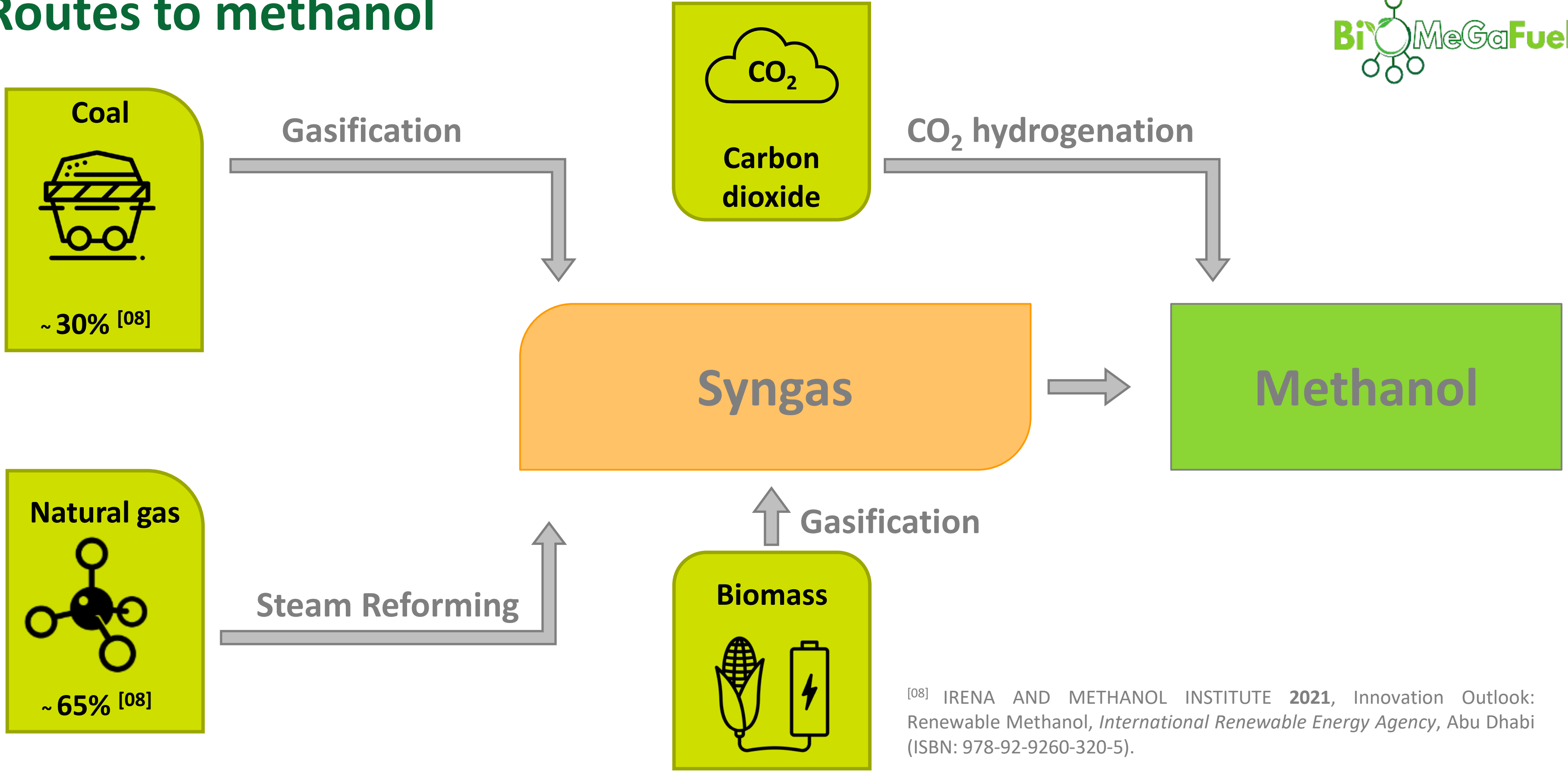




- *Methanol is a versatile biofuel and chemical building block*
- *One of the top 5 commodity chemicals globally*
- *Over 170 million metric tonnes/year produced (2023)* [06]
- *Supply shortage in Europe → opportunity for local production*

[05] Azhari et al., *Results Eng.* **2022**, 16, 100711
[06] GlobalData. In Statista. (May 28, **2024**). Production capacity of methanol worldwide.
[07] Ali et al., *Renew. Sustain. Energy Rev.* **2015**, 44, 508-518

Routes to methanol



[08] IRENA AND METHANOL INSTITUTE **2021**, Innovation Outlook: Renewable Methanol, *International Renewable Energy Agency*, Abu Dhabi (ISBN: 978-92-9260-320-5).

Bio-MeGaFuel Project

Figure 3. Bio-MeGaFuel value chain.

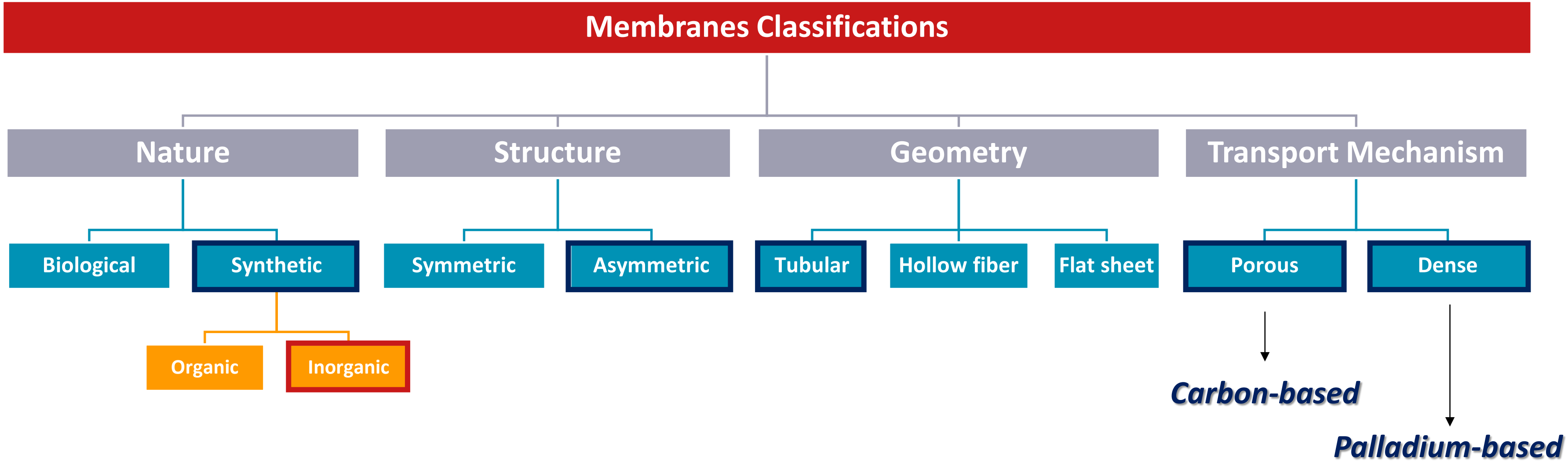
Process intensification strategy

Membrane reactors

- *Conventional process: packed-bed reactor with $Cu/ZnO/Al_2O_3$ catalyst.*
- *Methanol synthesis reaction is severely limited by its thermodynamic equilibrium.*
- *Membrane reactors offer the potential for simultaneous reaction and separation.*
- *Water removal drives equilibrium forward and improves performance.*

Introduction to Membranes

Classifications

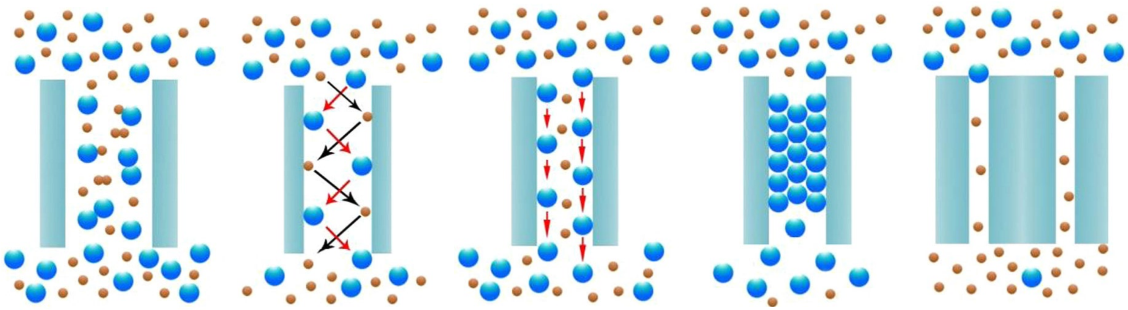


[09] P. Li et al., *J. Membr. Sci.* **2015**, 495, 130-168.
[10] Z. Dai et al., Green Energy Environ. **2016**, 1, 102-128.

Introduction to Membranes

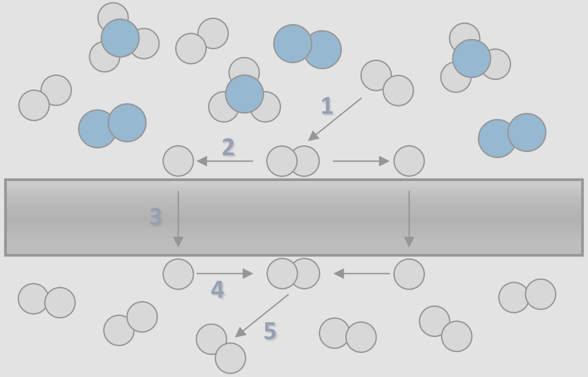
Transport mechanisms for inorganic membranes

Transport mechanisms of gases in porous media



Poiseuille flow	*Knudsen diffusion*	*Surface diffusion*	*Capillary condensation*	*Molecular sieving*

Transport mechanism of H_2 in dense media

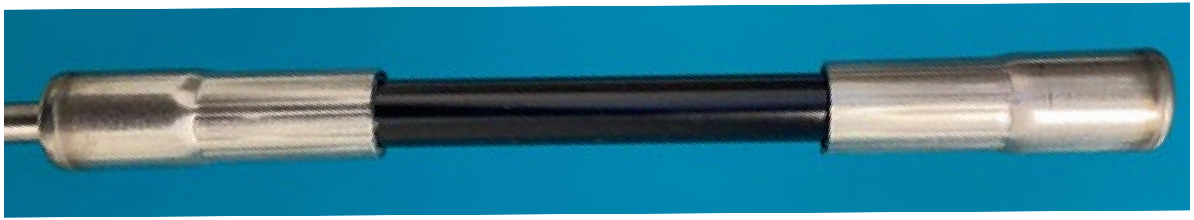


Solution diffusion

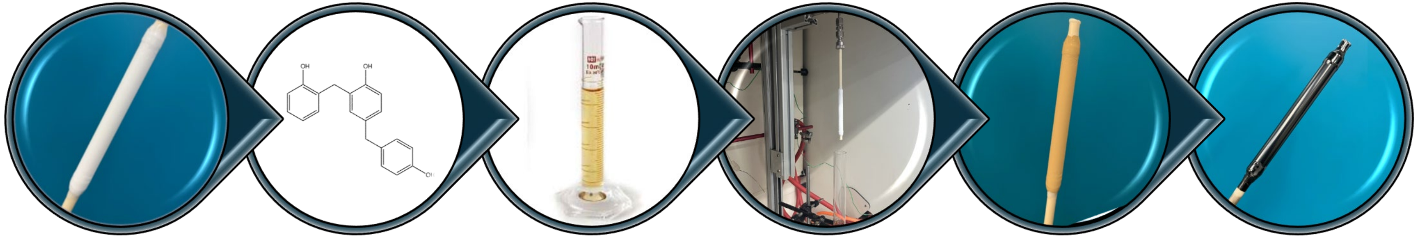
[09] P. Li et al., *J. Membr. Sci.* **2015**, 495, 130-168.
[10] Z. Dai et al., Green Energy Environ. **2016**, 1, 102-128.

Development of carbon membranes

Fabrication parameters



[11] Cechetto et al., Processes **2024**, 12(6), 1168.



Asymmetric porous Al_2O_3 support | Phenolic resin (NOVOLAC®) | Dipping solution | Dip coating | Rotary drying and polymerization | Carbonization

Development of carbon membranes

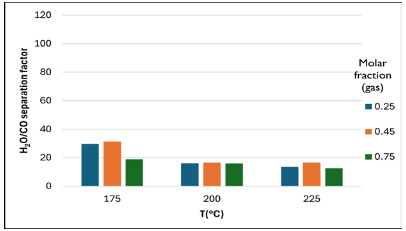
Membrane performance evaluation

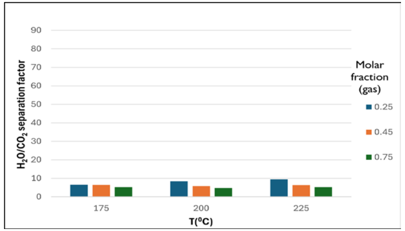
Separation Factor H_2O/CO

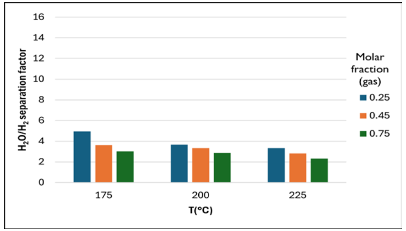
Separation Factor H_2O/CO_2

Separation Factor H_2O/H_2

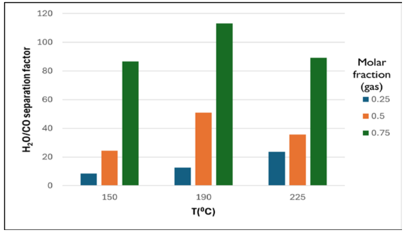
Benchmark membrane [4]
Polymer loading: 13 wt%
Alumisol loading: 0.80 wt%

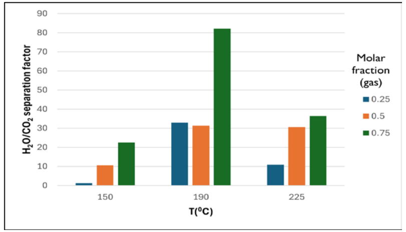


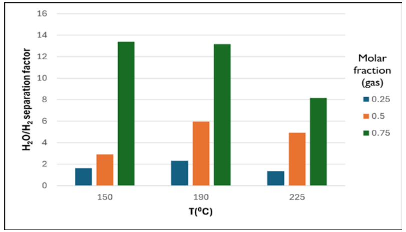




Best fabricated membrane
Polymer loading: 20 wt%
Alumisol loading: 0.70 wt%





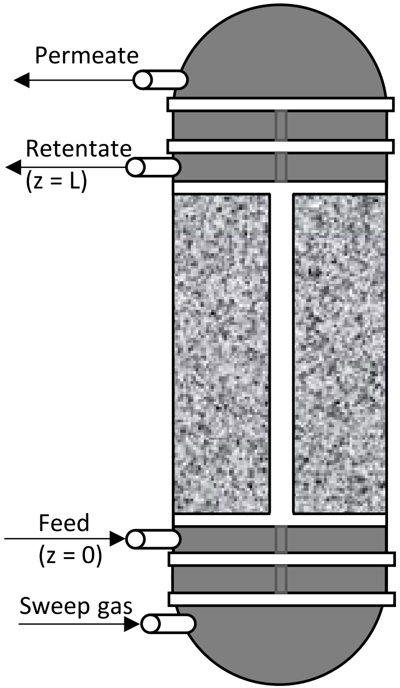


[12] Poto et al., *J. Membr. Sci.* **2023**,677, 121613.

Membrane reactor model

Reactor geometry and main assumptions

- *Steady-state operation*
- *1D ideal plug flow: axial and radial dispersion neglected for* $\frac{L}{d_p} \geq 50$ *and* $\frac{D}{d_p} \geq 25$ [13]
- *Pseudo-homogeneous phase: no intraparticle mass transfer limitations*
- *Negligible pressure drop on the permeate side*
- *Inert membrane material*
- *No reaction occurring on the permeate side*



[13] Poto et al., *Fuel.* **2021**, 302, 121080.

Membrane reactor model

Governing equations

❖ *Mass balance:*

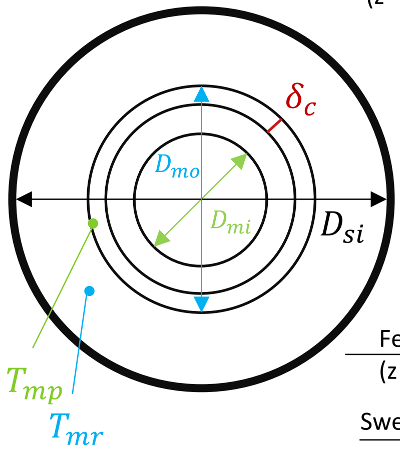
$$\frac{\partial F_i^R}{\partial z} = \rho_c(1-\varepsilon_b)\frac{\pi}{4}\left(D_{si}^2 - D_{mo}^2\right)\sum_{j=1}^{N_r} \nu_{ji} r_j - J_i \pi D_{mo}$$

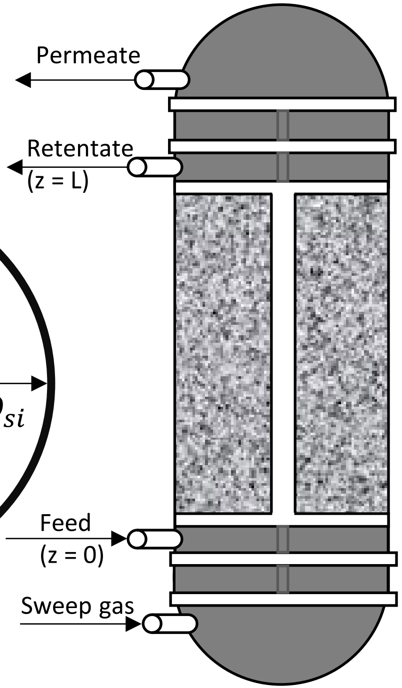
$$\frac{\partial F_i^P}{\partial z} = J_i \pi D_{mo}$$

$$J_i = \wp_i\left(P_i^R - P_i^P\right)$$

❖ *Momentum balance:*

$$\frac{dP^R}{dz} = -\left[\frac{150\mu(1-\varepsilon_b)^2 u}{{\varepsilon_b}^3 d_p^2} + \frac{1.75(1-\varepsilon_b)\rho u^2}{{\varepsilon_b}^3 d_p}\right]$$





Membrane reactor model

Governing equations

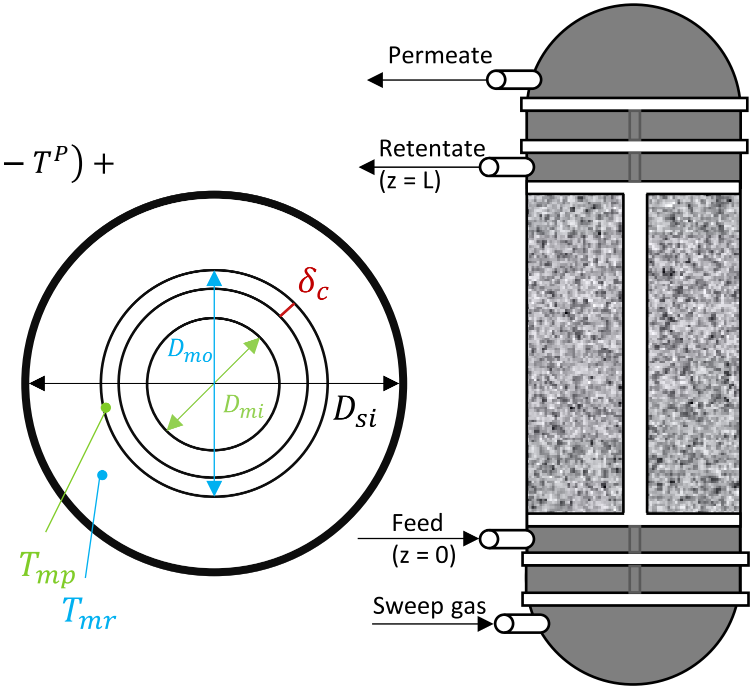
❖ *Energy balance:*

$$\sum_{i=1}^{N_s}\left(F_i^R C_{p,i}\right)\frac{dT^R}{dz} = \rho_c(1-\varepsilon_b)\frac{\pi}{4}\left(D_{si}^2 - D_{mo}^2\right)\sum_{j=1}^{N_r} r_j\left(-\Delta H_r(T^R)\right) - U\pi D_{mi}\left(T^R - T^P\right) + $$
$$- \pi D_{mo}\sum_{i=1}^{N_s}\left[J_i C_{p,i}\left(T^R - T_{mr}\right)\right]$$

$$\sum_{i=1}^{N_s}\left(F_i^P C_{p,i}\right)\frac{dT^P}{dz} = U\pi D_{mi}\left(T^R - T^P\right) + \pi D_{mo}\sum_{i=1}^{N_s}\left[J_i C_{p,i}\left(T_{mp} - T^P\right)\right]$$

❖ *Global heat transfer coefficient:*

$$\frac{1}{U} = \frac{1}{h_{mi}} + \frac{D_{mi}}{2}\frac{1}{k_m}\ln\left(\frac{D_{mo}}{D_{mi}}\right) + \frac{D_{mi}}{D_{mo}}\frac{1}{h_{mo}}$$

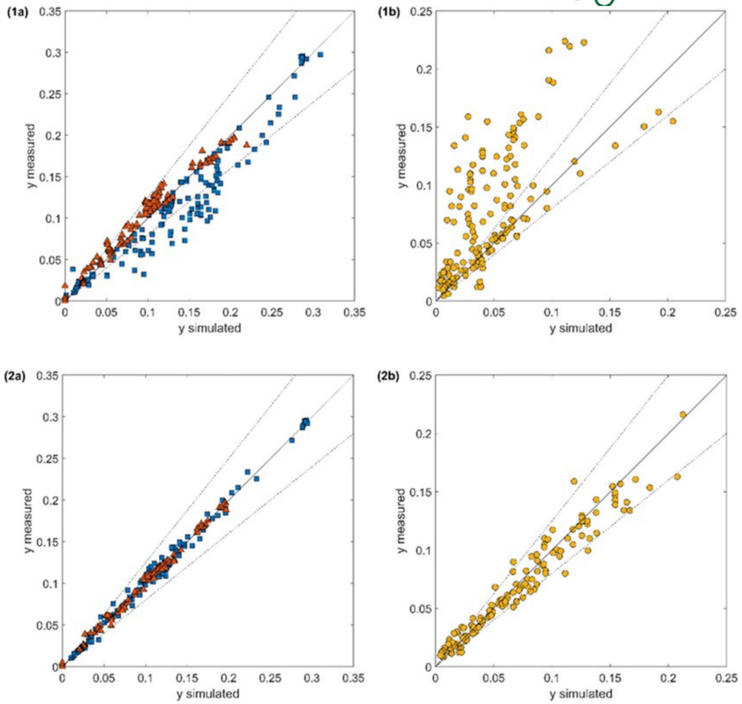


Membrane reactor model

Kinetic model validation

- *Model by Graaf et al. [14], with parameters refitted by Bisotti et al. [15]*
- *Higher accuracy in the range:*

  T = 210 – 340 °C, P = 20 – 90 bar



Parity plots of molar fractions in the product mixture: (a) CO_2 (blue square), CO (red triangle) and (b) methanol (yellow circle) for the original Graaf model (row 1) [14] and the refitted model (row 2).[15]

[14] Slotboom et al., *Chem. Eng. J.* **2020**, 389, 124181
[15] Bisotti et al., *Ind. Eng. Chem. Res.* **2021**, 60, 16032-16053

Membrane reactor model

Permeation model

- *In previous work:*

$$J_i = \wp_i(P_i^R - P_i^P)$$

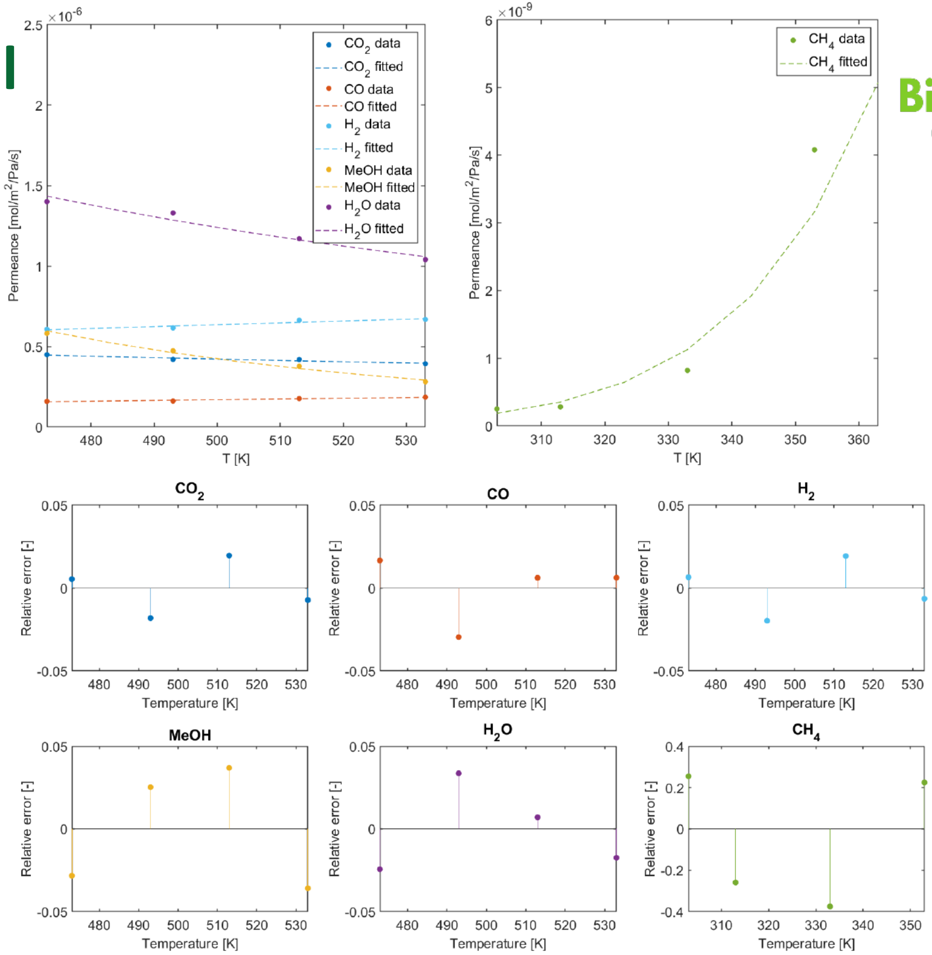
$$\wp_i(T^R) = C_1 e^{C_2 T^R}$$

- *New permeation model:*

$$\wp_i(T^R) = C_1 e^{C_2/T^R} \, ,$$

with C_1, C_2 fitted using data from

- *Gallucci et al.*[16]
- *Llosa Tanco et al.*[17] *(for CH_4)*



[16] Gallucci et al., *Catalysts* **2026**, 16(1), 53

[17] Llosa Tanco et al., *Int. J. Hydrog. Energy* **2015**, 40, 5653-5663

Feed composition

From biomass chemical looping gasification

Case	C_2-C_3 [vol.%]	CH_4 [vol.%]	CO [vol.%]	H_2 [vol.%]	CO_2 [vol.%]
1	1.0	9.0	24.0	38.0	28.0
2	1.0	9.0	20.0	36.0	34.0
3	1.0	9.0	18.0	32.0	40.0
4	0.7	7.0	20.0	15.0	55.0
5	0.7	7.0	20.0	7.0	67.0
6	0.7	7.0	20.0	1.0	72.0

Case	CH_4 [vol.%]	CO [vol.%]	H_2 [vol.%]	CO_2 [vol.%]
1	4.6	12.3	68.8	14.3
2	4.3	9.6	69.7	16.4
3	4.0	8.0	70.3	17.7
4	2.4	6.9	71.8	18.9
5	2.1	5.9	72.3	19.7
6	2.0	5.6	72.5	20.0

Removing C_2-C_3 and adding H_2 to reach $\mathrm{SN} = \frac{y_{H_2} - y_{CO_2}}{y_{CO} + y_{CO_2}} = 2.05$[15]

[15] Bisotti et al., *Ind. Eng. Chem. Res.* **2021**, 60, 16032-16053

Packed bed reactor model results

Performance indicators

- ***Packed Bed Reactor:***

$$X_{CO_2} = \frac{F^R_{CO_2,0} - F^R_{CO_2}}{F^R_{CO_2,0}} \qquad Y_{MeOH} = \frac{F^R_{MeOH}}{F^R_{CO_2,0}}$$

- ***Packed Bed Membrane Reactor [13]:***

$$X_{CO_2} = \frac{F^R_{CO_2,0} - F^R_{CO_2} + F_{CO_2,tmb}}{F^R_{CO_2,0} + F^*_{CO_2,tmb}} \qquad Y_{MeOH} = \frac{F^R_{MeOH} + F^P_{MeOH}}{F^R_{CO_2,0} + F^*_{CO_2,tmb}}$$

Transmembrane flow: $F_{CO_2,tmb} = F^P_{CO_2,0} - F^P_{CO_2}$

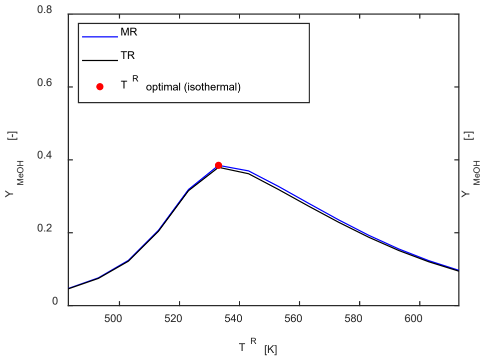
$$F^*_{CO_2,tmb} = \begin{cases} 0, \ F_{CO_2,tmb} \leq 0 \ (Reactant\ loss) \\ F_{CO_2,tmb}, F_{CO_2,tmb} > 0 \ (Reactant\ cofeeding) \end{cases}$$

Simulation conditions	
T^R [$^\circ C$]	270
P_R [bar]	90
GHSV [1/h]	10,000
D_{si} [m]	0.4
D_{mo} [mm]	14
D_{mi} [mm]	7
δ_c [m]	3E-6
L [m]	1.0
Sweep/feed ratio [-]	1
No. of membranes [-]	10
ΔP [bar]	0

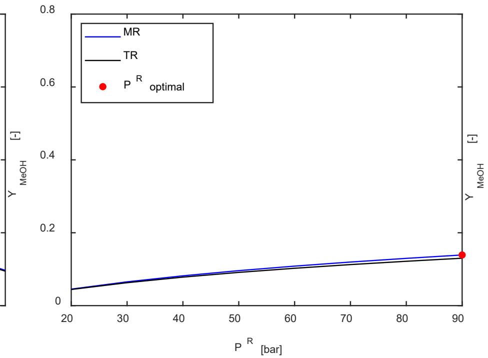
[13] Poto et al., *Fuel.* **2021**, 302, 121080.

PBMR Optimization

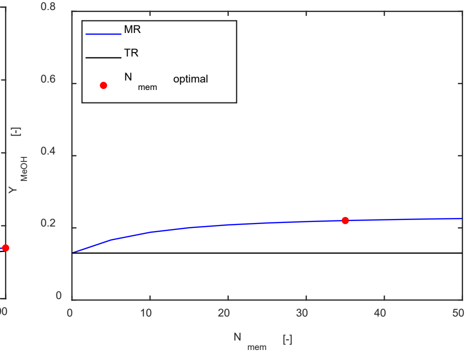
Optimization results for Feed case 1



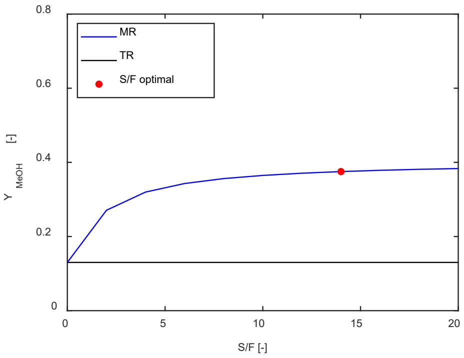
Effect of the **operating temperature** on the MeOH yield, under isothermal operation. Operating conditions: $P^R = 90$ bar, $N_{mb} = 1$, S/F = 1, $T^P = T^R$, $\Delta P = 0$. $T^R_{opt} = 533$ K



Effect of the **operating pressure** on the MeOH yield. Operating conditions: $T^R_{in} = T^P_{in} = 533$ K, $N_{mb} = 1$, S/F = 1, $\Delta P = 0$. $P^R_{opt} = 90$ bar



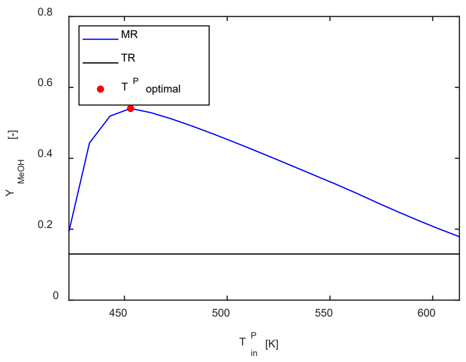
Effect of the **number of membranes** on the MeOH yield. Operating conditions: $T^R_{in} = T^P_{in} = 533$ K, $P^R = 90$ bar, S/F = 1, $\Delta P = 0$. $N_{mb,opt} = 35$



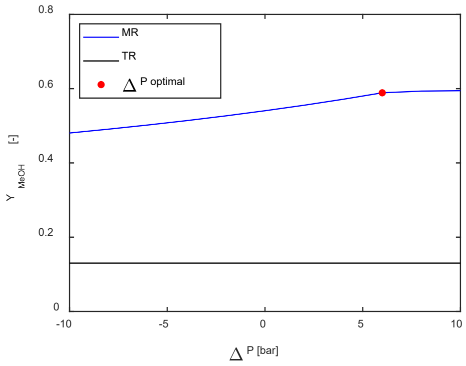
Effect of the **sweep-to-feed molar ratio** on the MeOH yield. Operating conditions: $T^R_{in} = T^P_{in} = 533$ K, $P^R = 90$ bar, $N_{mb} = 35$, $\Delta P = 0$. $S/F_{opt} = 14$

PBMR Optimization

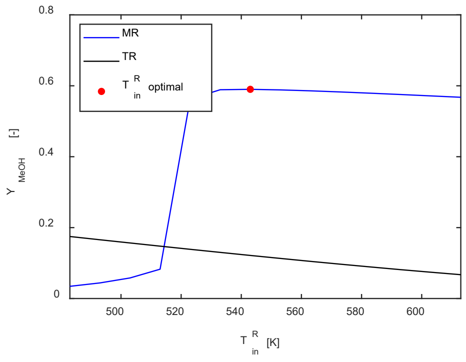
Optimization results – Feed case 1



Effect of the **inlet temperature of the sweep gas** on the MeOH yield. Operating conditions: $T_{in}^{R} = 533$ K, $P^{R} = 90$ bar, $N_{mb} = 35$, S/F = 14, $\Delta P = 0$. $T_{in,opt}^{P} = 453$ K



Effect of the **pressure difference across the membrane** on the MeOH yield. Operating conditions: $T_{in}^{R} = 533$ K, $T_{in}^{P} = 453$ K, $P^{R} = 90$ bar, $N_{mb} = 35$, S/F = 14. $\Delta P_{opt} = 6$ bar



Effect of **inlet temperature of the feed** on the MeOH yield. Operating conditions: $T_{in}^{P} = 453$ K, $P^{R} = 90$ bar, $N_{mb} = 35$, S/F = 14, $\Delta P = 6$ bar, $T_{in,opt}^{R} = 543$ K

PBMR Optimization

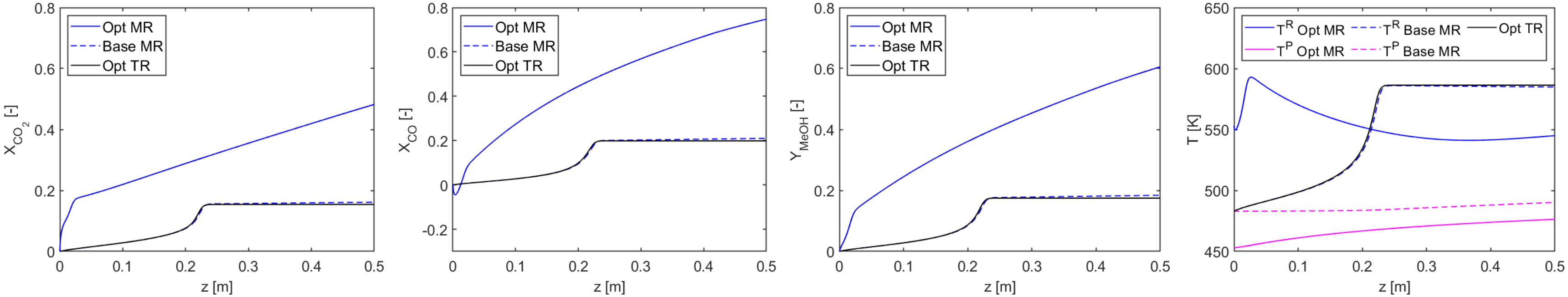
Optimization results

Parameter		Base case		Optimization	
		Feed 1	Feed 6	Feed 1	Feed 6
T^R	[K]	483	483	533	533
T_{in}^R	[K]	483	483	533	483
P_{in}^R	[bar]	90	90	90	90
N_{mb}	[-]	1	1	35	40
S/F	[-]	1	1	14	14
T_{in}^P	[K]	483	483	453	503
ΔP	[bar]	0	0	6	12
$m_{cat,MR}/A_{mb}$	[kg/m^2]	880	880	21	18
X_{CO2}	**[%]**	**15**	**22**	**48**	**69**
Y_{MeOH}	**[-]**	**17**	**19**	**0.6058**	**54**

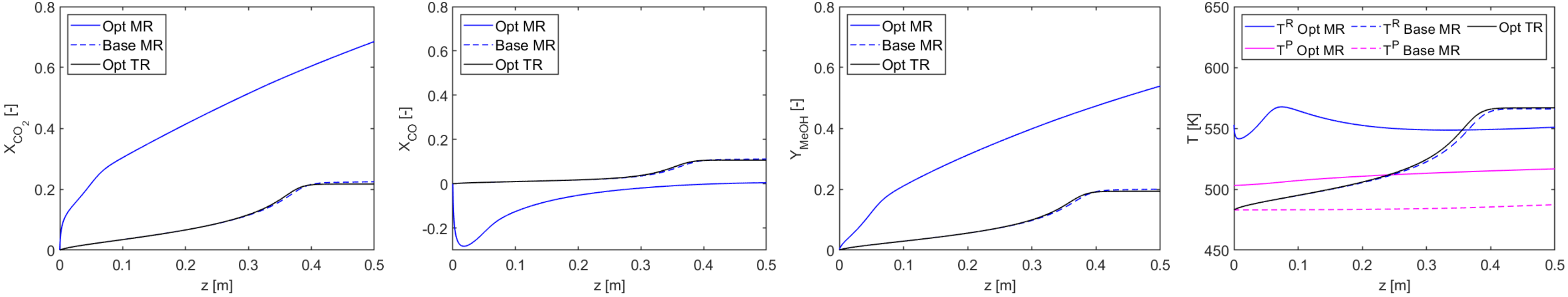
PBR vs PBMR comparison

Optimized conditions results

Feed 1



Feed 6



Conclusions and Outlook

- ✓ *Carbon membranes for H_2O separation were successfully produced, surpassing the performance of previous-generation membranes.*
- ✓ *A 1D carbon membrane reactor model for syngas to bio-methanol was successfully developed.*
- ✓ *Optimization of the membrane reactor led to a significant increase in CO_2 conversion and CH_3OH yield.*

  For the investigated optimal conditions (@ GHSV = 10 000 h^{-1}):
  - ✓ *X_{CO2} increased from 15% to 48% (+220%) for feed 1, and from 22% to 69% (+214%) for feed 6, respectively.*
  - ✓ *Y_{MeOH} increased from 17% to 61% (+260%) for feed 1, and from 19% to 54% (+184%) for feed 6, respectively.*

- ❑ *Hybrid PBR-PBMR system will be investigated.*
- ❑ *Techno-economic analysis integrating the developed predictive model into the Bio-MeGaFuel process.*

BioMeGaFuel

Contact us!

Thank you for your attention!

Any questions?

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