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BioMeGaFuel

1 CUBE

Membrane Reactors for Methanol Production

Prof. Fausto Gallucci, 1 Cube BV, High Tech Campus 37, Eindhoven, The Netherlands
CTO of ZEFIRA BV

- Who we are
- Why integrated reactors
- Methanol/CO_2 valorization
- Next steps

Outlook

Who we are

Welcome to Our Company

From 2021

1 Cube operates as a full - service consultancy, offering a comprehensive suite of services tailored to the diverse needs of EU projects

Who we are

Who are we?

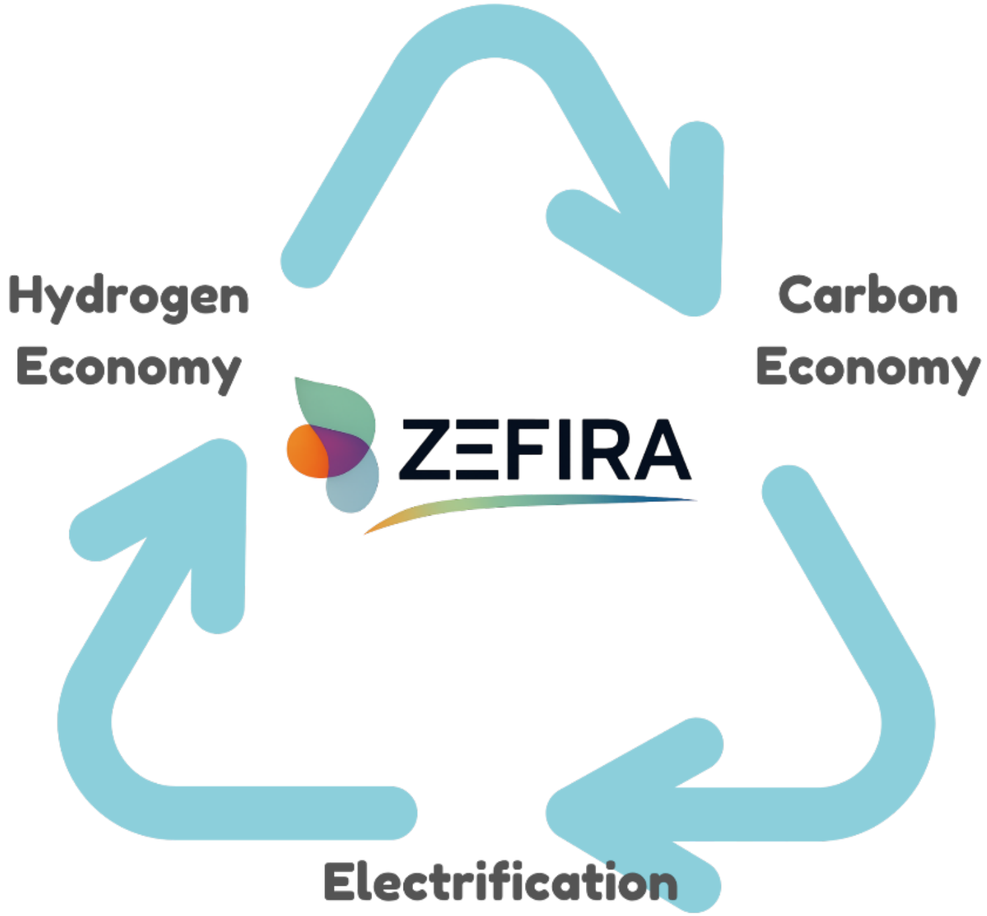
ZEFIRA B.V. is a cleantech company created in 2025 and based in Eindhoven, building on over 15 years of pioneering R&D conducted at TU/Eindhoven (NL)

Ambition

We combine advanced technologies to build the next generation of compact, efficient, and modular systems for CO_2 valorization.

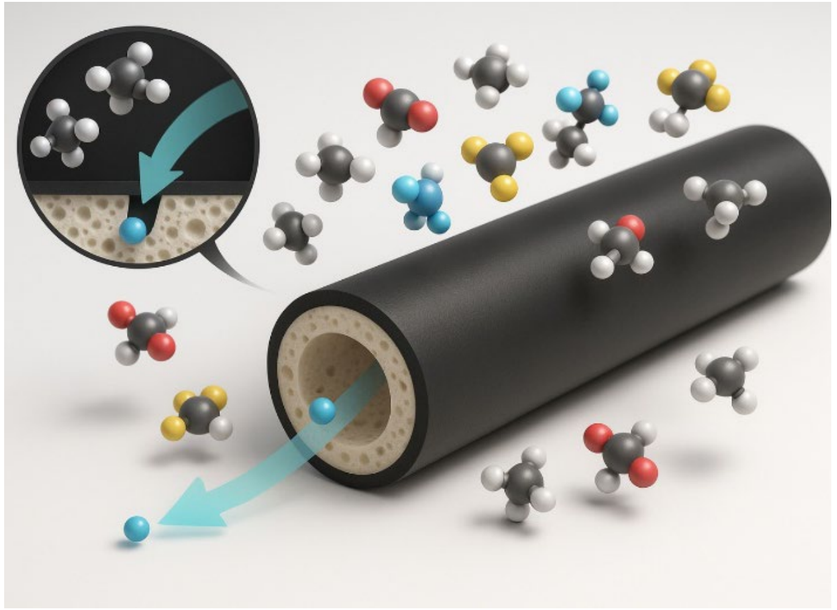
Why it matters?

Our solutions target the hardest-to-abate sectors e.g shipping, aviation, and heavy industry, where scalable, sustainable fuels are urgently needed.



Our products

Capturing CO_2. Recovering hydrogen. Producing circular fuels.



THREE MEMBRANE PRODUCT FAMILIES

- Dedicated to renewable gas recovery and membrane reactor (e/bio molecules) applications
- Patented technology
- TRL 6-7 at system level

EXTREME CHEMICAL STABILITY

- Tolerates pH of 0 to 14, sulfur tolerant
- Temperature range of -20°C to 700°C
- Wide pressure range, from ultra vacuum to 120 bar

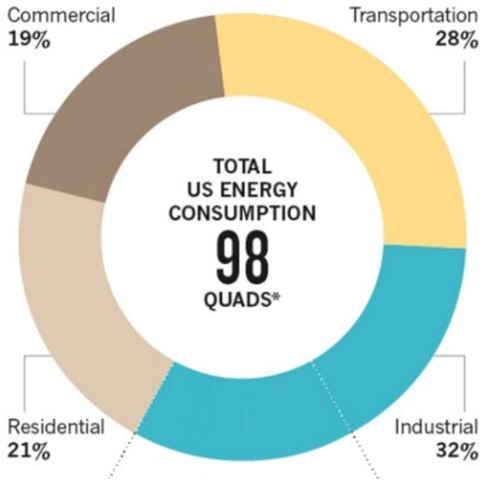
TUNABLE PROPERTIES

- Pore size distribution
- Hydrophobicity / hydrophylicity

SUSTAINABLE WITH LOWER COST

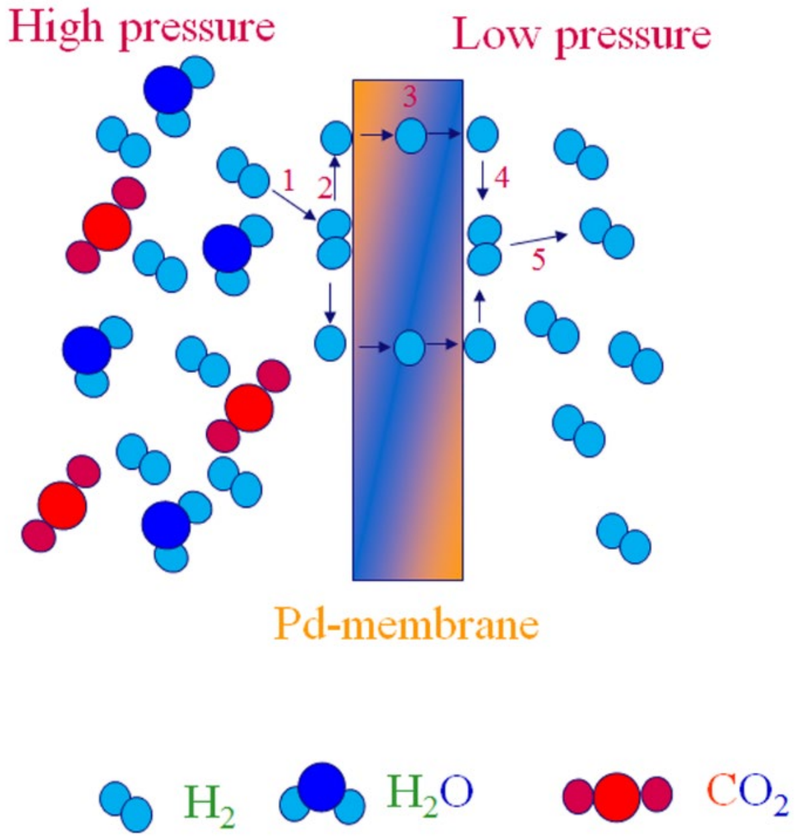
- No critical raw material needed
- Easy to recycle

A possible solution

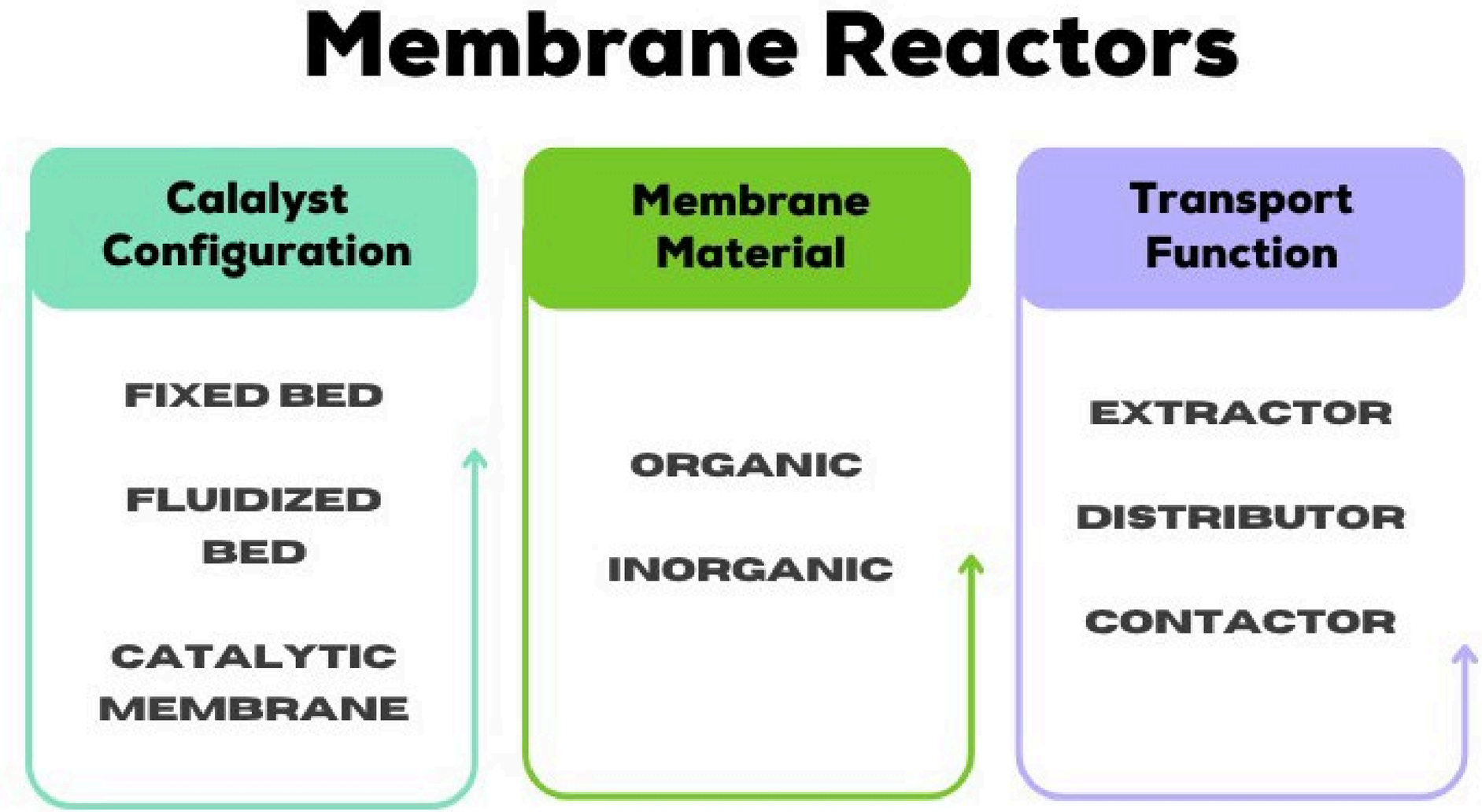


*A quad is a unit of energy equal to 10^{15} British Thermal Units (1 BTU is about 0.0003 kilowatt-hours).

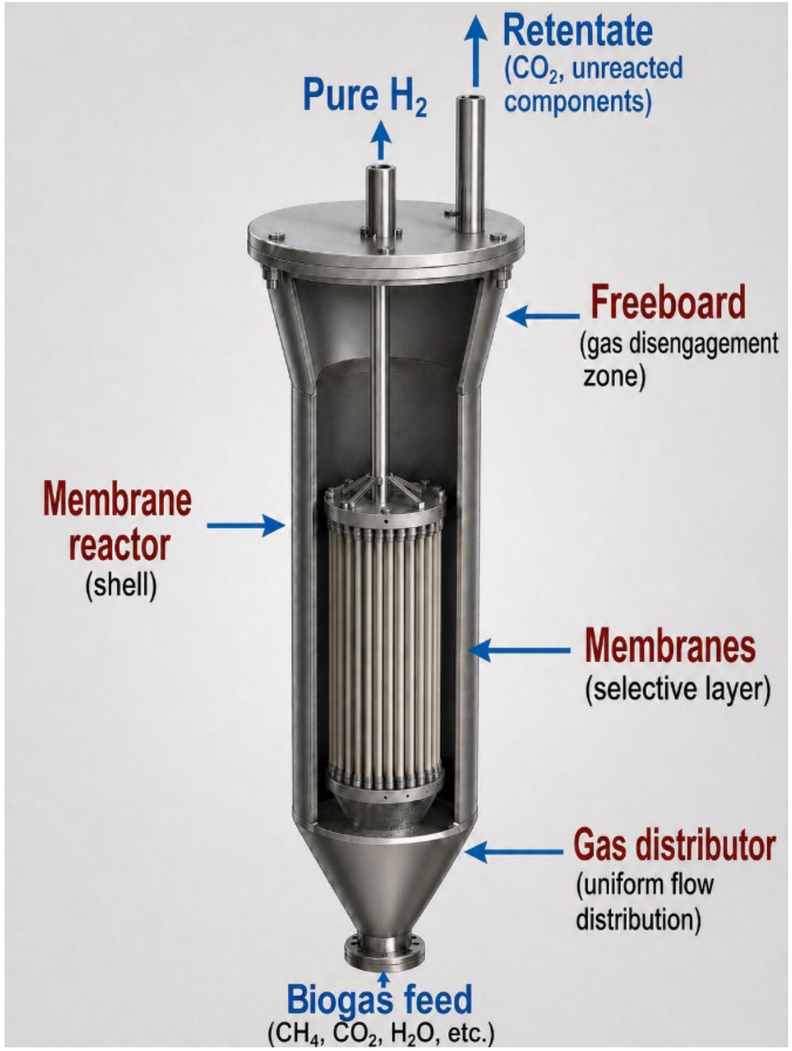
©nature

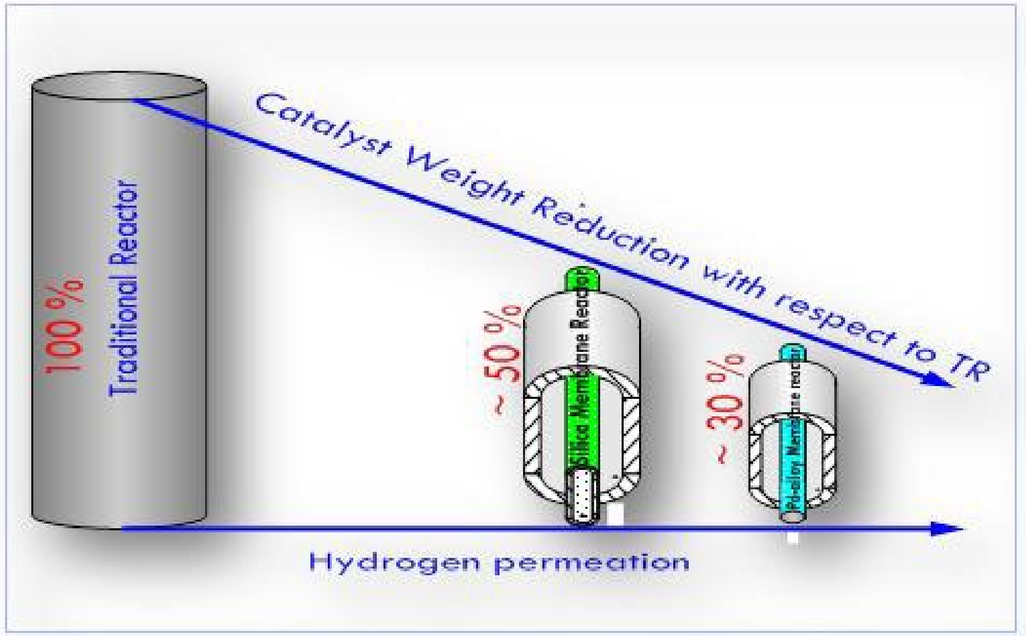


Classification



A membrane reactor

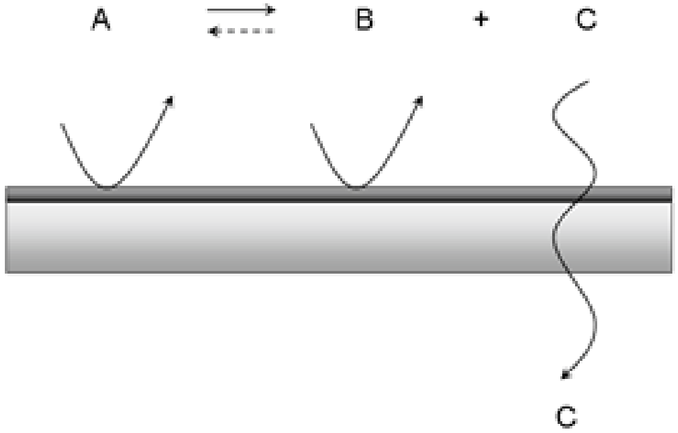


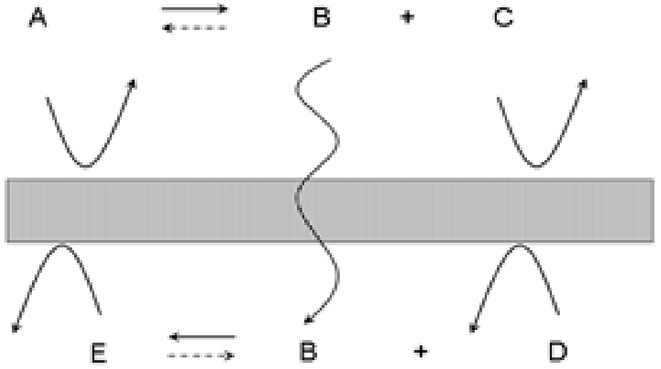


Brunetti A.; Caravella C.; Barbieri G.; Drioli E.; "Simulation study of water gas shift in a membrane reactor", *J. Membr. Sci.*, 2007, 306(1-2), 329-340

Why a membrane reactor?

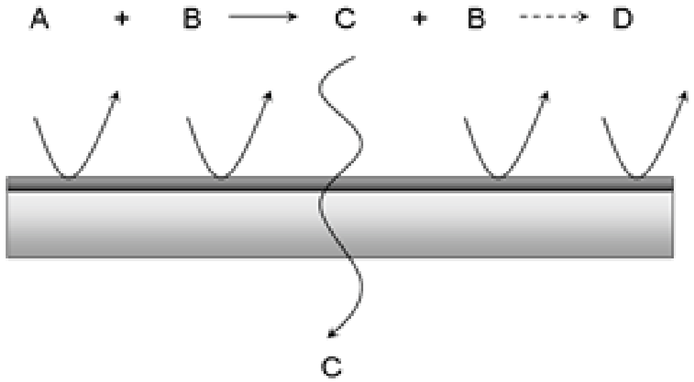
conversion enhancement by selective permeation of a reactant product of an equilibrium limited reaction

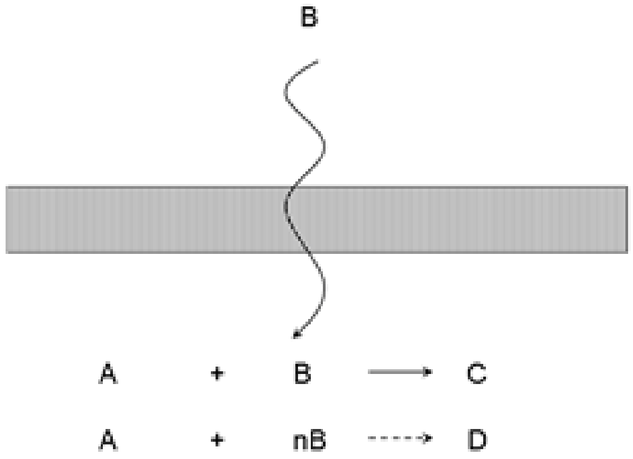




conversion enhancement by coupling of reactions

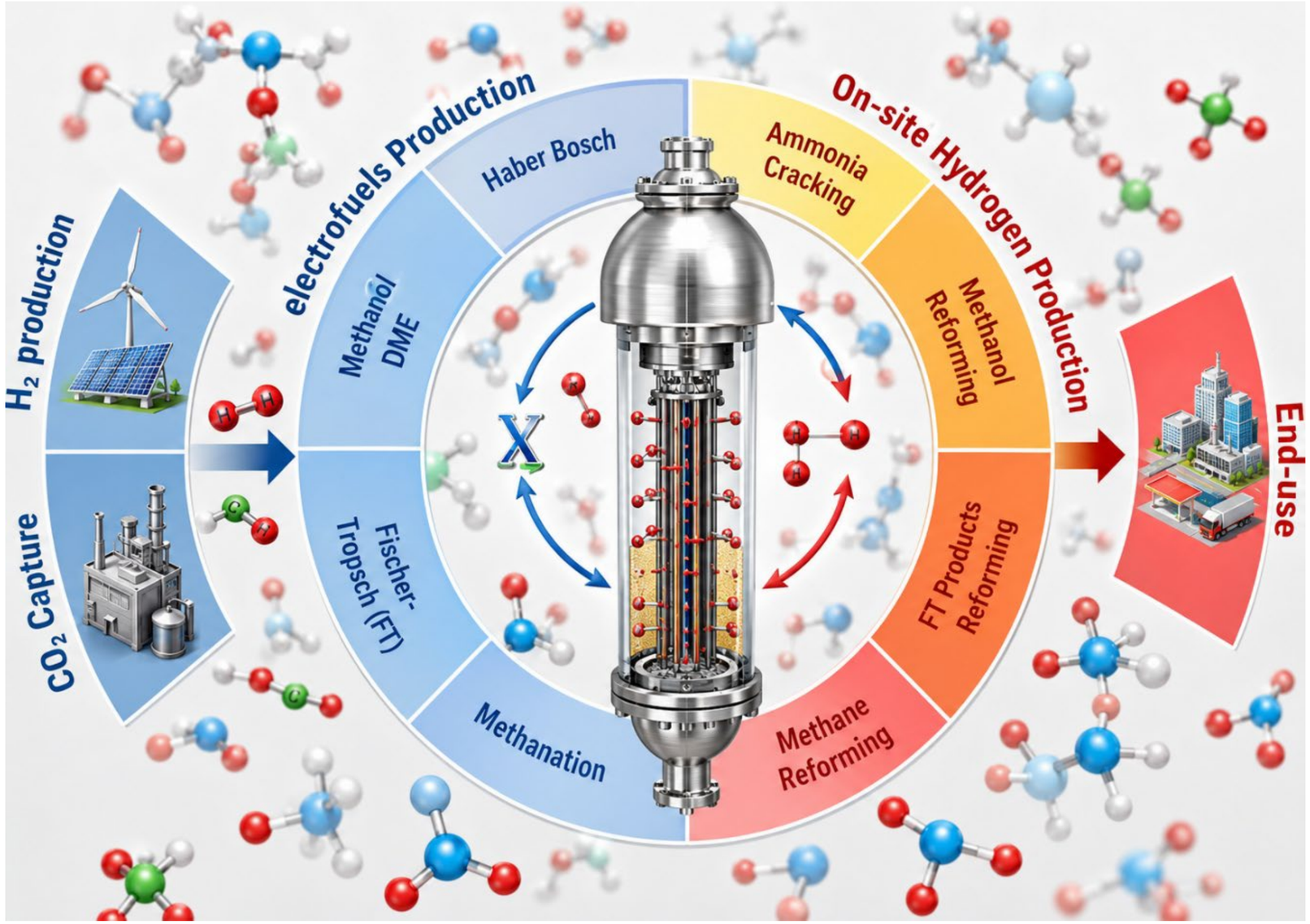
selectivity enhancement by selective permeation of an intermediate product





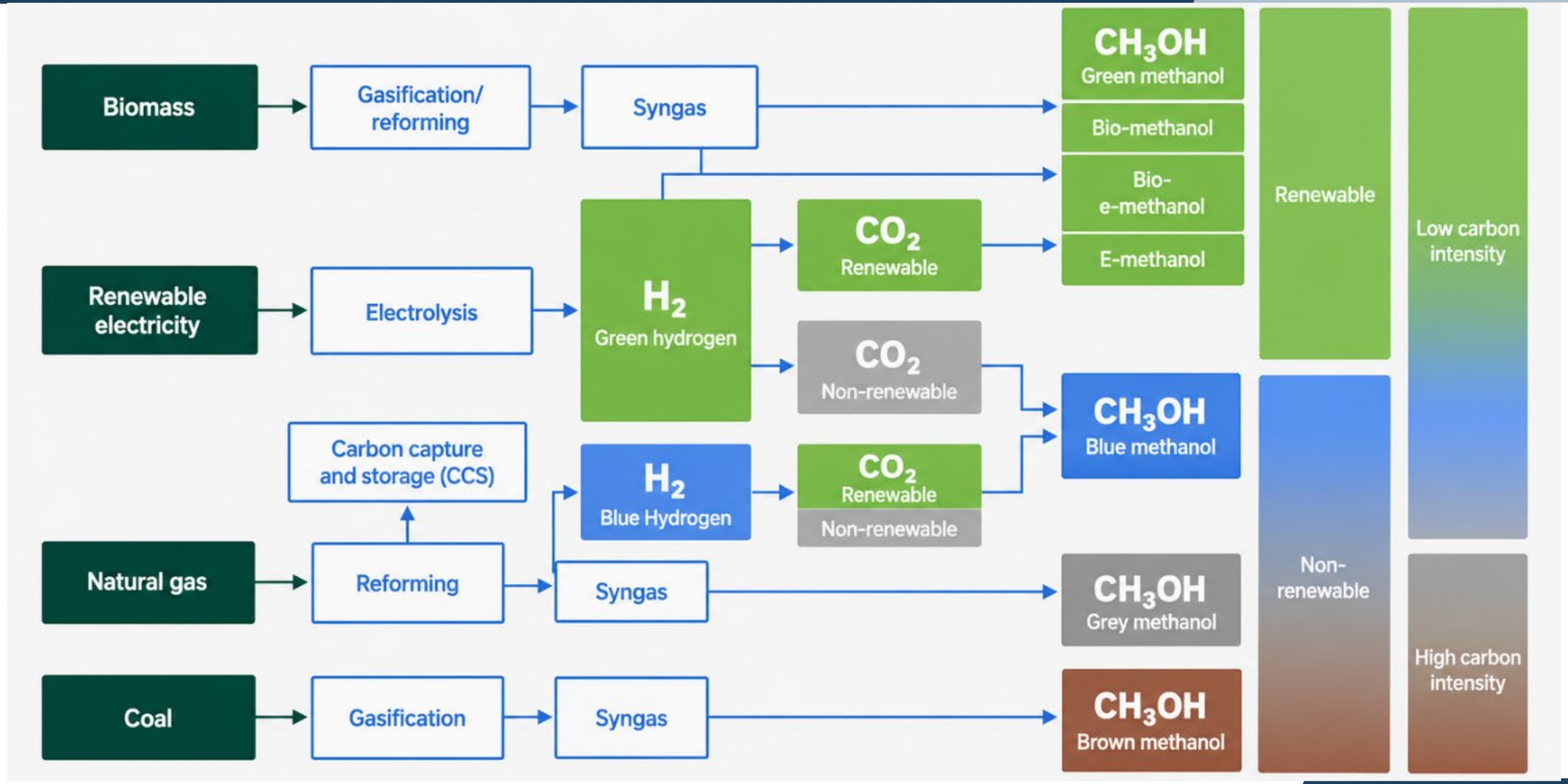
selectivity enhancement by dosing a reactant through the membrane

Use of MR



Simon Richard, PhD Thesis, TU/e 2025

Methanol



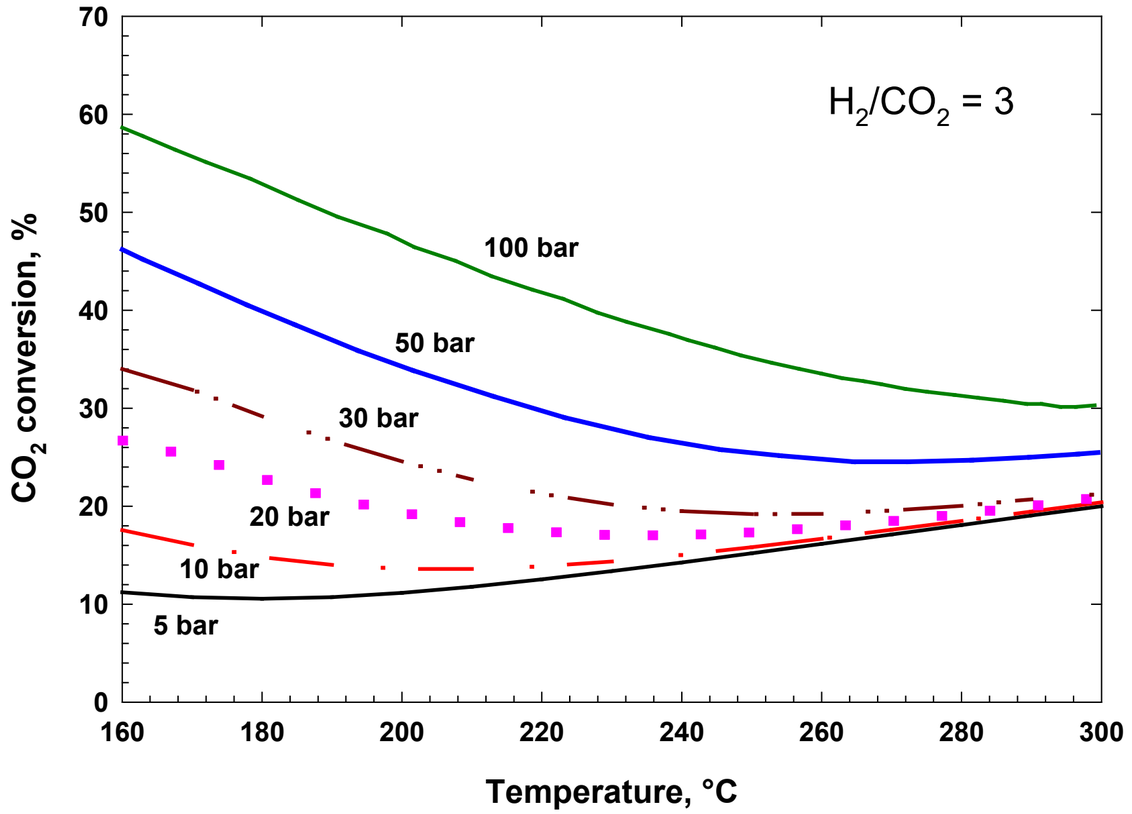
Kang, Seungwoo. *Innovation Outlook : Renewable Methanol*; International Renewable Energy Agency, 2021

Methanol

$CO_2 + 3H_2 \Leftrightarrow CH_3OH + H_2O$ $\Delta H = -49.5$ kJ/mol

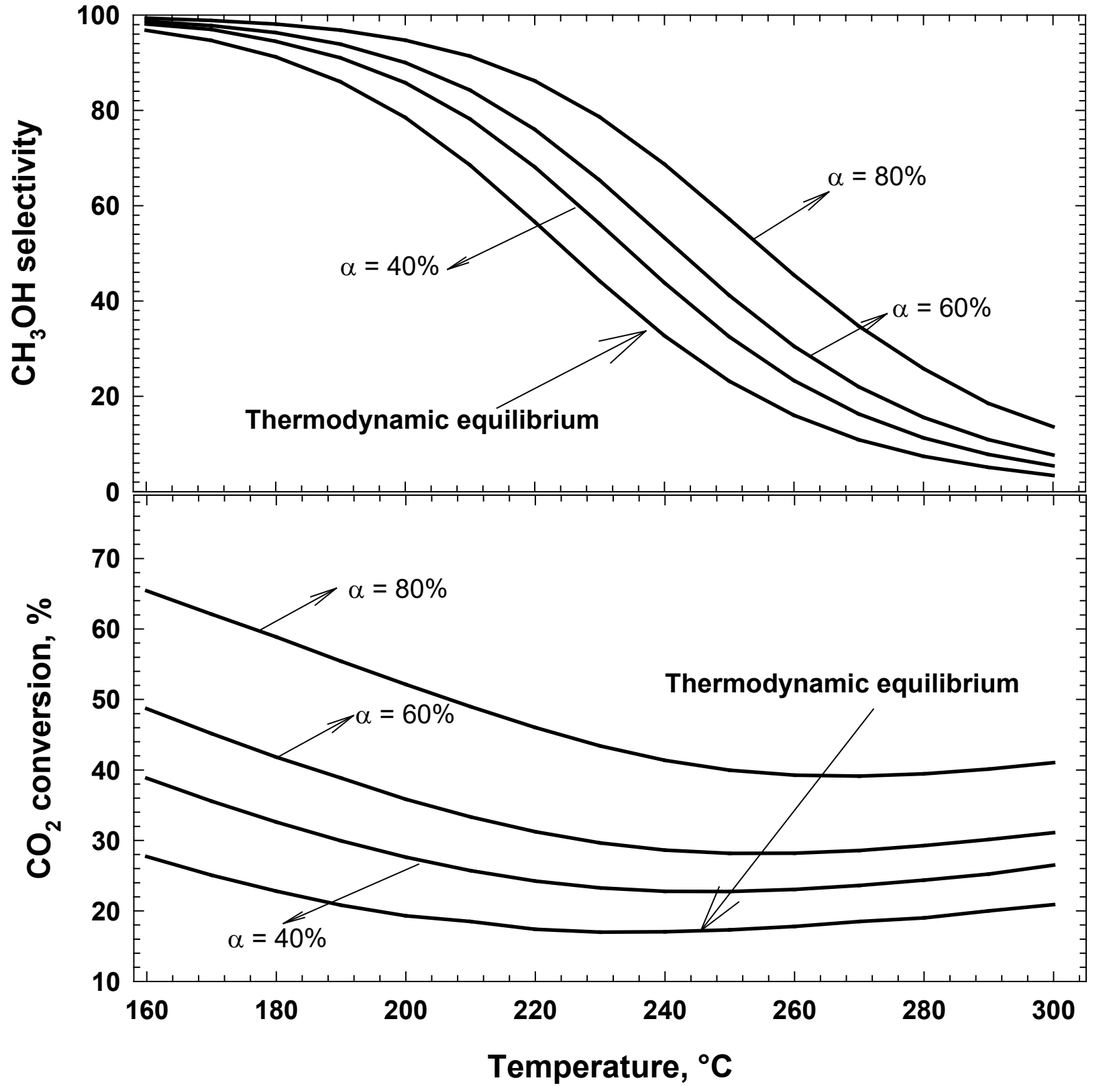
$CO + 2H_2 \Leftrightarrow CH_3OH$ $\Delta H = -90.7$ kJ/mol

$CO_2 + H_2 \Leftrightarrow CO + H_2O$ $\Delta H = +41.2$ kJ/mol



Gallucci et al. *International Journal of Hydrogen Energy,* 2007, 5050-5058

Methanol

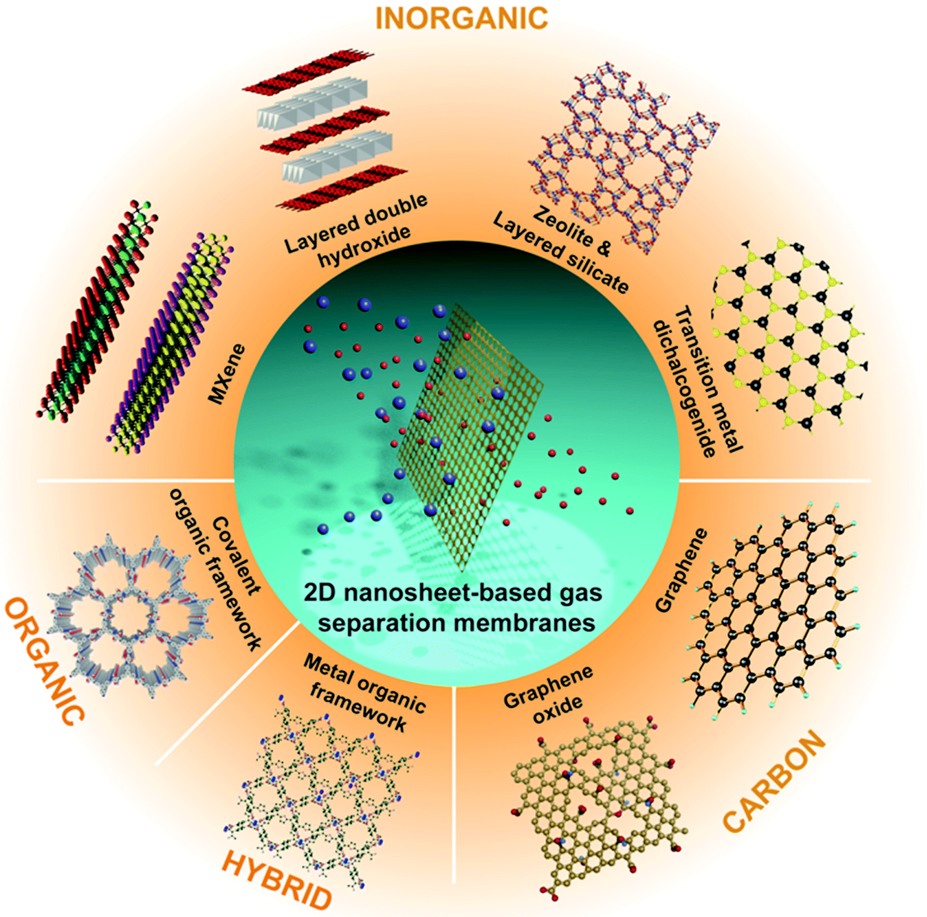


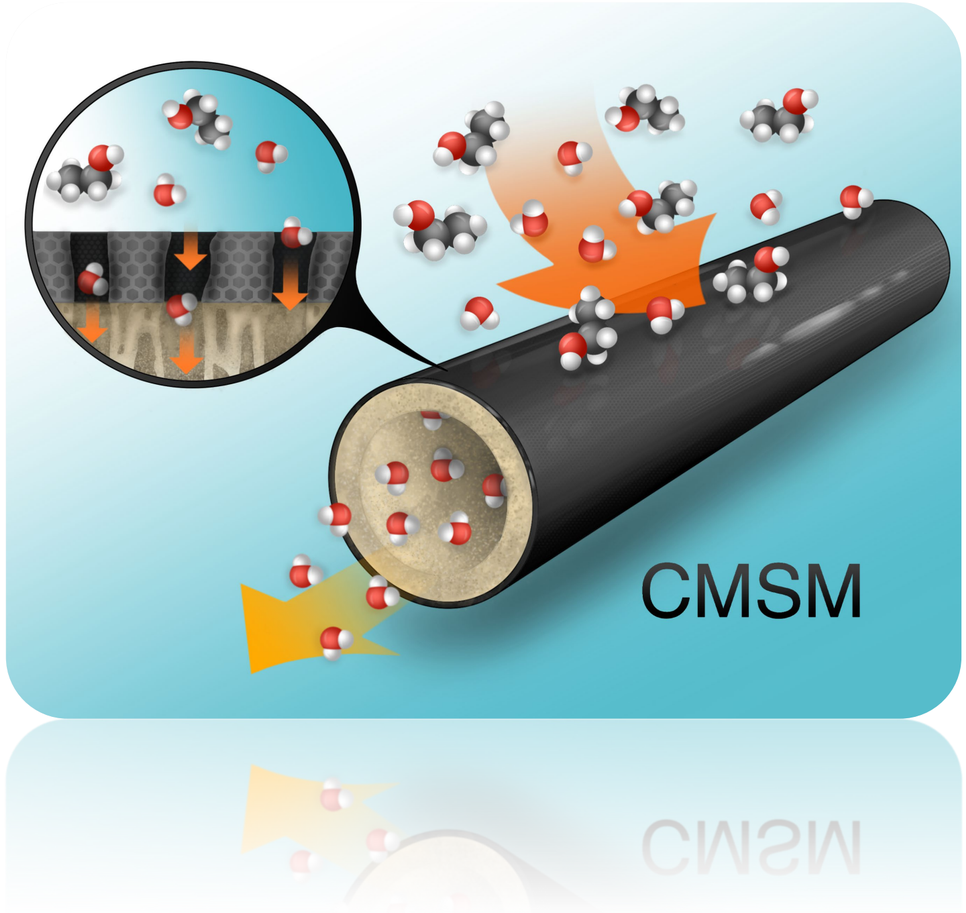
Gallucci et al. *International Journal of Hydrogen Energy,* 2007, 5050-5058

Membranes for methanol

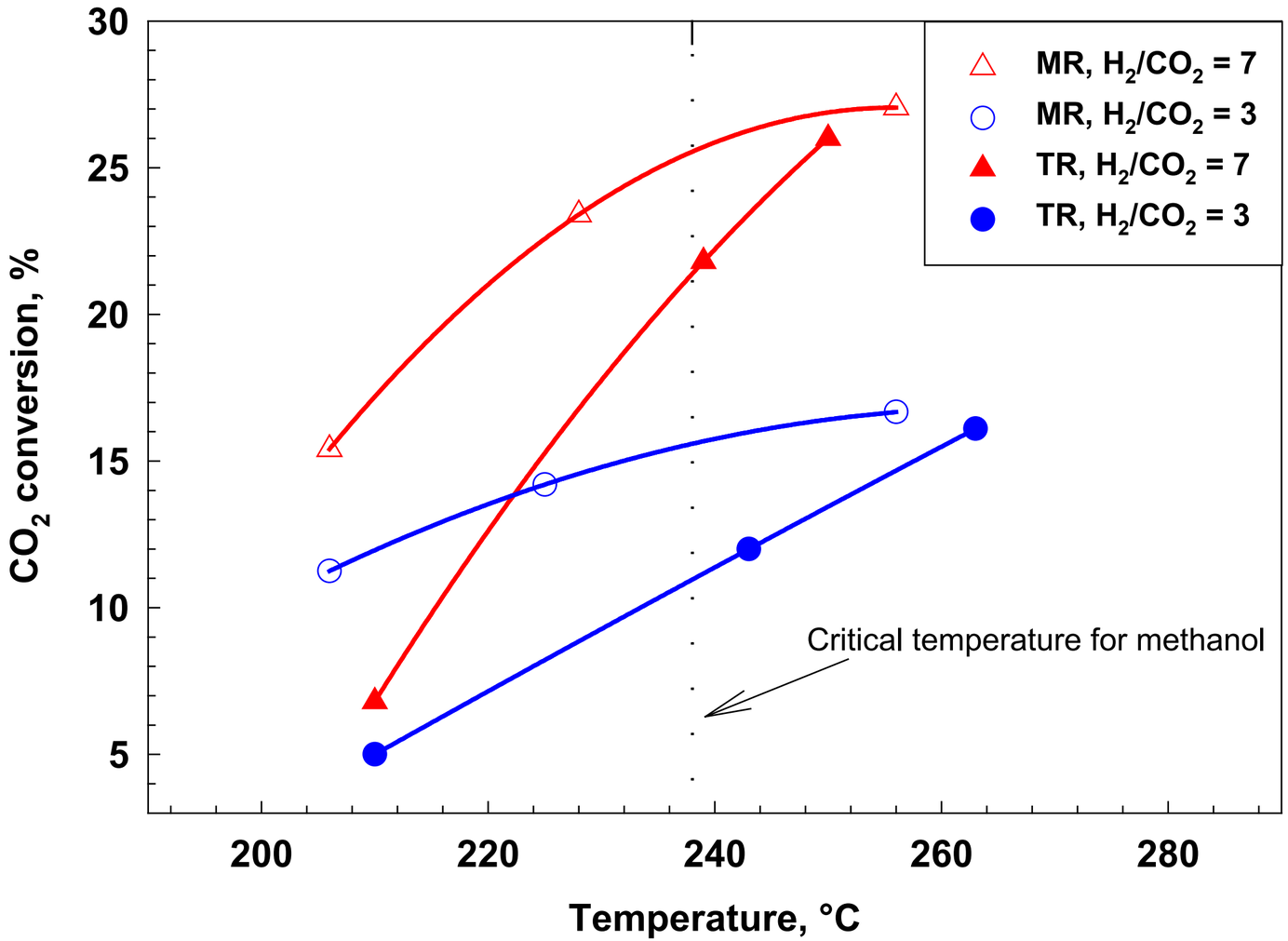
Material

1. Polymeric
2. Zeolites
3. Metallic
4. MOFs
5. 2D



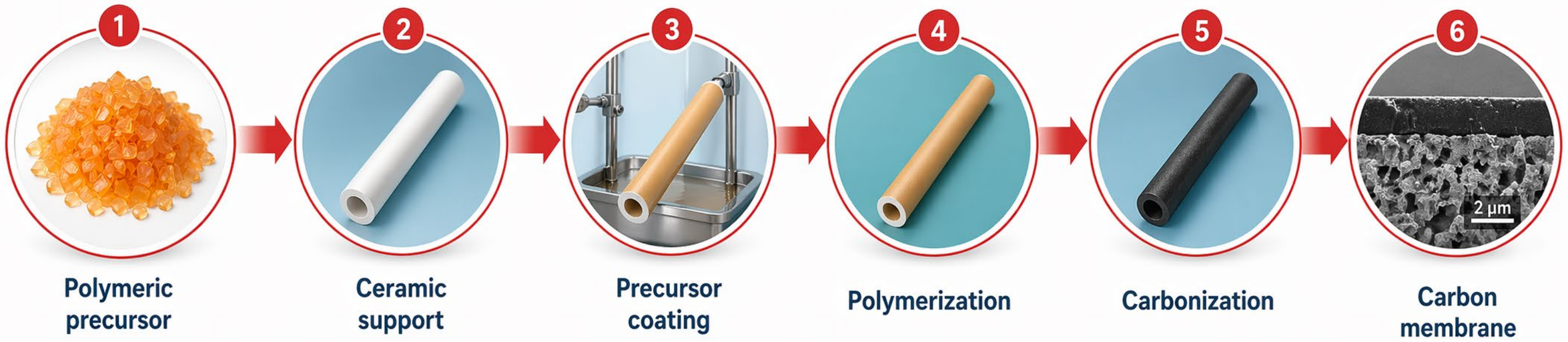


Methanol production in MR

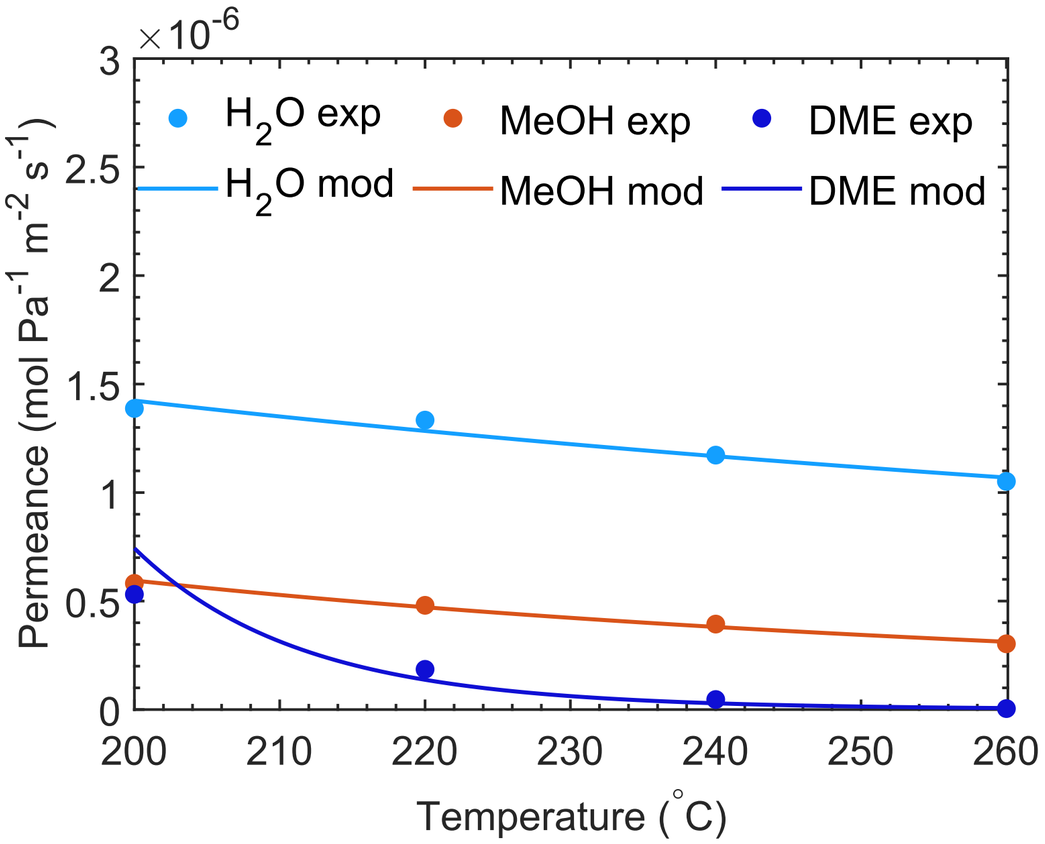


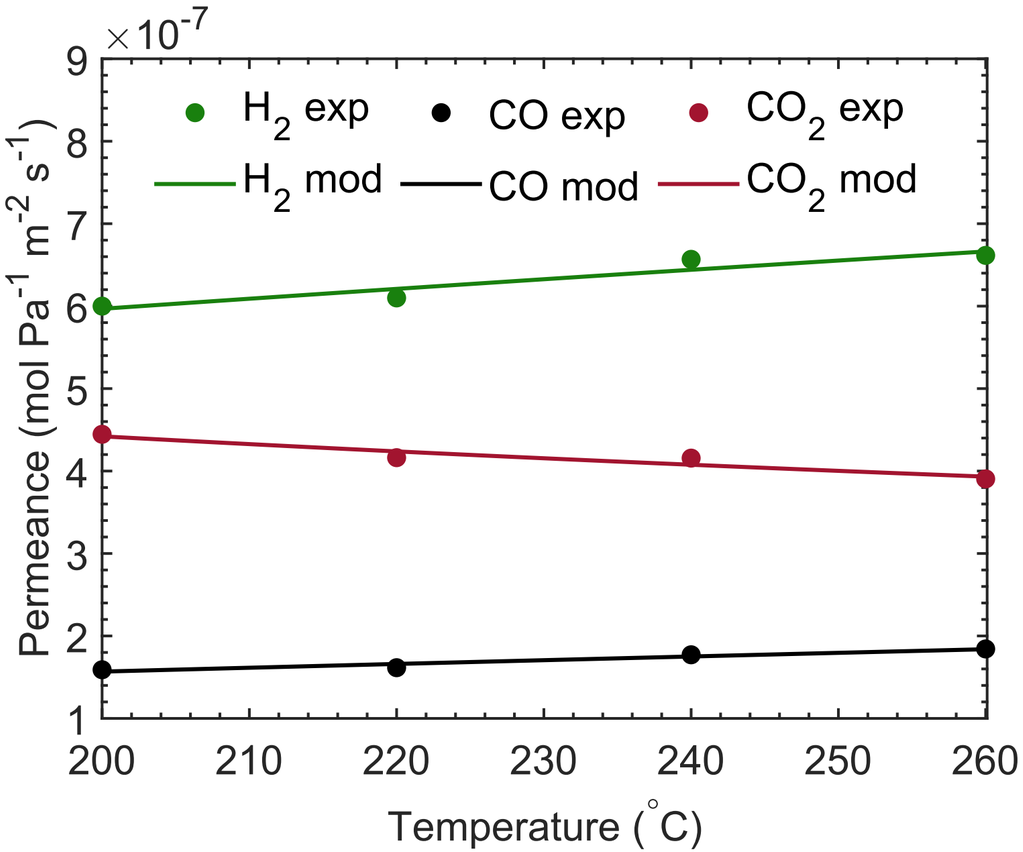
Gallucci et al. *Chemical Engineering and Processing* 2004, 1029-1036

Making CMSMs



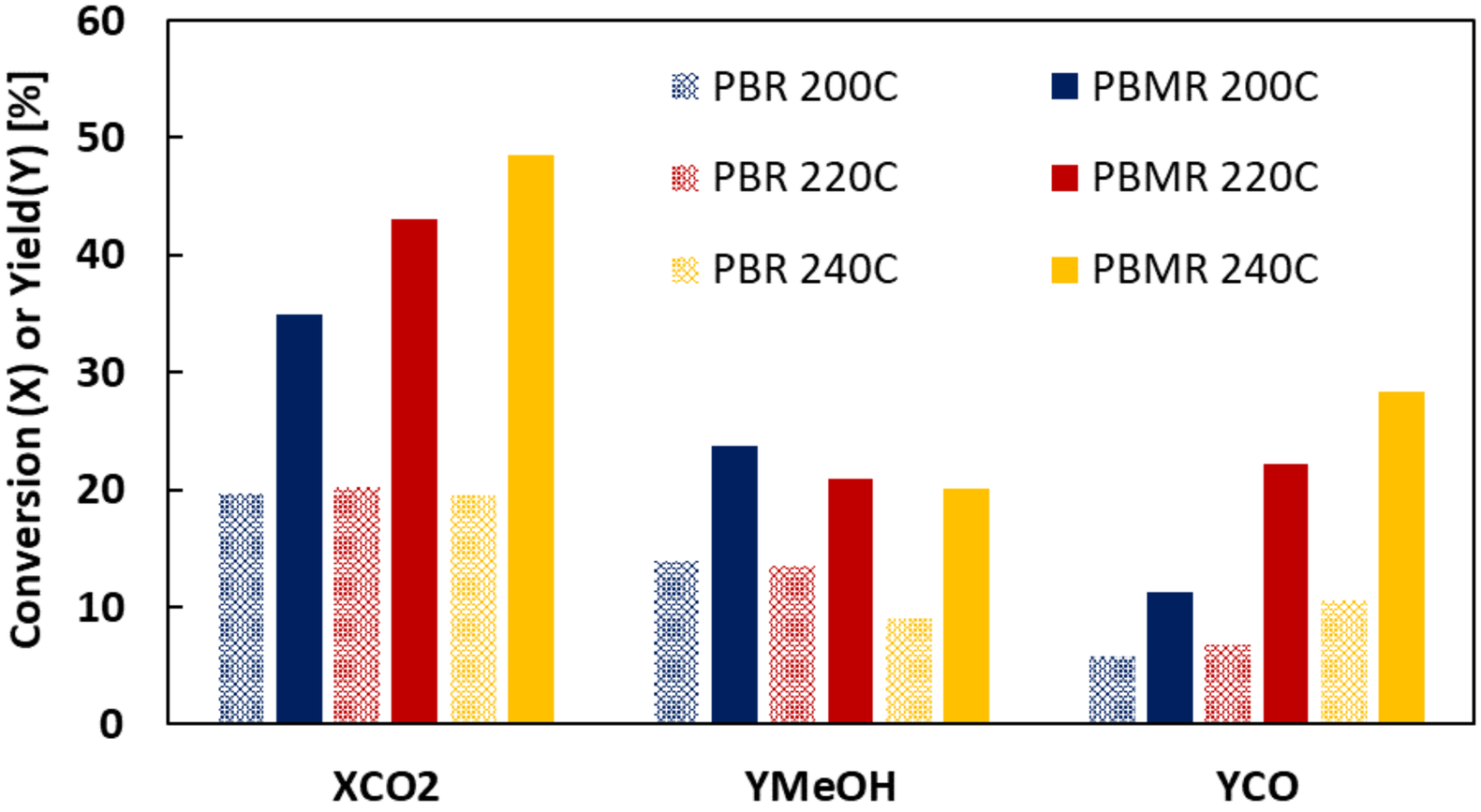
CMSM for methanol





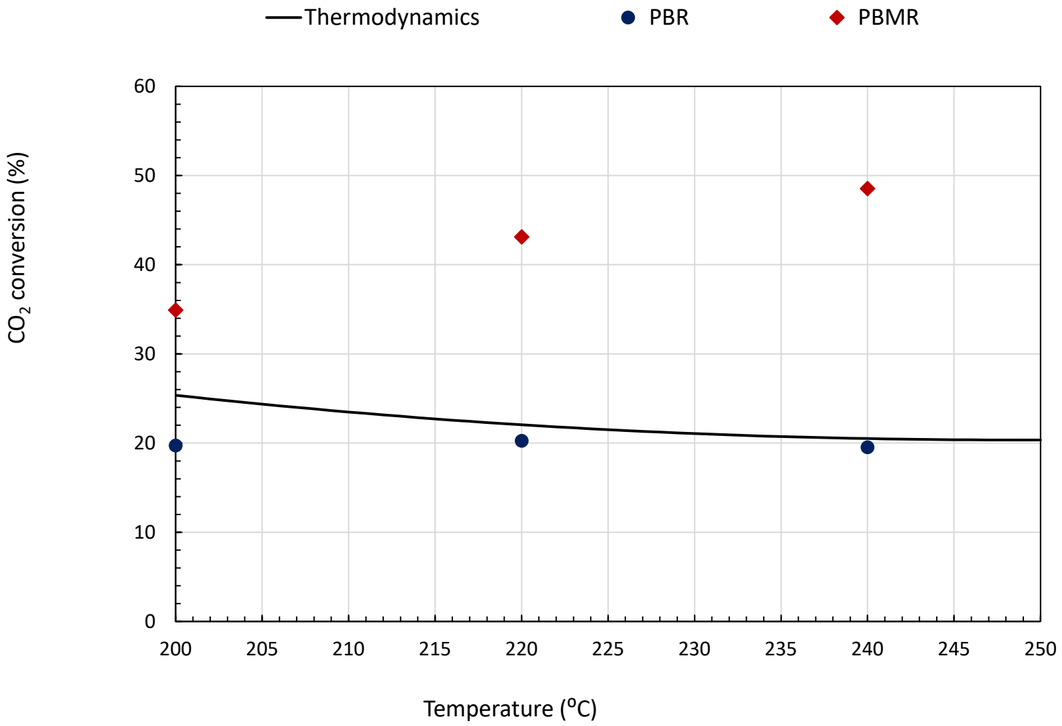
Gallucci et al. *Catalysts* **2026**, *16*(1), 53;

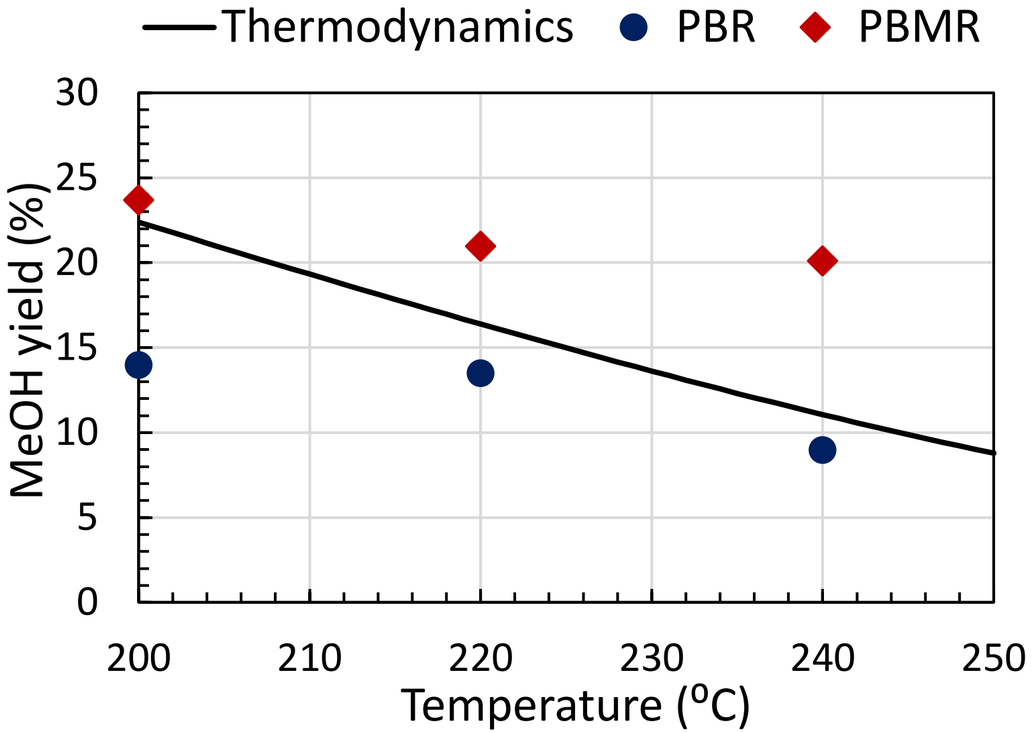
Methanol production in MR



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

Methanol production in MR

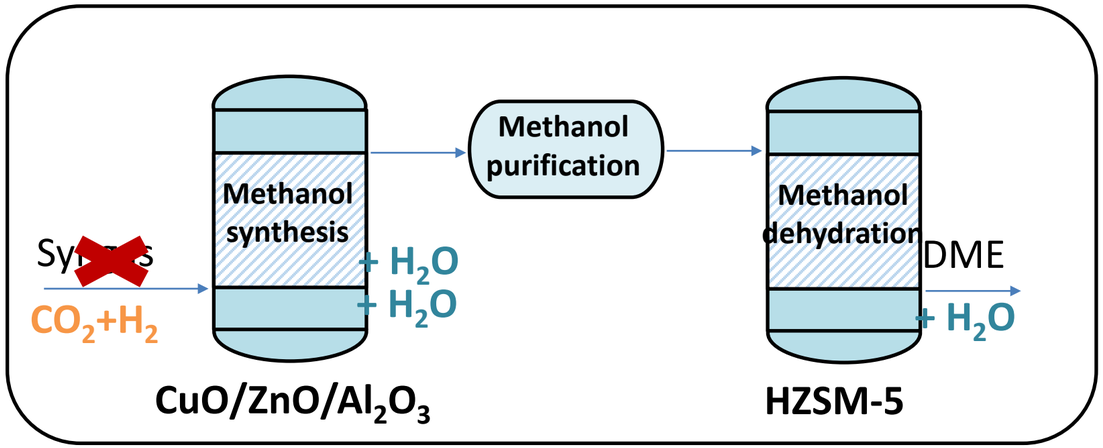




Gallucci et al. *Catalysts* **2026**, *16*(1), 53;

DME production

Benchmark process – indirect route



Reverse Water Gas Shift

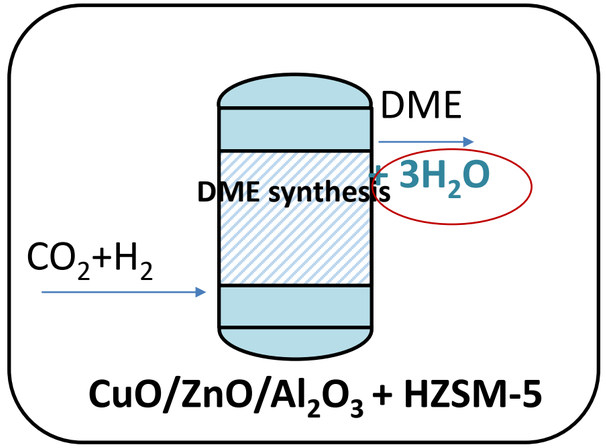
$CO_2 + H_2 \rightleftarrows CO + H_2O$

Challenge of replacing the carbon source with pure CO_2

Strong **thermodynamic limitation** due to large production of H_2O

How to reduce thermodynamic limitation

Direct route



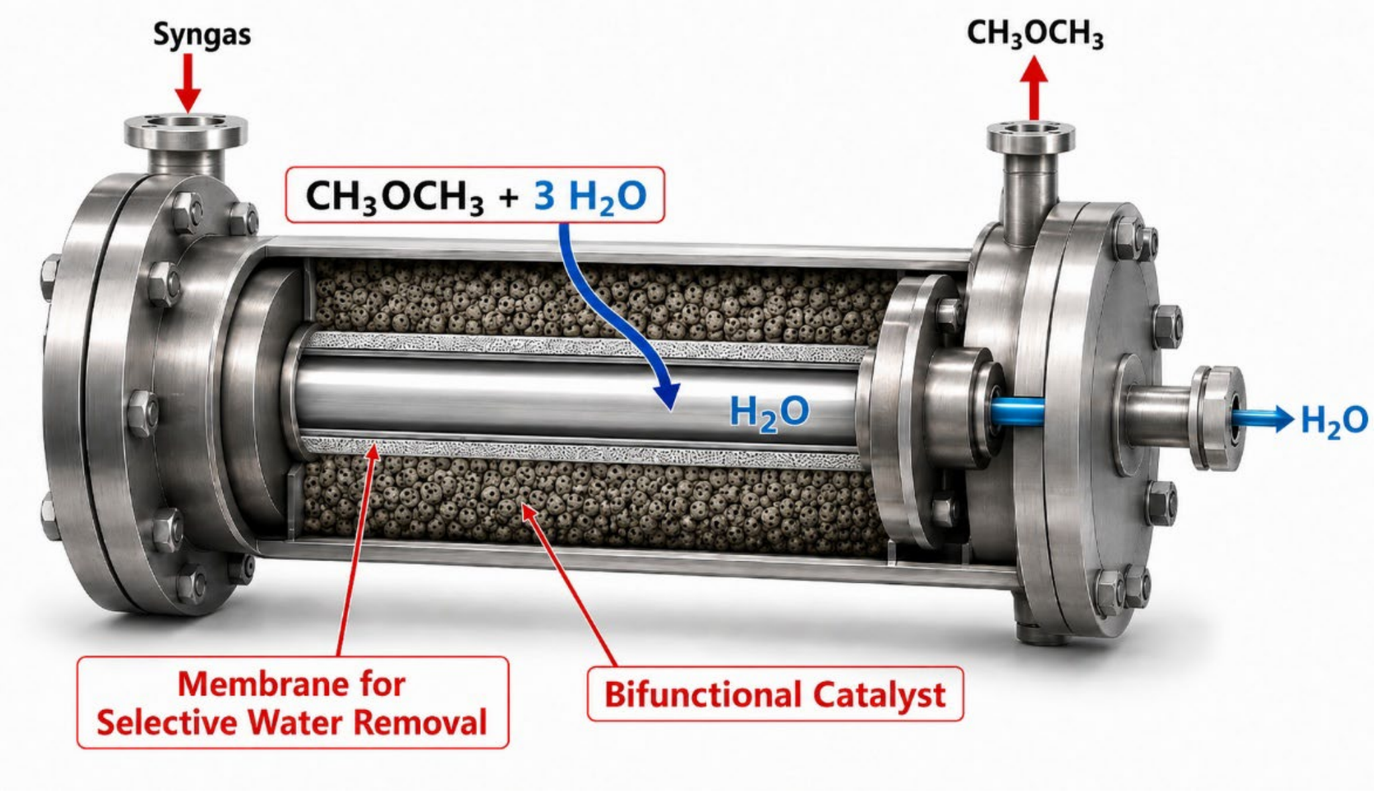
- One reactor: compact design
- Less limited by thermodynamic
- Higher energy efficiency
- Reduced catalyst stability with H_2O

Zeolites unstable with H_2O at high temperature (Al leaching)

Cu sintering and migration facilitated by H_2O

Membrane reactor for DME

Reaction and separation occur simultaneously



***In situ* removal of H_2O**

Le Chatelier's Principle

$$2CO_2 + 6H_2 \rightleftharpoons CH_3OCH_3 + 3H_2O$$

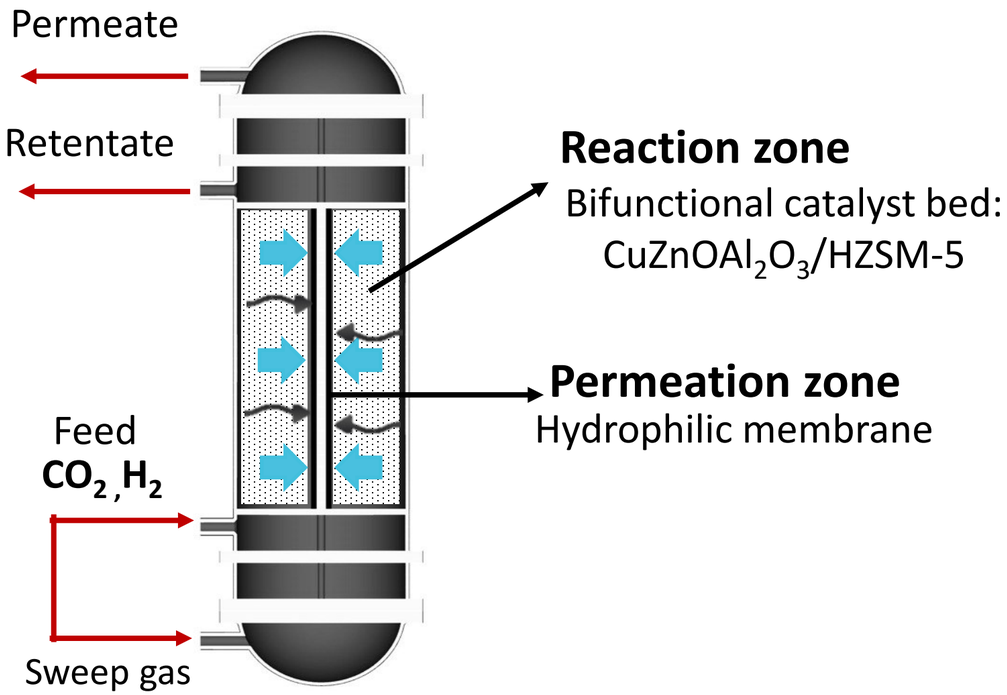
Equilibrium shifts to the right side

Advantages

- Overcome thermodynamic limitations
- Prevent catalyst deactivation
- Allow milder reaction conditions
- Decrease separation costs

Reactor features and model

Fixed bed membrane reactor



Trans-membrane flux :

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

Sweep gas (CO_2+H_2)

Water removal Heat removal

Co-current configuration

Model hypotheses

1. Steady state conditions
2. 1D plug flow (L/dp ≥ 50 and D/dp ≥ 25)
3. Kinetic control regime
4. Pseudo-homogeneous model
5. Reactor kinetic of conventional reactor valid
6. The membrane material is inert

Assessment of the membrane optimal properties

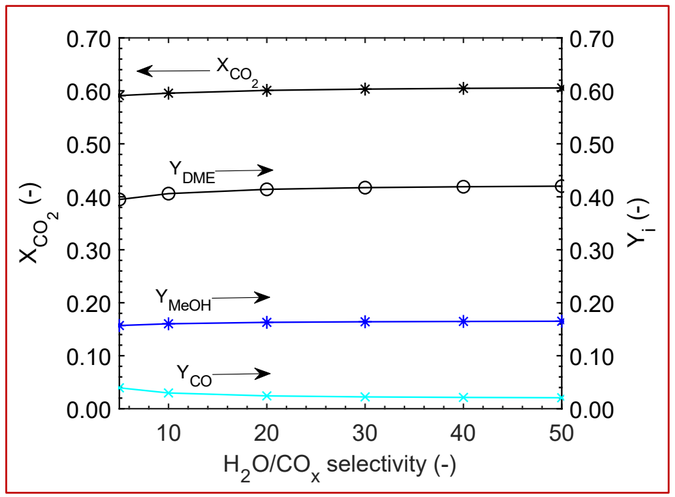
Membrane properties:

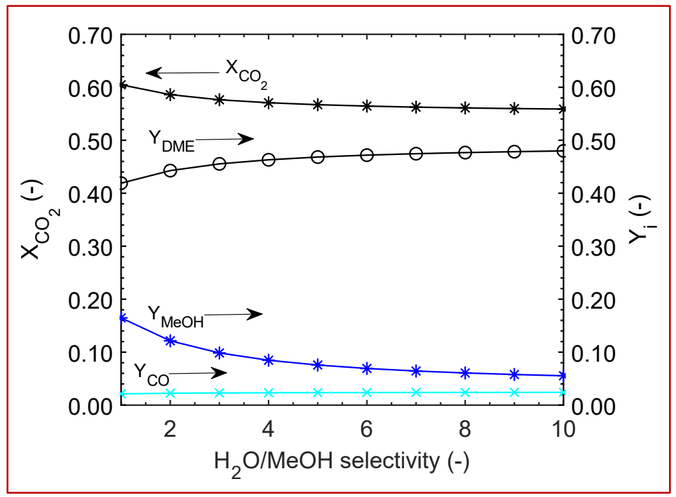
Permeance $\wp_i$ $[mol/(Pa \cdot m^2 \cdot s)]$

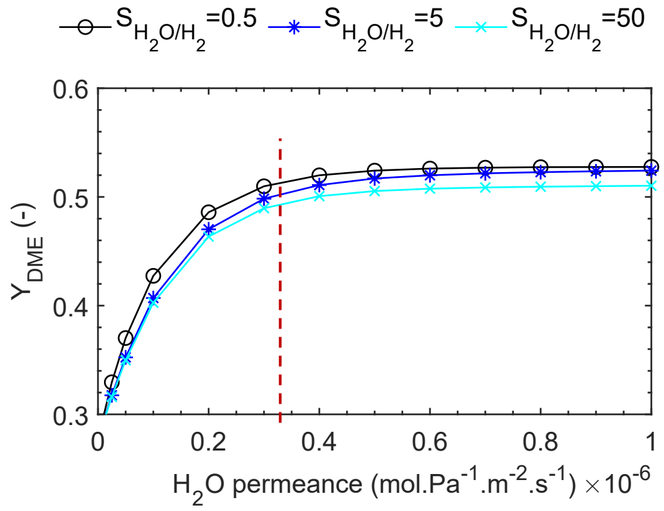
Selectivity $S_{H_2O,i} = \wp_{H_2O}/\wp_i$

Criteria

1. Maximize removal of water
2. Minimize reactant loss (H_2, CO_2 and MeOH)
3. Minimize removal of by-product (CO)







Membrane optimal properties		State-of-the-art (zeolites)
$\wp_{H_2O}$	$4 \cdot 10^{-7}$	$(0.6\text{-}10) \cdot 10^{-7}$
S_{H_2O,H_2}	50	2-50
S_{H_2O,CO_2}	30	2.45-17.7
$S_{H_2O,CO}$	30	3.7-19.6
$S_{H_2O,MeOH}$	10	1-9

Input for membrane development

Development of carbon membranes

Phenolic resin-based membranes

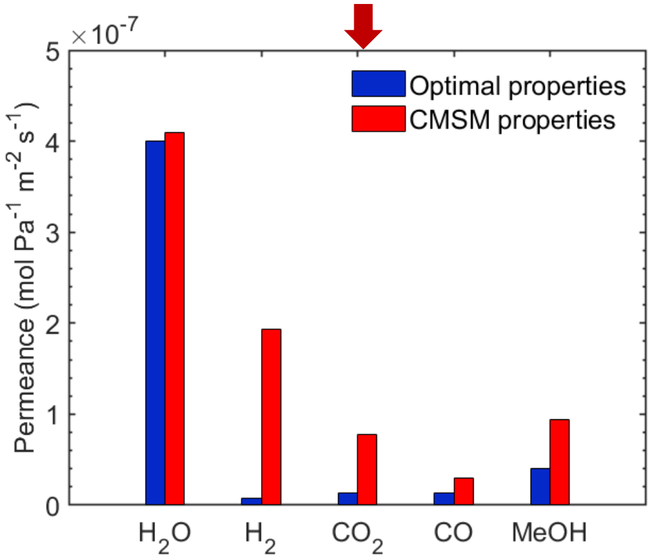
Studied effects:

- Carbonization temperature
- Hydrophilic inorganic fillers (boehmite)

Properties achieved

Target

Membrane optimal properties		Carbon Membranes[2]	
$\wp_{H_2O}$	$4 \cdot 10^{-7}$	$(1.2\text{-}7) \cdot 10^{-7}$	✓
S_{H_2O,H_2}	50	1.7-6.7	✗
S_{H_2O,CO_2}	30	5.9-14	✗
$S_{H_2O,CO}$	30	8.9-40	✓
$S_{H_2O,MeOH}$	10	2-8.7	✓



Selectivity target missed for H_2 and CO_2

- H_2 kinetic size too close to H_2O
- CO_2 affinity to the membrane surface

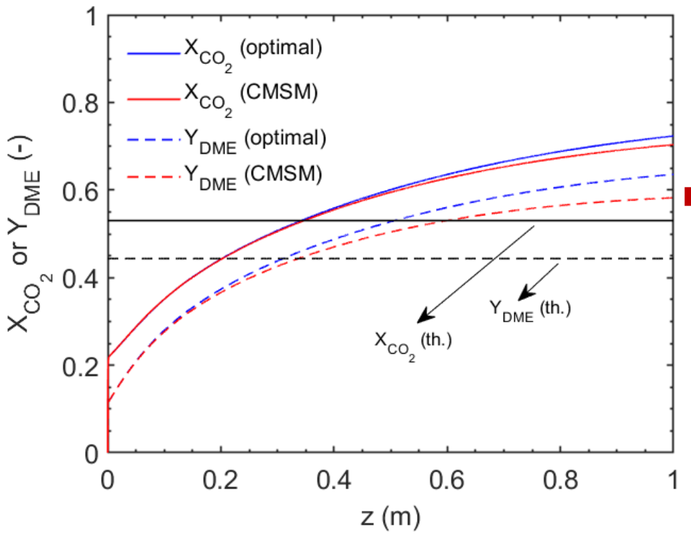
→ **What is the impact on reaction performance?**

Poto et al. *International journal of hydrogen energy* 47.21 (2022)

Membrane reactor performance

Optimal properties vs real carbon membrane properties

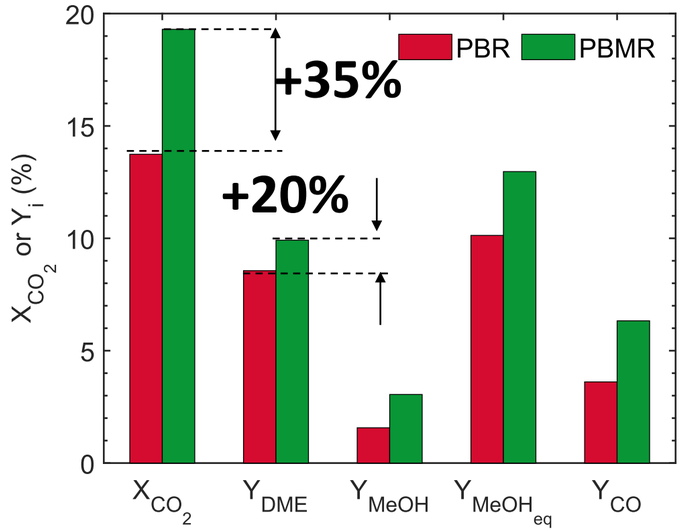
Simulation results[3]:



Improvement with optimal properties:

Y_{DME}	X_{CO_2}
+36%	+43%

Experimental results:



The reactant permeation limited via sweep gas circulation and low ΔP

For each membrane properties set, sweep gas and ΔP can be tuned to achieve optimal performance

- **Permeance** is more important than **selectivity**.
- **Poor selectivity** can be solved by tuning the driving force with the sweep gas
- **Experimental proof** of the **higher performance** of the packed bed membrane reactor (**PBMR**) over the conventional packed bed reactor (**PBR**)

3. Poto, Serena, et al. “Direct conversion of CO2 to dimethyl ether in a fixed bed membrane reactor: Influence of membrane properties and process conditions." *Fuel* 302, 13 p., 121080 (2021)

Follow our projects (on membrane reactors)

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Interested in membrane reactors?

18th International Conference on Catalysis in Membrane Reactors (ICCMR18) – Eindhoven October 2027

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1CUBE

Contact
f.gallucci@1cube.eu

+31620744662

www.1cube.eu

High Tech Campus 37, 5656AE Eindhoven