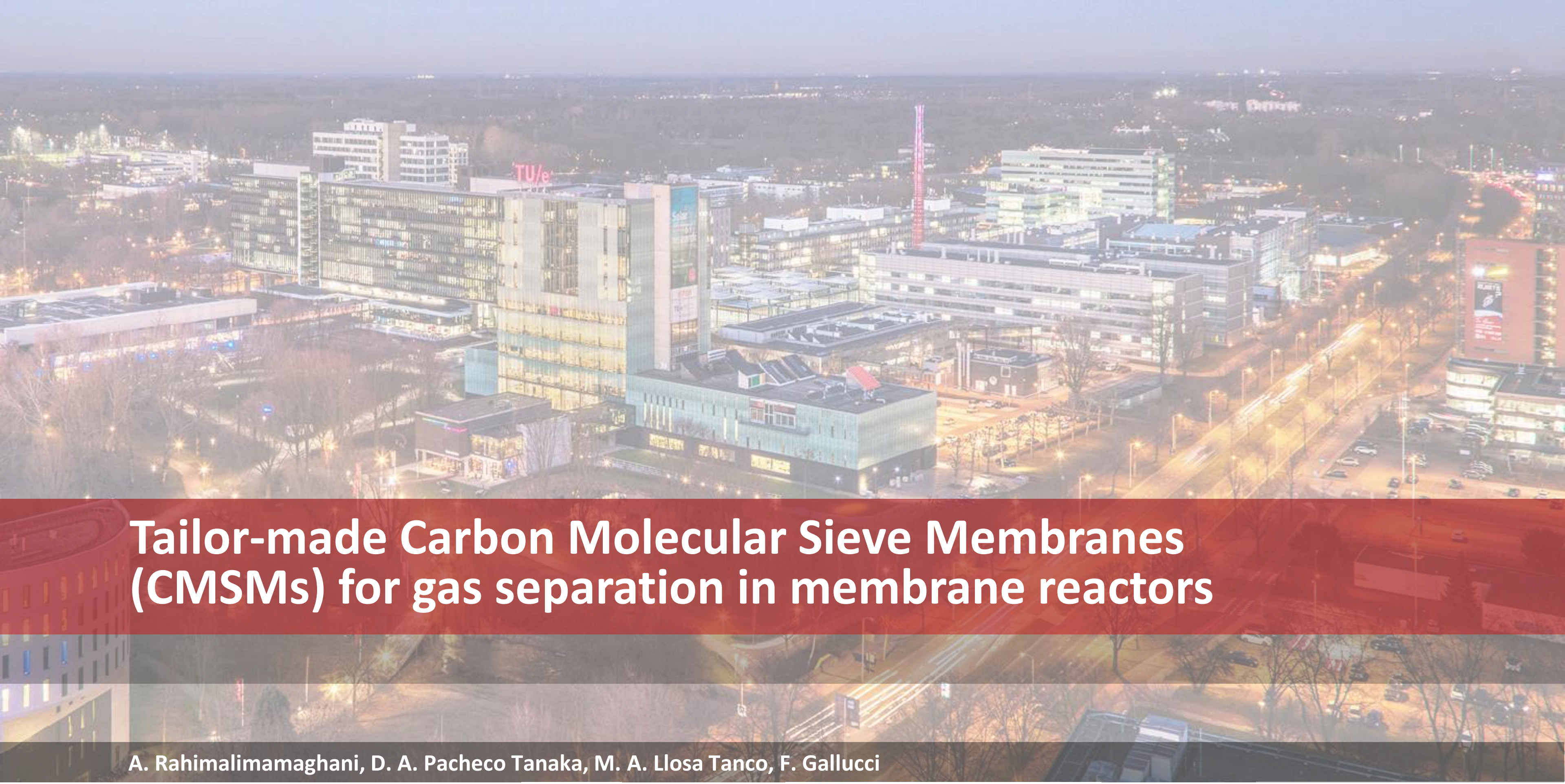

Tailor-made Carbon Molecular Sieve Membranes (CMSMs) for gas separation in membrane reactors

A. Rahimalimamaghani, D. A. Pacheco Tanaka, M. A. Llosa Tanco, F. Gallucci

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Outlook

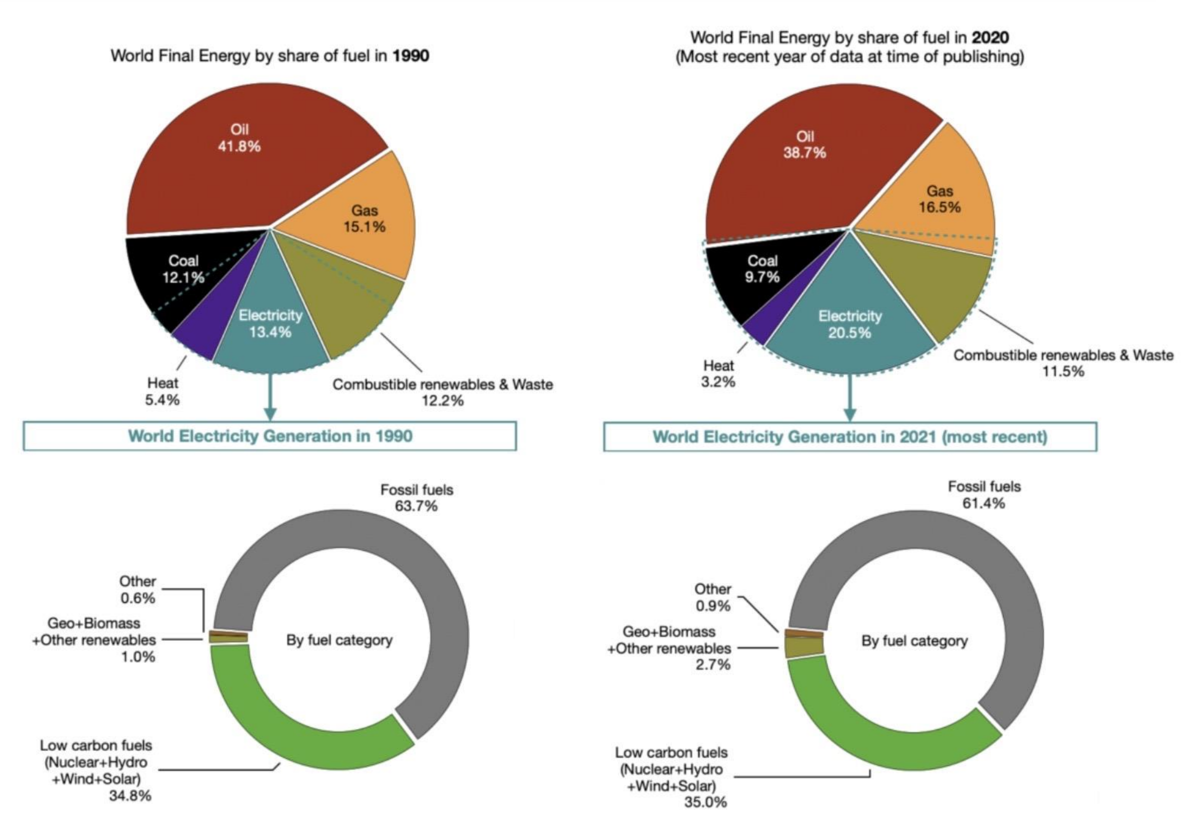
- Introduction
- CMSMs
- Applications of CMSMs
- Q&A

Inorganic Membranes & Membrane Reactors

Introduction

Energy resources

- The change in 30 years
- Dominated by fossil fuels (61%)
- Increased electricity production

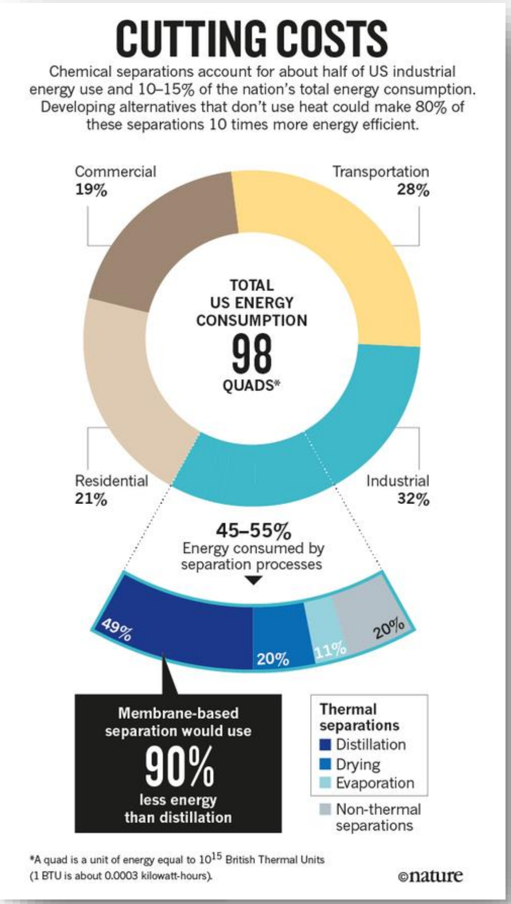


https://www.iea.org/data-and-statistics/data-product/world-energy-balances-highlights

Introduction

SEPARATION OF CHEMICALS

- 50% of US industrial energy use
- 10-15% of total energy consumption
- New technologies are required



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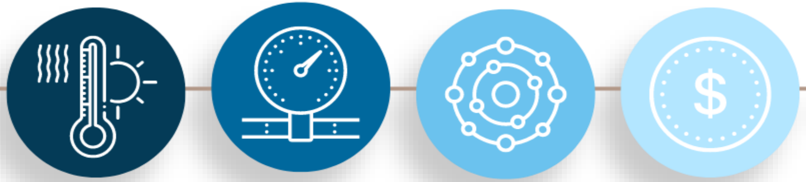
Introduction

MEMBRANE SEPARATION TECHNOLOGY

- Carbon Molecular Sieve Membranes (CMSMs)
- Separation based on molecular size and/or affinity
- Sub-nanometer range

~100.000 times smaller than human hair thickness

REQUIREMENTS



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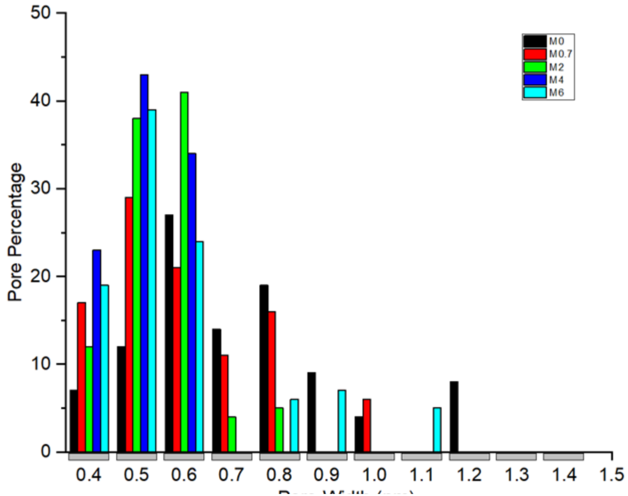
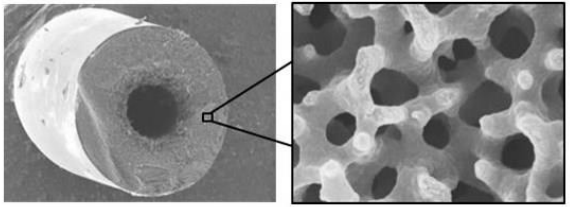
CMSMs

- Made via pyrolysis of a thermosetting polymer
  - Resorcinol- formaldehyde resin
  - Novolac
  - Polyimide based …
- Porous structure
- Modification of pore size and pore size distribution

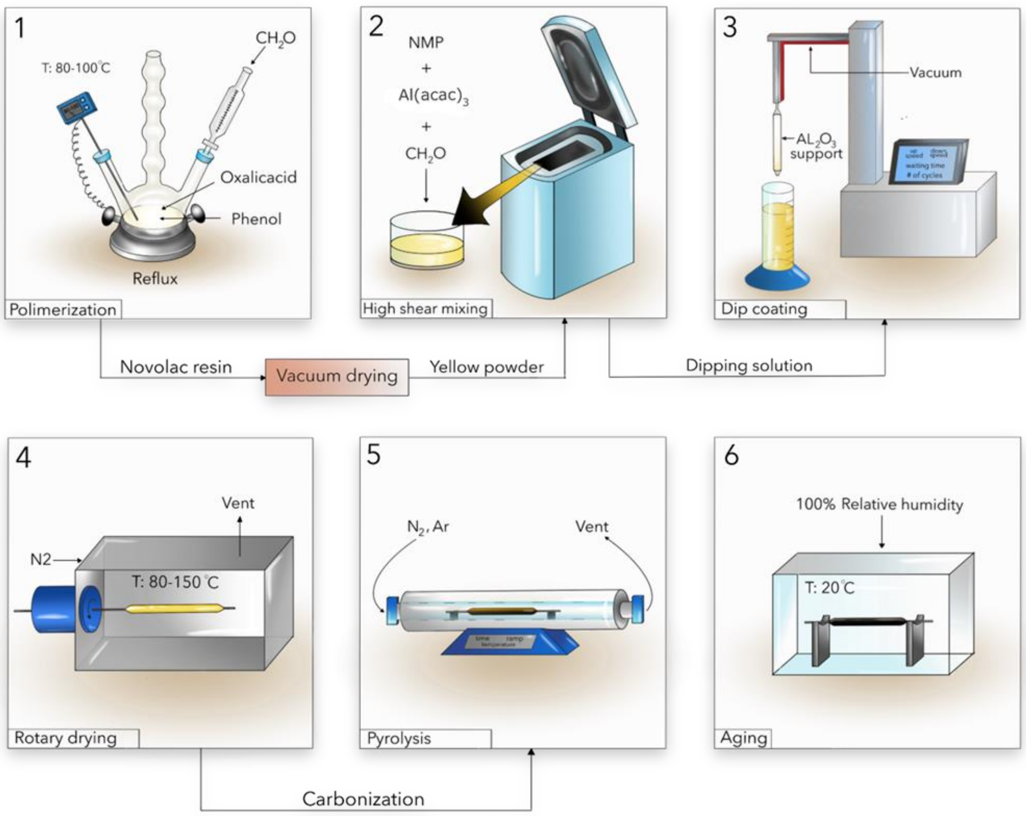




CMSMs

How is it made?

1. Precursor synthesis
2. Dipping solution preparation
3. Coating
4. Polymerization
5. Carbonization
6. Post treatment



Surface diffusion and molecular sieving are the common transport mechanisms

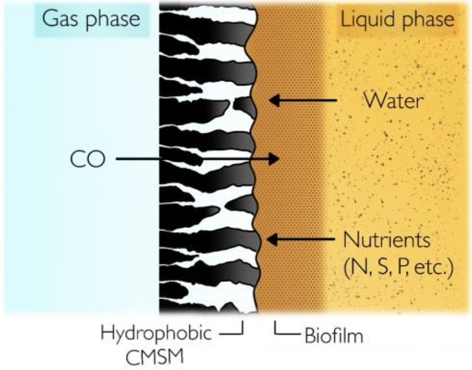
CMSMs

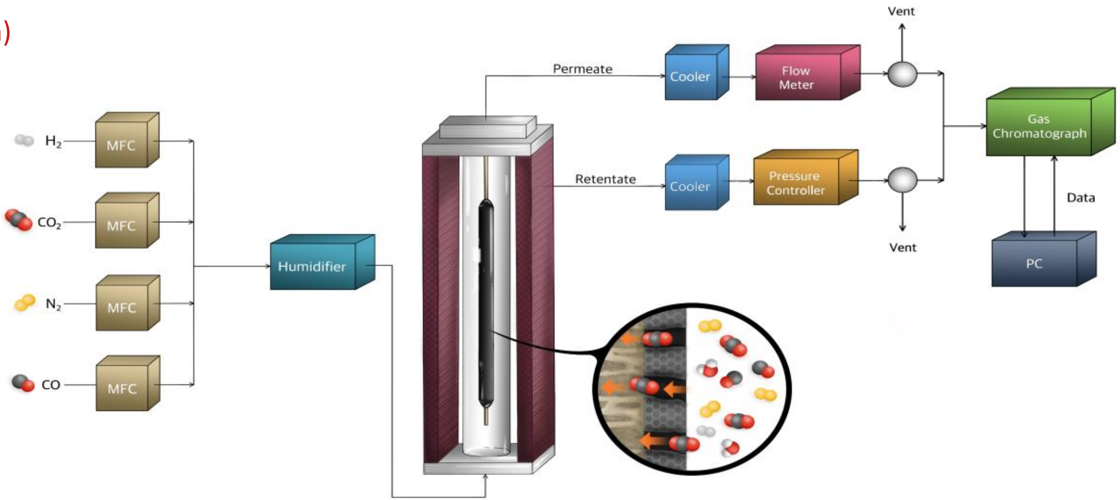
What could be separated?

Any desired molecule with different kinetic diameter compared to other molecules and/or difference in polarity (hydrophilicity/hydrophobicity)

Processes which have:

- Operational temperatures up to 700 °C (no oxygen)
- Operational pressures up to 200 Bar
- Configurations of
  a. Gas separation
  b. Pervaporation (liquid/vapor)
  c. Vapor permeation
  d. Selective gas distribution

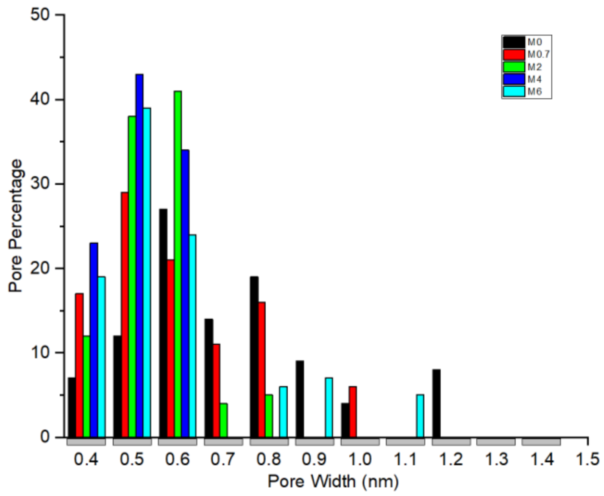


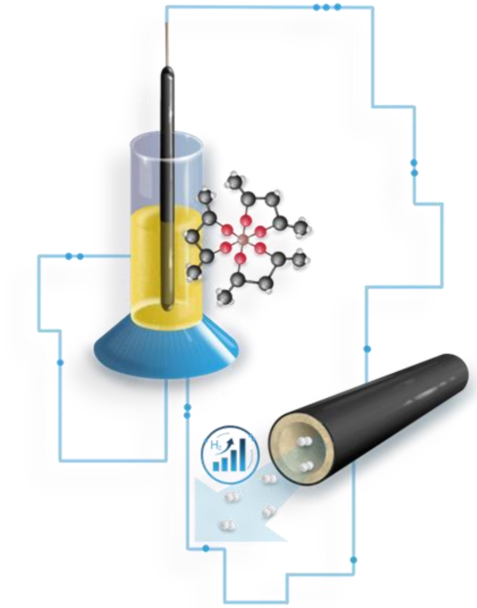


Applications CMSMs

H_2 separation

Al(acac)$_3$ effect on pore size distribution (PSD)





https://doi.org/10.1016/j.ijhydene.2022.02.198

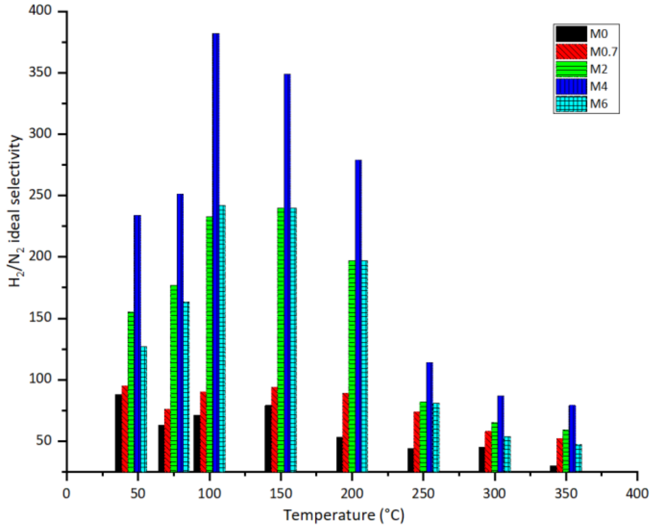
Narrow pore size distribution (PSD)

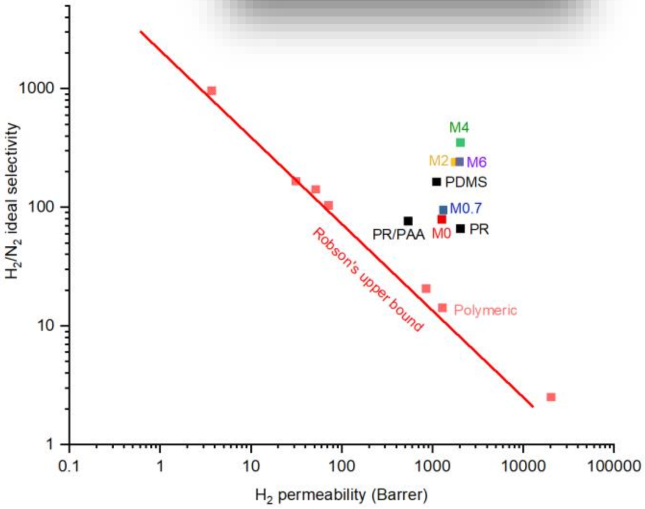
Applications CMSMs

H_2 separation

$Al(acac)_3$ effect on pore size distribution (PSD)

- 382 H_2/N_2 ideal selectivity
- Stable performance up to 350 °C





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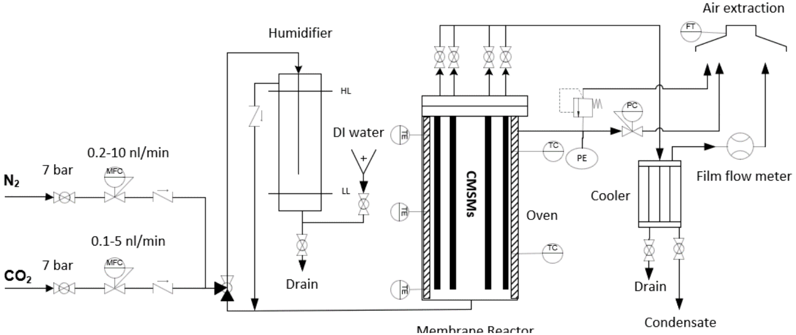
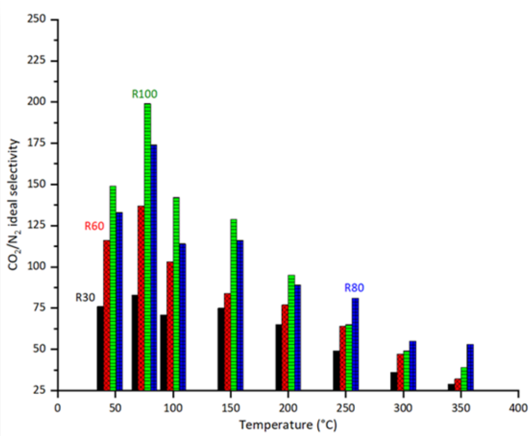
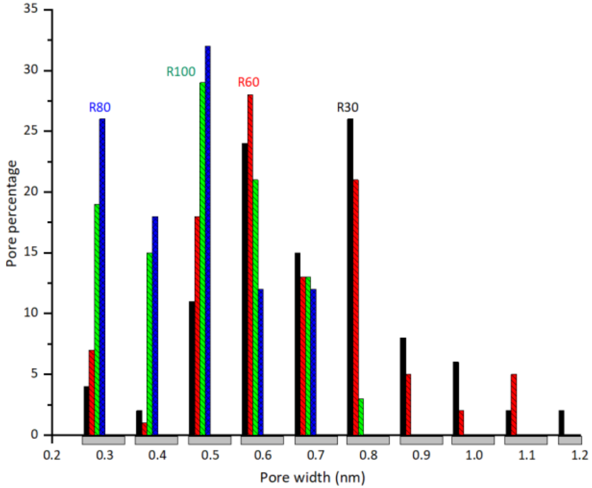
Applications CMSMs

CO_2 separation
CO_2/N_2

Effect of degree of polymerization on PSD
Resorcinol-formaldehyde resin







https://doi.org/10.3390/membranes12090847

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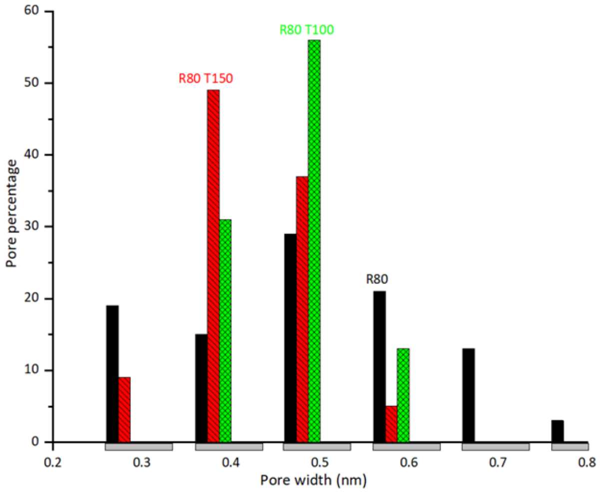
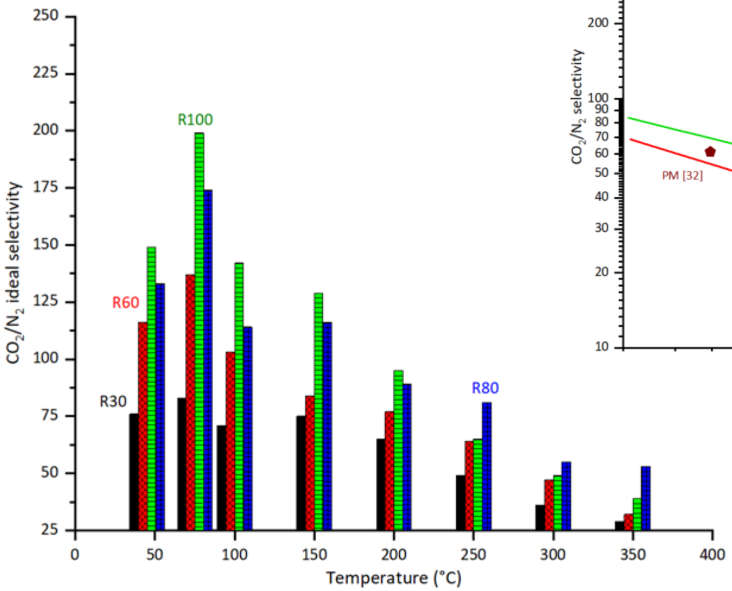
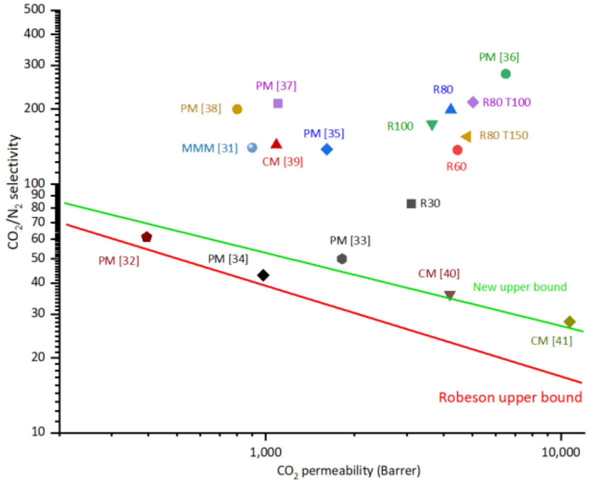
Applications CMSMs

CO_2 separation
CO_2/N_2

Post treatment with oxygen effect on PSD







Fine tuning the PSD with degree of polymerization and oxygen post treatment

https://doi.org/10.3390/membranes12090847

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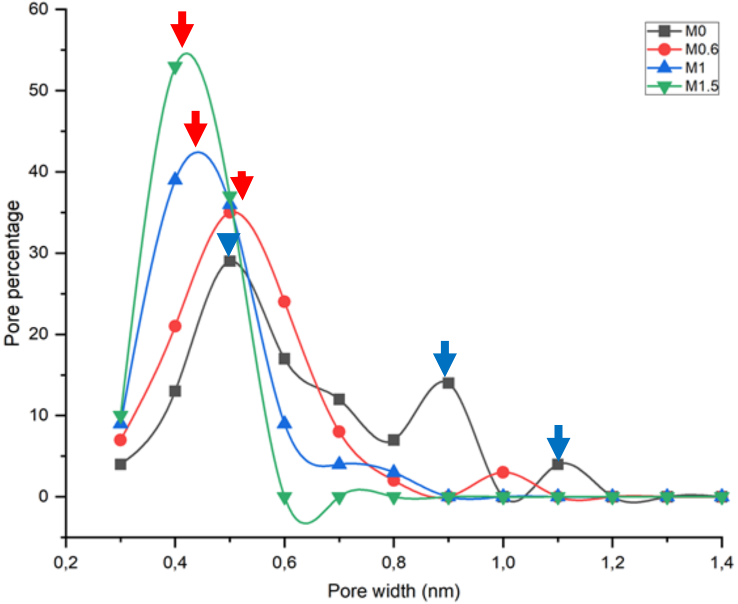
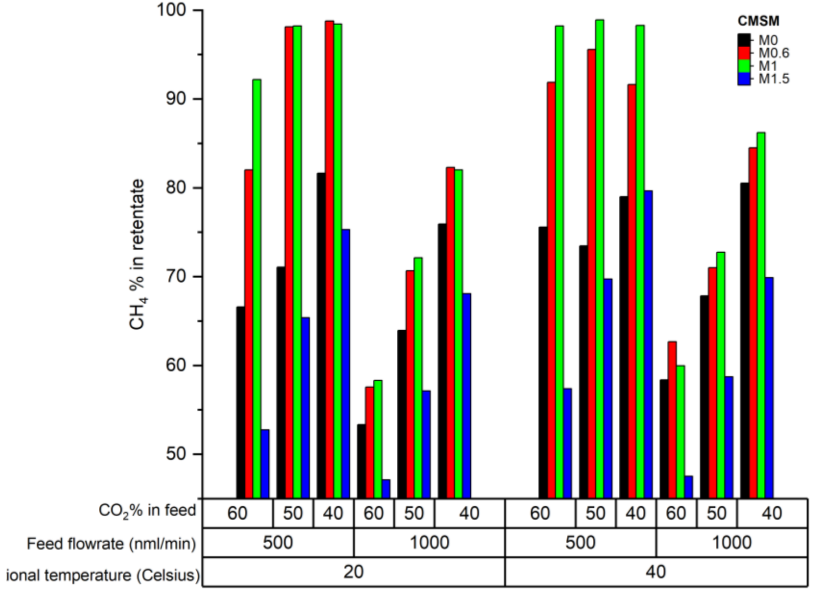
Applications CMSMs

CO_2 separation
CO_2/CH_4 (Biogas upgrading)





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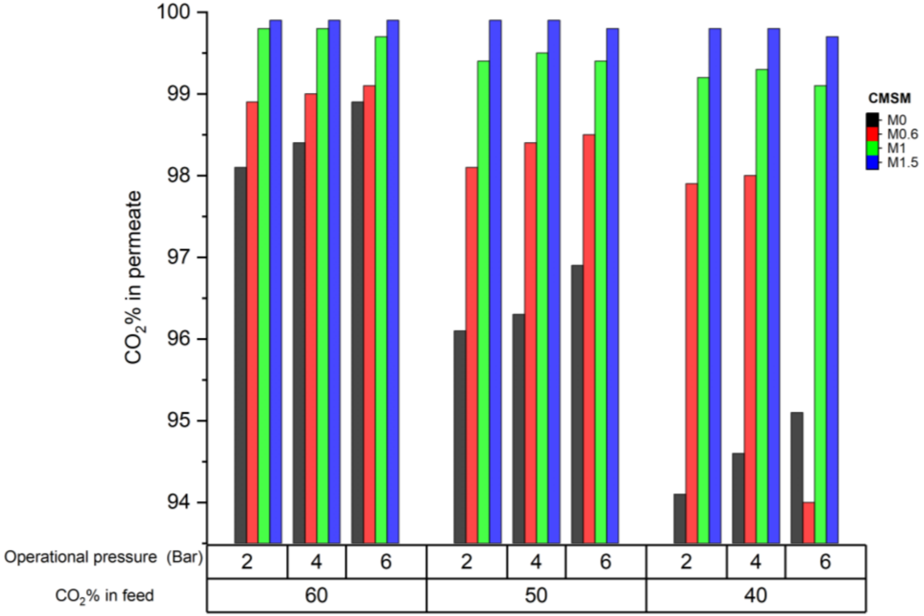
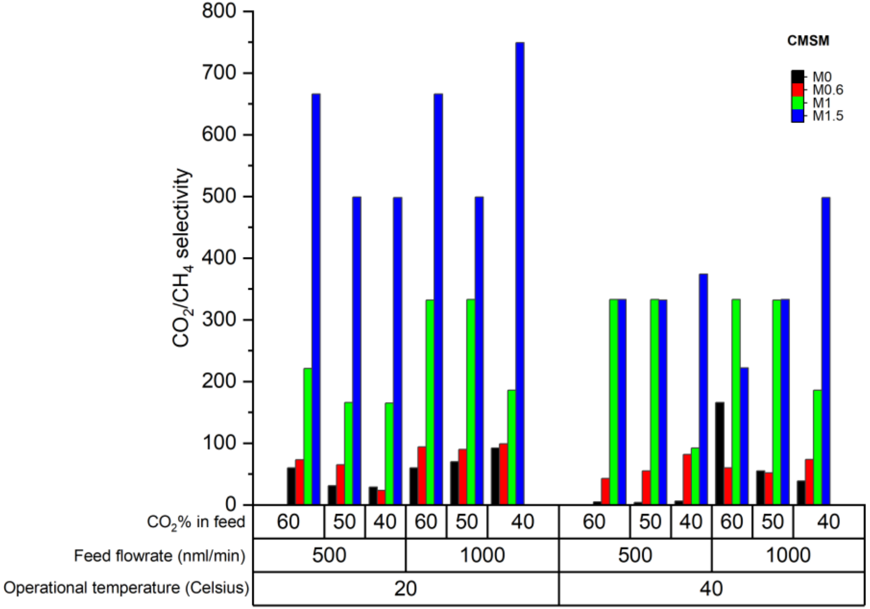
Applications CMSMs

CO_2 separation
CO_2/CH_4 (Biogas upgrading)





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Applications CMSMs

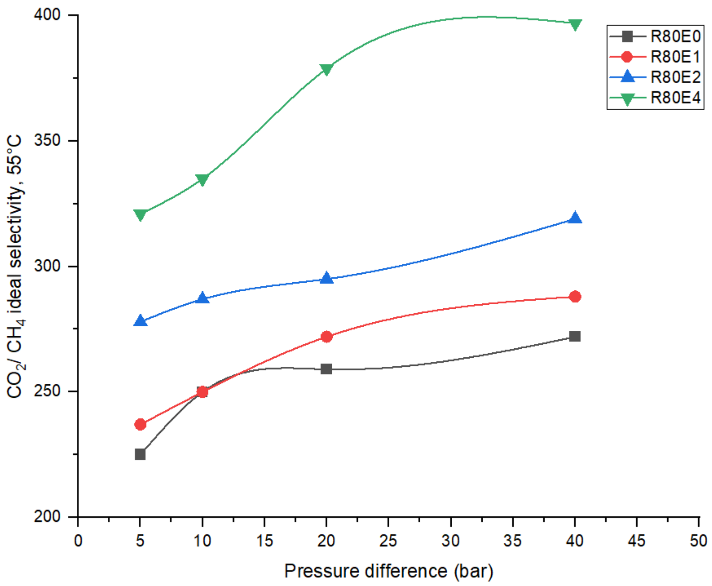
CO_2 separation
CO_2/CH_4 (Natural gas purification)

Effect of pressure on the CMSMs permselectivity

Increased CO_2/CH_4 ideal selectivity with increasing ethylenediamine content

- Increasing the ideal selectivity dependance on the operational pressure with increasing the ethylenediamine content in the dipping solution because of increased surface diffusion and adsorption sites

- Stable performance at 40 bar operational pressure



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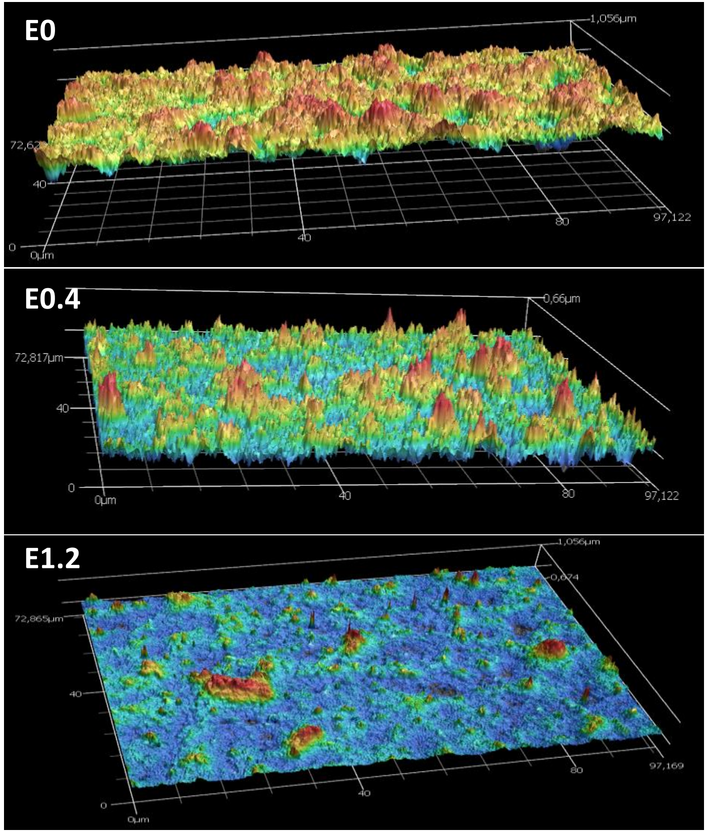
Applications CMSMs

CO_2 separation
CO_2/CH_4 (Natural gas purification)

Novolac – Ethylenediamine co-polymerization

3D laser confocal microscopy



Ethylenediamine effect:

- Reduction in surface roughness (Ra and Rz)
- Increase of membrane stability at higher temperatures and uniform permeance (less thickness variation)

Membrane	Surface roughness (3D laser microscopy)			
	50x (nm)		150 x (nm)	
	Ra*	Rz**	Ra	Rz
E 0	286	2021	202	1280
E 0.4	227	1429	69	475
E 1.2	100	734	94	652

* the average surface roughness, **difference between the tallest (peak) and deepest (valley) on the surface.

https://doi.org/10.1016/j.jcou.2022.102378

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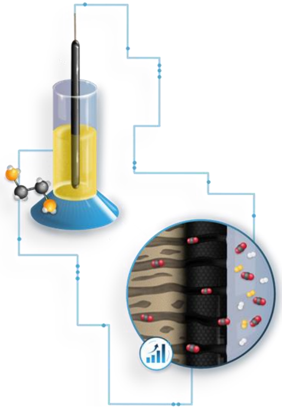
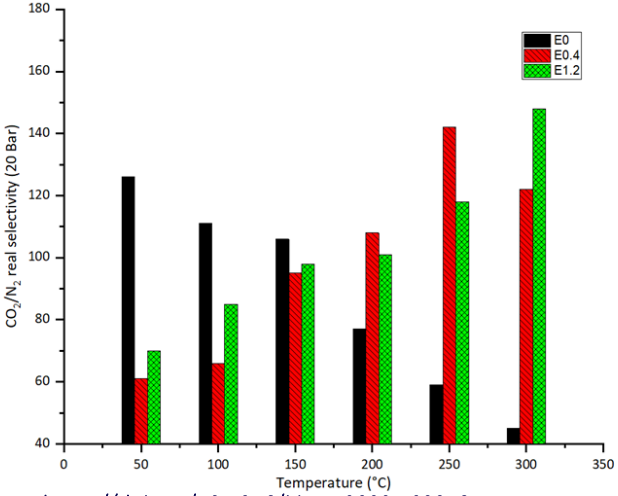
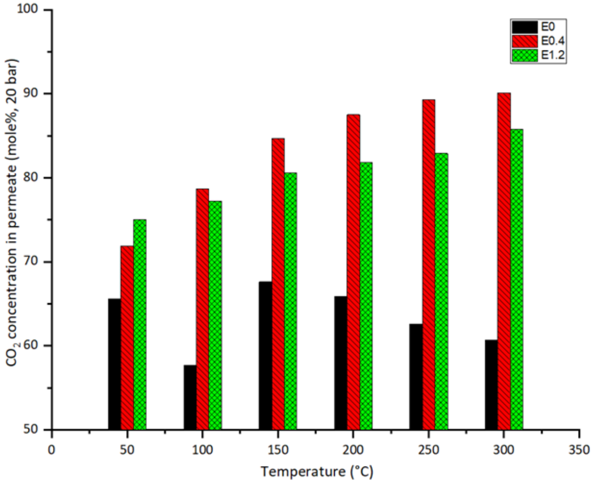
Applications CMSMs

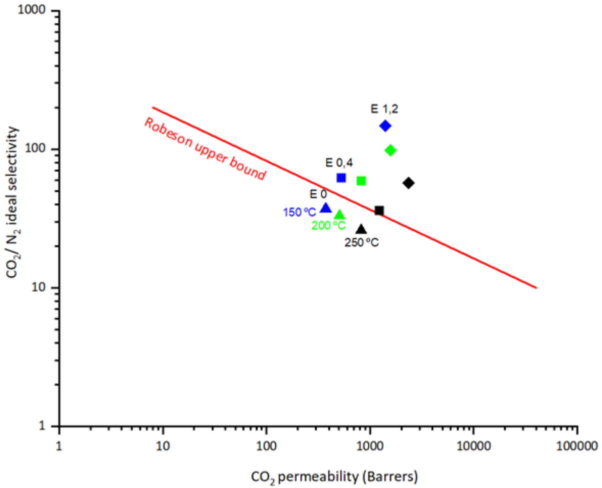


CO_2 separation at elevated pressures and temperatures
CO_2/Mix (Steel mill off gas)

- 152 CO_2/N_2 real selectivity at 300 °C
- 92 % CO_2 in the permeate
- Stable performance







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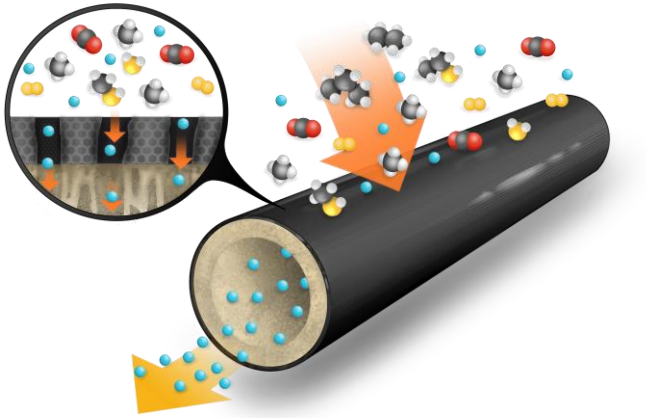
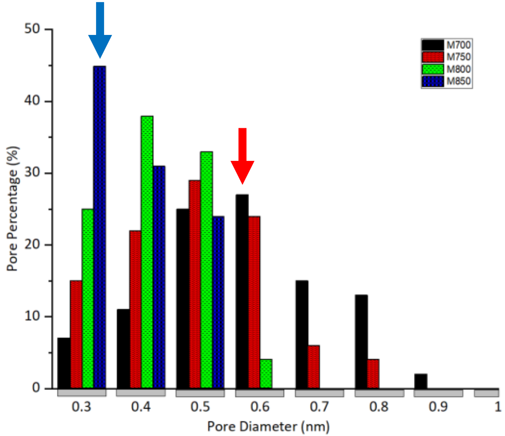
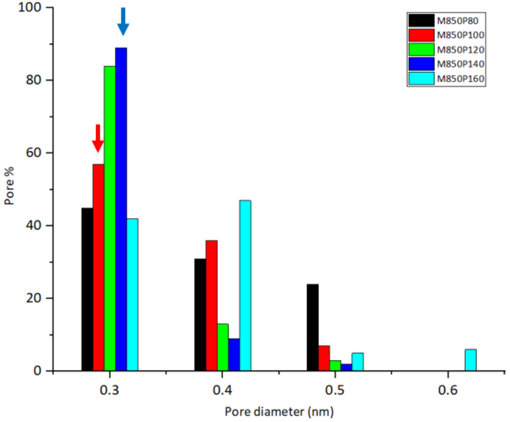
Applications CMSMs

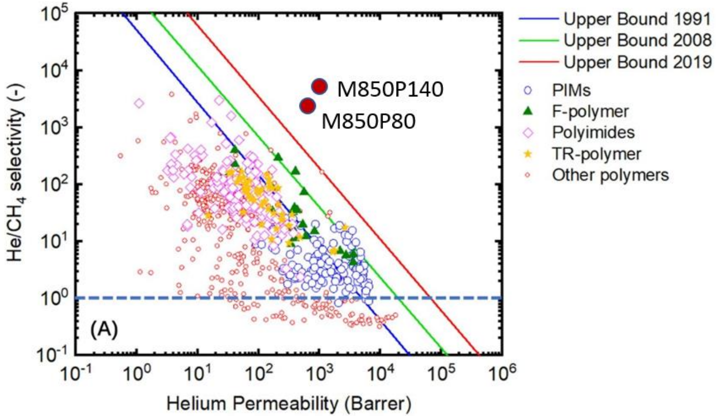


He separation from natural gas

- Shifting the smaller average pore size with increasing the polymerization temperature but there is an optimum
- CMSM carbonized at 850 °C and polymerized at 140 °C , contains 89% of the pores below 0.3 nm in diameter







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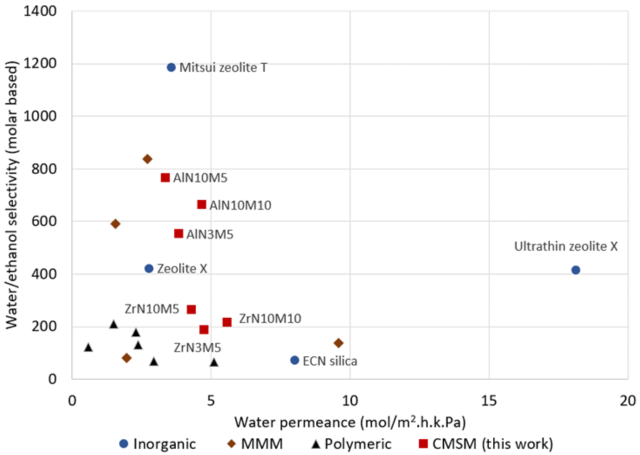
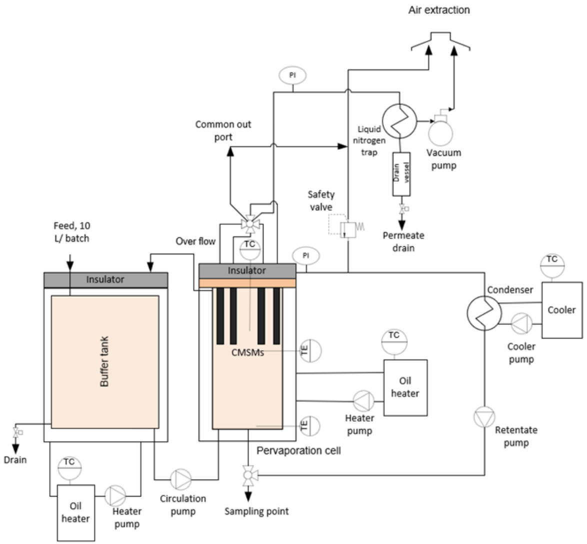
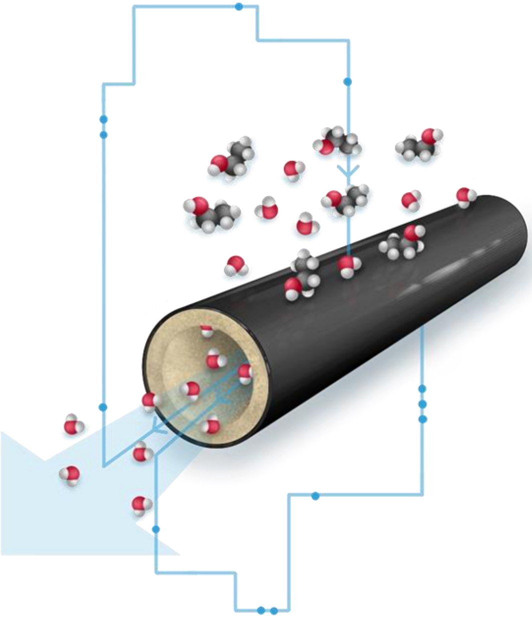
Applications CMSMs

Bioethanol dehydration via pervaporation (2021)

Effect of support roughness, coating parameters investigated
The higher oligomer's molecular weight resulted in higher water/ethanol selectivities.







https://doi.org/10.1016/j.cej.2022.134891

Thanks for your time and attention

Questions, suggestions are welcome

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