



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

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26-29 October 2025, Nanjing, China

- ❖ *Introduction*
- ❖ *Methodology*
- ❖ *Results*
- ❖ *Conclusions and Outlook*



Figure 1. The world's first commercial-scale CO<sub>2</sub>-to-methanol plant has started production in Anyang, Henan Province, China. [01]

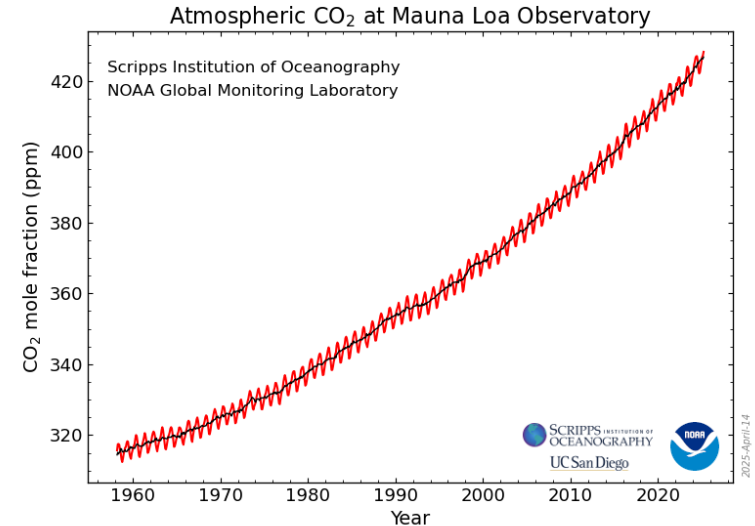
[01] Carbon Recycling International – press release, 2022-10-26

# Introduction

## Sub-title



- The intensive use of fossil fuels to meet the rise in global energy demand has led to severe environmental consequences.
- CO<sub>2</sub> levels in the atmosphere rise continuously.
- Predictions suggest around 570 ppm by 2100. [3]
- CO<sub>2</sub> valorization is gaining interest in scientific and industrial communities as a potential mitigation strategy.



**Figure 2.** Monthly mean CO<sub>2</sub> measured at Mauna Loa Observatory, Hawaii. The CO<sub>2</sub> data on Mauna Loa constitute the longest record of direct measurements of CO<sub>2</sub> in the atmosphere. [2]

[2] Dr. Xin Lan, NOAA/GML ([gml.noaa.gov/ccgg/trends/](http://gml.noaa.gov/ccgg/trends/)) and Dr. Ralph Keeling, Scripps Institution of Oceanography ([scrippsco2.ucsd.edu/](http://scrippsco2.ucsd.edu/)). Accessed: 23-04-2025

[3] Leonzio and Zondervan. - Carbon Dioxide to Methanol: A Green Alternative to Fueling the Future – Reference Module in Chemistry, Molecular Sciences and Chemical Engineering, (2025)

# Introduction

## Bio- MeGaFuel Project

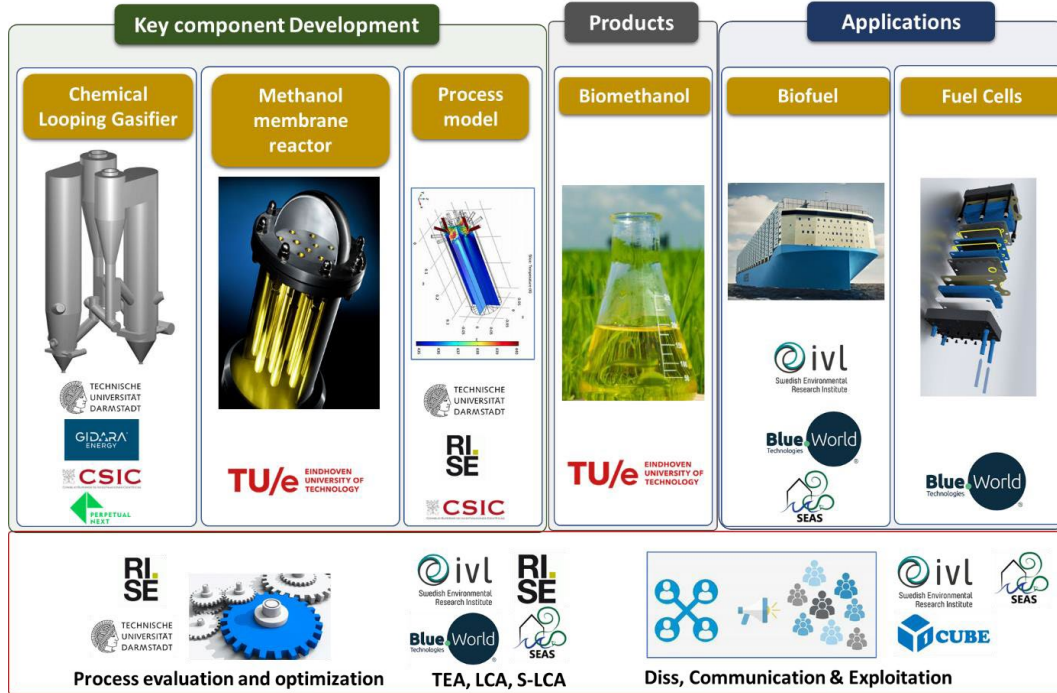
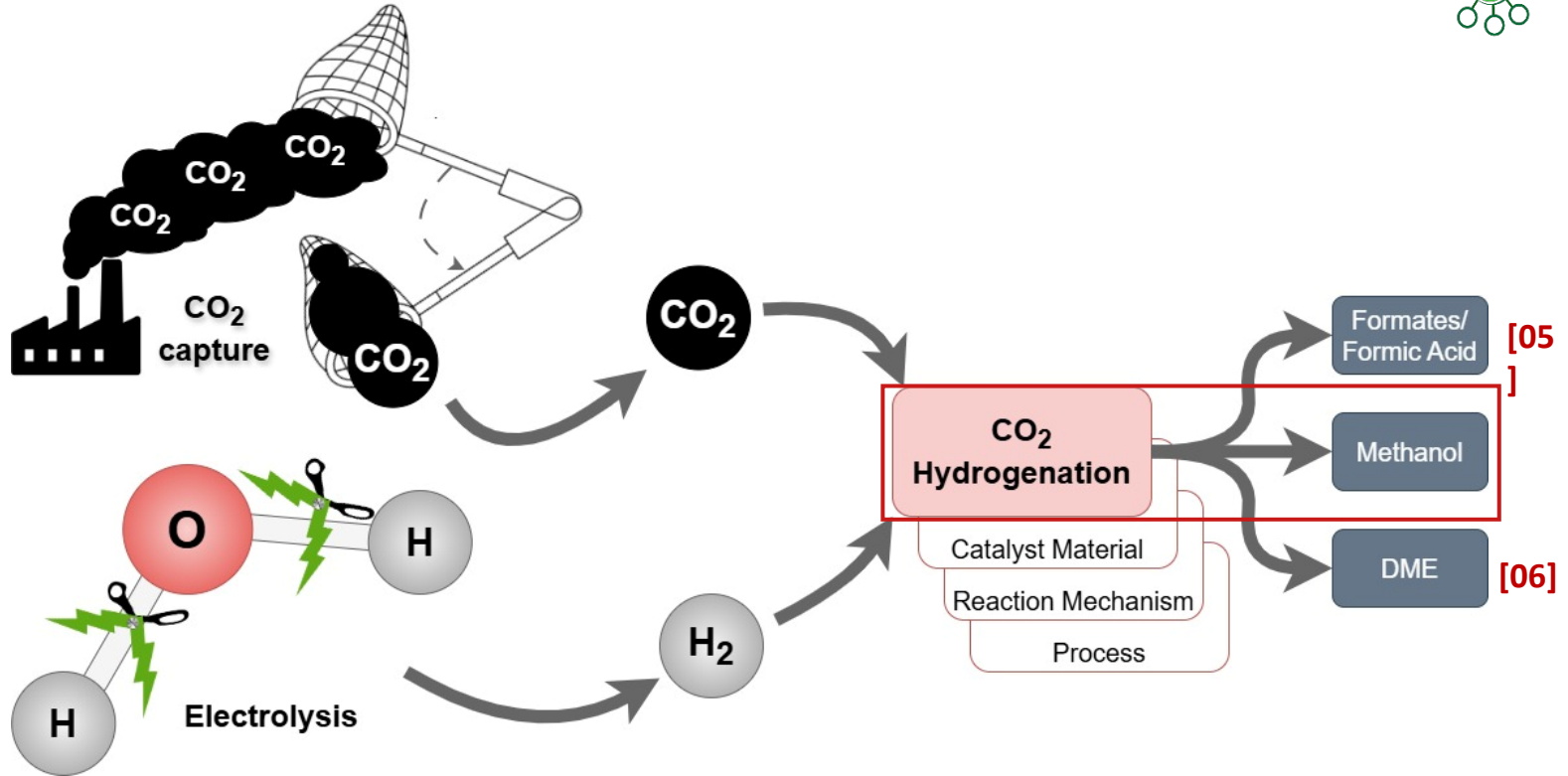


Figure 3. Bio-MeGaFuel value chain.

# Introduction



[05] de Leeuw den Bouter, A. W. N. - On the direct hydrogenation of CO<sub>2</sub> towards formic acid. [Dissertatie 1 (Onderzoek TU/e / Promotie TU/e), Chemical Engineering and Chemistry] – TU/e, (2025).

[06] Poto, S. - One-step CO<sub>2</sub> hydrogenation to dimethyl ether via packed bed membrane reactors. [Dissertatie 1 (Onderzoek TU/e / Promotie TU/e), Chemical Engineering and Chemistry] - TU/e, (2023).

# Introduction

## Why methanol?



One of the top five commodity chemicals shipped around the world.

- 92 Mt/y
- Supply shortage in Europe

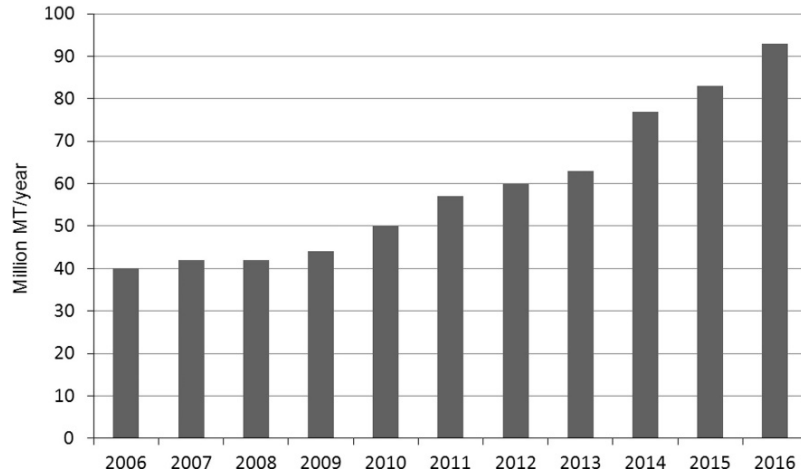
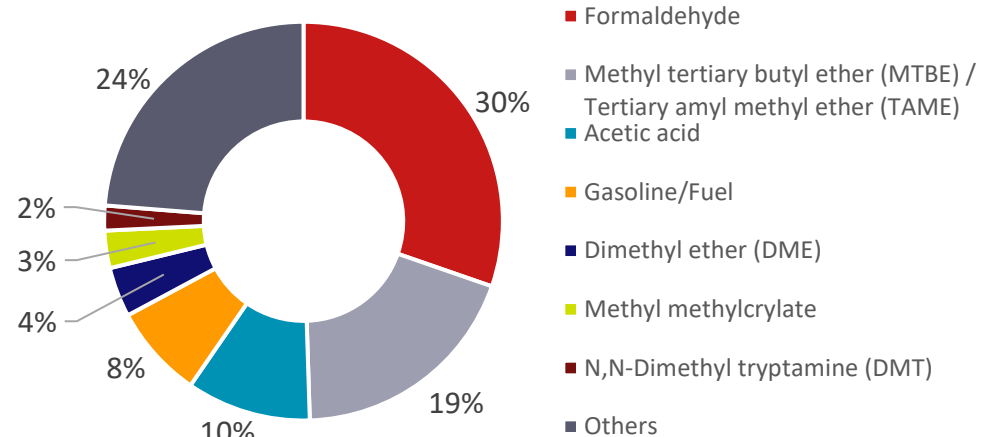


Figure 4. Methanol production from 1975 to 2016, as presented in Ali et al. [7].

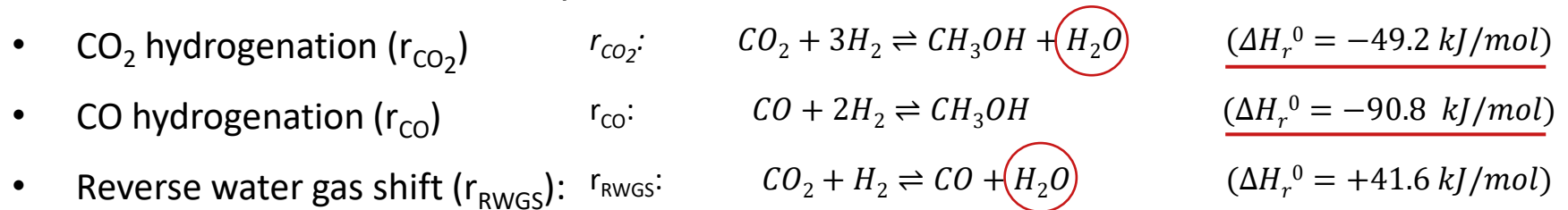


[7] Ali et al. - Recent development in catalytic technologies for methanol synthesis from renewable sources: A critical review. – Renewable and Sustainable Energy Reviews 44, (2015)

[8] Azhari et al. - Methanol synthesis from CO<sub>2</sub>: A mechanistic overview. - Results in Engineering 16, (2022)

- Conventional process: packed-bed reactor with Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst.

- Main reactions in methanol synthesis. [9]



- CO<sub>2</sub> conversion is severely limited by its thermodynamic equilibrium.

[9] Slotboom et al. - Critical assessment of steady-state kinetic models for the synthesis of methanol over an industrial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst. – Chemical Engineering Journal 389, 124181(2020)

# Process intensification strategy

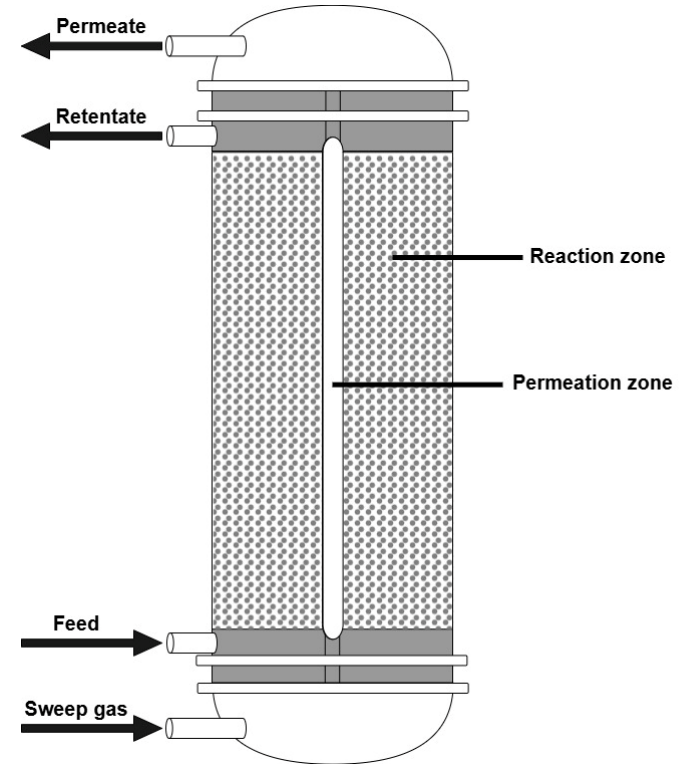
## Membrane reactors

Membrane reactors offer the potential for simultaneous reaction and separation.

- This drives equilibrium forward and improves performance.
- In this study, the membrane was used to remove the H<sub>2</sub>O side products.

### Objectives:

- Develop a 1D membrane reactor model for methanol synthesis.
- Validate the model
- Optimize for a 1 m length membrane reactor.

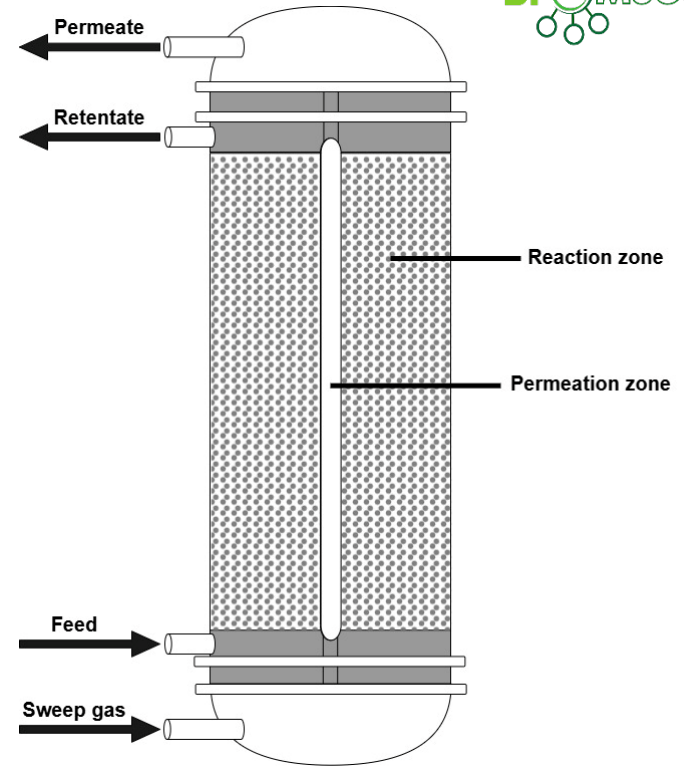


# Membrane reactor model

## Setup & main assumptions

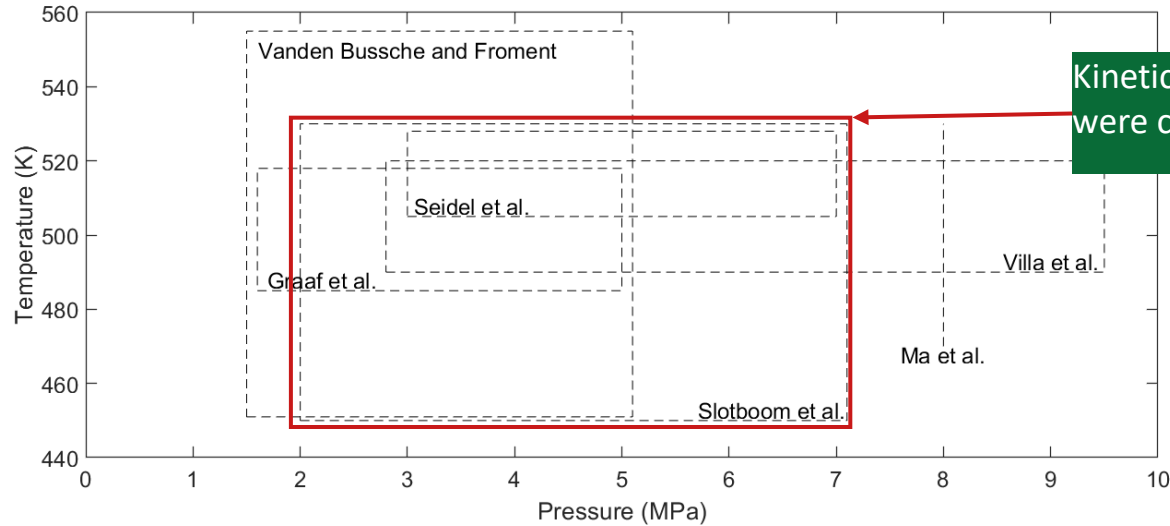
### Main assumptions:

- Steady state operation
- Co-current ideal plug flow
- Pseudo-homogeneous flow
- Negligible pressure drop in the permeation zone
- Inert membrane material under reaction conditions
- Kinetics are valid for both TR and MR
- No external heat transfer to the environment
- Inlet temperatures equal in both zones



# Membrane reactor model

## Kinetics overview



Kinetics of Slotboom et al. [9] were chosen for this study.

Combination of:

- Vanden Bussche and Froment. [11]
- Seidel et al. [12]

**Figure 5.** Overview of the experimental temperature and pressure ranges used for fitting the kinetic models of Vanden Bussche and Froment [11], Seidel et al. [12], Graaf et al. [13], Villa et al. [14], Ma et al. [15], and Slotboom et al. [9]. As presented in Slotboom et al. [9].

[9] Slotboom et al. - Critical assessment of steady-state kinetic models for the synthesis of methanol over an industrial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst. – Chemical Engineering Journal 389, 124181(2020)

[11] Vanden Bussche and Froment - A Steady-State Kinetic Model for Methanol Synthesis and the Water Gas Shift Reaction on a Commercial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> Catalyst. – Journal of Catalysis 161-1,(1996)

[12] Seidel et al. - Kinetic modeling of methanol synthesis from renewable resources. – Chemical Engineering Science 175,(2018)

[13] Graaf et al. - KINETICS OF LOW-PRESSURE METHANOL SYNTHESIS – Chemical Engineering Science 43-12, (1988)

[14] Villa et al. - Synthesis of alcohols from carbon oxides and hydrogen. 1. Kinetics of the low-pressure methanol synthesis - Industrial & Engineering Chemistry Process Design and Development 24-1, (1985)

[15] Ma et al. - Study on methanol synthesis from coal-based syngas. – Journal of Coal Science and Engineering (China) 15-1, (2009)

# Membrane reactor model

Kinetics Slotboom et al. [9]

- Langmuir-Hishelwood-type model.
- Methanol is only produced via  $\text{CO}_2$ .
- RWGS is considered for CO production.

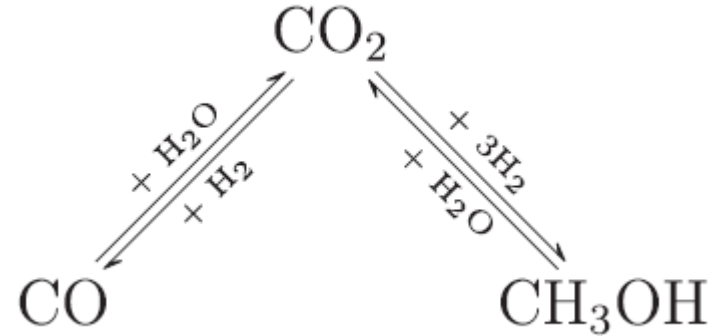
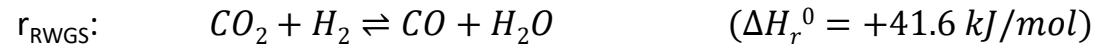
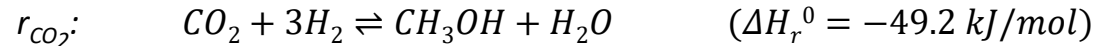


Figure 6. Reaction pathway of the kinetic model from Slotboom et al. [9].



# Membrane reactor model

## Mass balances

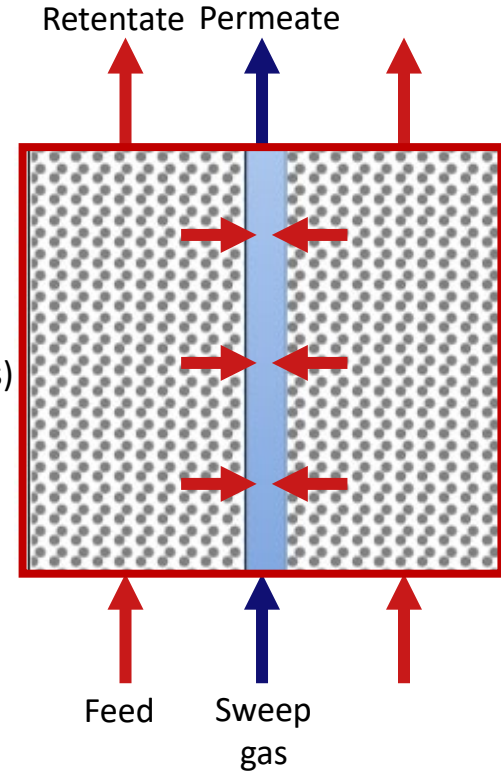


Reaction side:

$$\frac{\partial F_i^R}{\partial z} = \underbrace{\rho_c \cdot (1 - \epsilon) \cdot \frac{\pi}{4} \cdot (D_{si}^2 - N_{mem} \cdot D_{mo}^2)}_{\text{Reaction}} \cdot \sum_{j=1}^{N_r} (v_{ij} \cdot r_j) - \underbrace{J_i \cdot N_{mem} \cdot \pi \cdot D_{mo}}_{\text{Flux through membrane(s)}}$$

Permeation side:

$$\frac{\partial F_i^P}{\partial z} = \underbrace{J_i \cdot N_{mem} \cdot \pi \cdot D_{mo}}_{\text{Flux through membranes}}$$



# Membrane reactor model

## Energy balances



Reaction side:

$$\sum_{i=1}^{N_s} (F_i^R \cdot cp_i) \cdot \frac{\partial T^R}{\partial z} = \rho_c \cdot (1 - \epsilon) \cdot \frac{\pi}{4} \cdot (D_{si}^2 - N_{mem} \cdot D_{mo}^2) \cdot \sum_{j=1}^{N_r} r_j \cdot (-\Delta H_r(T^R)) - U \cdot N_{mem} \cdot \pi \cdot D_{mi} \cdot (T^R - T^P) +$$

Reaction heat

$$- N_{mem} \cdot \pi \cdot D_{mo} \cdot \sum_{i=1}^{N_s} (J_i \cdot cp_i \cdot (T^R - T_{mr}))$$

Heat transfer

Permeation side:

$$\sum_{i=1}^{N_s} (F_i^P \cdot cp_i) \cdot \frac{\partial T^P}{\partial z} = U \cdot N_{mem} \cdot \pi \cdot D_{mi} \cdot (T^R - T^P) + N_{mem} \cdot \pi \cdot D_{mo} \cdot \sum_{i=1}^{N_s} (J_i \cdot cp_i \cdot (T^R - T_{mp}))$$

Heat exchange at the membrane surfaces

Heat transfer

# Membrane reactor model

## Boundary conditions and performance indicators



Boundary conditions at  $z=0$ :

$$T^R = T^R(0)$$

$$T^P = T^P(0)$$

$$P^R = P^R(0)$$

$$F_i^R = F_i^R(0)$$

$$F_i^P = F_i^P(0)$$

Performance indicators [16]:

Conversion 
$$X_{CO_2} = \frac{F_{CO_2,in}^R - F_{CO_2,out}^R + F_{CO_2,tmb}}{F_{CO_2,in}^R + F_{CO_2,tmb}^*}$$

Yield 
$$Y_i = \frac{F_{i,out}^R + F_{i,out}^P}{F_{CO_2,in}^R + F_{CO_2,tmb}^*}$$

Selectivity 
$$S_i = \frac{Y_i}{X_{CO_2}}$$

CO<sub>2</sub> transmembrane flow 
$$F_{CO_2,tmb} = F_{CO_2,in}^P - F_{CO_2}^P$$

Reactant loss 
$$\text{If } F_{CO_2,tmb} \leq 0 \quad F_{CO_2,tmb}^* = 0$$

Reactant cofeeding 
$$\text{If } F_{CO_2,tmb} > 0 \quad F_{CO_2,tmb}^* = F_{CO_2,tmb}$$

[16] Rohde et al. –Membrane Application in Fisher-Tropsch Synthesis to Enhance CO<sub>2</sub> Hydrogenation. – Industrial & Engineering Chemistry Research 44,(2005)

# Kinetic validation

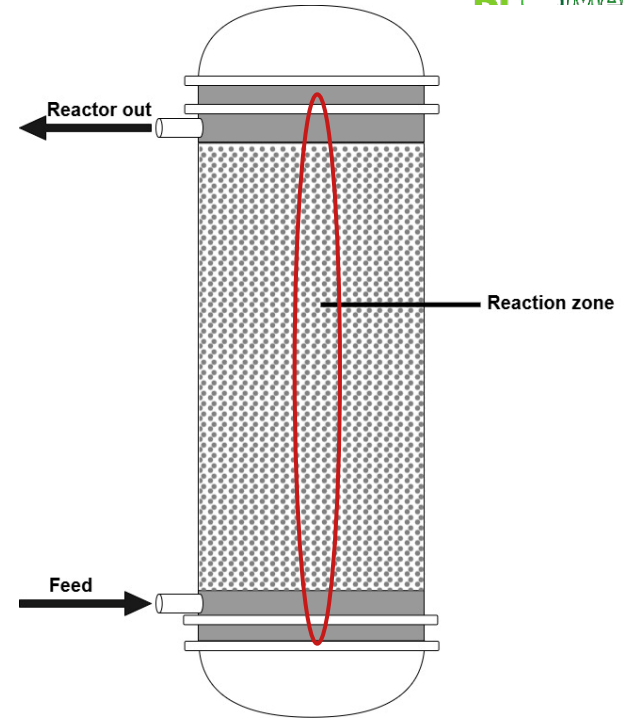
## Packed bed reactor

Reproducing experiments from Slotboom et al. [9]

- Tubular reactor
- No permeation zone
- Isothermal operation
- Feed ratio  $H_2/CO_2 = 3$
- $GHSV = 3000 \text{ h}^{-1}$

Determining temperature and pressure profile

- Peng-Robinson (PR) EoS [17]
- Modified Soave-Redlich-Kwong (SRK) EoS [18]



[9] Slotboom et al. - Critical assessment of steady-state kinetic models for the synthesis of methanol over an industrial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst. – Chemical Engineering Journal 389, 124181(2020)

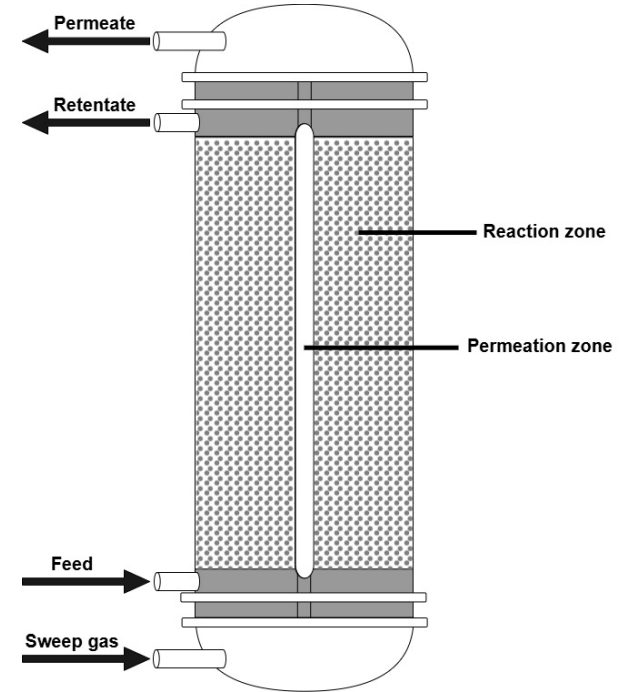
[17] Peng and Robinson - A New Two-Constant Equation of State. - Industrial and Engineering Chemistry Fundamentals 15-1, (1976)

[18] Bennekoum et al. - Modeling and Experimental Studies on Phase and Chemical Equilibria in High-Pressure Methanol Synthesis. - Industrial & Engineering Chemistry Research 51-38, (2012)

# Membrane reactor validation

## *Packed-bed membrane reactor*

- Membrane reactor
- Isothermal operation
- Feed ratio  $H_2/CO_2 = 3$
- $P^R = 27$  bar
- $GHSV = 476$   $h^{-1}$
- Permeation data Poto et al. [19] used for modeling of the membrane.
- PR EoS used.



[19] Poto et al. - Experimental investigation of a packed bed membrane reactor for the direct conversion of CO<sub>2</sub> to dimethyl ether. – Journal of CO<sub>2</sub> Utilization 72,(2023)

# Optimization

## Parameters and goal



- The goal is to maximize the methanol yield ( $Y_{\text{MeOH}}$ ).
  - 'fmincon' function in MATLAB
  - Parametric study
- GHSV =  $10\,000\text{ h}^{-1}$ , based on work by de Boed [20].
- $P^R = 70\text{ bar}$
- $D_{\text{si}} = 0.1\text{ m}$  to fit multiple membranes
- Each optimized value is used in the following tests.

Variable	Unit	Lower bound	Initial Value	Upper bound
$T_{\text{in}}^R$	[K]	450	493	513
$N_{\text{mem}}$	[-]	1	1	10
S/F	[-]	1	1	20
$T_{\text{in}}^P$	[K]	450	493	513
$\Delta P$	[bar]	-10	0	10

Determine the optimal ratio between catalyst mass and membrane area.

[20] De Boed, P. – Membrane-Assisted Carbon Dioxide Valorization to Methanol: A Techno-Economical Study [Master graduation project, Chemical Engineering and Chemistry]. – TU/e, (2025).



# Optimization

Number of membranes



Constraint  $N_{mem}$ :

$$\rho_{pack} \leq \rho_{pack,max}$$

$$\rho_{pack} = \frac{A_{mem}}{A_{Reactor}}$$

$$A_{mem} = N_{mem} \cdot \frac{\pi}{4} \cdot D_{mo}^2$$

$$A_{Reactor} = \frac{\pi}{4} \cdot D_{si}^2$$

$$\rho_{pack,max} = 0.68 [19]$$

[19] Pirl.- Der Mindestabstand von n in der Einheitskreisscheibe gelegenen Punkten. – Mathematische Nachrichten, 40 (1969)

# Kinetic validation

## Temperature profile

EoS average relative errors:

- PR: 5.80%
- SRK: 5.08%

For PR in temperature range  
450 – 550 K

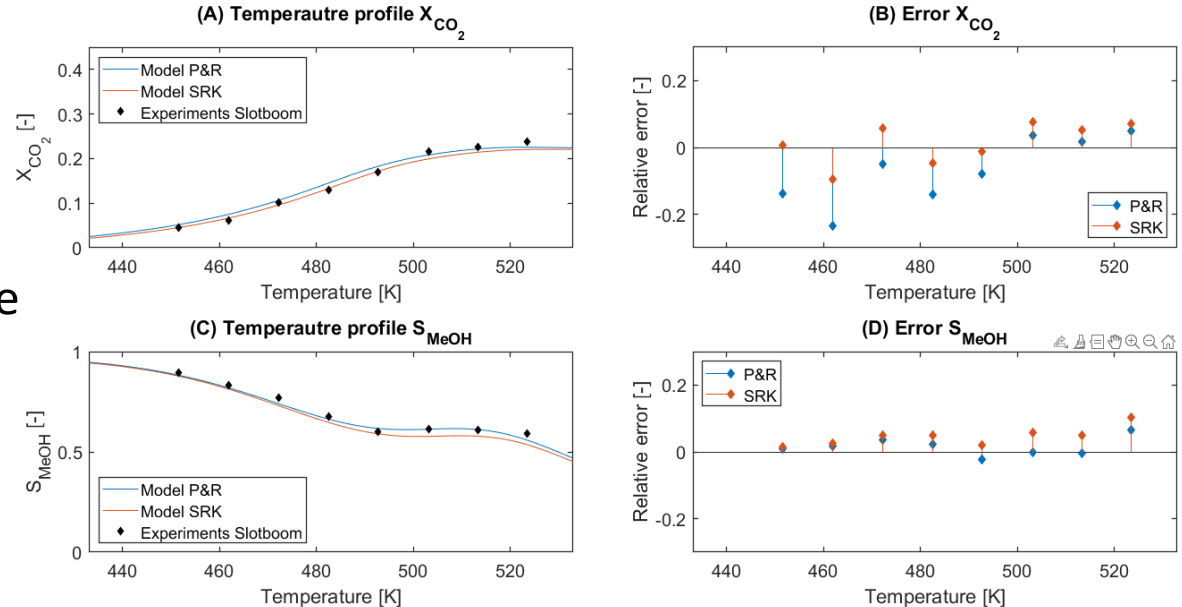
- $X_{\text{CO}_2}$ : 0.05 - 0.23
- $S_{\text{MeOH}}$ : 0.89 - 0.31

Operating conditions:

$P = 40 \text{ bar}$ ,

$\Phi_{\text{V}}^{\circ} = 100 \text{ ml min}^{-1} / \text{GHSV} = 3000 \text{ h}^{-1}$ ,

$\text{CO}_2/\text{H}_2 = 25/75 \text{ mol}\%$



**Figure 5.** Temperature profile with errors of CO<sub>2</sub> conversion and MeOH selectivity. Experimental results are obtained from Slotboom et al. [9].

[9] Slotboom et al. - Critical assessment of steady-state kinetic models for the synthesis of methanol over an industrial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst. – Chemical Engineering Journal 389, 124181(2020)

# Kinetic validation

## Pressure profile



EoS average relative errors:

- PR: 4.11%
- SRK: 3.90%

For PR in pressure range  
1 – 80 bar

- $X_{\text{CO}_2}$ : 0.05 - 0.23
- $S_{\text{MeOH}}$ : 0.03 - 0.76

Operating conditions:

$T = 493 \text{ K}$ ,

$\Phi_V^0 = 100 \text{ ml min}^{-1} / \text{GHSV} = 3000 \text{ h}^{-1}$ ,

$\text{CO}_2/\text{H}_2 = 25/75 \text{ mol}\%$

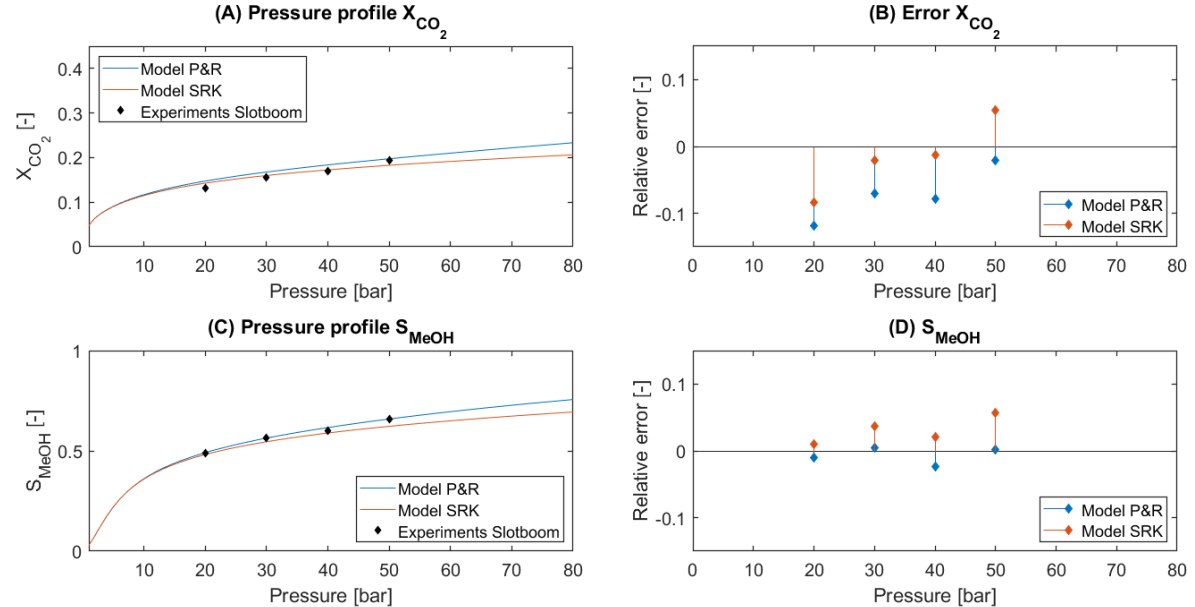
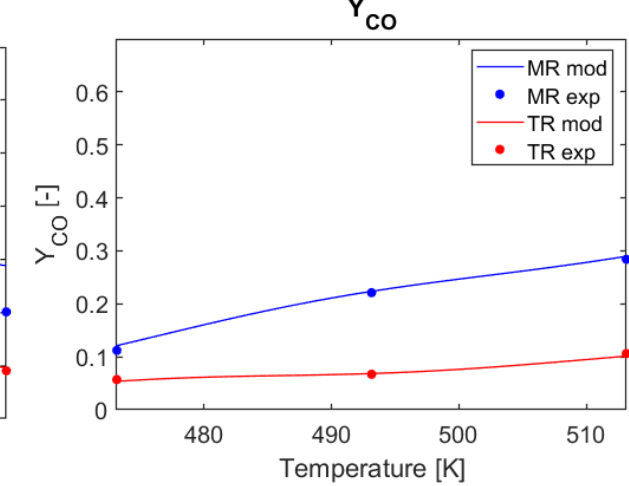
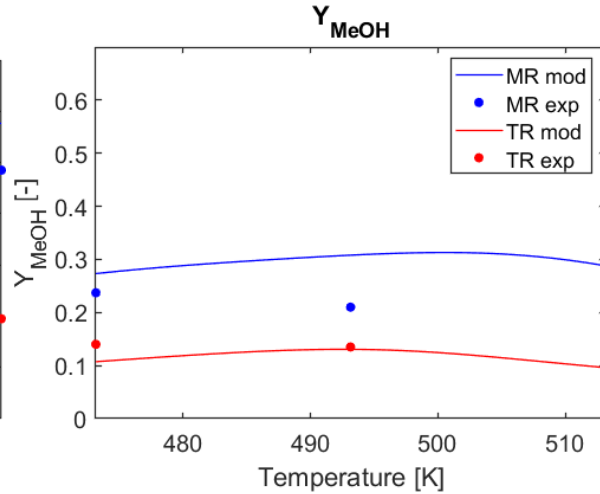
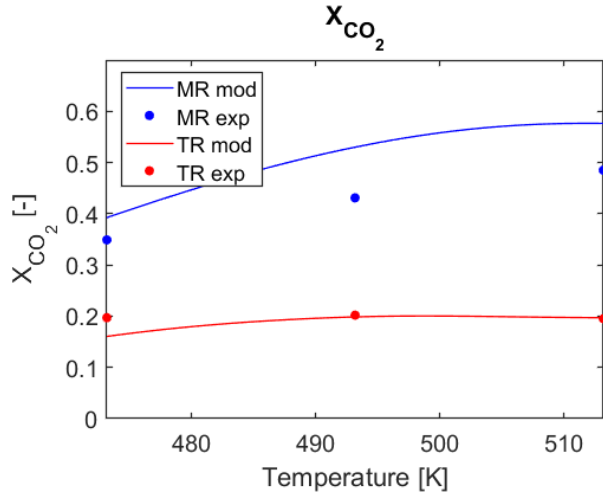


Figure 6. Pressure profile with errors of CO<sub>2</sub> conversion and MeOH selectivity. Experimental results are obtained from Slotboom et al. [9].

[9] Slotboom et al. - Critical assessment of steady-state kinetic models for the synthesis of methanol over an industrial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst. – Chemical Engineering Journal 389, 124181(2020)

# Validation Membrane Reactor

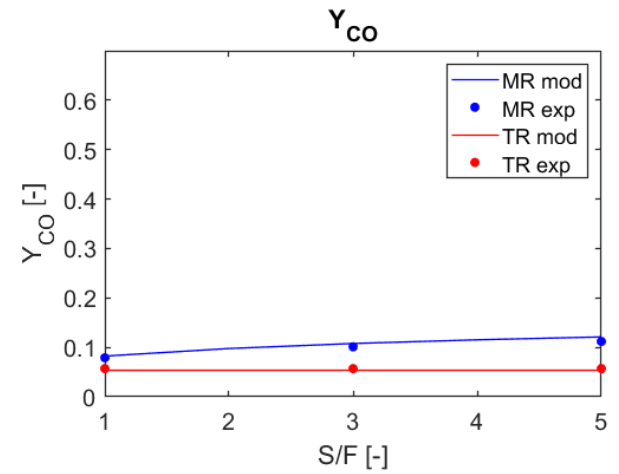
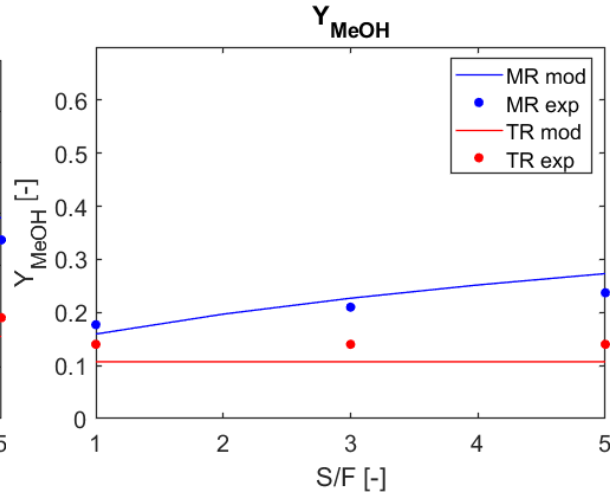
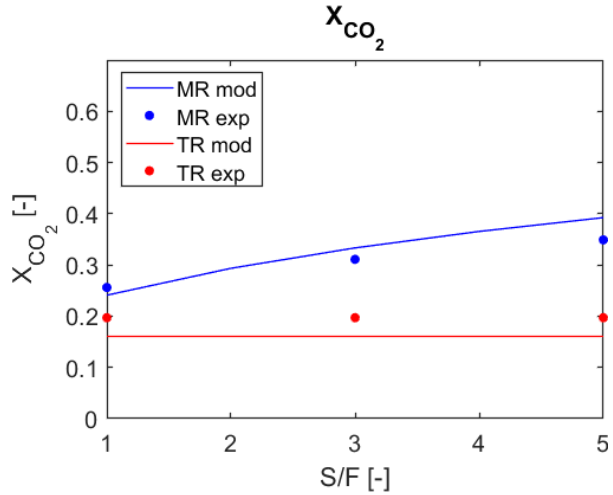
Results temperature profile



Parameter	GHSV [h <sup>-1</sup> ]	T <sub>in</sub> <sup>R</sup> [K]	PR [bar]	N <sub>mem</sub> [-]	S/F [-]	T <sub>in</sub> <sup>P</sup> [K]	ΔP [bar]	e <sub>avg</sub> [-]
Value	476	473 – 513	27	1	5	T <sub>in</sub> <sup>R</sup>	0	0.19

# Validation Membrane Reactor

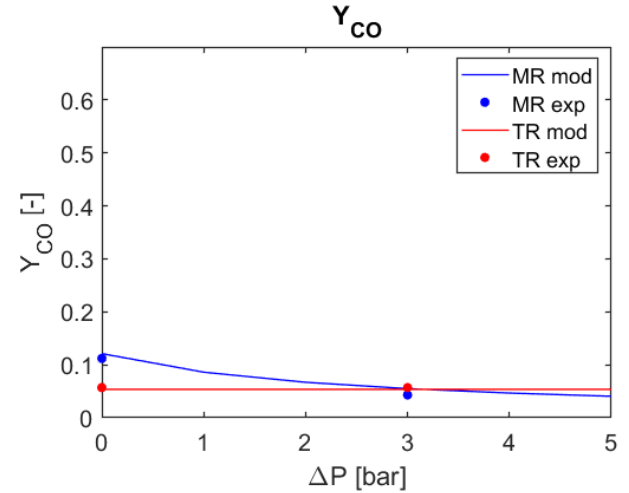
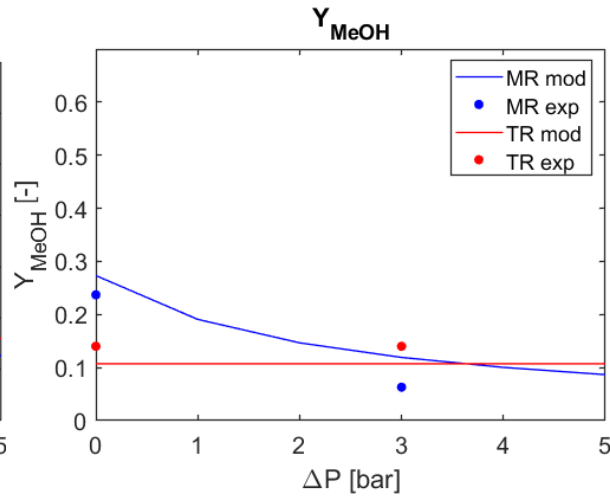
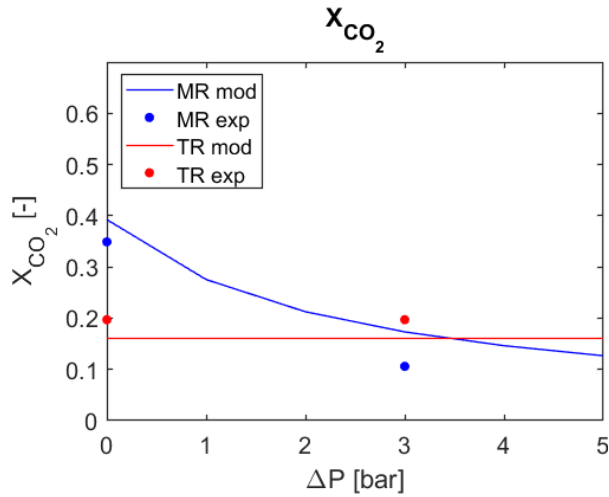
Results S/F profile



Parameter	GHSV [h <sup>-1</sup> ]	T <sub>in</sub> <sup>R</sup> [K]	PR [bar]	N <sub>mem</sub> [-]	S/F [-]	T <sub>in</sub> <sup>P</sup> [K]	ΔP [bar]	e <sub>avg</sub> [-]
Value	476	473	27	1	1 - 5	473	0	0.09

# Validation Membrane Reactor

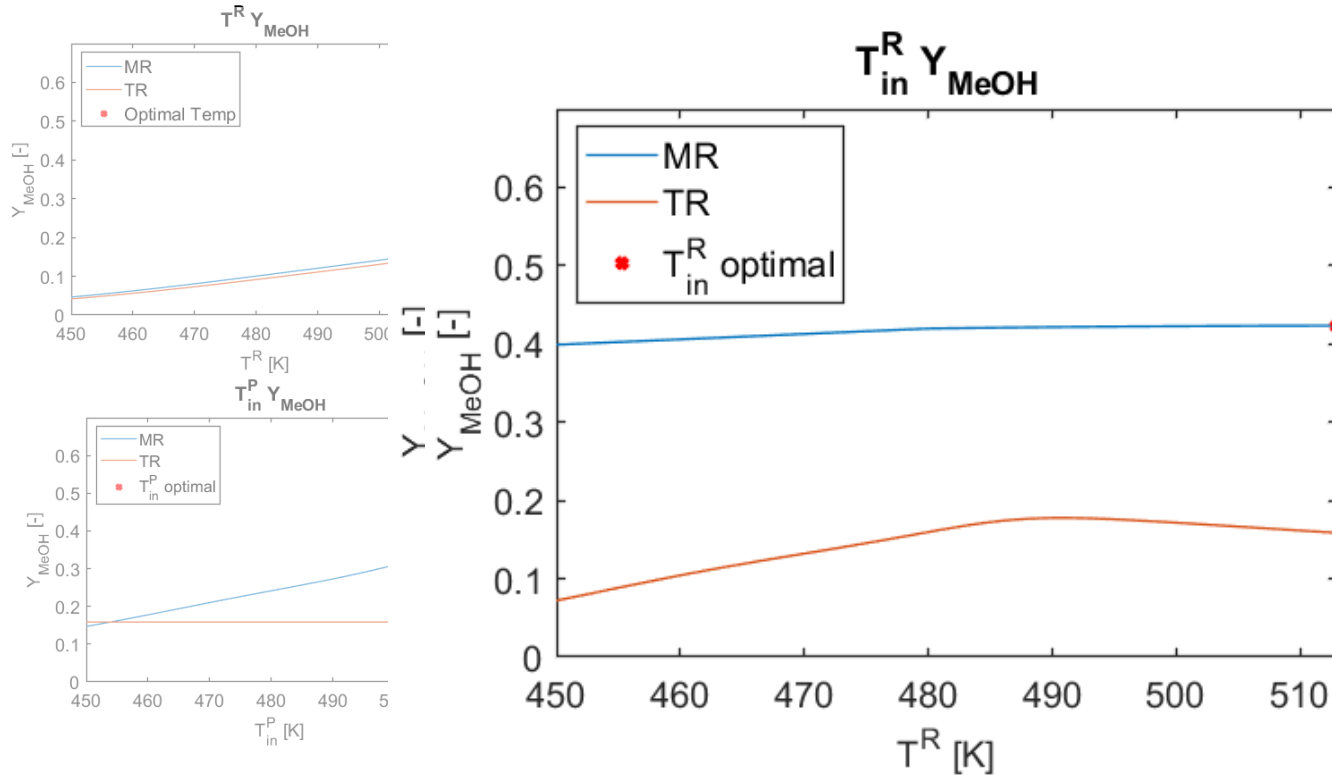
Results S/F profile



Parameter	GHSV [h <sup>-1</sup> ]	T <sub>in</sub> <sup>R</sup> [K]	PR [bar]	N <sub>mem</sub> [-]	S/F [-]	T <sub>in</sub> <sup>P</sup> [K]	ΔP [bar]	e <sub>avg</sub> [-]
Value	476	473	27	1	5	473	0 - 3	0.39

# Optimization Membrane Reactor

## Parametric study



Isothermal operation

Parameter	Results
$T^R_{in}$ [K]	450–513
$N_{mem}$ [-]	10
S/F [-]	20
$T^P_{in}$ [K]	513
$\Delta P$ [bar]	10
<b>Optimal parameter</b>	
$T^R_{in,opt}$ [K]	513
$Y_{MeOH}$ [-]	0.42

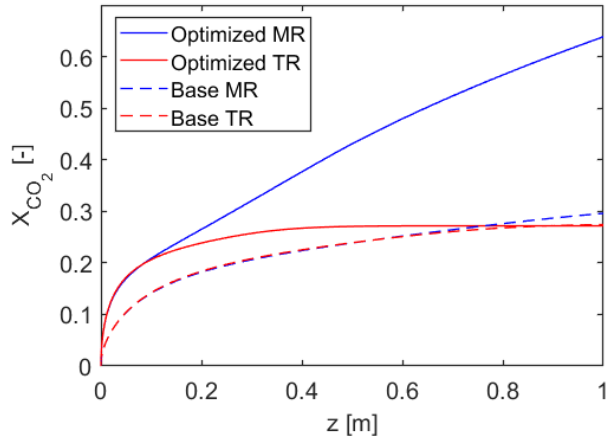
# Comparison Traditional Reactor and Membrane Reactor

Optimization results

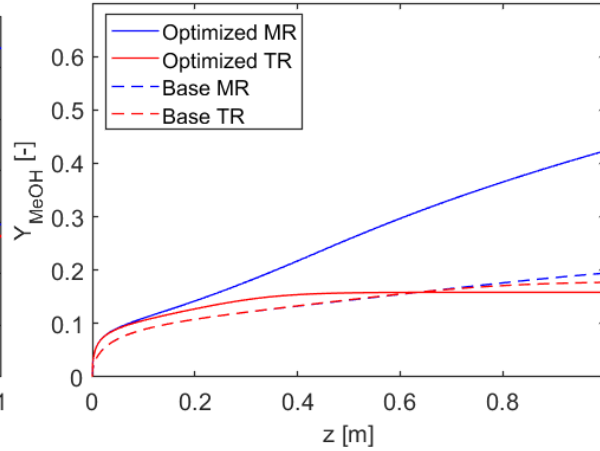


Isothermal operation

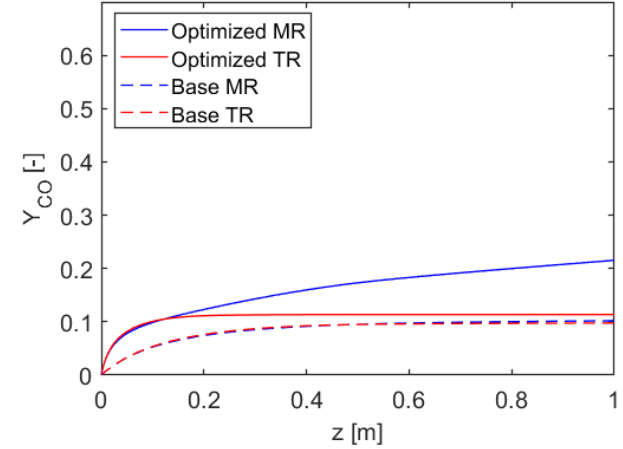
Comparing  $X_{CO_2}$



Comparing  $Y_{MeOH}$



Comparing  $Y_{CO}$



Parameter	$T_{in}^R$ [K]	$P^R$ [bar]	$N_{mem}$ [-]	S/F [-]	$T_{in}^P$ [K]	$\Delta P$ [bar]	$Y_{MeOH,opt}$
Value	513	70	10	20	513	10	TR: 0.18 MR: 0.42

- ❖ *A 1D carbon membrane reactor model was implemented successfully, using experimental data of a carbon membrane.*
- ❖ *Traditional Reactor: Verified and kinetically validated.*
- ❖ *Permeation module validation could not be concluded.*
- ❖ *Membrane Reactor: Validated using experimental results, though with significant errors.*
- ❖ *The reactor was optimized by changing operating conditions:*
  - ❖ *An increase in  $Y_{MeOH}$  of 160% compared to the traditional reactor and of 120% compared to the base case, at the same operating conditions were achieved.*
  - ❖ *Resulting ratio catalyst mass to membrane area was  $17 \text{ kg}_{cat} \cdot \text{m}_{mem}^{-2}$ , an 83% decrease compared to the base case.*

- ❖ *Permeation module validation using a newly fabricated membrane.*
- ❖ *Membrane reactor model re-validation with experimental results new independent experimental results.*
- ❖ *Extend the model to different feed composition to include streams from gasification.*
- ❖ *Membrane Reactor: Validated using experimental results, though with significant errors.*
- ❖ *Techno-economic analysis integrating this predictive model into the Bio-Megafuel process: coupling chemical looping gasification and membrane reactors for converting low-value biomass to bio-methanol.*



Contact us!



Thank you for your attention!

Any questions?



Bio-MeGaFuel, project N° 101147737. Funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or CINEA. Neither the European Union nor the granting authority can be held responsible for them.

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