Inorganic Membranes
& Membrane Reactors

1CUBE

Membranes and Membrane reactors for CO_2 hydrogenation

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Professor Inorganic Membranes and Membrane Reactors

BioMeGaFuel MEMCAT

Outlook

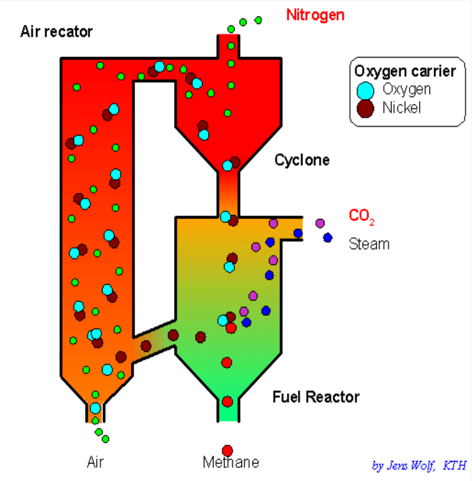
- Who we are
- Why integrated reactors
- CO_2 to methanol…and others
- Next steps

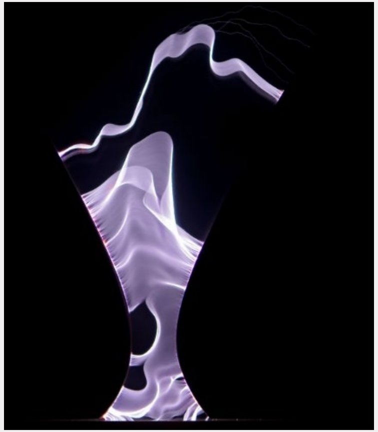
Research themes - SIR

Novel intensified reactor concepts via:

- ➢ Integration reaction and separation (membrane reactors, chemical looping)

- ➢ Integration reaction and heat/energy management (endo/exothermic, plasma systems)





• **Research approach:** combination experimental PoC and modelling

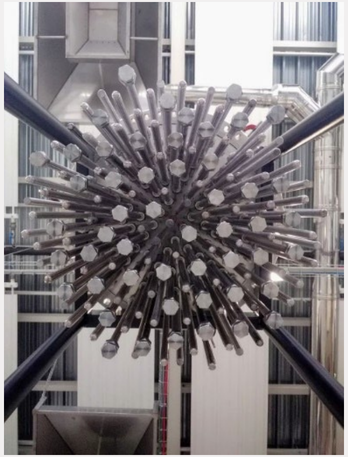
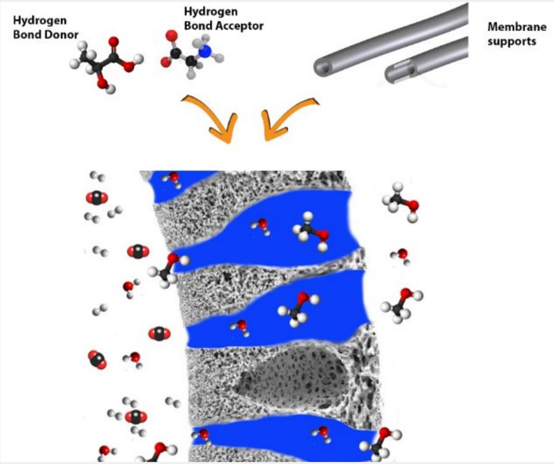
Research themes - SIR

Integration reaction + separation

Packed bed and fluidized bed membrane reactors

(H_2, syngas, oxidative dehydrogenations, partial oxidations)

- Use membranes to improve fluidization and fluidization to improve membrane flux
- Liquid supported membranes

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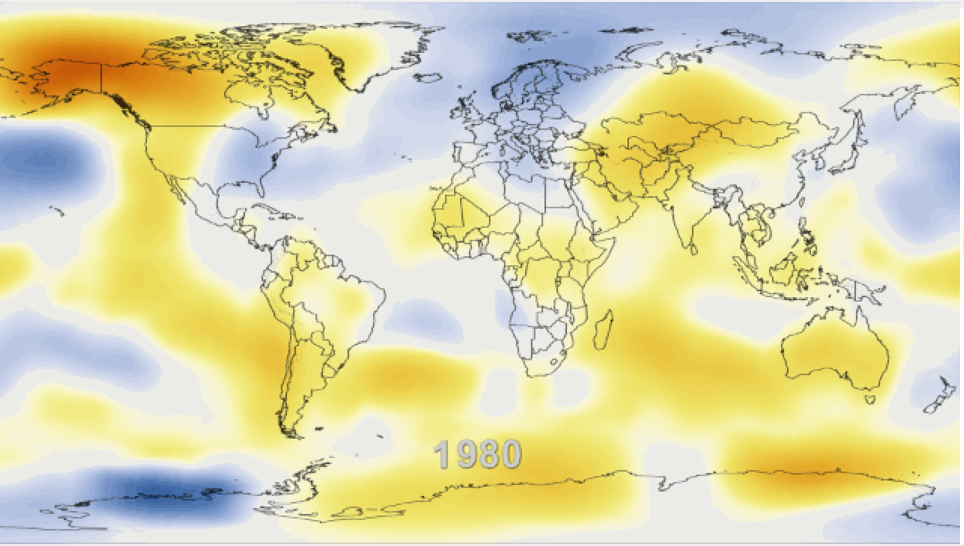
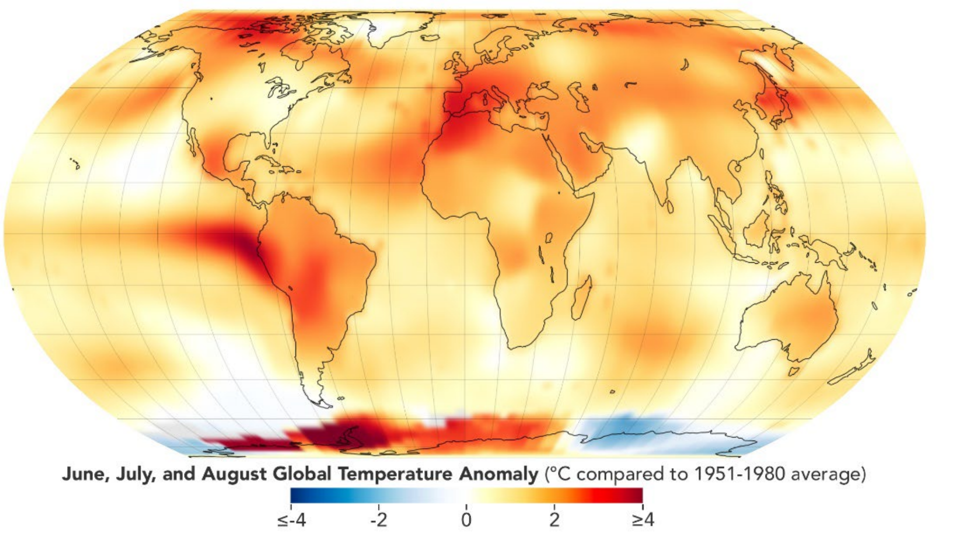
One of our challenges



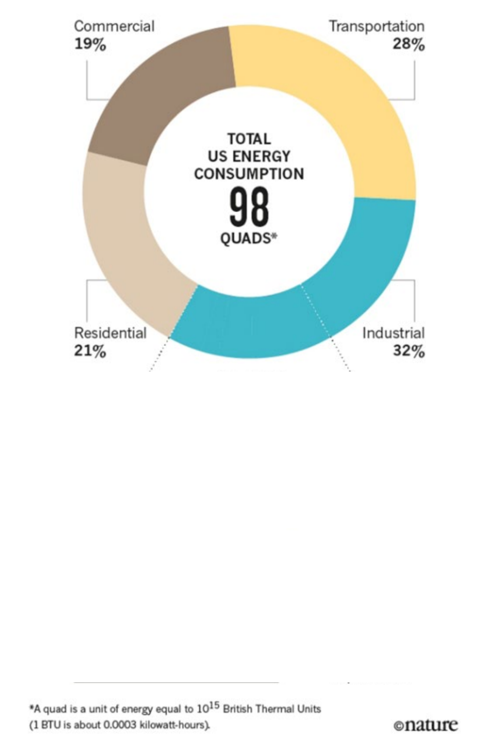


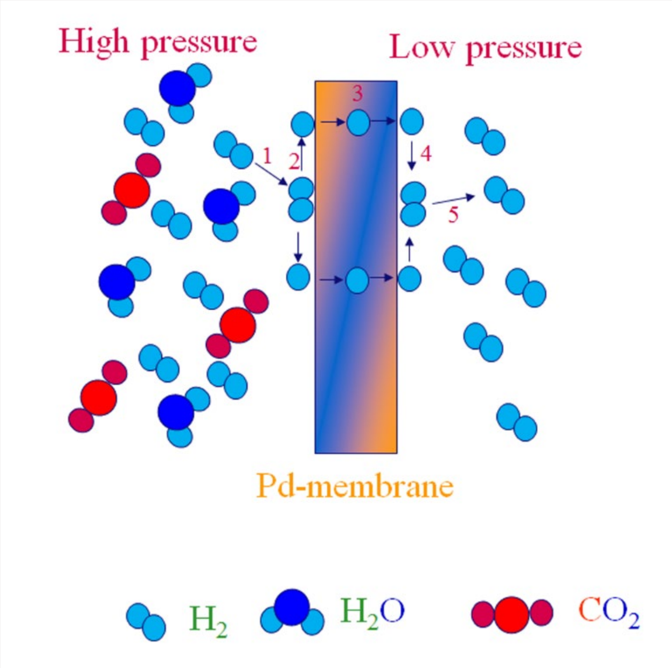
https://kaiserscience.wordpress.com/2019/06/24/the-discovery-of-global-warming/

https://climate.nasa.gov/news/3282/nasa-announces-summer-2023-hottest-on-record/

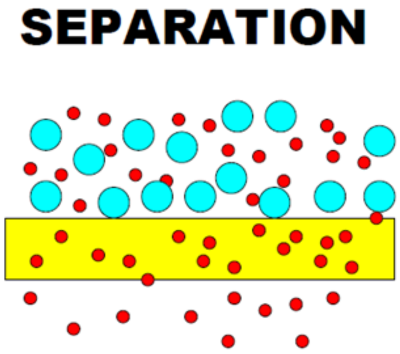
Earth = 4,54 By Homo sapiens = 300000 y Industrial revolution = 100 y

A possible solution

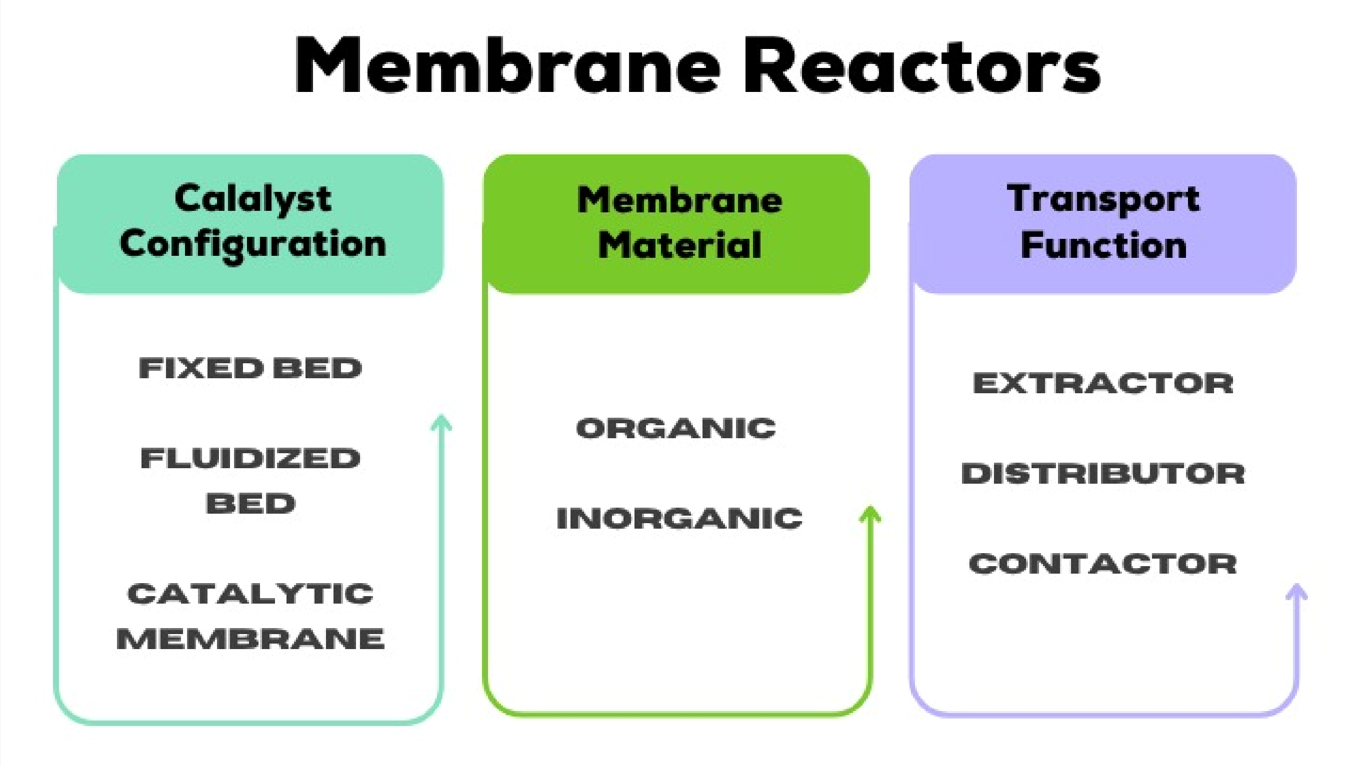




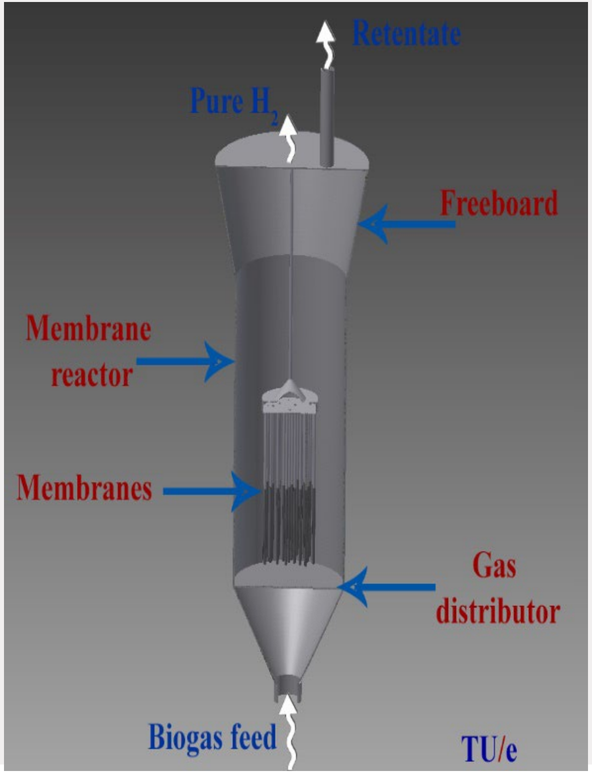
Membrane functions

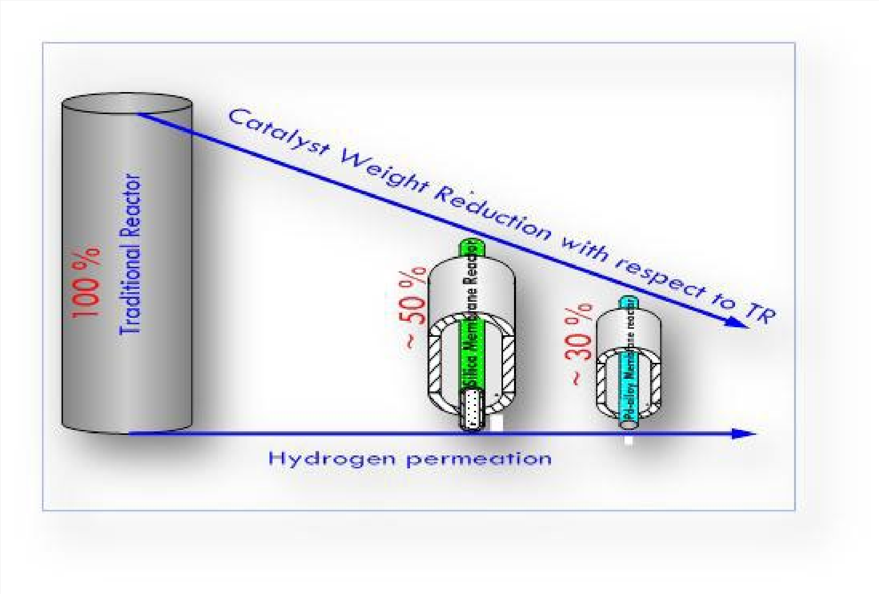


Classification



A membrane reactor

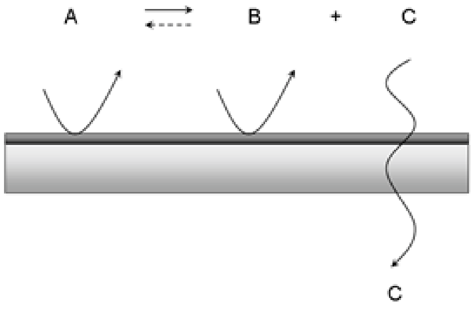


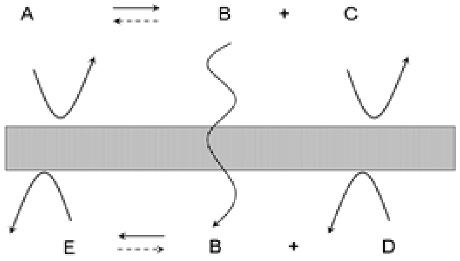


Brunetti A.; Caravella C.; Barbieri G.; Drioli E.; "Simulation study of water gas shift in a membrane reactor", *J. Membr. Sci.*, 2007, 306(1-2), 329-340

Why a membrane reactor?

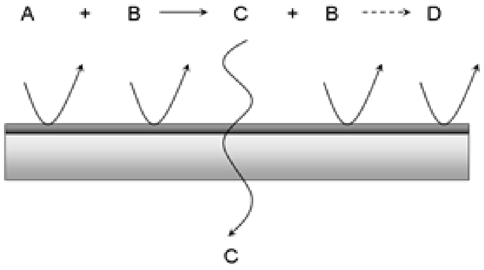
conversion enhancement by selective permeation of a reactant product of an equilibrium limited reaction

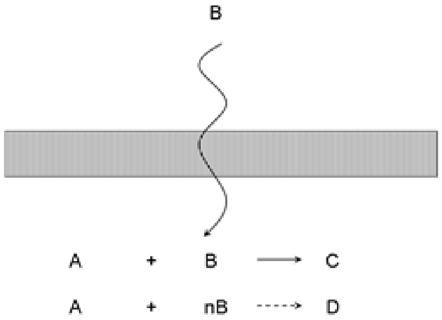




conversion enhancement by coupling of reactions

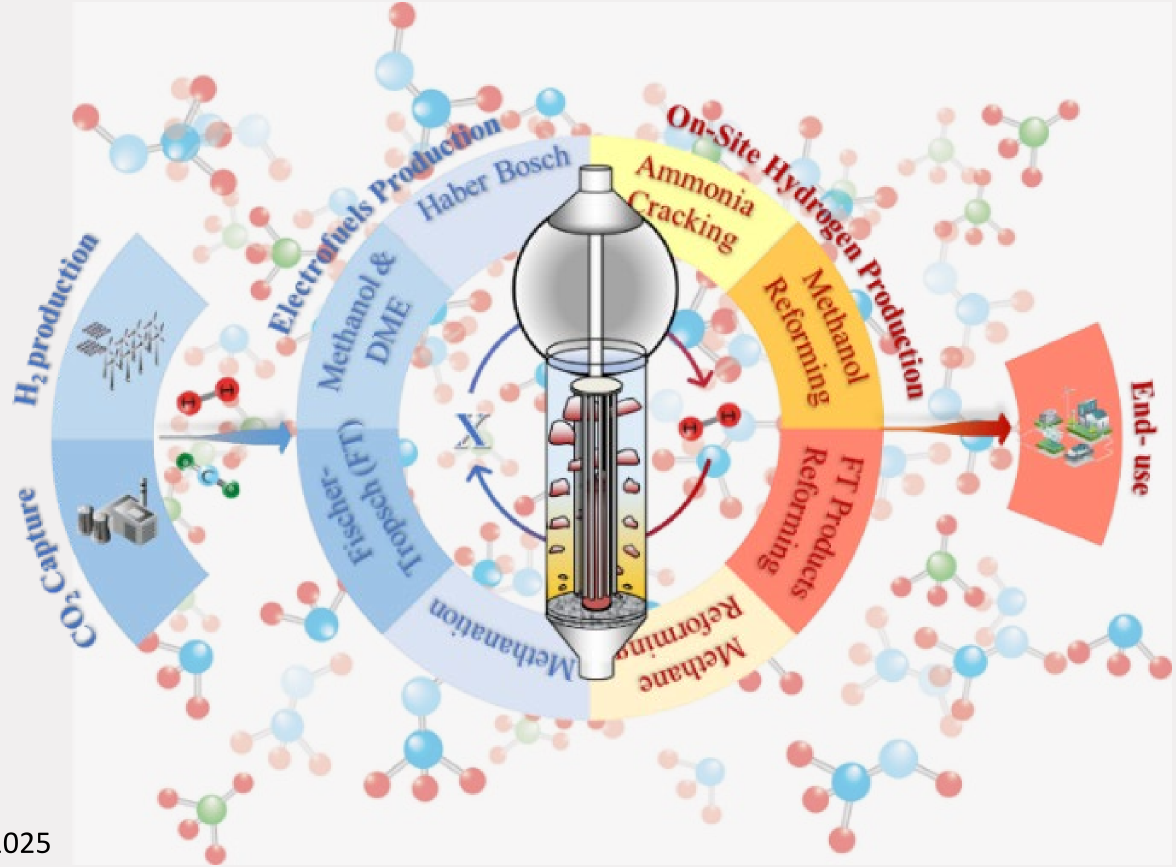
selectivity enhancement by selective permeation of an intermediate product





selectivity enhancement by dosing a reactant through the membrane

Use of MR



Simon Richard, PhD Thesis, TU/e 2025

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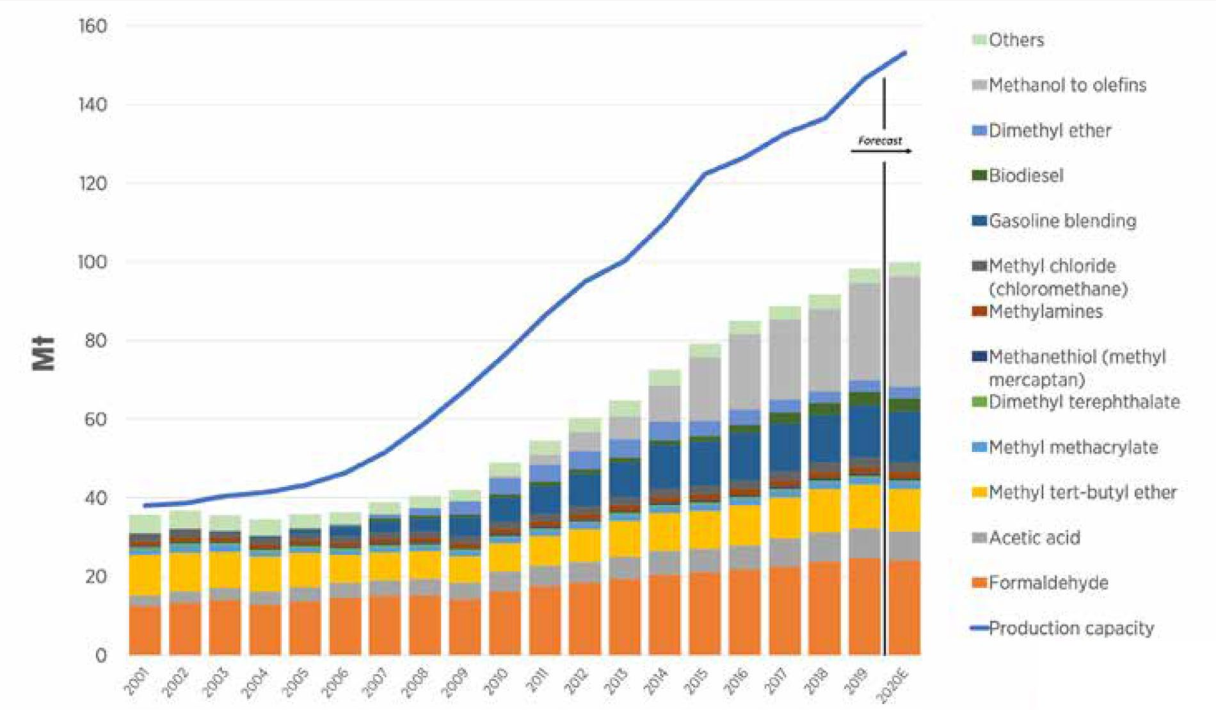
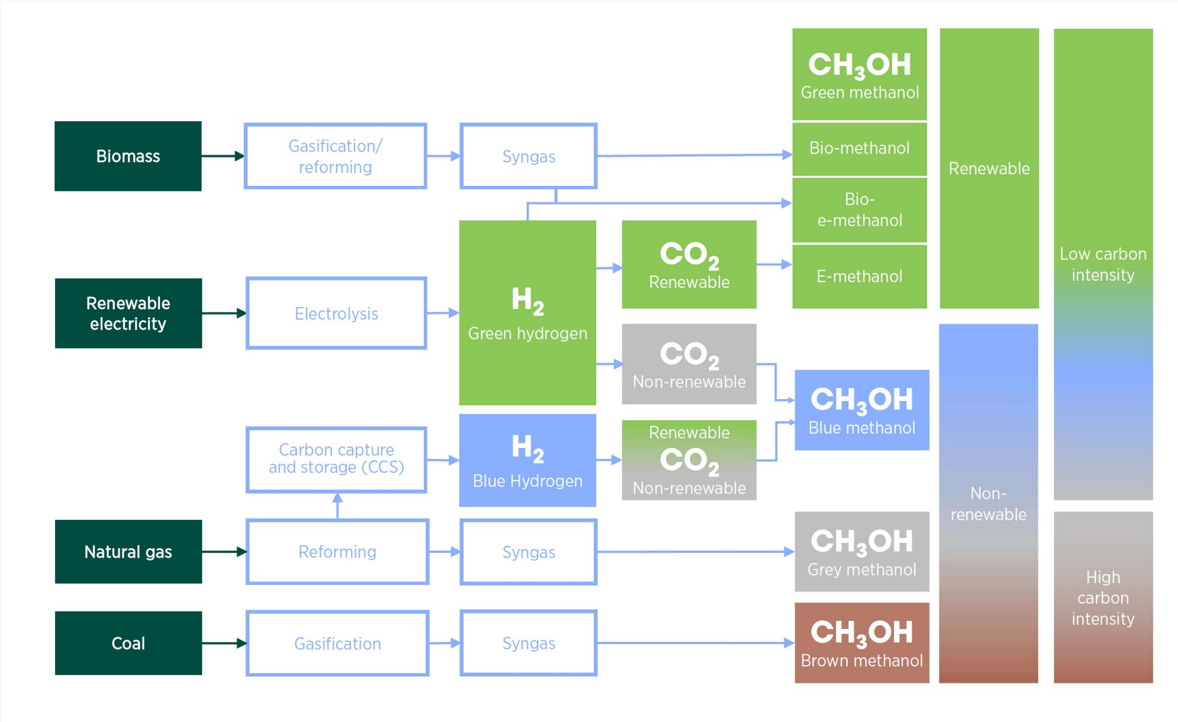
Methanol



Global methanol demand and production capacity. Kang, Seungwoo. Innovation Outlook : Renewable Methanol; International Renewable Energy Agency, 2021

Methanol



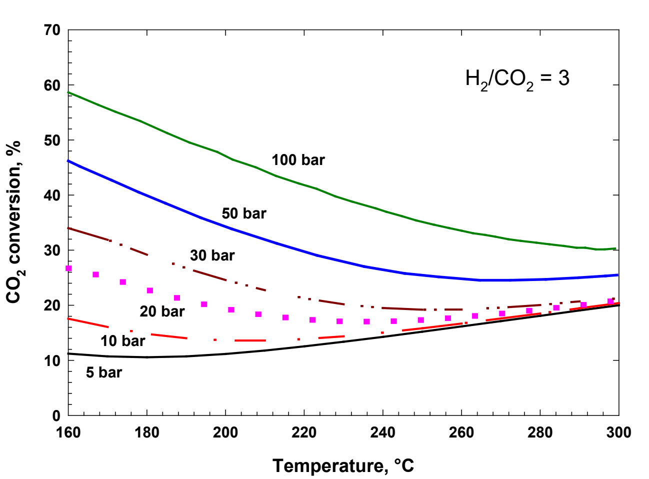
Kang, Seungwoo. Innovation Outlook : Renewable Methanol; International Renewable Energy Agency, 2021

Methanol

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

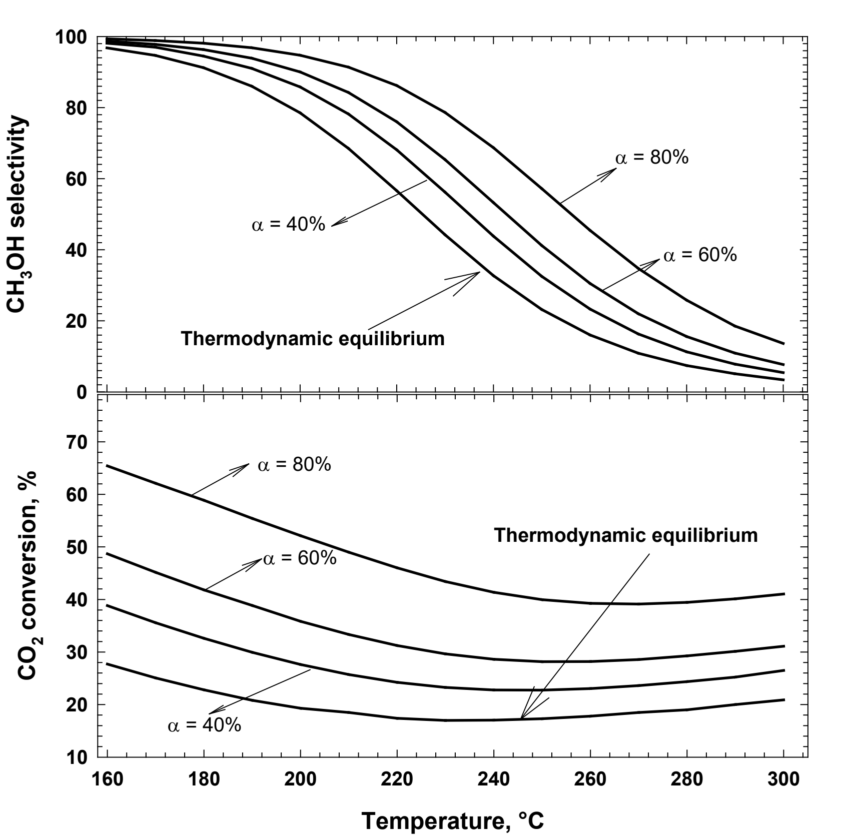
$CO + 2H_2 \Leftrightarrow CH_3OH$ $\Delta H = -90.7$ kJ/mol

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



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

Methanol

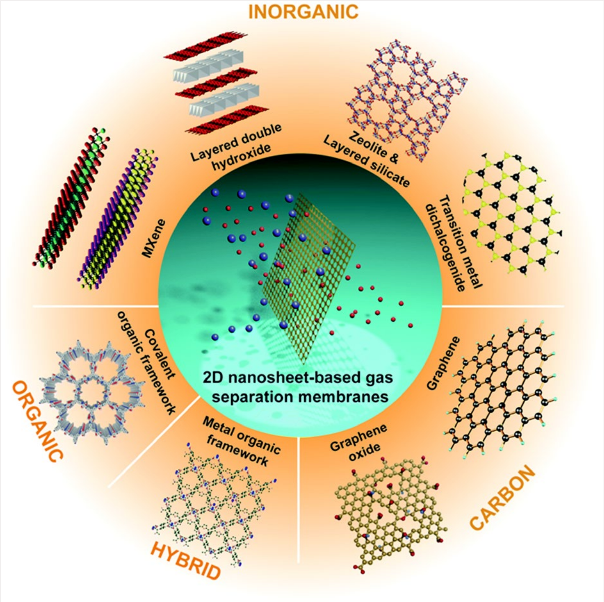


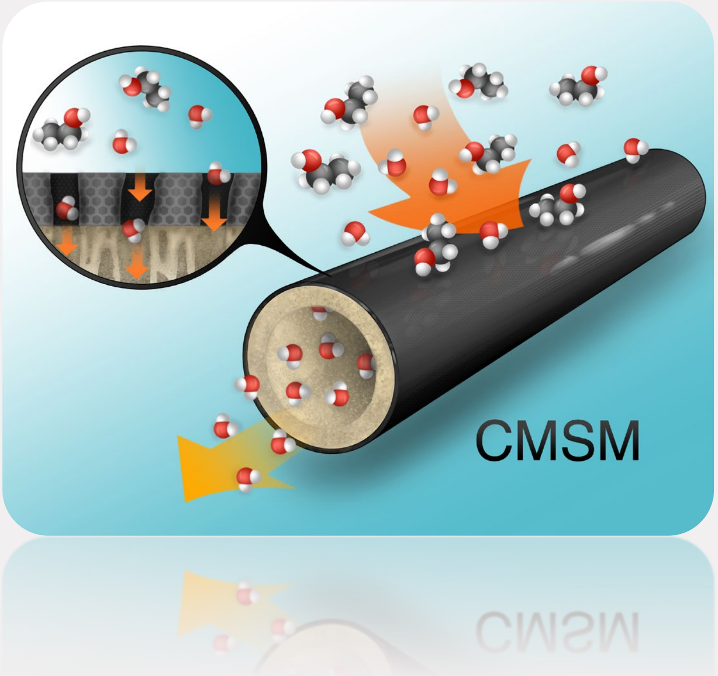
Gallucci et al. *International Journal of Hydrogen Energy,* 2007, 5050-5058

Membranes for methanol

Material

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





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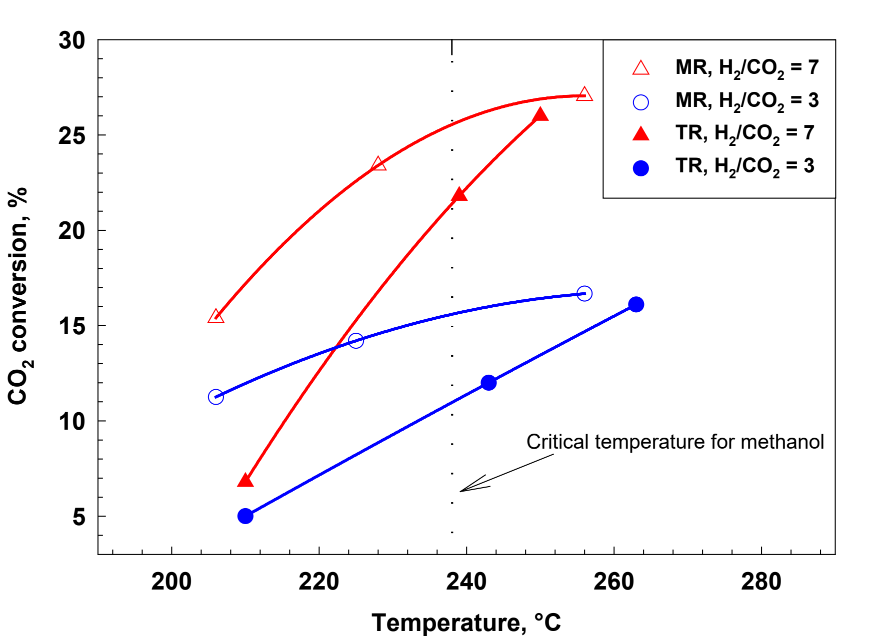
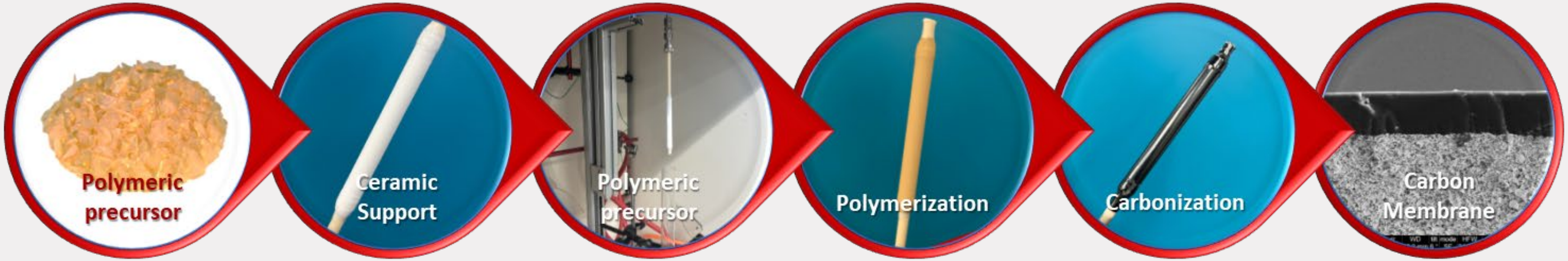
Methanol production in MR

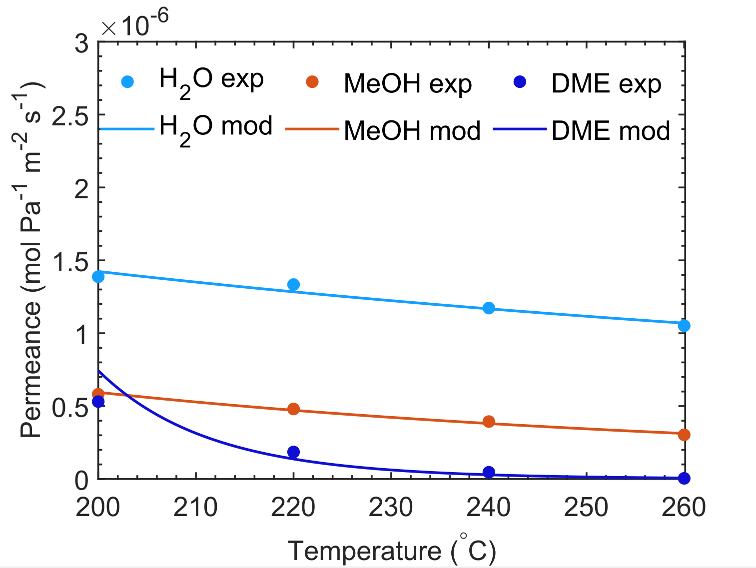


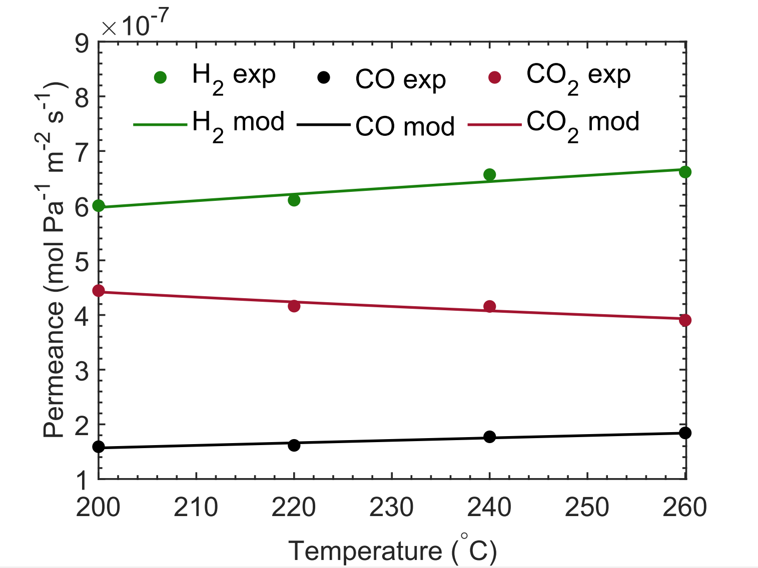
Gallucci et al. *Chemical Engineering and Processing* 2004, 1029-1036

Making CMSMs



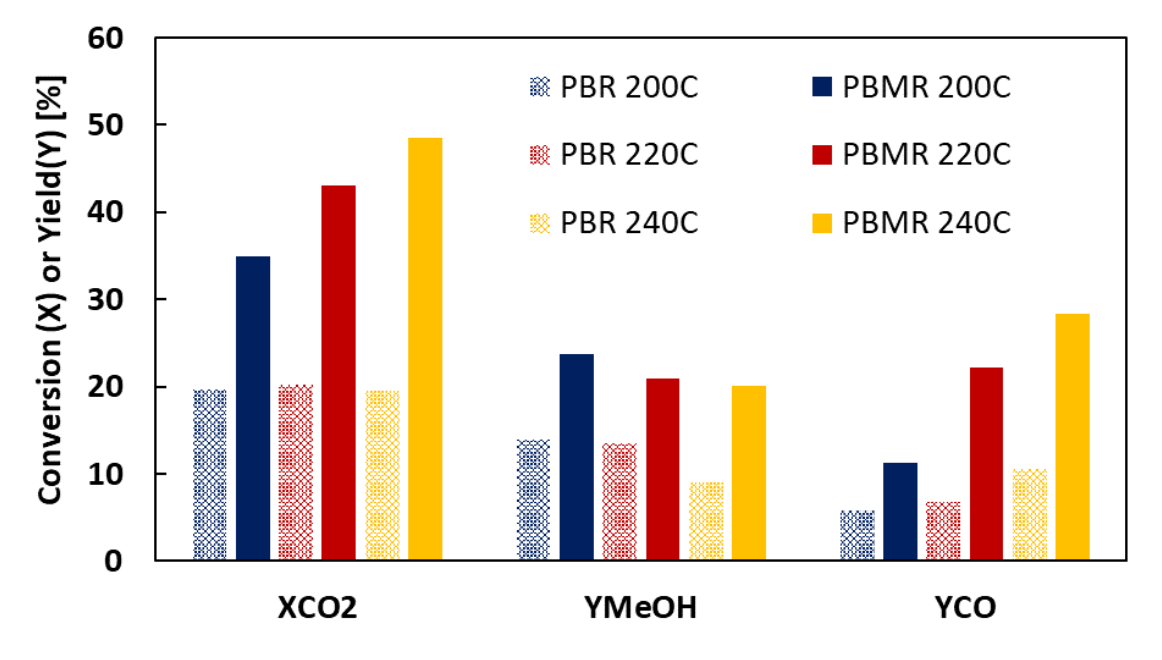
Methanol production in MR





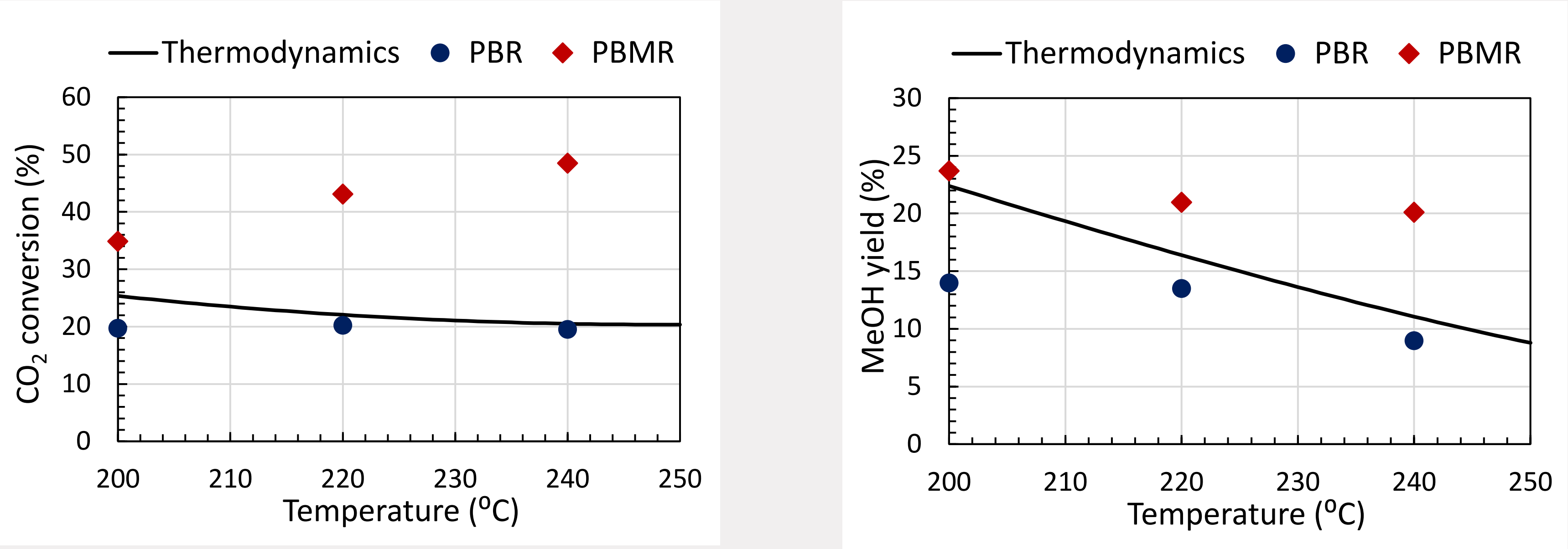
Gallucci et al. *Catalysts* **2026**, *16*(1), 53;

Methanol production in MR



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

Methanol production in MR



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

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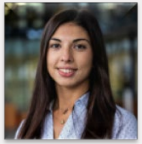
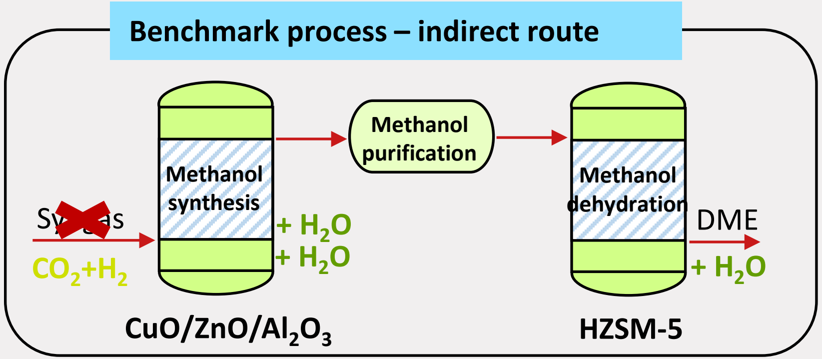
What's next

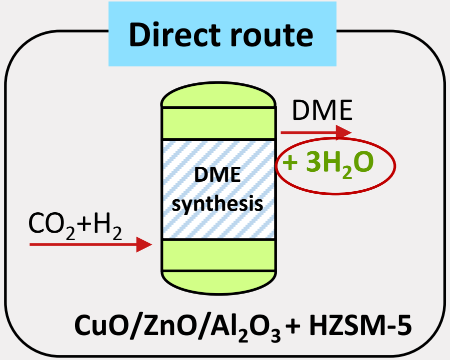
- Techno-economics
- Detailed design of systems, most probably distributed
- Scale-up of systems
- Application to other reaction systems – DME, Ethylene….

DME production



How to reduce thermodynamic limitation





Reverse Water Gas Shift

$CO_2 + H_2 \rightleftarrows CO + H_2O$

Water Gas Shift

$CO + H_2O \rightleftarrows CO_2 + H_2$

Challenge of replacing the carbon source with pure CO_2

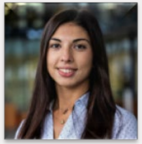
Strong **thermodynamic limitation** due to large production of H_2O

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

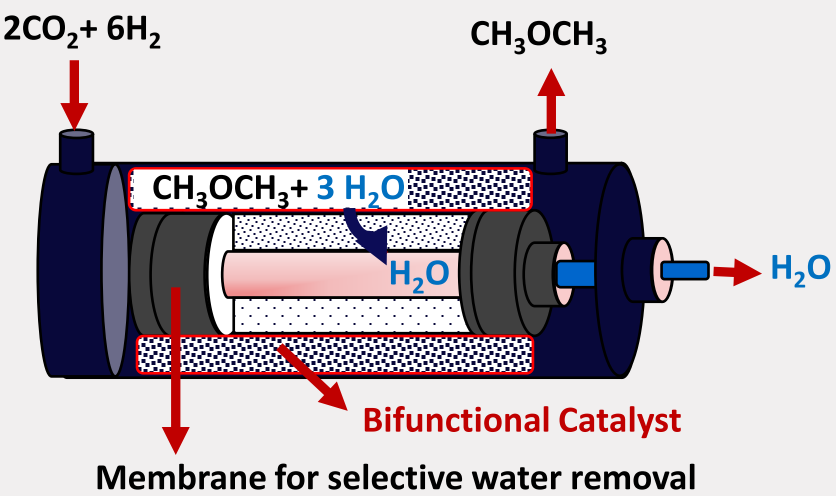
Zeolites unstable with H_2O at high temperature (Al leaching)

Cu sintering and migration facilitated by H_2O

Membrane reactor



Reaction and separation occur simultaneously



In situ **removal of H_2O**

Le Chatelier's Principle

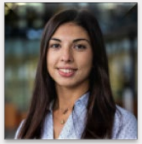
$$2CO_2 + 6H_2 \rightleftarrows CH_3OCH_3 + 3H_2O$$

Equilibrium shifts to the right side

Advantages

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

Membrane requirements



Stability (thermal, mechanical, chemical) **+ Hydrophilicity + High vapor/gas selectivity**

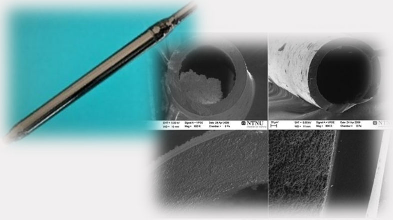
Polymeric membranes

- High permeability
- Low thermal stability

$\wp_{H_2O} = 4 \cdot 10^{-7} \text{mol s}^{-1}\text{m}^{-2}\text{Pa}^{-1}$ @ 50 ℃

$\wp_{H_2O} = 4 \cdot 10^{-8} \text{mol s}^{-1}\text{m}^{-2}\text{Pa}^{-1}$ @ 200 ℃

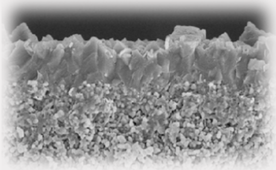
Carbon membranes



- Possible hydrophilicity (surface functionalization)
- Stability (thermal, chemical)
- Possibility to tune properties

Ceramic membranes

(zeolite, alumina, etc.)



- High permeability/selectivity
- Low stability (hot humid environment)

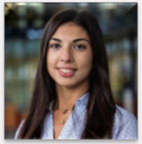
$\wp_{H_2O} \approx 10^{-7} \text{mol s}^{-1}\text{m}^{-2}\text{Pa}^{-1}$

Carbonization of a **thermosetting polymer**

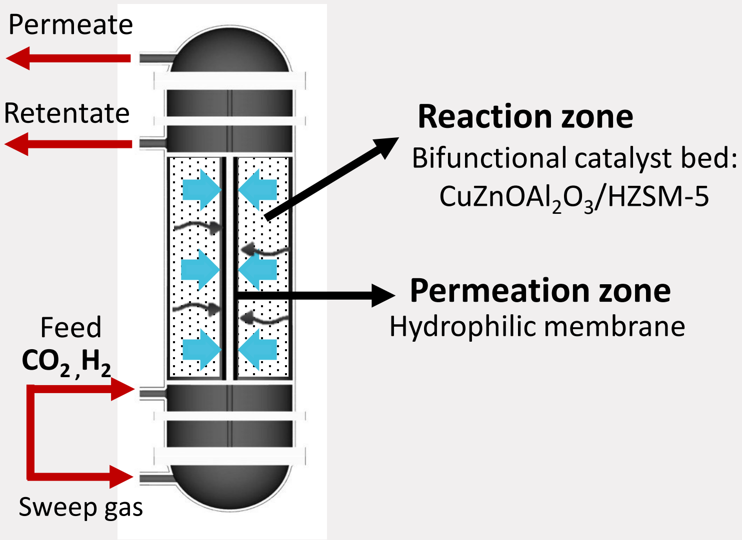
Formation of a **porous structure**

Derive from polymer: **Surface functionality**

Reactor features and model hypotheses



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

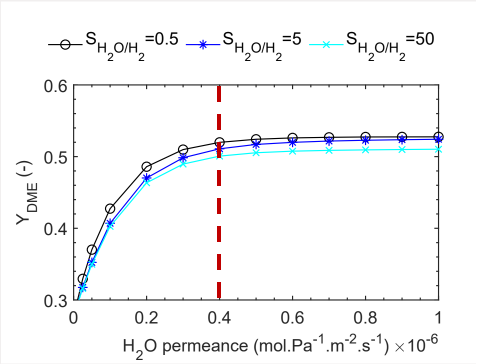
Membrane properties:

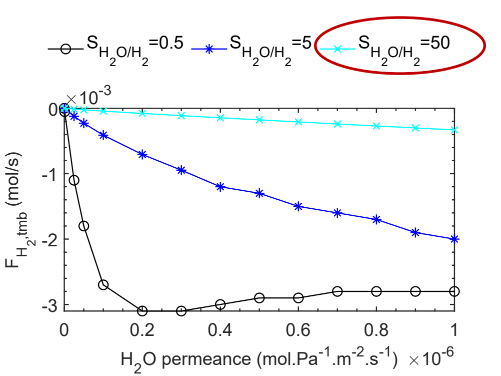
Permeance $\wp_i \quad [mol/(Pa \cdot m^2 \cdot s)]$

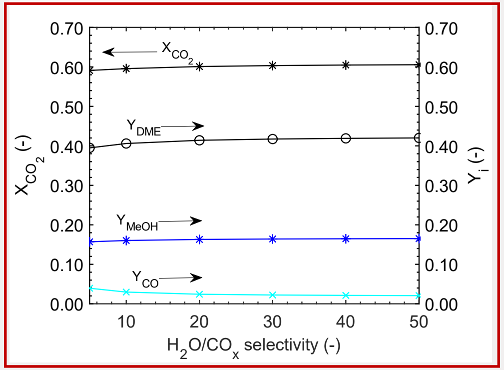
Selectivity $S_{H_2O,i} = \wp_{H_2O}/\wp_i$

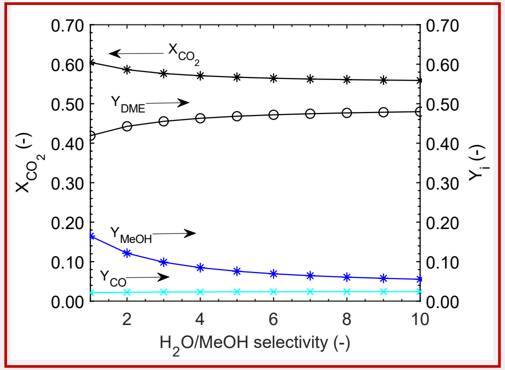
Criteria

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



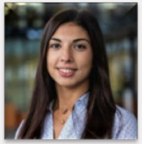




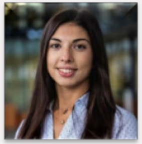


Membrane optimal properties		**State-of-the-art (zeolites)**
$\wp_{H_2O}$	$4 \cdot 10^{-7}$	$(0.6\text{-}10) \cdot 10^{-7}$
S_{H_2O,H_2}	50	2-50
S_{H_2O,CO_2}	30	2.45-17.7
$S_{H_2O,CO}$	30	3.7-19.6
$S_{H_2O,MeOH}$	10	1-9

Input for membrane development



Development of carbon membranes



Phenolic resin-based membranes

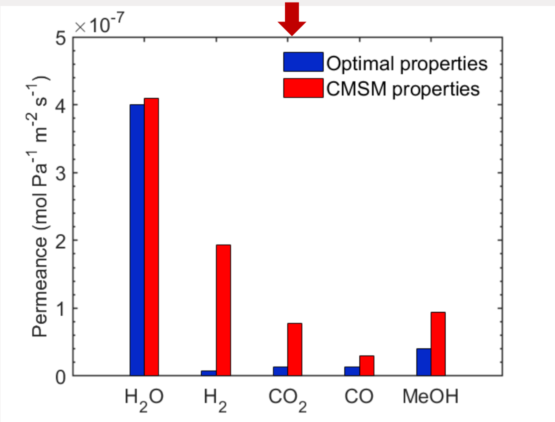
Studied effects:

- Carbonization temperature
- Hydrophilic inorganic fillers (boehmite)

Target / **Properties achieved**

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	✔

Average properties:



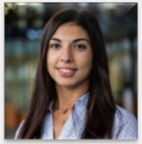
Selectivity target missed for H_2 and CO_2

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

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

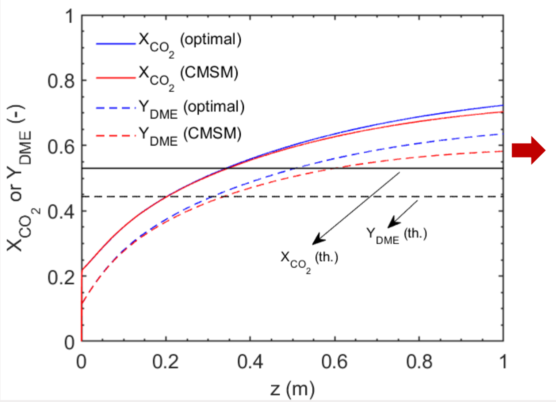
Poto et al. *International journal of hydrogen energy* 47.21 (2022)

Membrane reactor performance



Optimal properties vs real carbon membrane properties

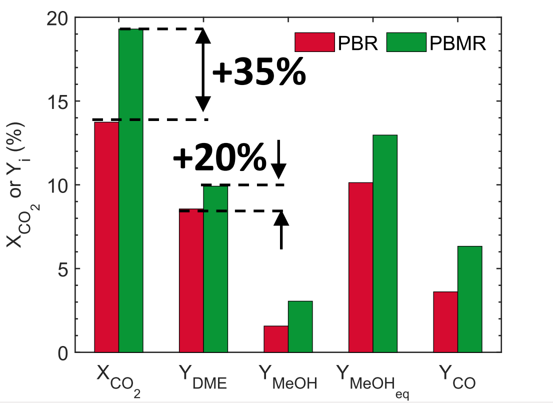
Simulation results[3]:



Improvement with optimal properties:

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

Experimental results:



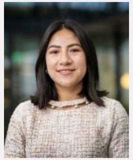
The reactant permeation limited via sweep gas circulation and low ΔP

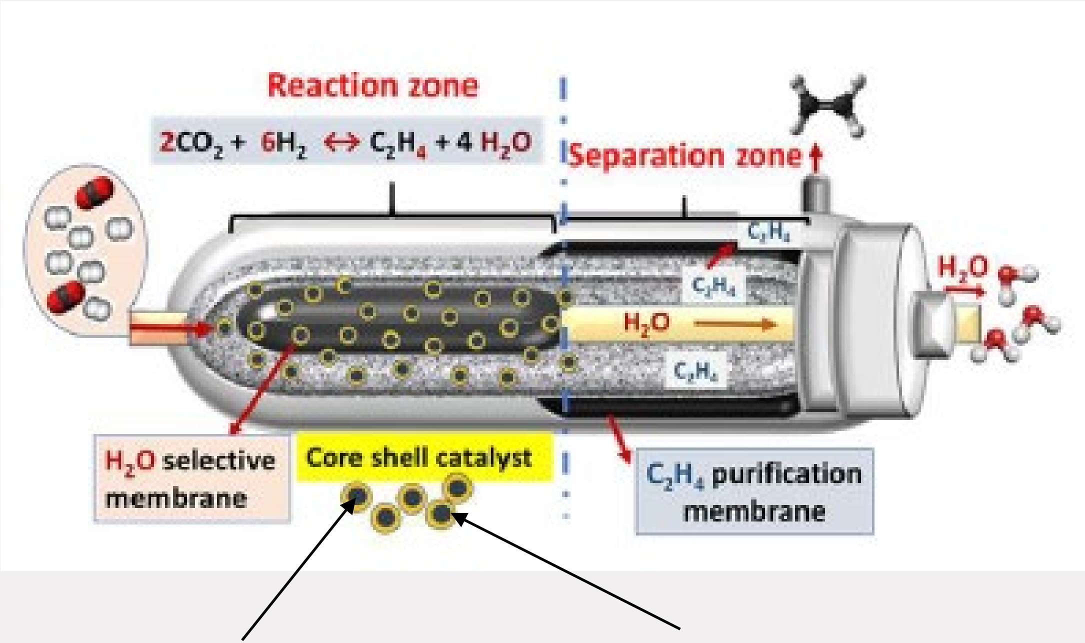
For each membrane properties set, sweep gas and ΔP can be tuned to achieve optimal performance

- **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)

Ethylene



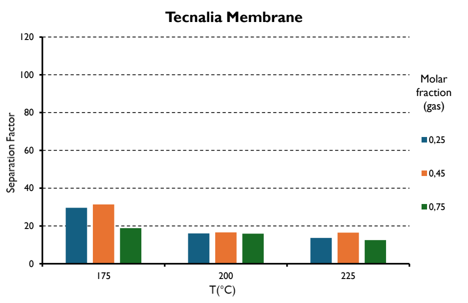


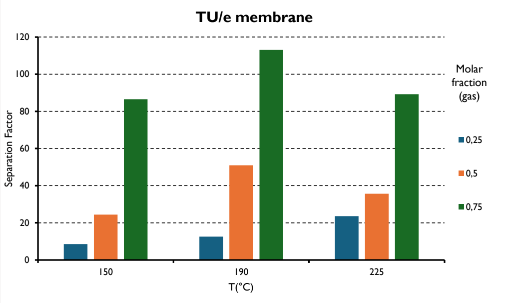
Cu, Zn, Zr and Al

Zeolite type

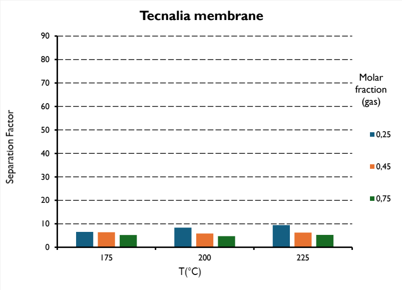
Membrane development

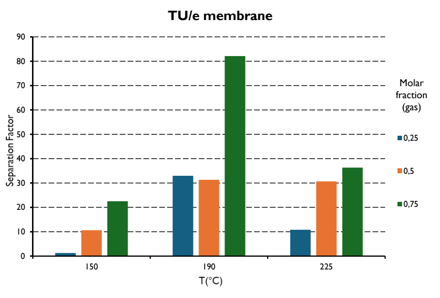
H_2O/CO



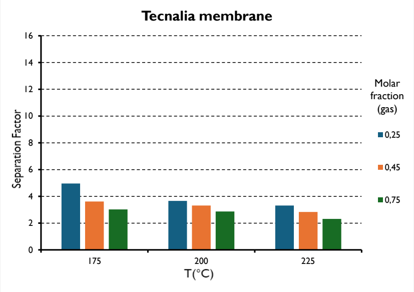


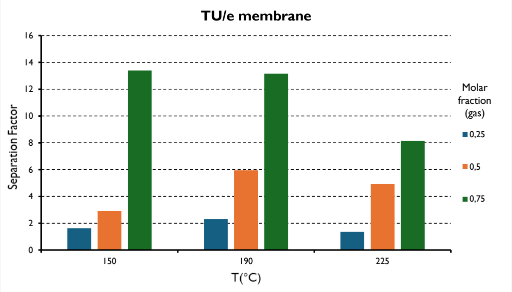
H_2O/CO_2





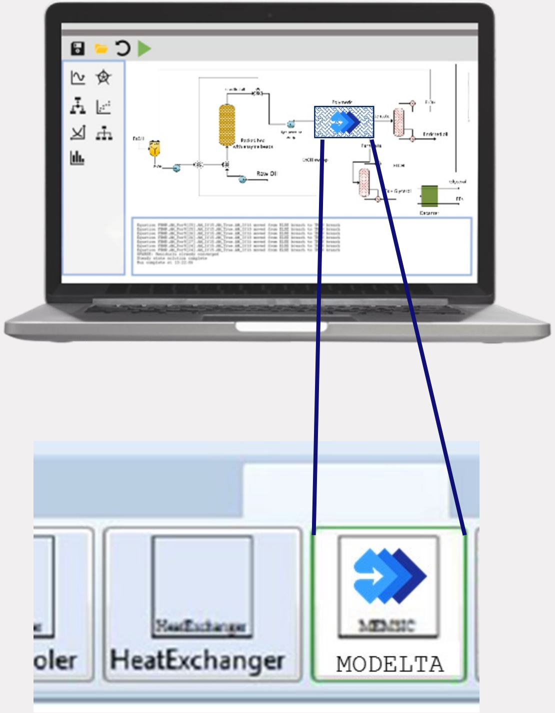
H_2O/H_2





Go to Market

Modelta cloud-based unit operation

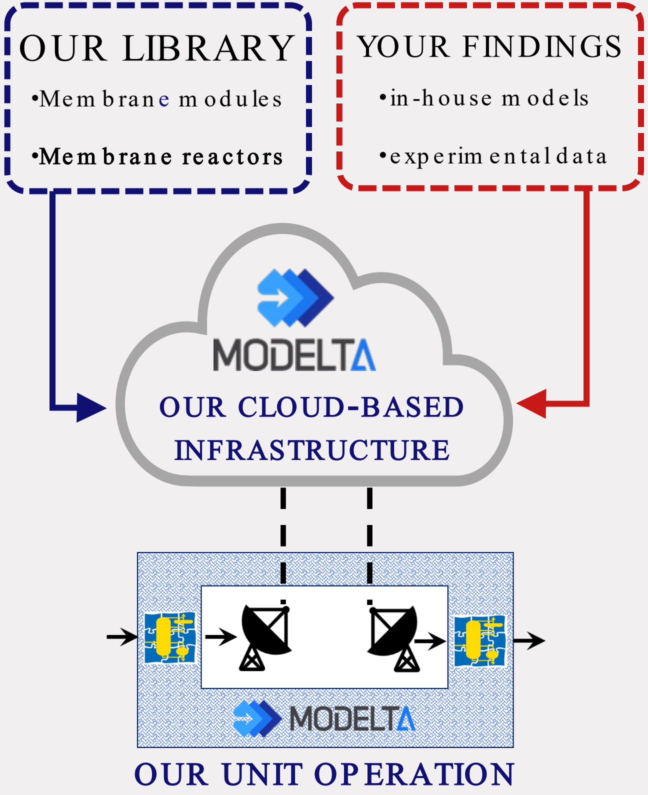


Just one block
in the flowsheet

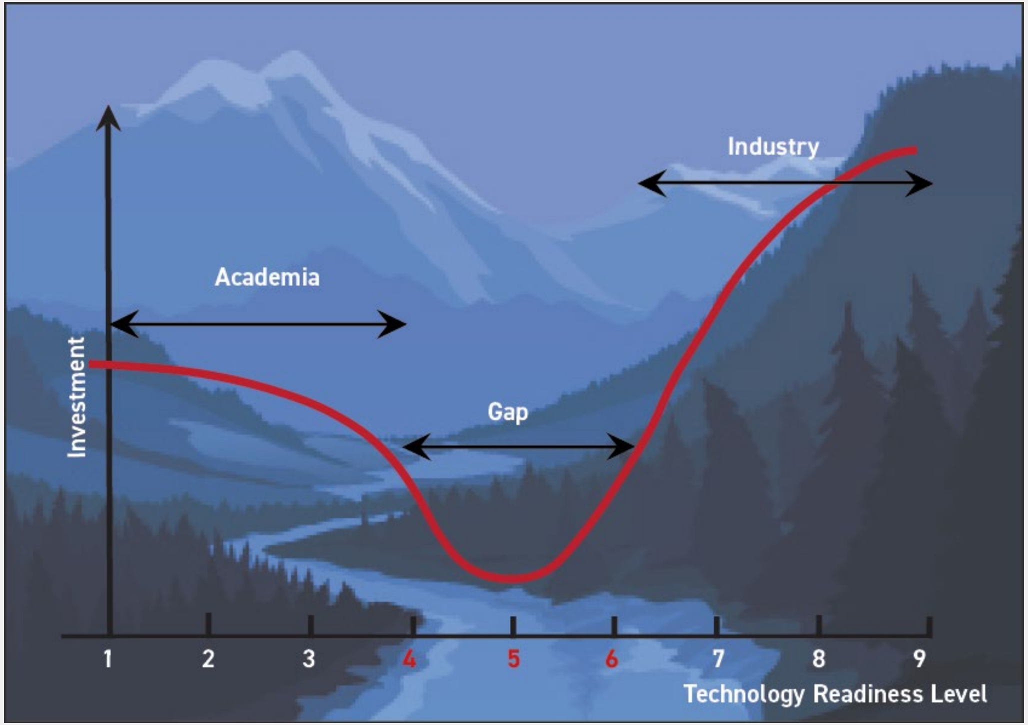
a whole library of
models available

that *we can swiftly*
customize via cloud

and *combine with*
your own models



Next steps


Industry
Academia
Investment
Gap
1
2
3
4
5
6
7
8
9
Technology Readiness Level

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MEMCAT

BiOMeGaFuel