MEMBER

ADVANCED **MEMB**RANES AND MEMBRANE ASSISTED PROC**E**SSES FOR PRE- AND POST-COMBUSTION CO_2 CAPTU**R**E

H2020 GRANT AGREEMENT NUMBER: 760944

Start date of project: 01/01/2018 **Duration: 4 years**

WP08 - Dissemination and communication

Webinar on "Process modelling, design and scale-up for CO_2 capture processes" Booklet

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Funding scheme: Innovation action t
Call identifier: H2020-NMBP-2016-2017

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v11	03-03-2022	Final version	TECNALIA	J.L. Viviente

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Dissemination Level		
PU	Public	X
PP	Restricted to other programme participants (including the Commission Services)	
RE	Restricted to a group specified by the consortium (including the Commission Services)	
CO	Confidential, only for members of the consortium (including the Commission Services)	
CON	Confidential, only for members of the Consortium	

(*) for generating such code please refer to the Quality Management Plan, also to be included in the header of the following pages

(**) indicate the acronym of the partner that prepared the document

Content

1. EXECUTIVE SUMMARY

1.1. Description of the deliverable content and purpose

The present document includes the presentation of the webinar on "Process modelling, design and scale-up for CO2 capture processes" organised by the project MEMBER on February 23rd, 2022. The webinar was hosted by TUE. The agenda is shown in the figure hereafter.

Webinar: Process modelling, design and scale-up for CO_2 capture processes

February 23th, 2022 at 10:30 (CET)

Agenda

10:30 – 10:50 Introduction to the MEMBER project
José Luis Viviente (TECNALIA)

10:50 – 11:10 Aspects of modelling MOF-based mixed matrix membranes
Freek Kapteijn (TUDELFT)

11:10 – 11:30 Gas separation through post and pre-combustion membranes - mathematical modelling in Comsol Multiphysics.
Magdalena Malankowska (DTU, before UNIZAR)

11:30 – 11:50 Membrane and system modelling
Hans ten Dam (HYGEAR)

11:50 – 12:10 Modelling of MA-SER reactor for H_2 production with CO_2 capture
Stefan Pouw (TU/e)

12:10 – 12:30 Advances on membrane technologies in hydrocarbon processing industry
Vittoria Cosentino (KT)

12:30 – 12:40 Final remarks and closure
Jose Luis Viviente

Figure 1. Agenda of the webinar organised by MEMBER

2. Presentations

2.1. Introduction to the MEMBER project (José Luis Viviente – TECNALIA)

MEMBER WEBINAR ON:
Modelling of membranes materials and systems

Advanced MEMBranes and membrane assisted procEsses for pre- and post- combustion CO_2 captuRe

MEMBER

https://member-co2.com/

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 760944

Duration: 4.5 years. *Starting date: 01 January 2018*

Budget: € 9 596 541,50 *EU contribution: €7 918 901*

Contact: joseluis.viviente@tecnalia.com

Outline

1. Project Objectives
2. Partnership
3. Overall approach and methodology
4. Expected results
5. Design and modelling in MEMBER

1. Project Objectives

The key objective of the MEMBER project is the **scale-up and manufacturing of advanced materials** and their demonstration at industrially relevant conditions (TRL6) in **novel membrane-based technologies that outperform current technologies for pre- and post-combustion CO_2 capture in power plants as well as H_2 generation with integrated CO_2 capture and meet the targets of the European SET plan.**

Three different technological solutions involving advanced materials will be developed and demonstrated at three different end user's facilities:

- Advanced Mixed Matrix Membranes (MMMs) for pre- and post-combustion CO_2 capture in power plants (H_2/CO_2 & CO_2/N_2 respect.)
- A combination of metallic hydrogen membranes and CO_2 sorbent integrated into an advanced Membrane Assisted Sorption Enhanced Reforming (MA-SER) process for pure H_2 production with CO_2 capture.

1. Project Objectives

Targets

Prototype A

Pre-combustion capture in power plants using MMMs at HYGEAR reforming equipment.

CCR	Capture Cost
> 90%	**< 30 €/ton**

Prototype B

Post-combustion capture in power plants using MMMs at the 8.8 MW CHP facilities of Agroger (GALP, Portugal).

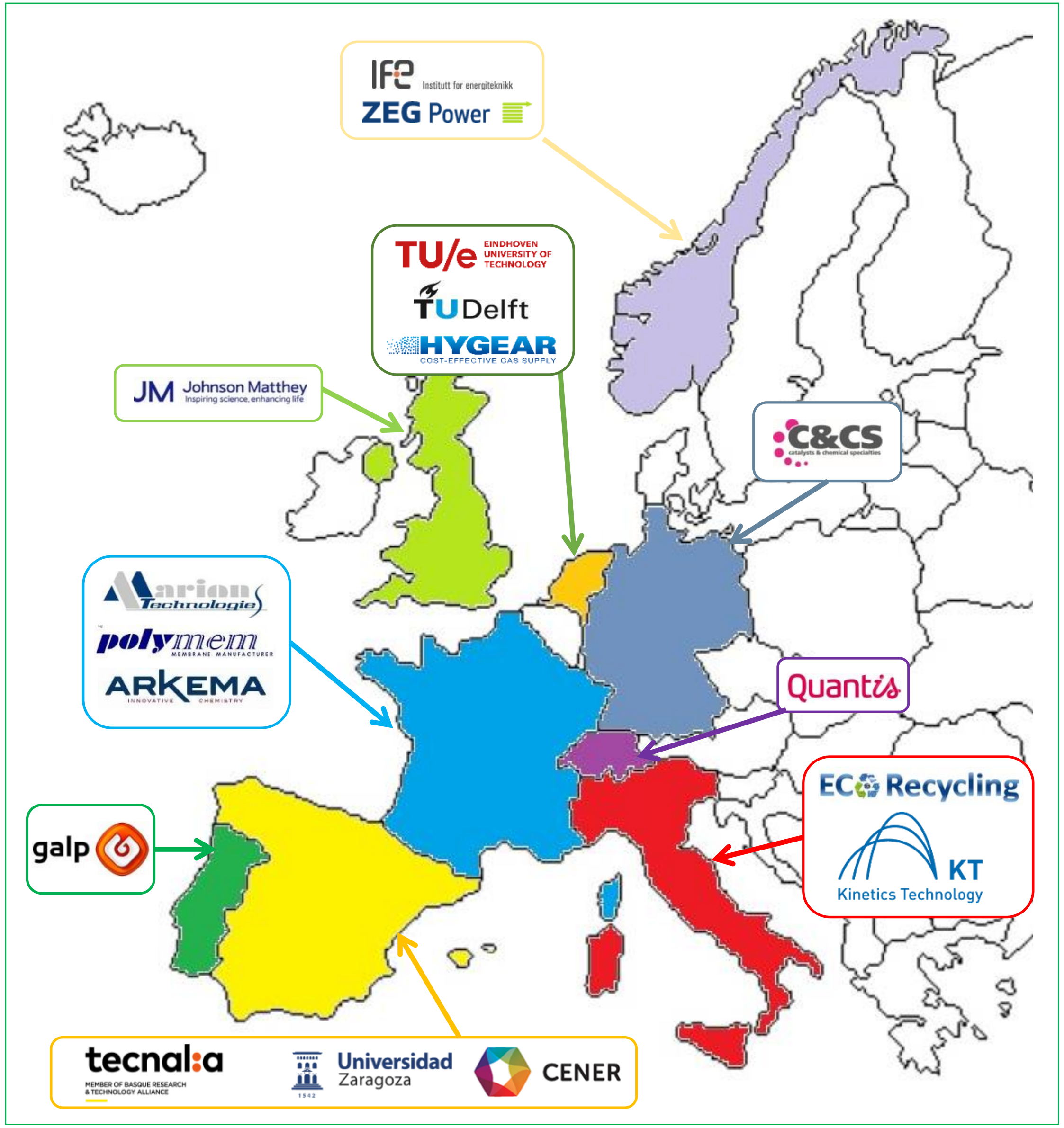
CCR	Capture Cost
> 90%	**< 40 €/ton**

Prototype C

Pure hydrogen production with integrated CO_2 capture using MA-SER at the IFE-HyNor (Norway) under the supervision of ZEG POWER.

CCR	Capture Cost
> 90%	**< 30 €/ton**

2. Partnership



- Multidisciplinary and complementary team.
- 17 partners from 9 countries.
- Industrial oriented (65%): 11 SME/IND + 6 RTO/HES
- 7 SMEs (41%) & 4 IND (24%)

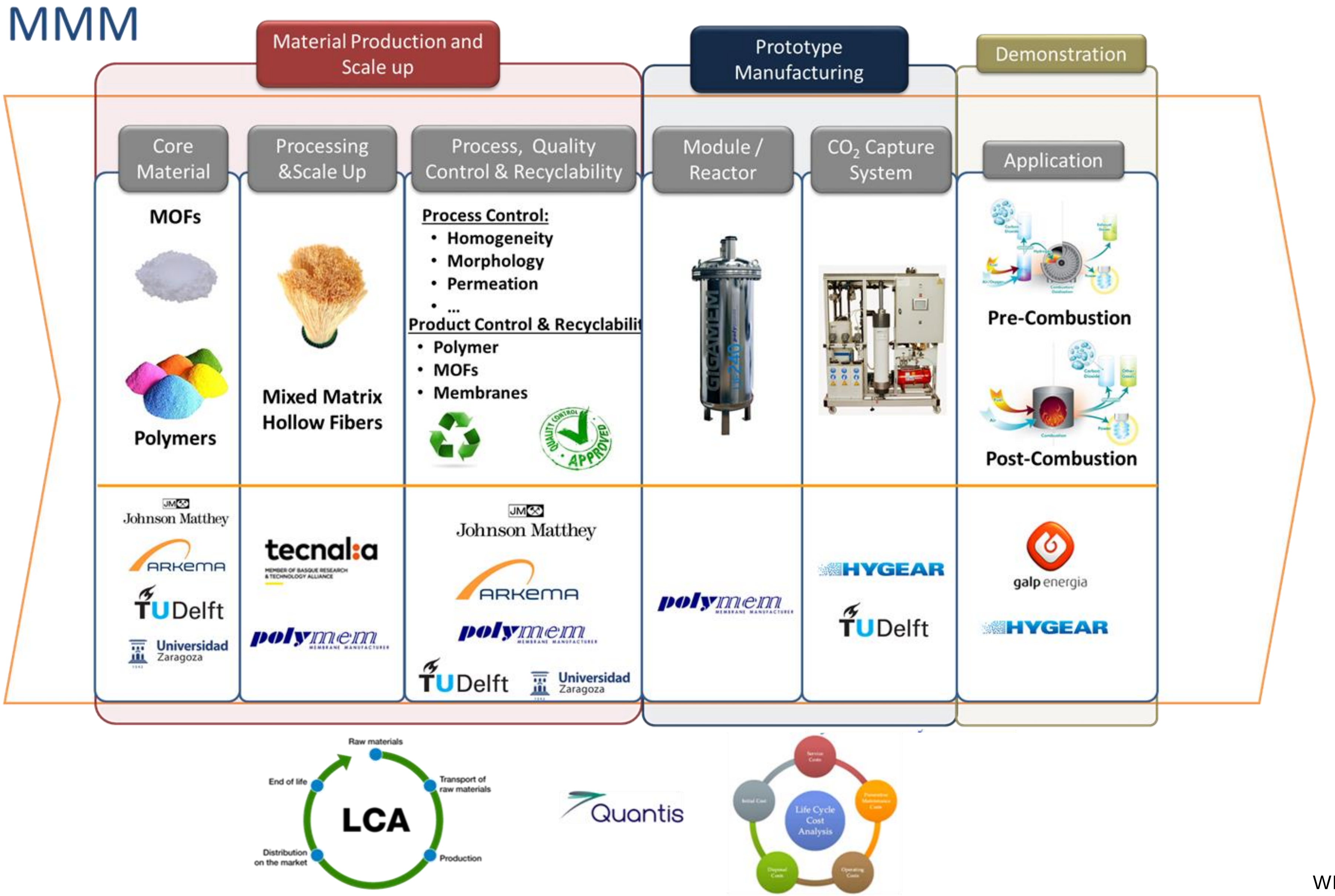
1 TECNALIA, RTO, Spain
2 TUE, HES, Netherlands
3 TUDELFT, HES, Netherlands
4 IFE, RTO, Norway
5 UNIZAR, HES, Spain
6 CENER, RTO, Spain
7 MTEC, SME, France
8 C&CS, SME , Germany
9 POLYMEM, SME, France
10 HYGEAR, SME, Netherlands
11 ECOREC, SME, Italy
12 ZEG, SME, Norway
13 QUANTIS, SME, Switzerland
14 KT, IND, Italy
15 GALP, IND, Portugal
16 ARKEMA, IND, France
17 JM, IND, United Kingdom

2. Partnership: Consortium synergies

MEMBER gathers the entire value chain:

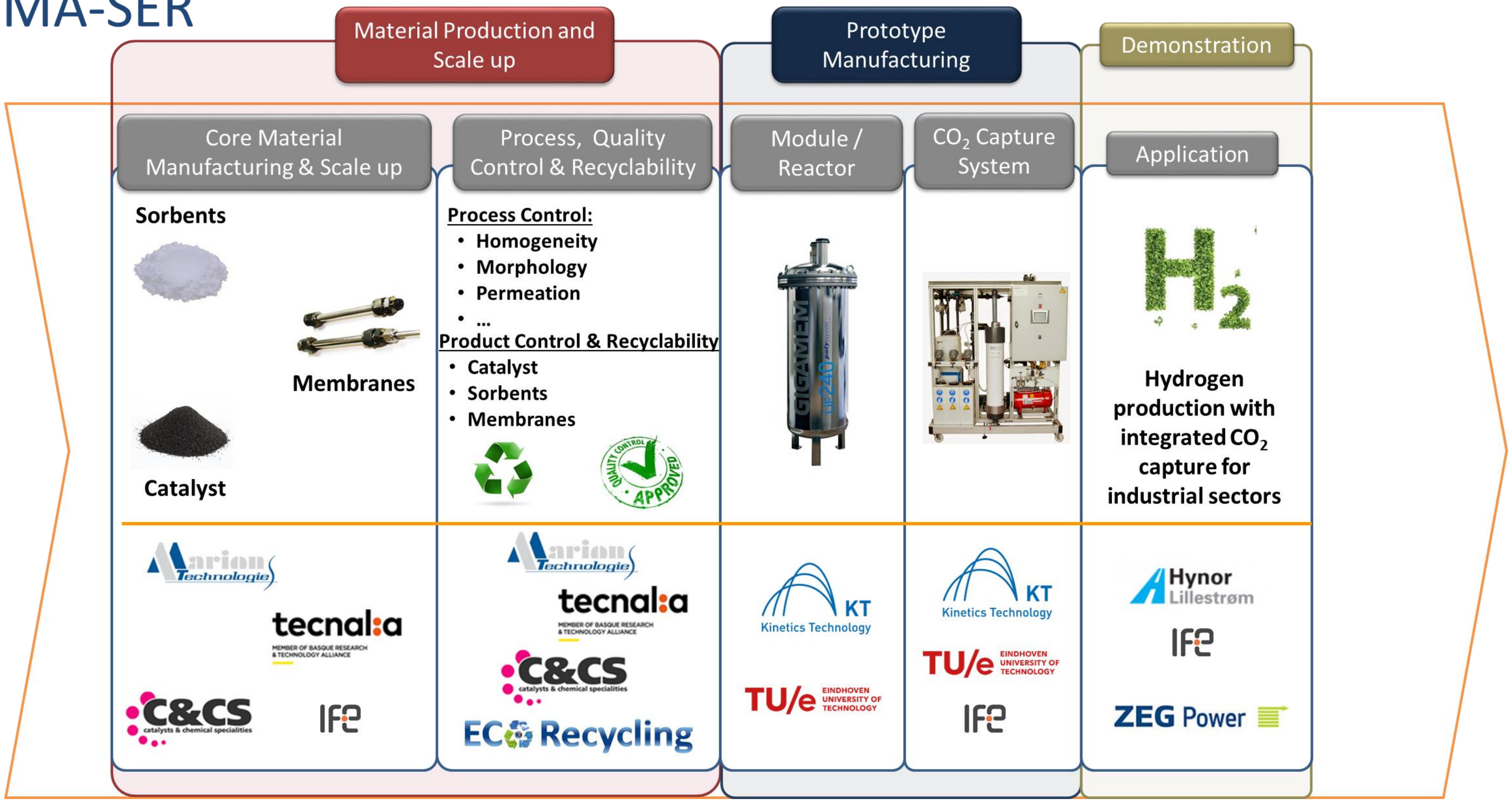
- Commercial actors in Materials development, processing and supply (JM for MOFs, ARKEMA for polymers, C&CS for catalysts and MTEC for Sorbents)
- one industrial partner focused on membrane manufacturing (POLYMEM),
- two engineering companies focused on system design and integration (HYGEAR and KT),
- 4 partners for the demonstration of the technologies (HYGEAR and GALP for MMMs for pre-and post-combustion CO_2 capture respectively, and IFE-HYNOR H_2 Technology Center under the supervision of ZEG POWER for MA-SER concept),
- one SME focused on sustainability and recyclability of materials produced (ECO RECYCLING)
- one SME for Life Cycle Assessment (QUANTIS).
- industrial partners supported by recognized research organizations experts in the fields of material development (IFE, TUDELFT and UNIZAR), membrane development (TECNALIA) and process engineering (TUe).

3. Overall approach and methodology

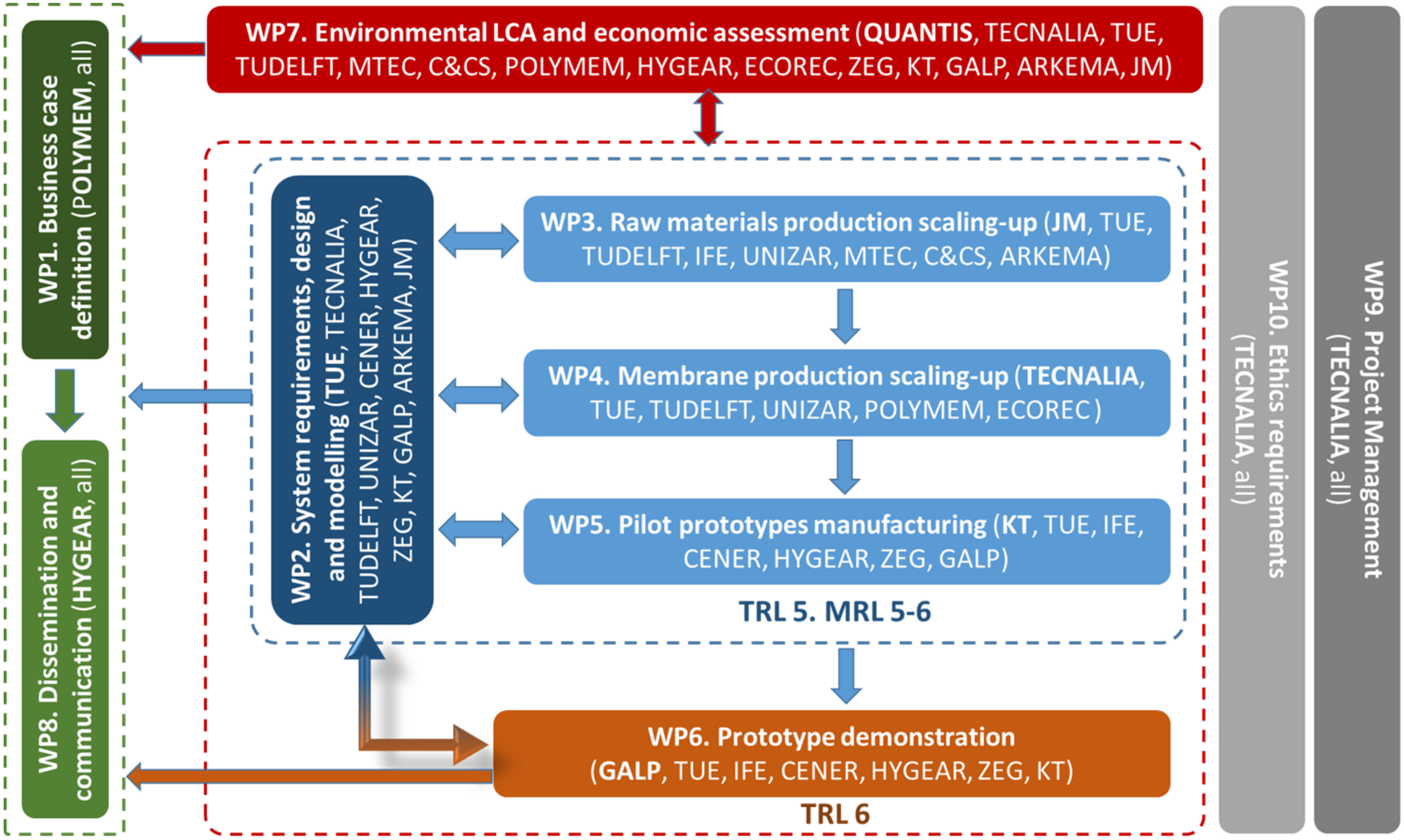


3. Overall approach and methodology

MA-SER



3. Overall approach and methodology



4. Expected results

#	Main exploitation product/ technologies/ others
1	MMM based system for pre-combustion CO_2 capture
2	MMM based system for post-combustion CO_2 capture
3	MA-SER system for pure H_2 production with integrated CO_2 capture
4	Advanced polymers for post-combustion MMMs
5	Advanced MOFs for pre- and post-combustion MMMs
6	Advanced MMMs for pre- and post-combustion
7	Advanced sorbents for MA-SER
8	Advanced catalysts for MA-SER
9	Advanced Pd-based H_2 membranes for MA-SER
10	Software tool for Membrane reactor and SER design. Membrane separation modules
11	Consulting services on LCA of CO_2 capture

5. Design and modelling in MEMBER

- Industrial requirements
- Membrane modelling
  - Polymeric membranes (flat sheet and HF)
  - MMMs membranes (flat sheet and HF)
  - Pd-based membranes
- Reactor modelling (MA-SER concept)
- Pre- and Post-combustion CO_2 capture systems modelling (MMMs concept)
- Technical and economical assessment and comparison with benchmark technologies

Modelling of pre-combustion gas permeation through flat sheet and HF membranes

COMSOL

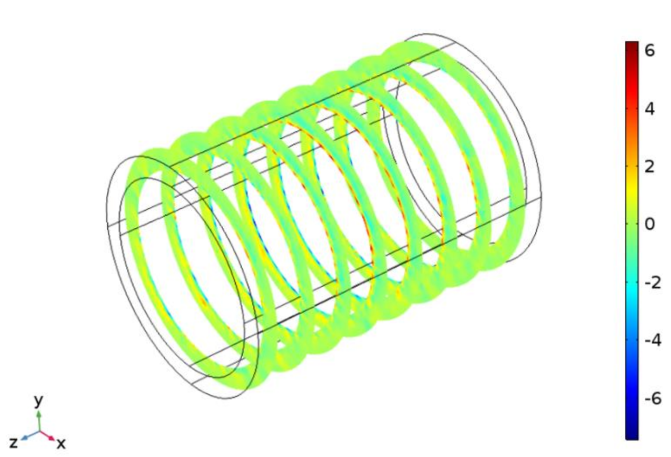
$$\rho(\mathbf{u}\cdot\nabla)\mathbf{u} = \nabla\cdot\left[-p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T) - \frac{2}{3}\mu(\nabla\cdot\mathbf{u})\mathbf{I}\right] + \mathbf{F}$$

$$\nabla\cdot(\rho\mathbf{u}) = 0$$

$$\mathbf{u}\cdot\nabla c_i = D\cdot\nabla^2 c_i$$

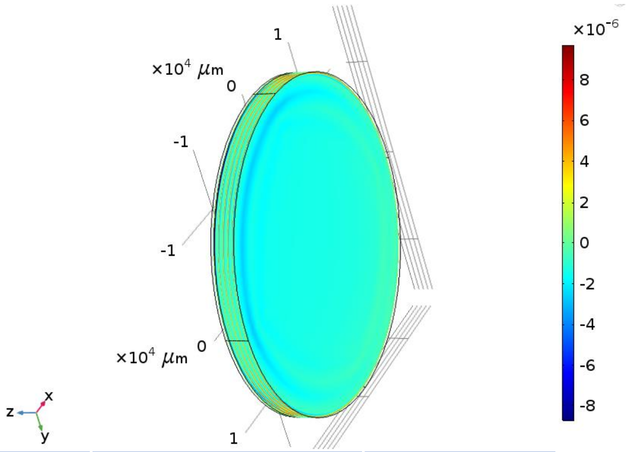
CO_2 total flux (convective+diffusive) through a PBI HF membrane

Total flux [mol/m²*s]



CO_2 total flux (convective + diffusive) through a PBI flat sheet membrane

Total flux [mol/m²*s]



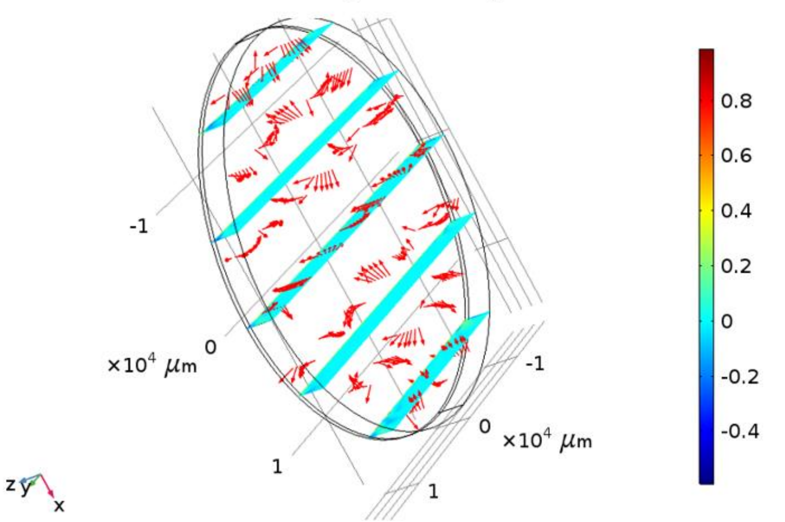
Total flux CO_2 (mol/m²·s)	Total flux H_2 (mol/m²·s)	Sel H_2/CO_2	
$1.18\cdot10^{-4}$	$6.83\cdot10^{-4}$	5.8	Exp
$1.20\cdot10^{-4}$	$6.00\cdot10^{-4}$	5.0	Model
$7.33\cdot10^{-3}$	$7.52\cdot10^{-2}$	10.2	Exp
$5.80\cdot10^{-3}$	$6.30\cdot10^{-2}$	10.9	Model

5. Design and modelling in MEMBER

Modelling of post-combustion gas permeation through flat sheet and HF membranes

CO_2 total flux (convective+diffusive) through a Pebax 1657 flat sheet membrane

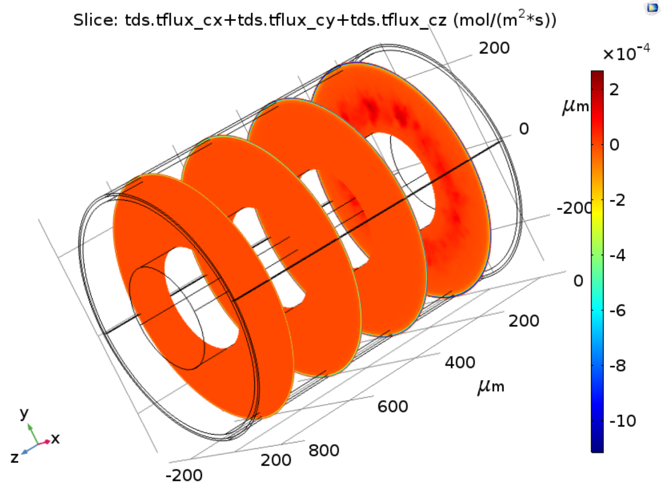
Total flux [mol/m²*s]



Total flux CO_2 (mol/m²·s)	Total flux N_2 (mol/m²·s)	Sel CO_2/N_2	
$2.68 \cdot 10^{-5}$	$4.69 \cdot 10^{-6}$	32.3	**Exp**
$3.30 \cdot 10^{-5}$	$6.10 \cdot 10^{-6}$	30.7	**Model**

CO_2 total flux (convective + diffusive) through a Psf/PDMS/Pebax 1657 HF membrane

Total flux [mol/m²*s]

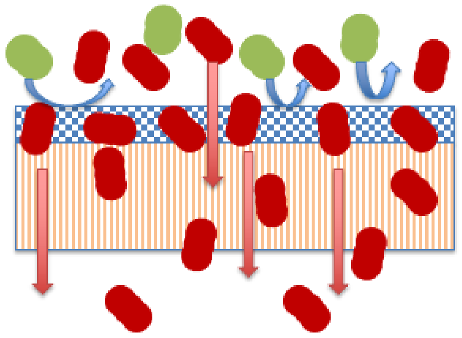


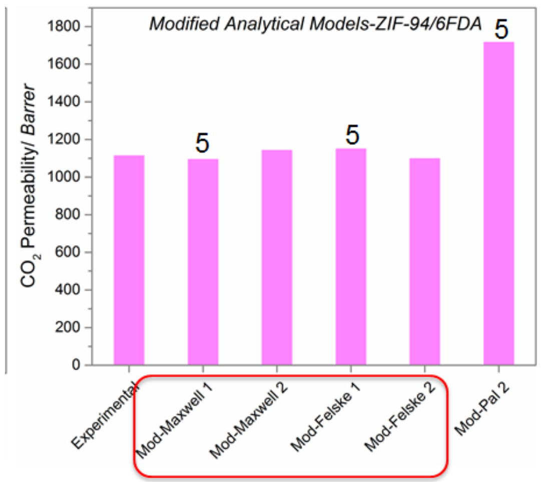
Total flux CO_2 (mol/m²·s)	Total flux N_2 (mol/m²·s)	Sel CO_2/N_2	
$1.90 \cdot 10^{-4}$	$3.52 \cdot 10^{-5}$	30.7	**Exp**
$2.70 \cdot 10^{-4}$	$3.41 \cdot 10^{-5}$	44.9	**Model**

5. Design and modelling in MEMBER

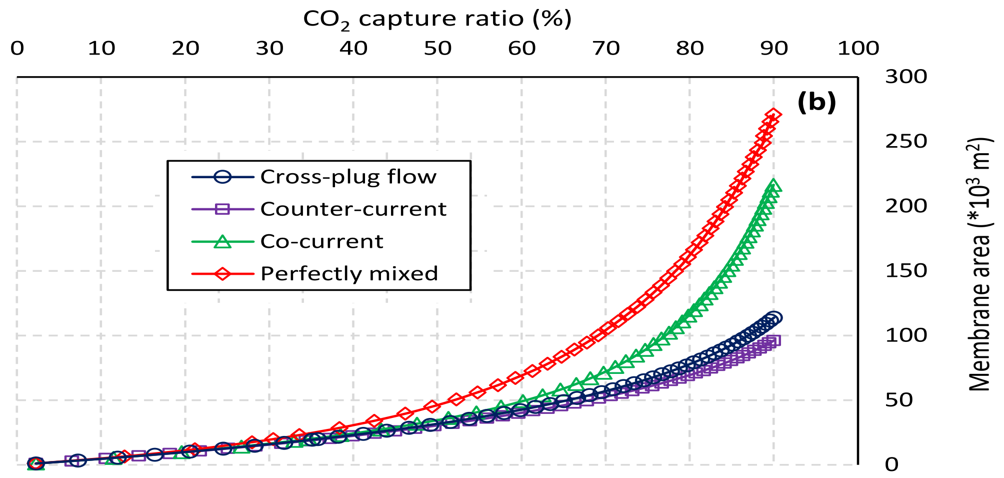
Modelling Modelling MMM – Mixed Matrix Membranes

- Selective layer models
- Inclusion porous support
- Contacting flow pattern

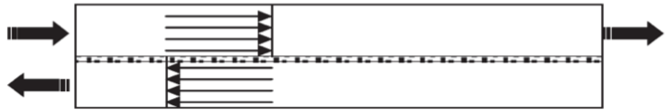




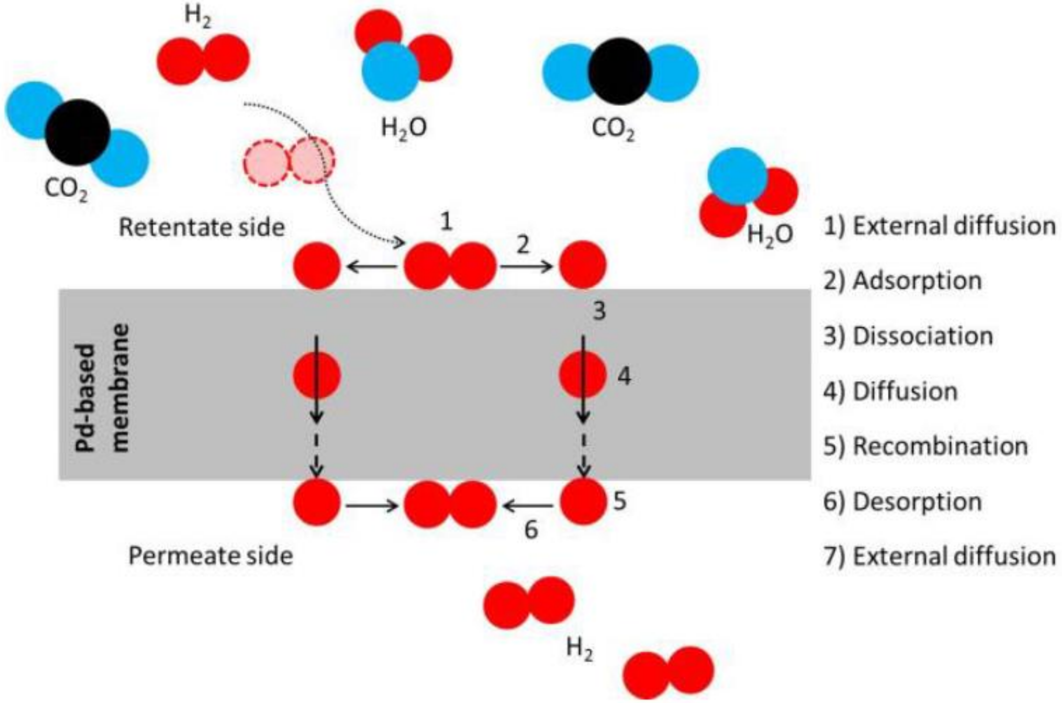
- Felske and modified Felske and Maxwell models describe MMM data best
- Sorption & diffusion p,T incorporation
- Knudsen transport support



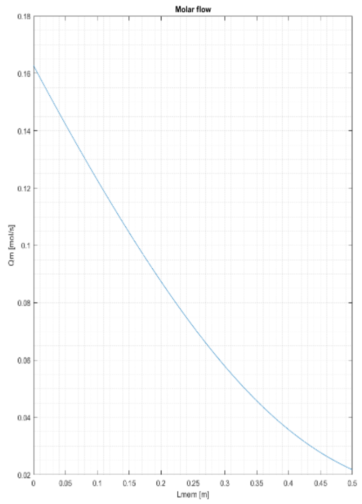
- Countercurrent operation optimal

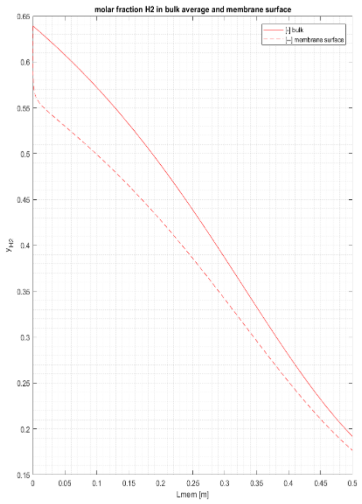


Dense membrane module modelling



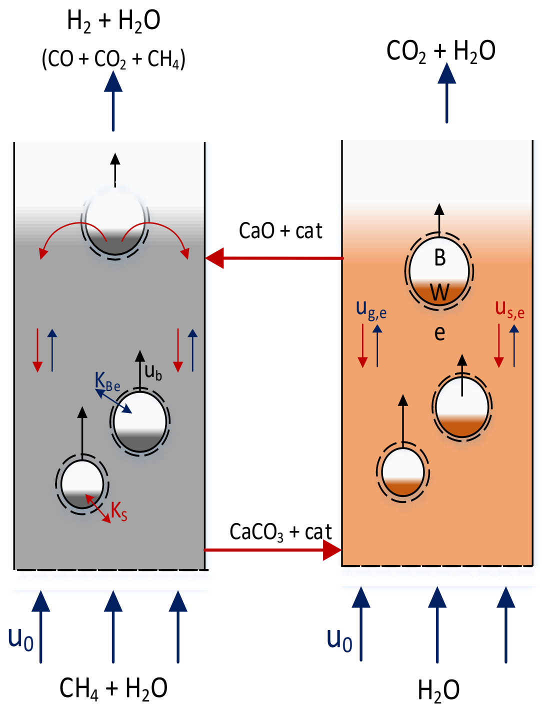
- Identified the transport mechanisms throughout the membrane module
- Determined the largest transfer resistance
- Modelled the dense membrane module for H_2 separation

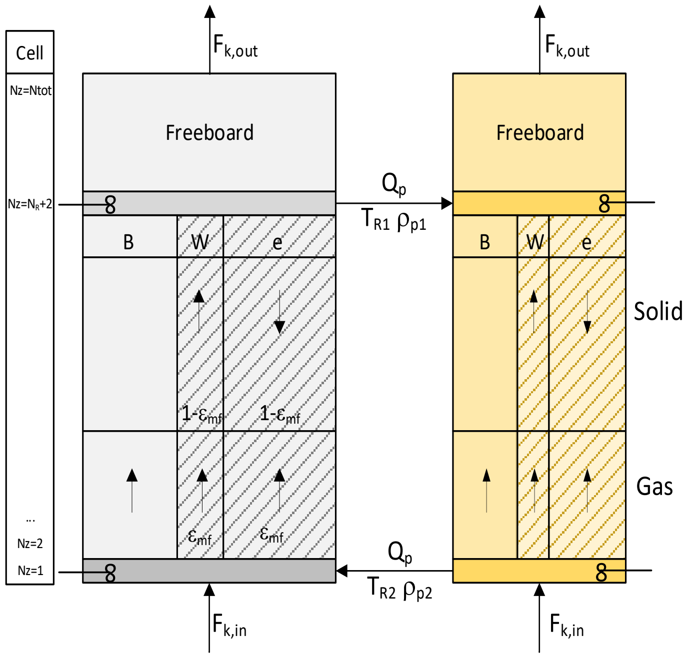




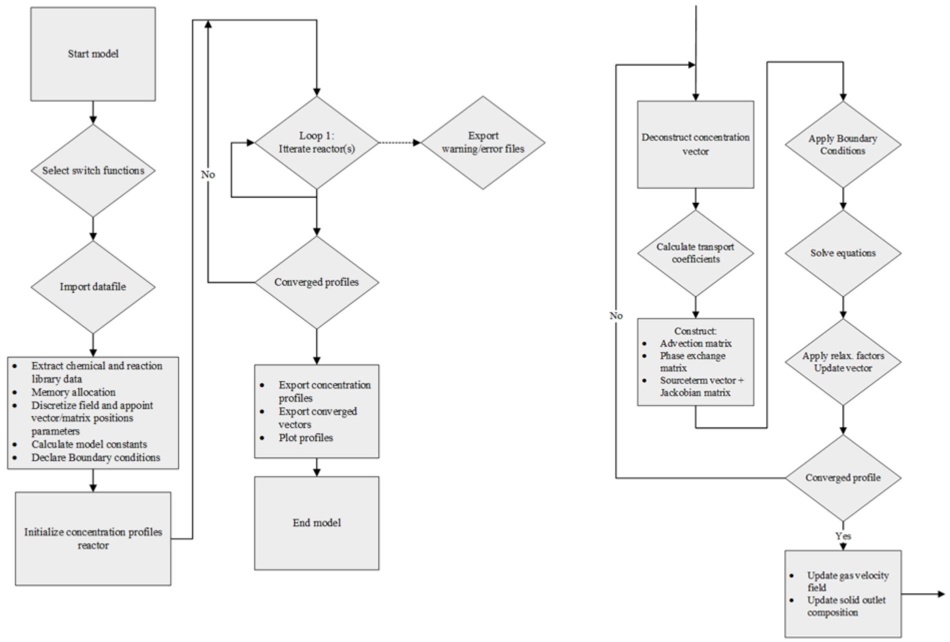
5. Design and modelling in MEMBER

MA-SER reactor modelling





- Modelled the MA-SER reactor system using phenomenological model
- Analyzed the reactor performance for improvement based on process limitations
- Model can be used for full scale process simulations for (dual) fluidized bed design



(a) Model code construction (b) Loop 1: Reactor evaluation

5. Design and modelling in MEMBER

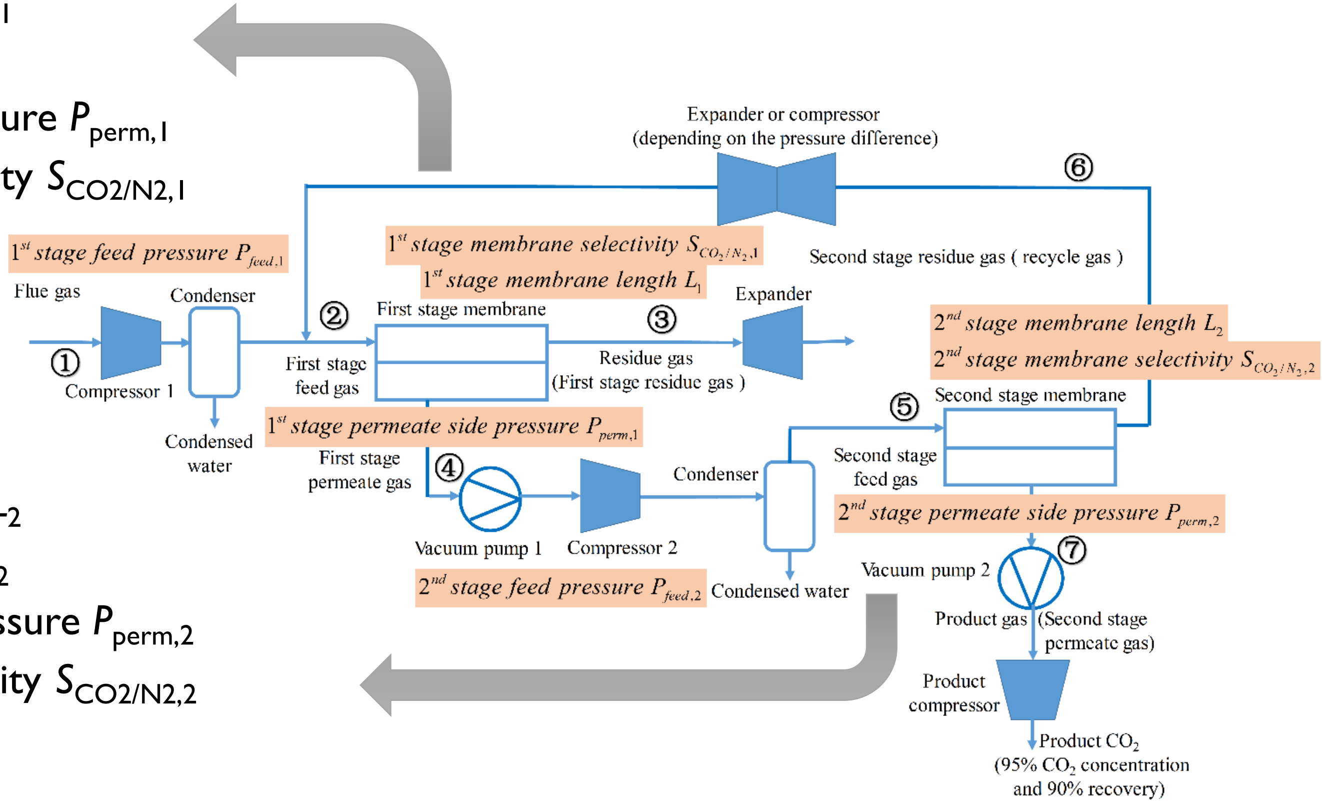
MMM systems modelling

- Genetic Algorithm for process optimization
  - For the typical two-stage membrane separation process, **eight** independent variables are to be optimized:

- 1st stage membrane length L_1
- 1st stage feed pressure $P_{feed,1}$
- 1st stage permeate gas pressure $P_{perm,1}$
- 1st stage membrane selectivity $S_{CO2/N2,1}$

Multivariable Optimization

- 2nd stage membrane length L_2
- 2nd stage feed pressure $P_{feed,2}$
- 2nd stage permeate side pressure $P_{perm,2}$
- 2nd stage membrane selectivity $S_{CO2/N2,2}$



Genetic Algorithm is instrumental in optimizing the multivariable CO_2 capture processes

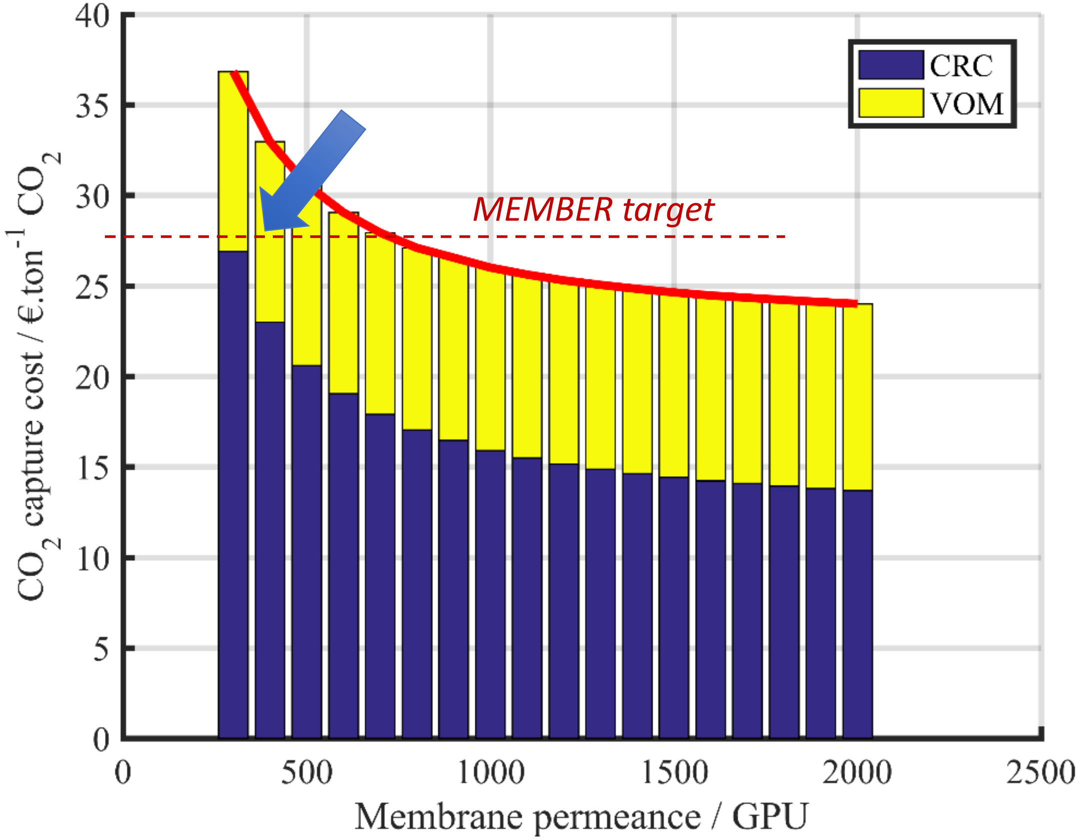
5. Design and modelling in MEMBER

Technical and economic assessment Prototype A & B

- Based on GA system lay-outs, includes:
  - Sensitivity analysis regarding
    - Permeance
    - Selectivity
  - Cost breakdown
  - Reference: 300 GPU/ 70 Sel.

CO_2 capture cost

VOM -- Variable Operating and Maintenance
CRC -- Capital Related Cost



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12:10 – 12:30	Advances on membrane technologies in hydrocarbon processing industry – Vittoria Cosentino (KT)

Thank you for your attention

https://member-co2.com/

Contact:

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Acknowledgement: For the CO2 molecule used in the logo:The original uploader was Frederic Marbach at French Wikipedia [GFDL (http://www.gnu.org/copyleft/fdl.html)

2.2. Aspects of modelling MOF-based mixed matrix membranes (Freek Kapteijn – TU Delft)

Aspects of modelling MOF-based mixed matrix membranes

Mixed Matrix Membranes for CO_2 capture - II

Freek Kapteijn

Catalysis Engineering

Delft University of Technology

Member workshop Eindhoven 15 January 2020

Mixed Matrix Membranes for CO_2 capture

Practical aspects of

membrane performance testing

and interpretation

Freek Kapteijn

Catalysis Engineering

Delft University of Technology

What you can expect…..

- Objective
- Basics quick wrap-up
  - Definitions
  - The Maxwell model analysed
  - Issues and beyond
- Recent directions
- Take home message

Objective lecture

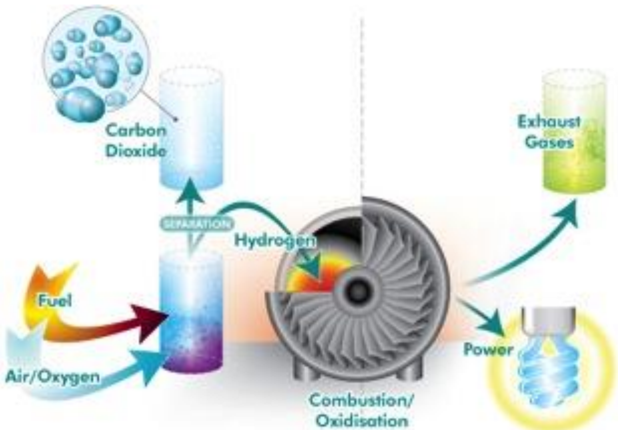
Focus on selective layer

- Modeling basics of mixed matrix membranes
  - Predictive?
  - Message
- Directions development reaching targets CCS
  - MOF-type based MMMs

Prototypes A and B

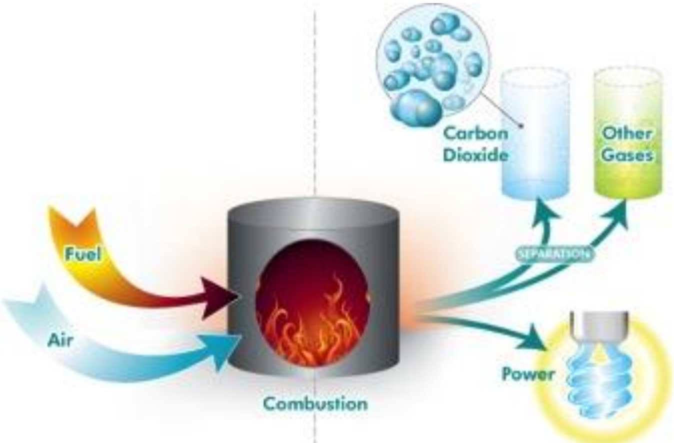
Membrane separation ≡ Energy efficiency

Pre-combustion CO_2 capture



CO_2 / H_2 mixtures

Post-combustion CO_2 capture



CO_2 / N_2 mixtures

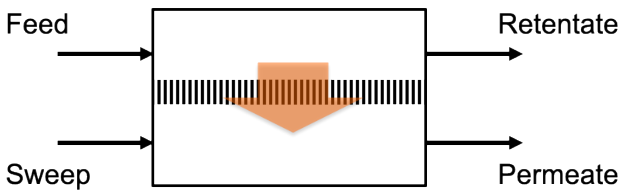
Bio-gas, natural gas upgrading CO_2 / CH_4 mixtures

H_2 selective membranes

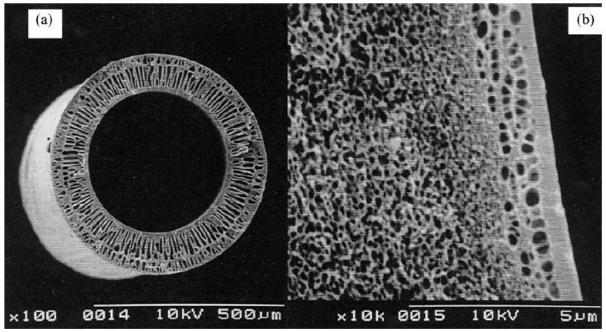
CO_2 selective membranes

Membrane performance

- Characterization membrane in operation
  - **Flux** through membrane (mol s^{-1} m^{-2})
    - of a specific component
      - as single component, in a mixture
    - dependency on operational variables
      - (partial) pressures, temperature
  - Separation of a mixture
  - Comparison with other systems
    - Normalization
      - Applied partial pressure difference - **Permeance**
      - Membrane thickness - **Permeability**



Definitions



SI units

- Flux
  - molar transport rate of a component per unit membrane area

$$J_i = \frac{N_i}{A} \qquad \frac{\text{mol}}{\text{s} \cdot \text{m}^2}$$

- Permeance *membrane performance property, HF membrane*
  - Flux normalized for partial pressure difference of component over membrane

$$P_i = \frac{J_i}{\Delta p_i} \qquad \frac{\text{mol}}{\text{s} \cdot \text{m}^2 \cdot \text{Pa}}$$

GPU

- Permeability *materials property, slab membrane*
  - Permeance normalized for thickness separation layer of membrane

$$\mathcal{P}_i = P_i \cdot d \qquad \frac{\text{mol} \cdot \text{m}}{\text{s} \cdot \text{m}^2 \cdot \text{Pa}}$$

Barrer

Definitions – other units

SI units

- Flux
  - molar transport expressed in ml_{STP} (1 mmol = 22.4 cm^3 @ 0°C, 1 atm)

$$\frac{cm^3_{STP}}{s \times cm^2} \qquad 0.446 \frac{mol}{s \times m^2}$$

- Permeance
  - **Gas Permeation Unit** $GPU = 10^{-6} \frac{cm^3_{STP}}{s \times cm^2 \times cmHg}$ $\quad 3.346 \times 10^{-10} \frac{mol}{s \times m^2 \times Pa}$

- Permeability
  - **Barrer**

$$Barrer = 10^{-10} \frac{cm^3_{STP} \times cm}{s \times cm^2 \times cmHg} \qquad 3.346 \times 10^{-16} \frac{mol \times m}{s \times m^2 \times Pa}$$

Units interconversion - relation

- Relation between GPU (permeance) and Barrer (permeability):
  - Membrane of thickness 1 μm (10^{-4} cm) and 1 Barrer permeability has a permeance of 1 GPU:

$$\mathcal{P}_i = \frac{P_i}{d}$$

$$\frac{1\ \text{Barrer}}{10^{-4}\ \text{cm}} = 10^{-10}\frac{\text{cm}^3_{STP}\times\text{cm}}{\text{s}\times\text{cm}^2\times\text{cm Hg}}\times 10^{4}\ \text{cm}^{-1} = 10^{-6}\frac{\text{cm}^3_{STP}}{\text{s}\times\text{cm}^2\times\text{cm Hg}} = 1\ \text{GPU}$$

(re-)MEMBER Targets

- Protoytype A – Precombustion
  - Permeance H_2 = 100 GPU
  - H_2/CO_2 selectivity = 18

- Prototype B – Post-combustion
  - Permeance CO_2 = 300 GPU
  - CO_2/N_2 selectivity = 70

Thickness *variable*

Comparison properties-performance

- Barrer — GPU

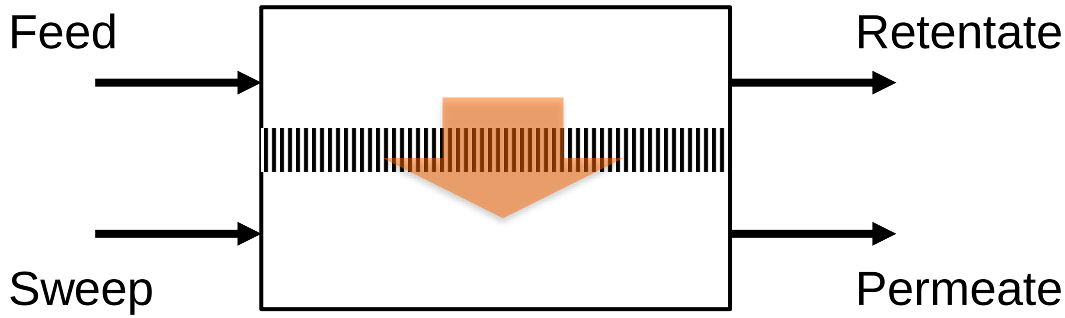
$$P_i = \frac{P_i}{d}$$

thickness 0.3 μm (3.10^{-5} cm)

Barrer	GPU
– 30	100
– 90	300
– 500	1667
– 800	2667
– 1200	4000

$$\frac{1\ \text{Barrer}}{3 \times 10^{-5}\ \text{cm}} = 10^{-10}\ \frac{\text{cm}^3_{STP} \times \text{cm}}{\text{s} \times \text{cm}^2 \times \text{cm Hg}} \times \frac{10^5}{3}\ \text{cm}^{-1} = 3.3 \times 10^{-6}\ \frac{\text{cm}^3_{STP}}{\text{s} \times \text{cm}^2 \times \text{cm Hg}} = 3.3\ \text{GPU}$$

Other nomenclature membranes



- Separation factor

mixed gas selectivity

$$a_{AB} = \frac{(X_A / X_B)_{permeate}}{(X_A / X_B)_{retentate}}$$

- Ideal separation factor

$$ideal\ S_F(AB) = \frac{P_A}{P_B}$$

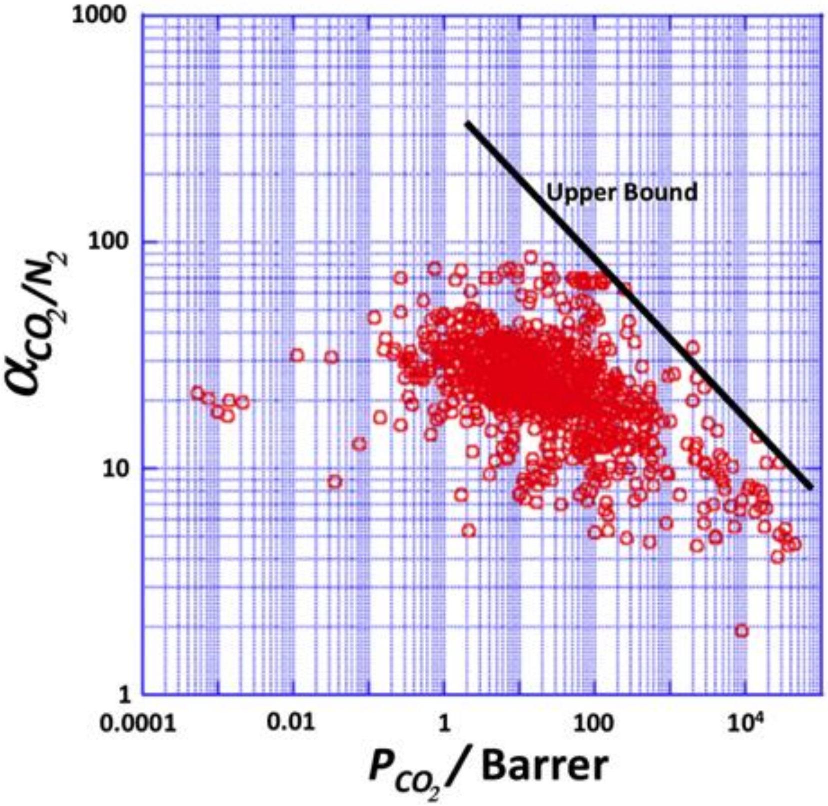
ideal selectivity, pure gases

PureApplChem 68(1996)1479-1489 IUPAC-Membranes
W.J. Koros, Y.H. Ma, and T. Shimidzu

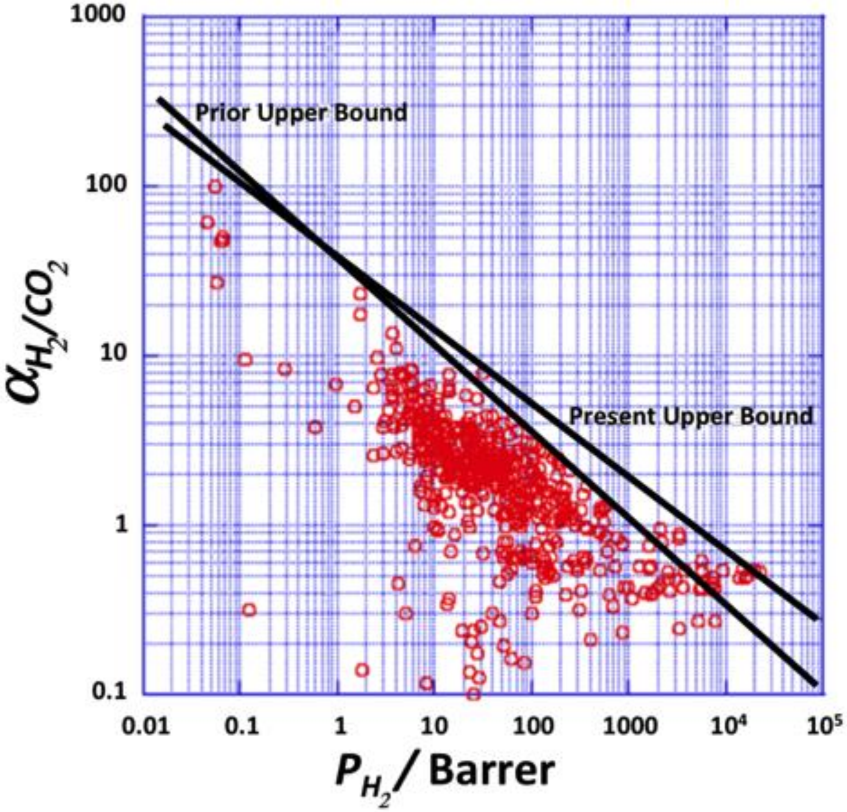
Membrane performances - polymers

Robeson upper bounds

Post-combustion



Pre-combustion

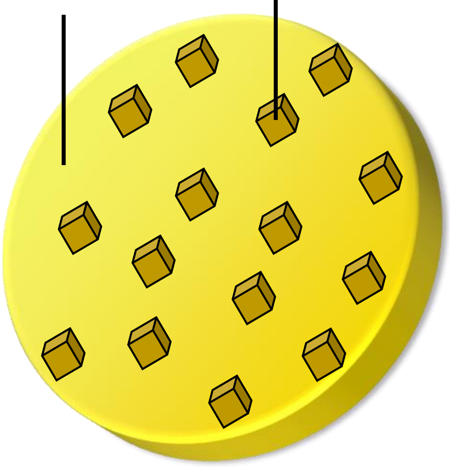


- Ideal separation factor – single gas permeation
- Room temperature

Delft University of Technology

L.M. Robeson / Journal of Membrane Science 320 (2008) 390–400

What is a Mixed-Matrix Membrane?



- Silica, Alumina
- Carbon, CMS
- Clays
- Zeolites
- CNT
- **MOFs, COFs, HOFs**

Polymeric membrane
(continuous phase)

containing an inorganic '**Filler**'

Combination is expected/desired
to exhibit an improved *performance:*

- **Permeability**
- **Separation selectivity**
- Stability
  - Less plasticization
  - No loss performance

Mixed Matrix Membranes (MMMs)

Polymeric Membranes

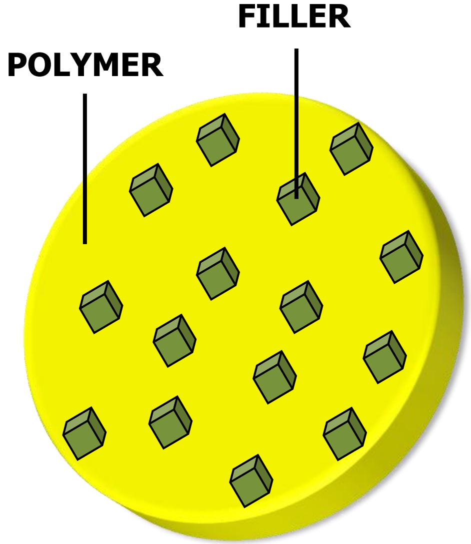
Pros:
- Mechanical stability
- Easy processing and low price

Cons:
- Thermal and chemical stability
- Low permeability

Inorganic Membranes

Pros:
- Chemical stability
- Gas sieving properties

Cons:
- Mechanical stability (brittle)
- Complex processing and expensive



Mixed Matrix Membranes

Filler (Molecular sieve)
+
Matrix (Polymer)

- Mechanical stability
- Easy processing and low price

- Chemical stability
- Gas sieving properties

Improvement?

Chung, T. S.; Jiang, L. Y.; Li, Y.; Kulprathipanja, S., *Prog. Polym. Sci.* 32 **(2007)** 483-507
Zimmerman, C. M.; Singh, A.; Koros, W. J., *J. Membr. Sci.* 137 **(1997)** 145-154.

Transport modeling

Sorption and Diffusion

Polymeric membranes:

$$P_i \approx D_i \cdot S_i$$

$$\alpha_{A/B} \approx \frac{D_A \cdot S_A}{D_B \cdot S_B}$$

Mixed matrix membranes:

Homogeneous distribution filler

Combined result filler & polymer performance

Sorption and **diffusivity** filler can affect
permeability and selectivity
often counter-effective

T. Singh et al. Journal of Membrane Science 448 (2013) 160
M. Rezakazemi et al. Progress in Polymer Science 39 (2014) 817
D. Schneider PHYS. REV. APPLIED 12, 044034 (2019)

Transport modeling

Sorption and Diffusion – Maxwell model

Mixed matrix membranes:

Homogeneous distribution filler
Combined result filler & polymer performance
Individual properties preserved (no barriers)

$$\frac{P_{\text{eff}}}{P_m} = \frac{2(1-\phi) + (1+2\phi)P_f/P_m}{(2+\phi) + (1-\phi)P_f/P_m}$$

Φ : volume fraction filler in polymer matrix
invalid at >>0.2
(then Lewis-Nielsen model more correct)

Generalized:

$$\frac{P_{\text{eff}}}{P_m} = 1 + \frac{(1+G)\phi}{\frac{P_f/P_m + G}{P_f/P_m - 1} - \phi}$$

G geometric factor (0 - ∞, sphere = 2)

D. Schneider PHYS. REV. APPLIED 12, 044034 (2019)
Vinh-Thang, & Kaliaguine, *Chemical reviews* **2013,** *113* (7) 498

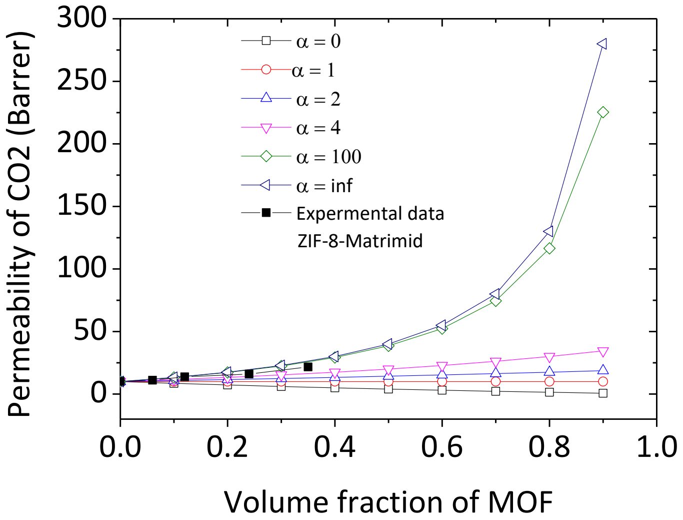
Maxwell model - effect filler on permeability

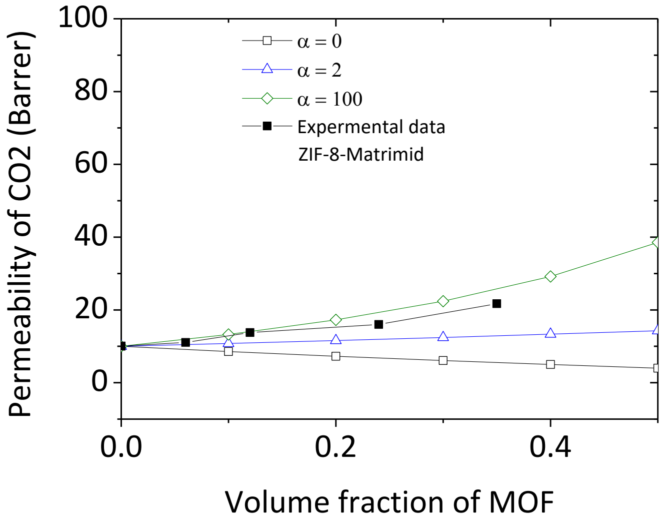
Maxwell model

$$P_{MMM} = P_c \left[\frac{1 + 2\phi_d (\alpha - 1)/(\alpha + 2)}{1 - \phi_d (\alpha - 1)/(\alpha + 2)} \right]$$

α is the permeability ratio, P_d/P_c

System	Permeability (Barrer)
ZIF-8	1192
Matrimid	10





Permeability ratios > ~100 no further improvement
Gain limited

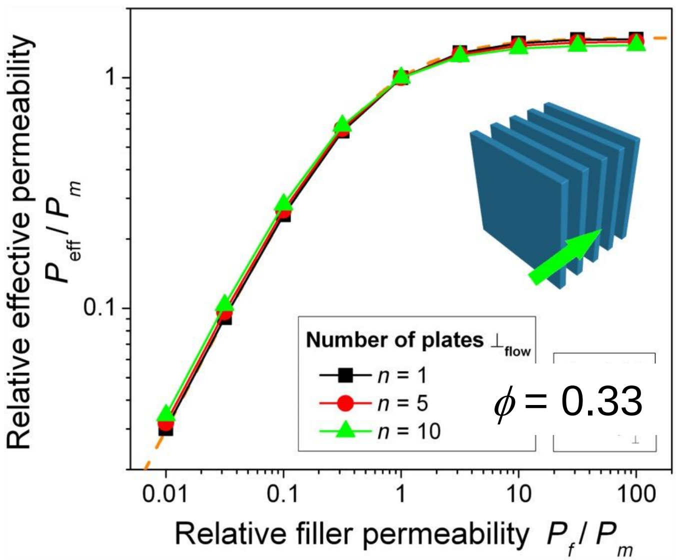
H. Bux et al., J. Am.Chem. Soc., 131 (2009) 16000–16003
S. Shahid et al., J. Membr. Sci., 470 (2014) 166-177

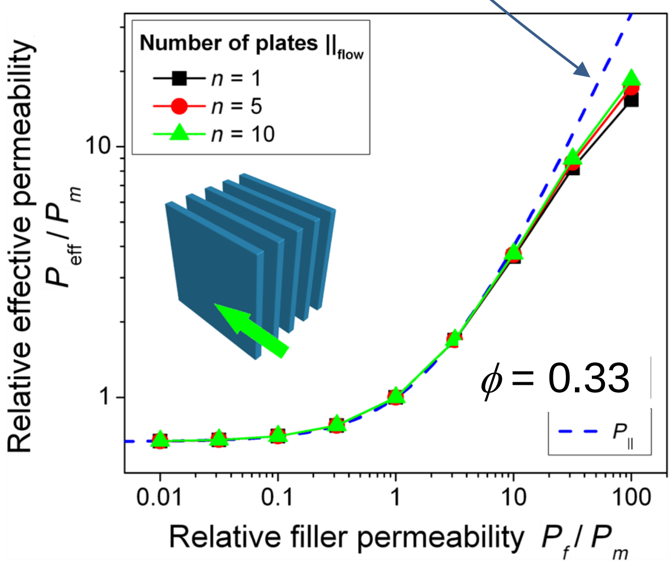
Kinetic Monte Carlo approach

Single component

- Cubic geometry, variations of relative permeability
  - Limiting cases (parallel and perpendicular plates)
  - Distribution (random, homogenenous), loading
  - Particle size, particle shape and orientation
  - Overlapping particles

Maxwell model





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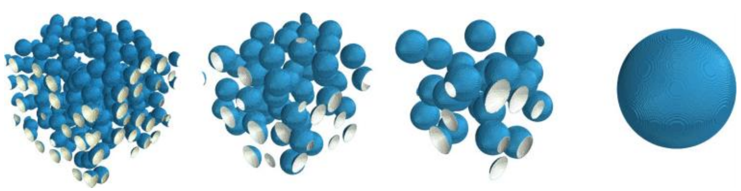
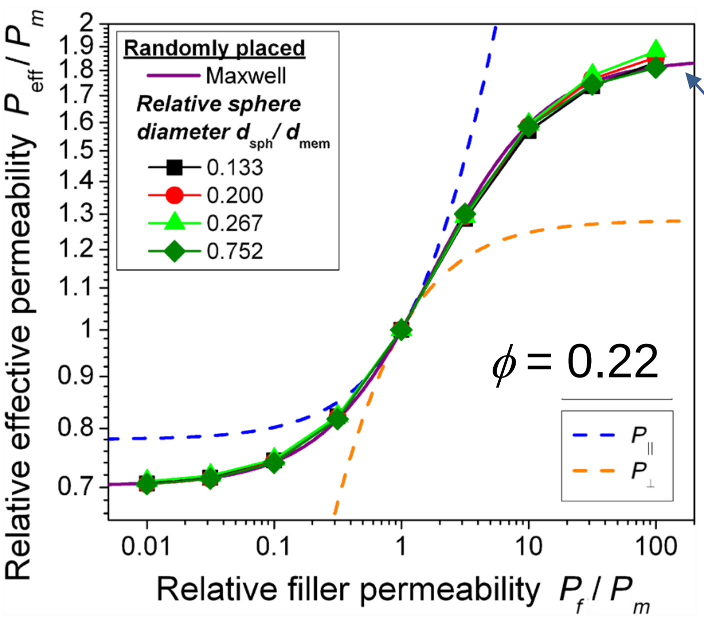
Kinetic Monte Carlo approach

Single component

- Cubic geometry, variations of relative permeability
  - Distribution (random, homogenenous), loading
  - Particle size, particle shape and orientation, loading
  - Overlapping particles





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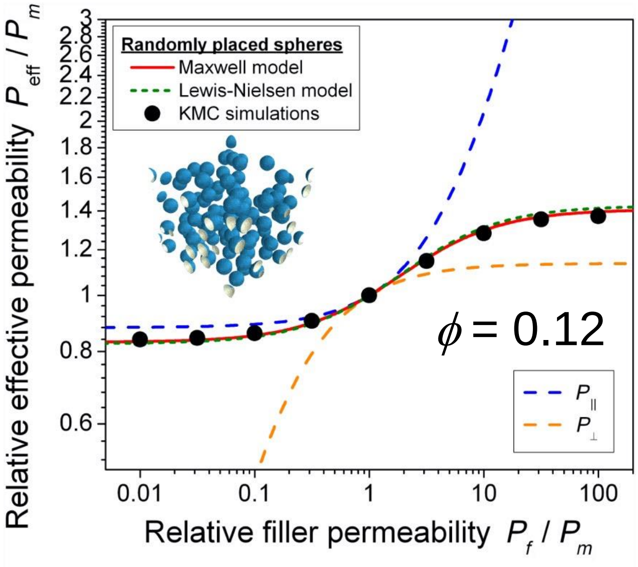
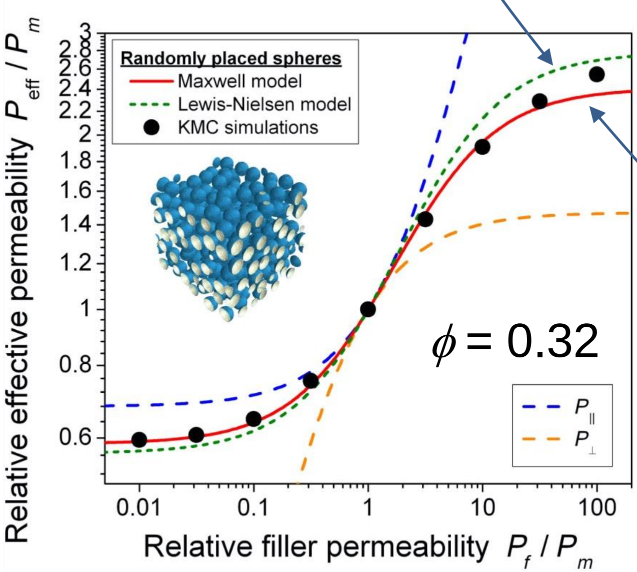
Kinetic Monte Carlo approach

Single component

- Cubic geometry, variation relative permeability filler/polymer
  - Distribution (random, homogenenous), loading
  - Particle size, particle shape and orientation
  - Overlapping particles





Lewis-Nielsen model

Maxwell model

Deviation at higher loading and relative filler permeability

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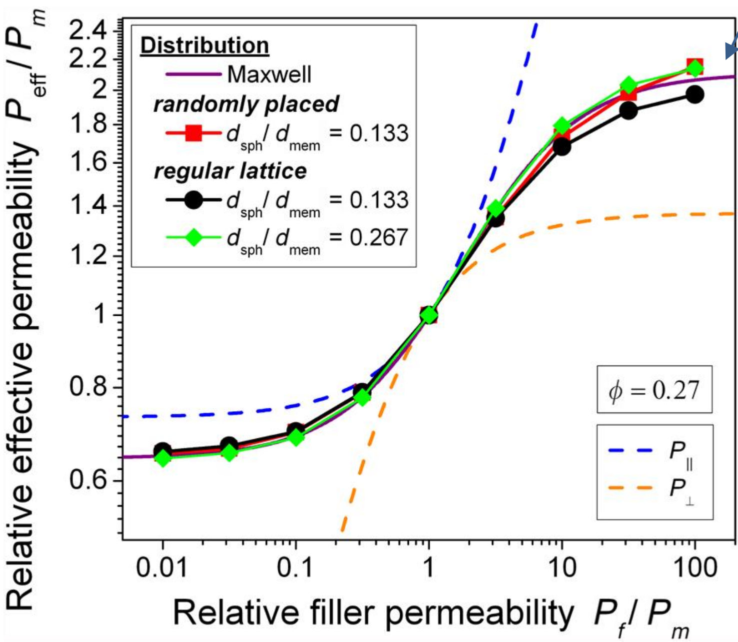
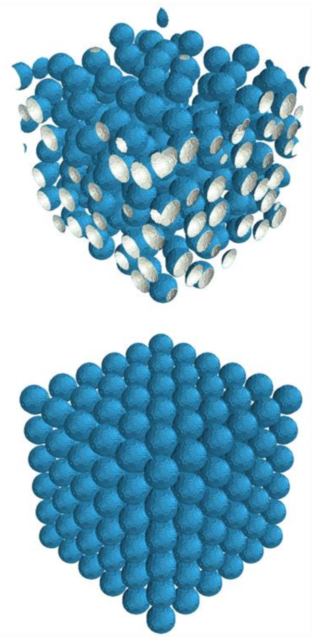
Kinetic Monte Carlo approach

Single component

- Cubic geometry, variations of relative permeability
  - Distribution (random, homogenenous), loading
  - Particle size, particle shape and orientation
  - Overlapping particles

Maxwell model





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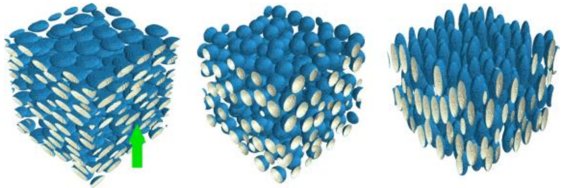
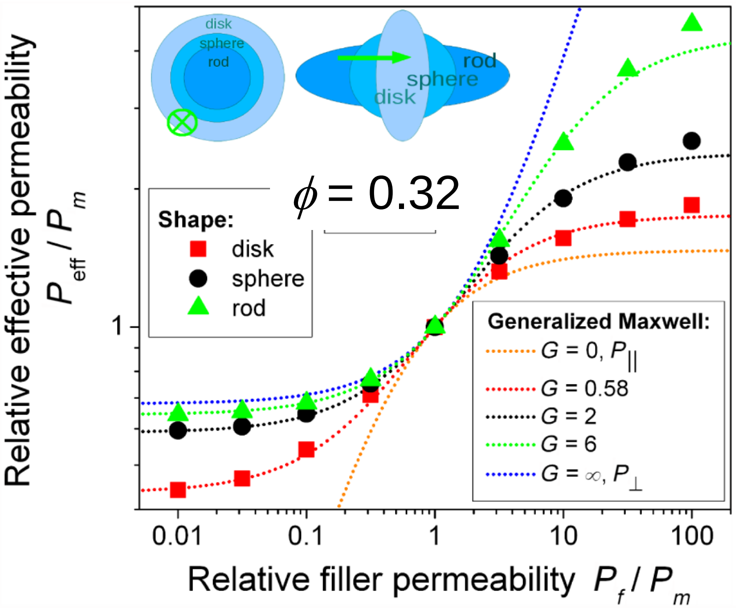
Kinetic Monte Carlo approach

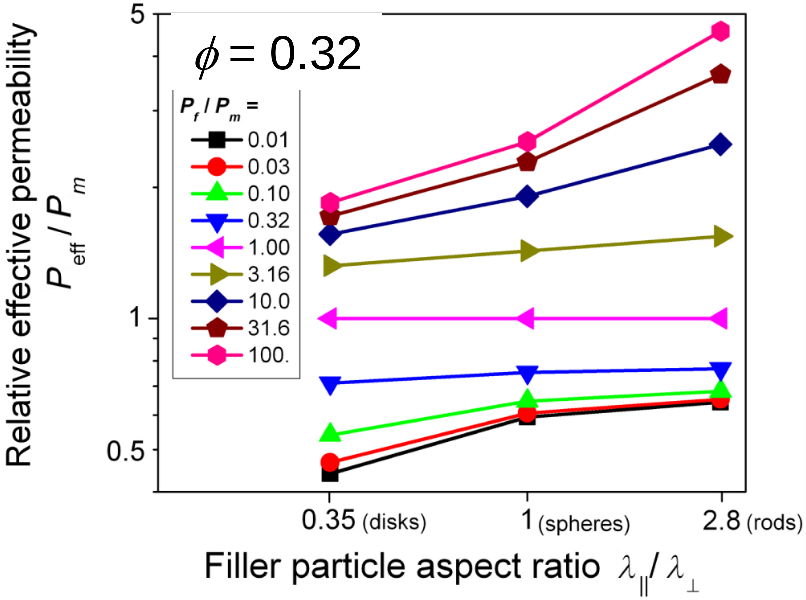
Single component

- Cubic geometry, variations of relative permeability
  - Distribution (random, homogenenous), loading
  - Particle size, particle aspect ratio and orientation, loading



Generalized Maxwell model





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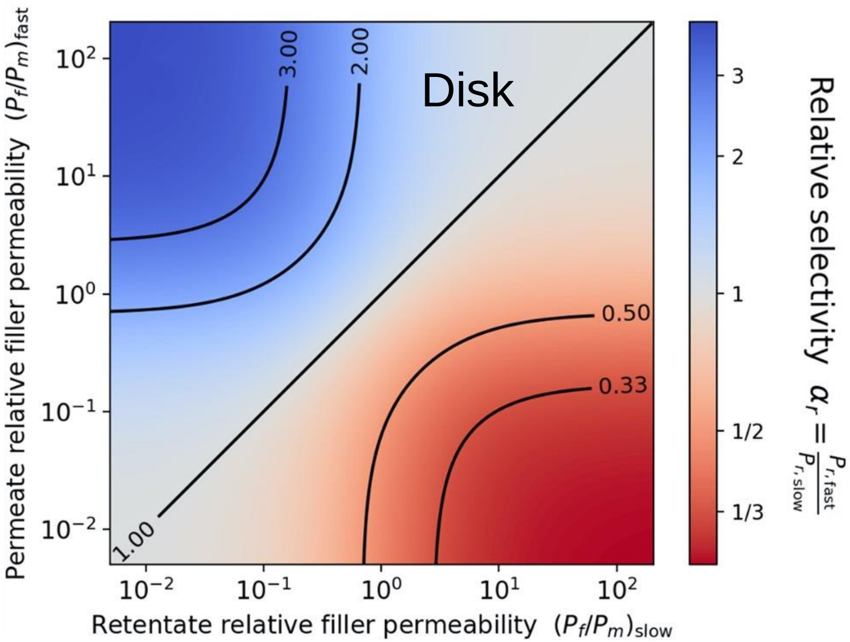
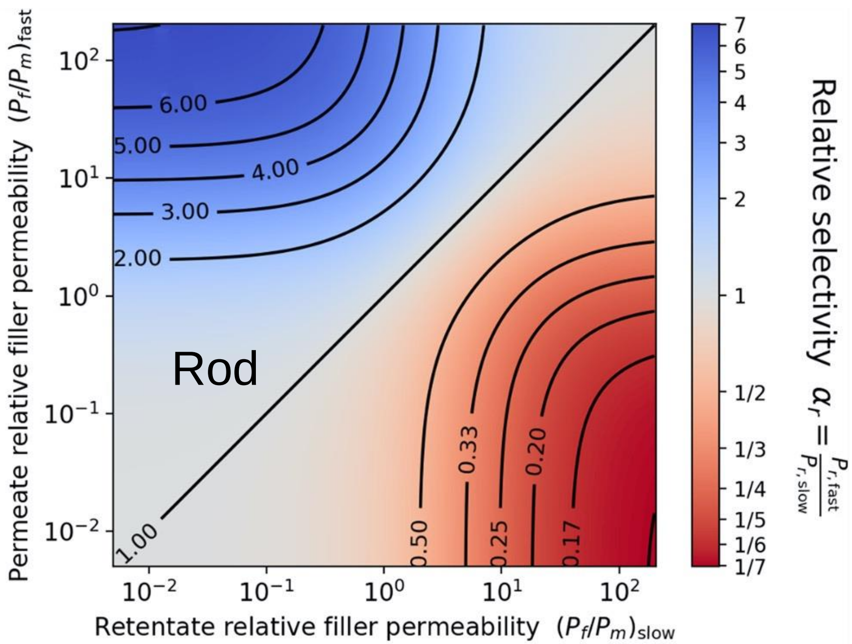
Kinetic Monte Carlo approach

Permselectivity fast/slow

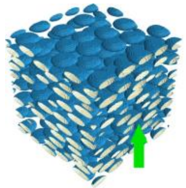
- Selectivity improvement
  - relative permeability (filler/polymer) *fast* versus *slow* component $\phi = 0.32$

Fast

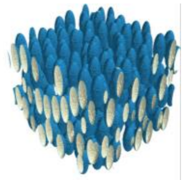




Slow



- Only better selectivity if fast component improves more than slow
- Absolute selectivity = polymer selectivity x improvement
- Rod shape yields better improvement



D. Schneider PHYS. REV. APPLIED 12, 044034 (2019)

General observations

- Maxwell works well, but… practical deviations
- Voids
  - Poor adherence filler-polymer
  - Agglomeration filler, sedimentation

Faster transport
No selectivity

Percolation danger

- Rigidification, chain orientation
- Pore blocking

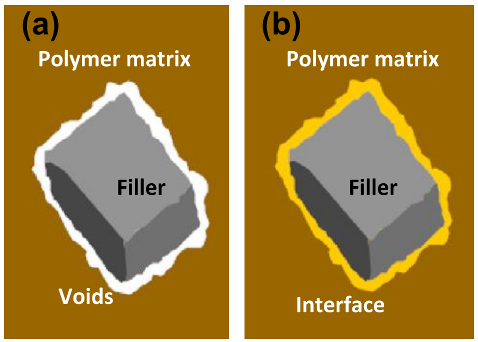
Changing properties: + or -

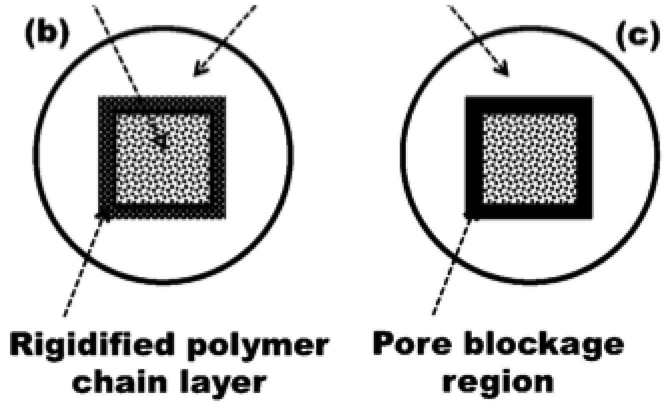
- *Surface modifications for interaction improvement*
- *Modified permeation models – non-predictive*
- ***Control?***

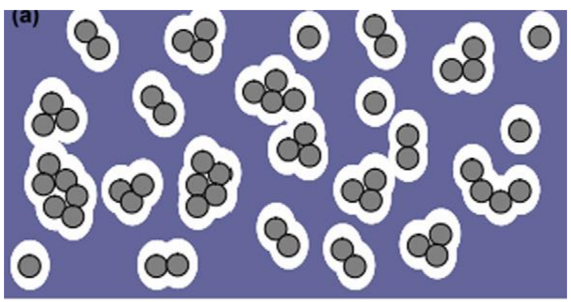
T.T. Moore, W.J. Koros / Journal of Molecular Structure 739 (2005) 87
S.A. Hashemifard et al., Chemical Engineering Journal 172 (2011) 581

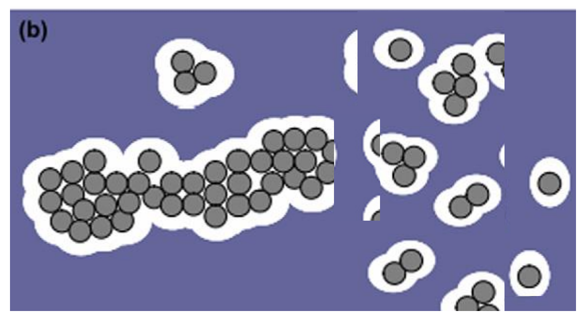
General observations

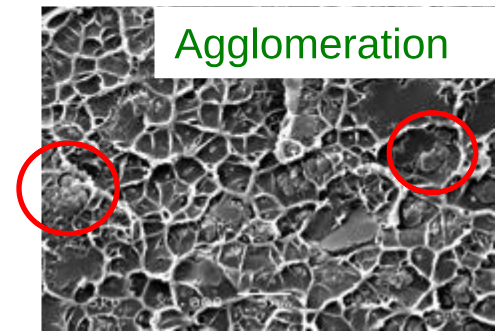
Deviations from ideal membrane system

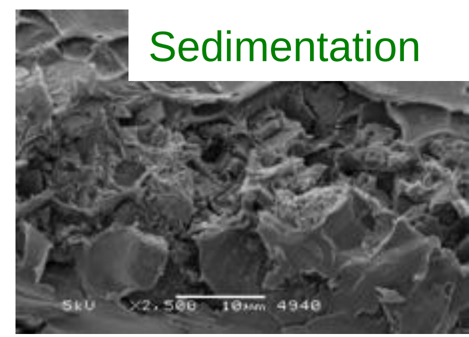






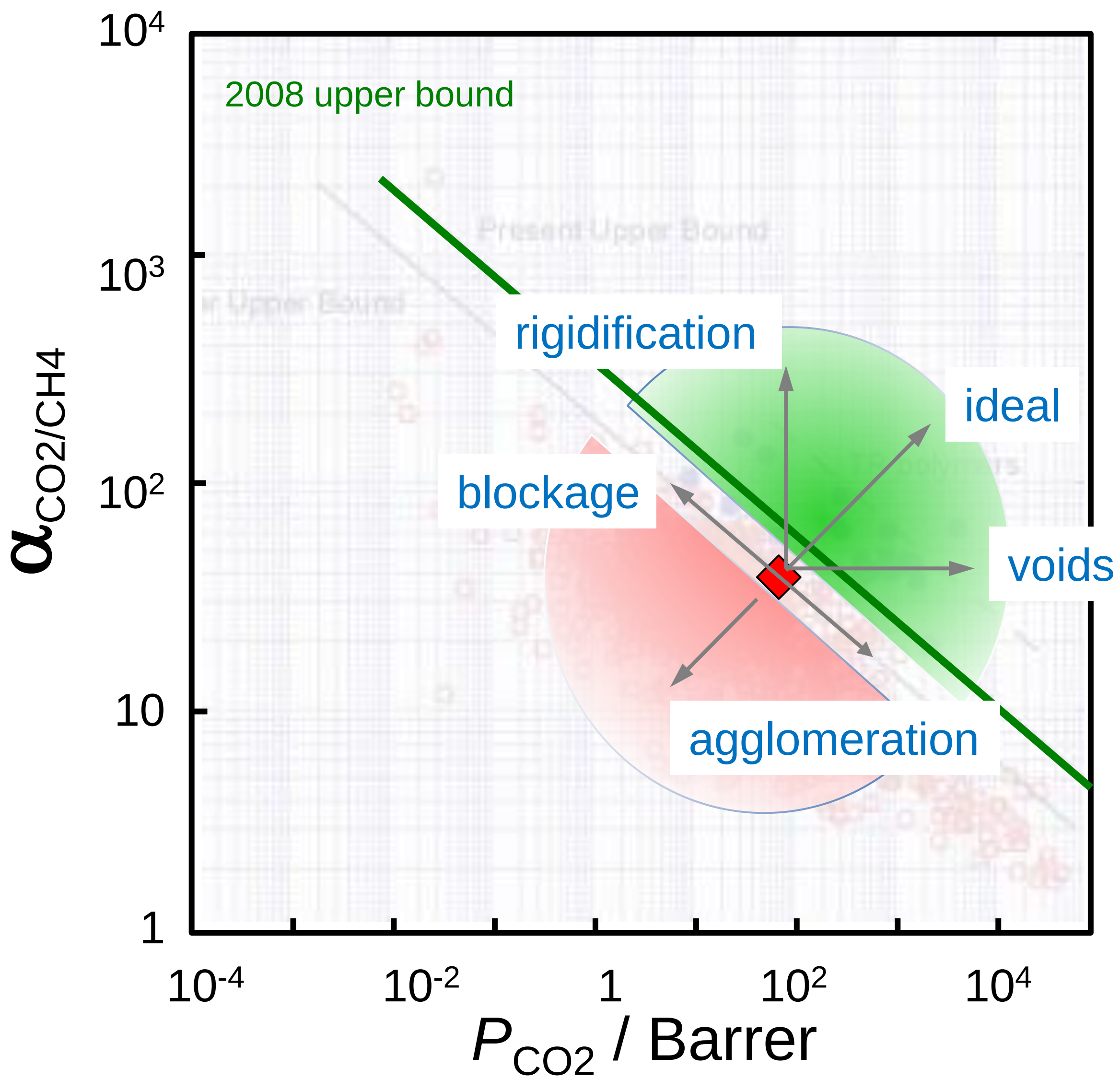






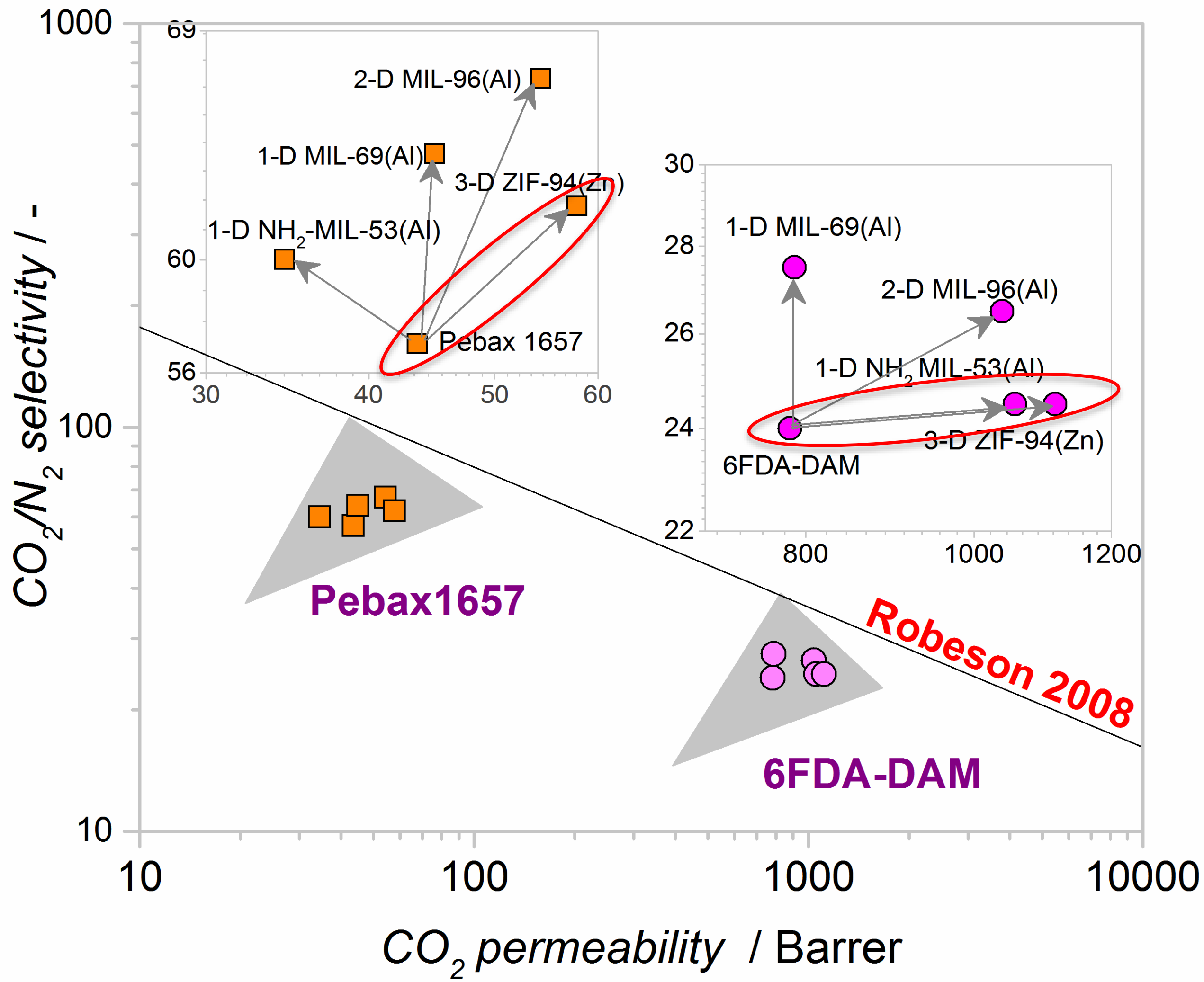
S.A. Hashemifard et al., Chemical Engineering Journal 172 (2011) 581
P.S. Goh et al., Separation and Purification Technology 81 (2011) 243
Vinh-Thang, & Kaliaguine, *Chemical reviews* **2013,** *113* (7) 498

Robeson plot – effect of filler



MMMs performance *vs.* Robeson plot

Feed conditions: 15/85 CO_2/N_2 at 25 C and 2 bar



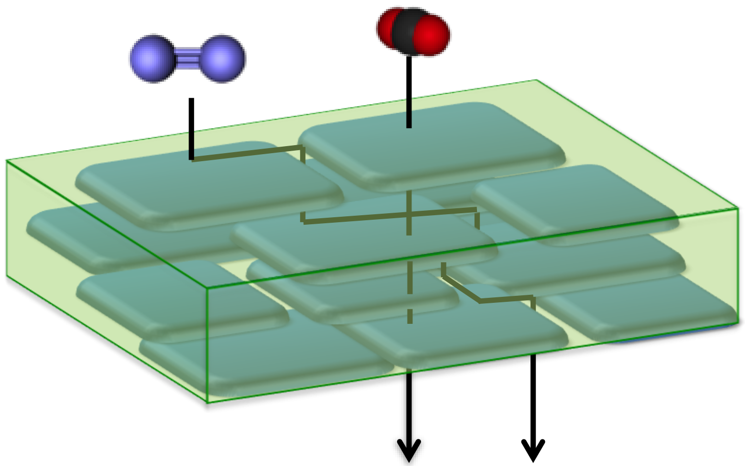
*Sabetghadam et al., Chemistry–A European Journal, 24 (**2018**), 7949-7956.*

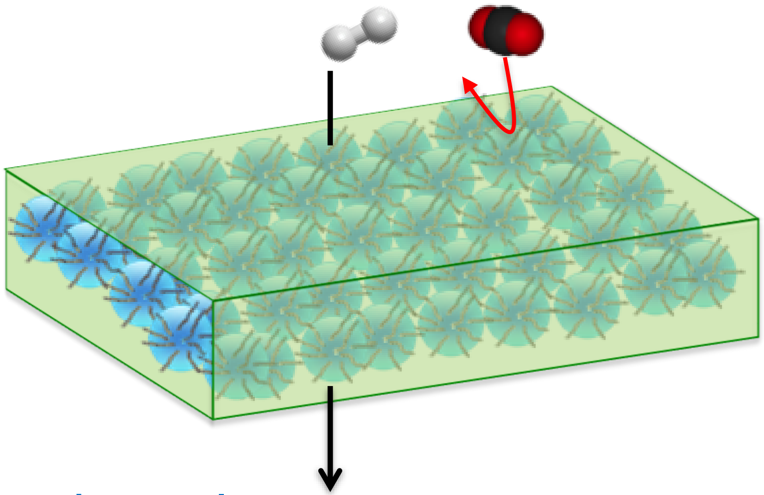
What M^4 configuration do we want?
What properties of materials?
How to seize control?

- Models/theory
  - Volume fraction filler important parameter - loading
  - Control transport pathways - sorption diffusion
- Highly dispersed MOF, nanoparticles
  - Large pore – polymer penetration?
  - Large aspect ratio filler (3rd gen.)
  - Hollow spheres, core shell (3rd gen.)
  - Polymer chain orientation
- Molecular sieving (H_2) - MOF, polymer
- Adsorption-diffusion (CO_2) - high polymer permeability selective adsorption

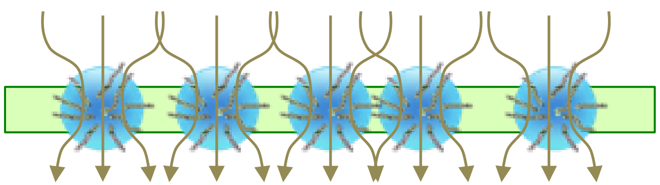
TU Delft
Delft University of Technology

Flux - Selectivity improvements





Selective polymers:
- Flux improvements
  - Hollow spheres
  - Mesoporous, good adsorption
- Shorter effective path-lengths

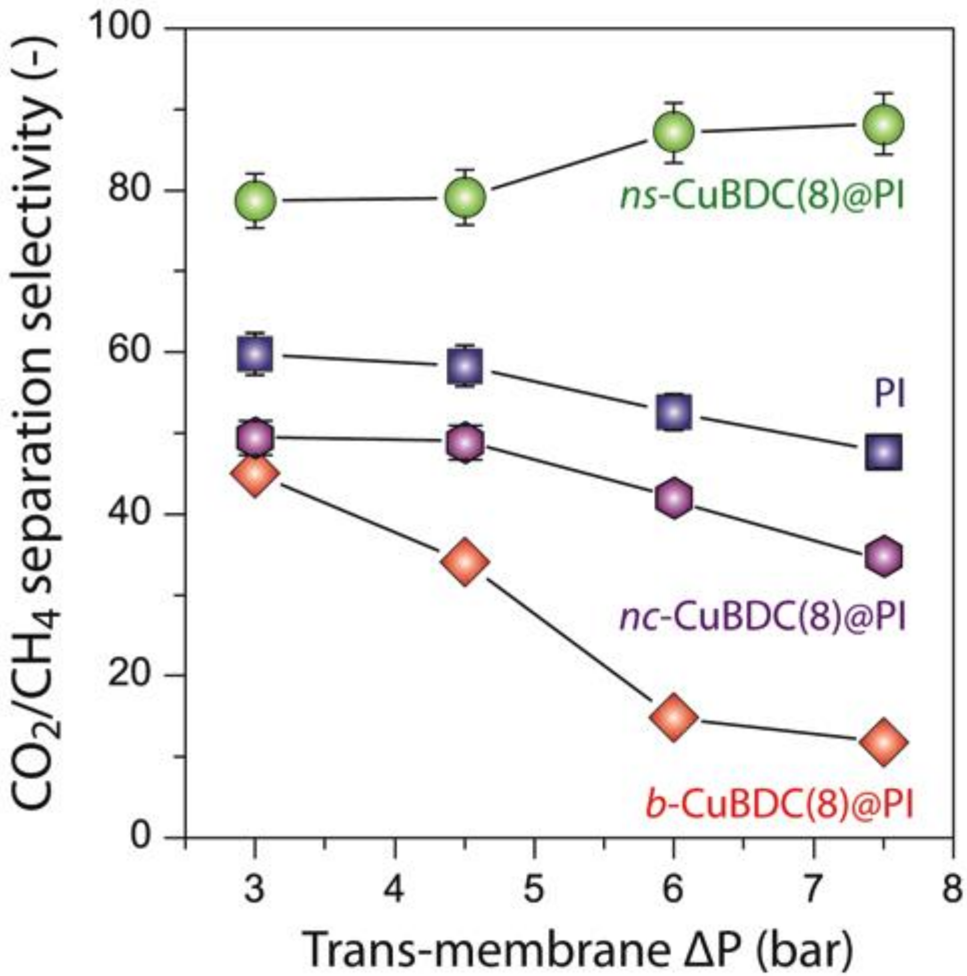


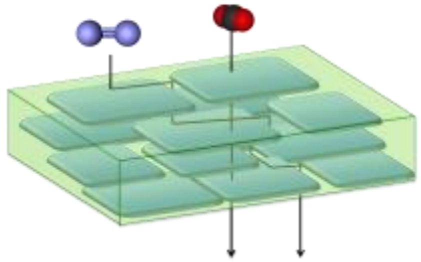
- Percolation membranes

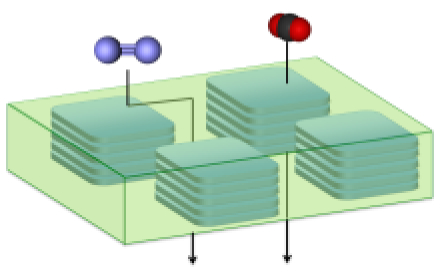
High flux polymers:
- Selective fillers
  - Increased path-lengths
    - tuned aspect ratio
  - Adsorption selective

Rodenas *et al.* Nature Materials 14, 48–55 (2015)
Sabetghadam *et al.* J Membrane Science 570–571 (2019) 226–235

Separation performance





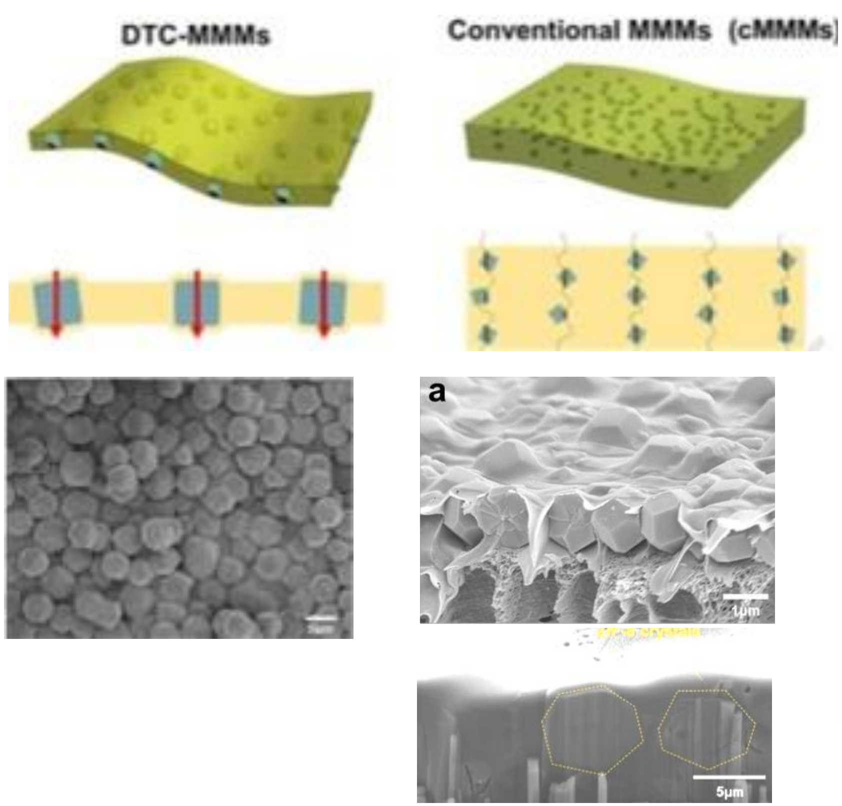


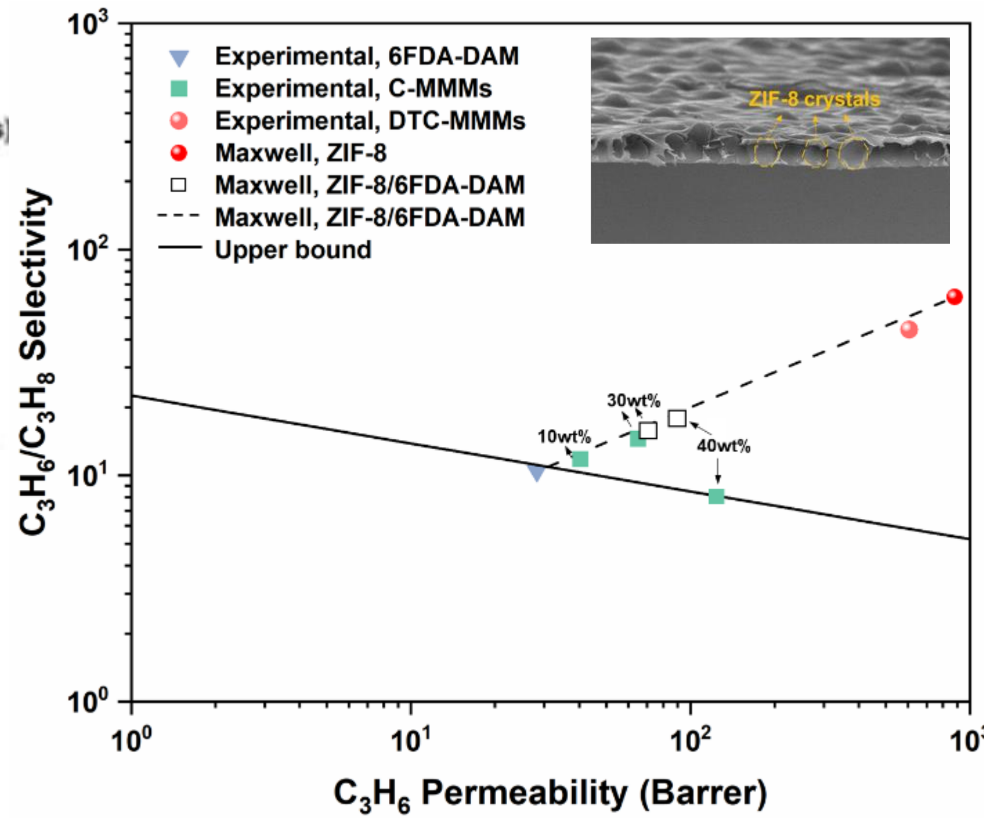
Rodenas *et al.* Nature Materials 14, 48–55 (2015)

Percolation membranes

'direct-through channels'

Propene/propane separation
ZIF-8 in 6FDA-DAM





S. Song; H. Jiang; H. Wu; M. Zhao; Z. Guo; B. Li; Y. Ren; Y. Wang; C. Ye; M.D. Guiver; G. He; Z. Jiang, *Weakly pressure-dependent molecular sieving of propylene/propane mixtures through mixed matrix membrane with ZIF-8 direct-through channels*. *J. Membr. Sci.* **2022**, 120366.

Delft University of Technology

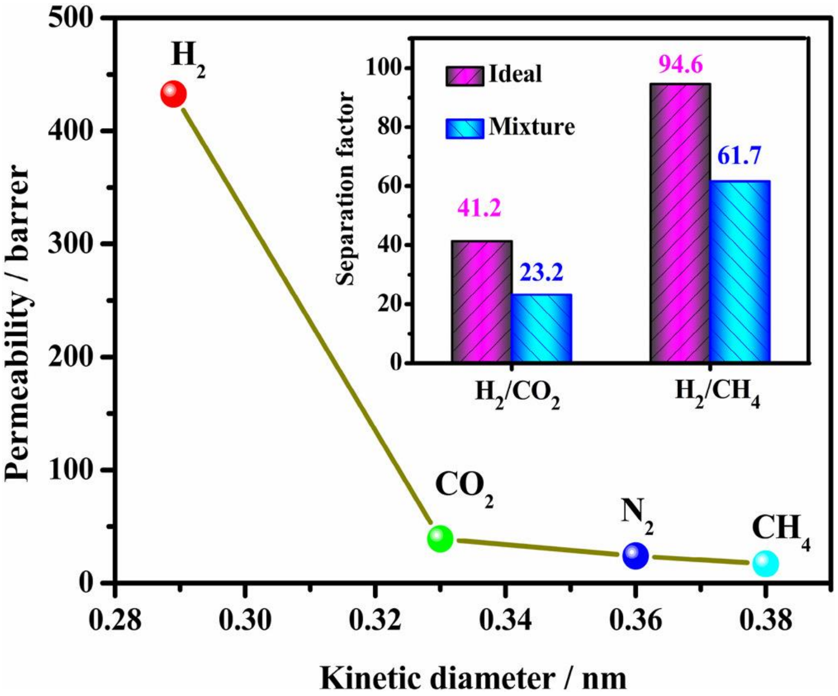
Improve interaction MOF-polymer

Y. Pu; Z. Yang; V. Wee; Z. Wu; Z. Jiang; D. Zhao, *Amino-functionalized NUS-8 nanosheets as fillers in PIM-1 mixed matrix membranes for CO_2 separations*. *J. Membr. Sci.* **2022,** *641*, 119912.

10 wt% NUS-8-NH_2 showed CO_2 permeability of ~14000 Barrer and CO_2/N_2 selectivity of ~30

W. Li; Y. Li; J. Caro; A. Huang, *Fabrication of a flexible hydrogen-bonded organic framework based mixed matrix membrane for hydrogen separation*. *J. Membr. Sci.* **2022,** *643*, 120021

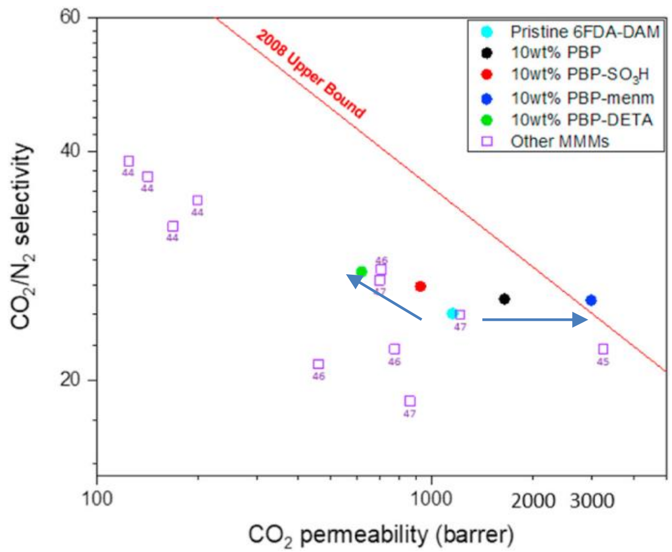
A HOF-30@PI MMM with 10 wt% HOF-30 exhibits a high hydrogen permeability of 428.1 barrer and H_2/CH_4 separation factor of 61.7.



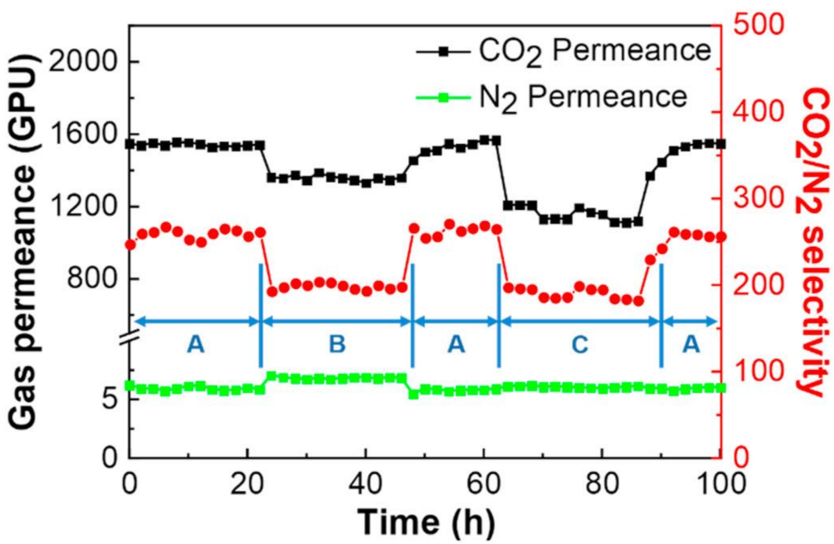
Improve MOF-polymer system

Y. Liu; W. Xie; S. Liang; X. Li; Y. Fan; S. Luo, *Polyimide/ZIFs mixed matrix membranes with tunable interfacial interaction for efficient gas separation*. *J. Membr. Sci.* **2022,** *646*, 120240.

The optimized membrane of 6FDA-DAM:DABA (1:1)/10 wt.% ZIF-8-90(30) has enhanced H_2/CH_4 and CO_2/CH_4 ideal selectivities of 75.4 and 43.6, respectively, with H_2 and CO_2 permeabilities of 222 Barrer and 128 Barrer



Y. Lee; C.Y. Chuah; J. Lee; T.-H. Bae, *Effective functionalization of porous polymer fillers to enhance CO_2/N_2 separation performance of mixed-matrix membranes*. *J. Membr. Sci.* **2022,** *647*, 120309



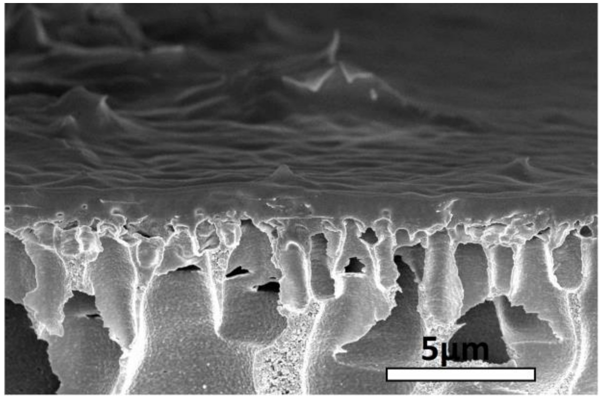
Y. Yuan; Z. Qiao; J. Xu; J. Wang; S. Zhao; X. Cao; Z. Wang; M.D. Guiver, *Mixed matrix membranes for CO_2 separations by incorporating microporous polymer framework fillers with amine-rich nanochannels*. *J. Membr. Sci.* **2021,** *620*, 118923

Take home message

- Modelling
  - (Generalized) Maxwell model works best for ‘behaving systems’
    - Improvement limited
    - Simulations show direction
  - Generally, a posteriori model description, nonpredictive
- 3rd generation membranes under development
  - Pathway control, percolation membranes

Modeling of gas separation in thin supported membranes

- The permeability of MMMs comprising ZIF-94 & NH_2-MIL-53(Al) and Pebax 1657 & 6FDA-DAM were calculated by analytical models (using calculated filler diffusivity), which were in the range of experimental permeation values with 3-4% deviation
- The permeation data from modified analytical models were used to predict the permeation of supported thin mixed matrix membrane by taking the following assumptions:
- 1 µm thin layer on top of the support,
- Knudsen diffusion through the porous support
- Applying series model



$$P^S_{CO_2} = P^S_{N_2} \times \sqrt{\frac{M_{N_2}}{M_{CO_2}}} = 0.798 \times P^S_{N_2}$$

$$P^C_{CO_2} = \left(\frac{\delta_F}{P^F_{CO_2}} + \frac{1}{P^S_{CO_2}} \right)^{-1} \qquad P^C_{N_2} = \left(\frac{\delta_F}{P^F_{N_2}} + \frac{1}{P^S_{N_2}} \right)^{-1}$$

δ_A Thickness

Mi Molecular weight

P^C_i Permeance of species *i* in composite membrane

P^S_i Permeance of species *i* in support

Modeling of gas separation in thin supported membranes

By applying Knudsen diffusion relation, the CO_2 permeance of the PAN support based on its experimental N_2 permeance was calculated.
(P_{N2}~ 45776 GPU at 1 bar and 25°C)

CO_2 and N_2 permeation of the PAN support

P_{N2} (GPU)	Assumptions	P_{CO2} (GPU)
45776	Assuming Knudsen selectivity of the PAN support	36529.248

CO_2 and N_2 permeation of the thin PAN supported MMMs (MMM CO_2 permeation from modified analytical models prediction).

MMMs	PCO2 – selective layer	Assumption	P_{CO2} – PAN supported MMMs
ZIF-94/PEBAX	55	Thin layer thk=1 µm	55
ZIF-94/6FDA	1150	Thin layer thk=1 µm	1115
NH2-MIL-53/PEBAX	40	Thin layer thk=1 µm	40
NH2-MIL-53/6FDA	1100	Thin layer thk=1 µm	1068

- The influence of PAN support resistance on the permeation performance of thin MMMs is more significant in case of high permeable membranes.

*Sabetghadam et al., Journal of Membrane Science, 570 (**2018**), 226-235.*

2.3. Gas separation through post and pre-combustion membranes - mathematical modelling in Comsol Multiphysics (Magdalena Malankowska – DTU (before UNIZAR))

Webinar: Process modelling, design and scale-up for CO_2 capture processes

February 23th, 2022 at 10:30 (CET)

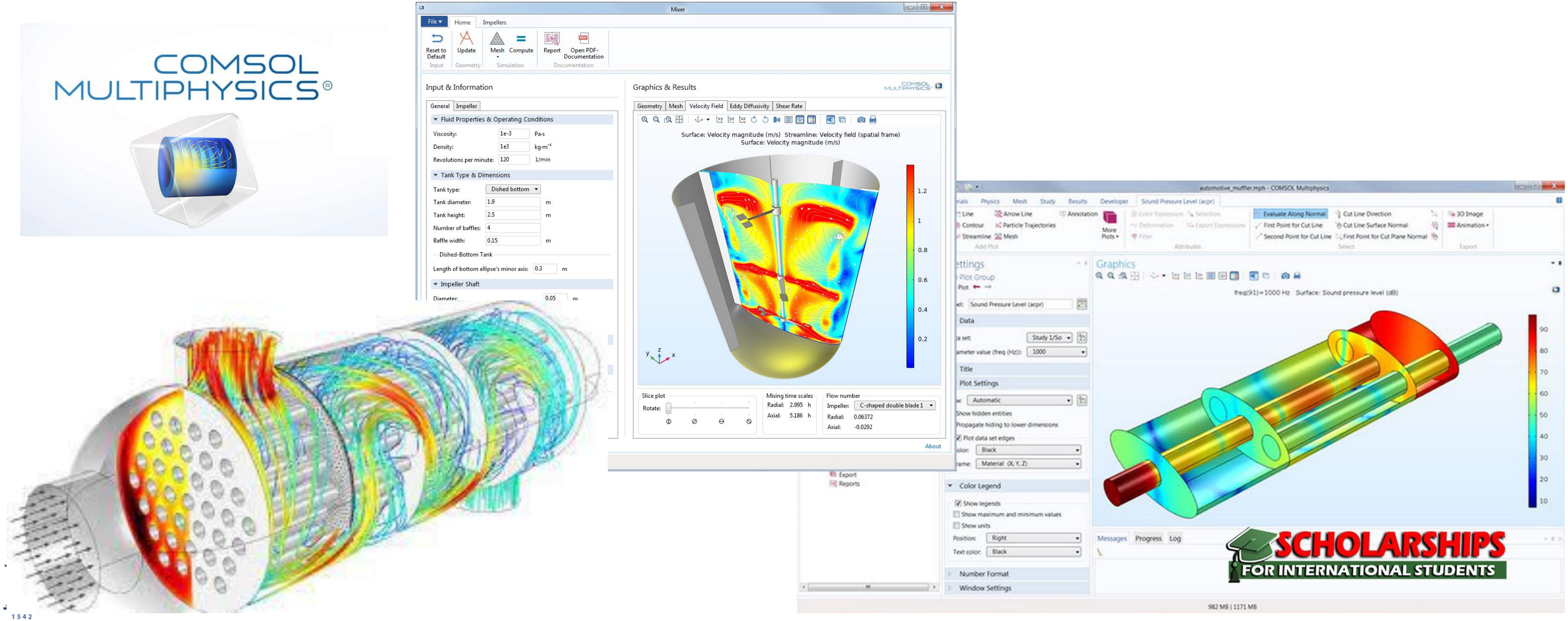
Gas separation through post and pre-combustion membranes - mathematical modelling in Comsol Multiphysics

Magdalena Malankowska

Universidad Zaragoza 1542

Comsol Multiphysics

COMSOL Multiphysics is a cross-platform finite element analysis, solver and multiphysics simulation software. It allows conventional physics-based user interfaces and coupled systems of partial differential equations (PDEs). COMSOL provides a unified workflow for electrical, mechanical, fluid, acoustic, and chemical applications.



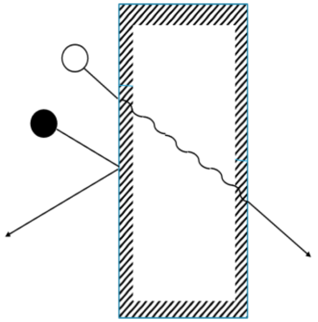
Separation by membrane technology – Transport mechanisms

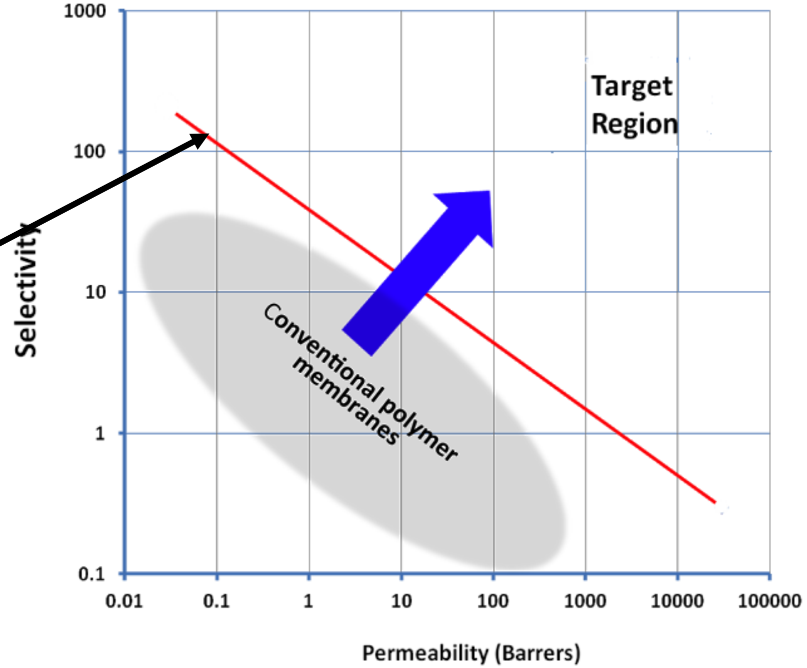
Types of membranes

Nonporous dense membrane

Transport

Solution-diffusion model





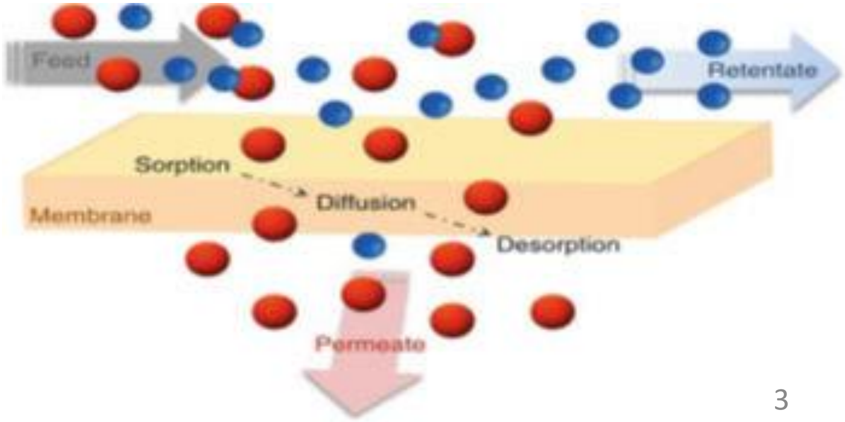
Robbeson upper bound

Mass transfer according to solution-diffusion mechanism

1. Selective sorption of the gas into the membrane at the feed-membrane interface

2. Selective diffusion of the gas through the membrane

3. Desorption from the membrane-permeate interface to the permeate stream (very fast process)



Transport mechanism + Modelling

Flux through dense membrane

$$J = \frac{D \cdot S(p_0 - p_l)}{l}$$

D – diffusivity [cm^2/s]
S – solubility [$cm^3/cm^3 \cdot cmHg$]
l – membrane thickness
p – partial pressure of a component on either side of the membrane [cmHg]

Selectivity

$$\alpha_{ij} = \frac{P_i}{P_j}$$

α_{ij} – selectivity of a component i over j
P_i – permeability of component i
P_j – permeability of component j

Mathematical models used

- The momentum conservation for laminar flow of incompressible fluids with the mass conservation (Navier-Stokes equations):

$$\rho(\mathbf{u} \cdot \nabla)\mathbf{u} = \nabla \cdot \left[-p\mathbf{I} + \mu(\nabla\mathbf{u} + (\nabla\mathbf{u})^T) - \frac{2}{3}\mu(\nabla \cdot \mathbf{u})\mathbf{I}\right] + \mathbf{F}$$

$$\nabla \cdot (\rho\mathbf{u}) = 0$$

- The mass balance and transport equation solved from a standard convection-diffusion mass transfer expression under steady state conditions:

$$\mathbf{u} \cdot \nabla c_i = D \cdot \nabla^2 c_i$$

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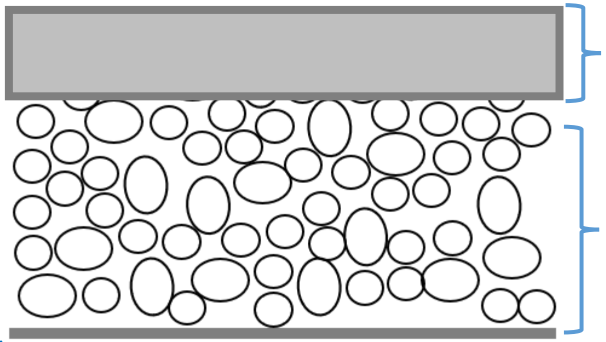
4

Transport mechanism + Modelling

Post-combustion

1 Thin-film composite membrane



Selective dense layer

Pebax 1657

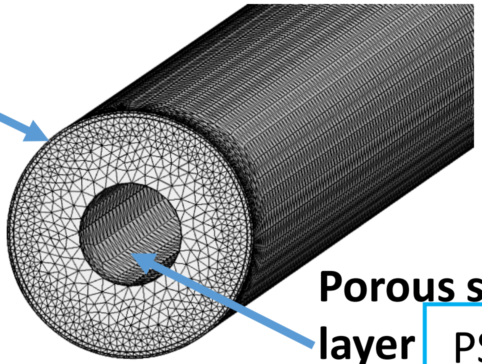
Porous supportive layer

PSF

2 Hollow fiber membrane

Selective dense layer

Pebax 1657



Porous supportive layer

PSF

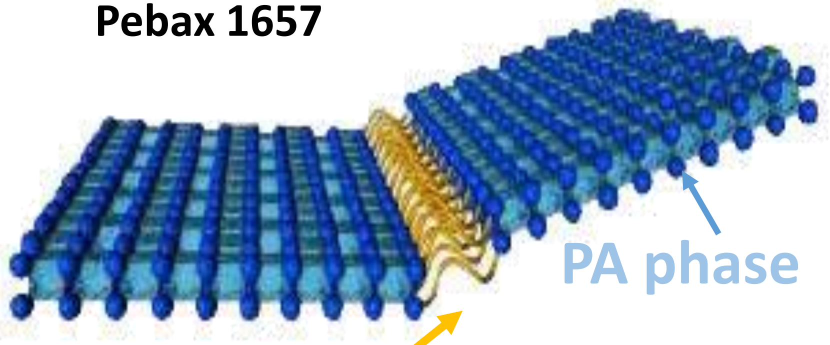
Pre-combustion

1 Dense self-standing membrane

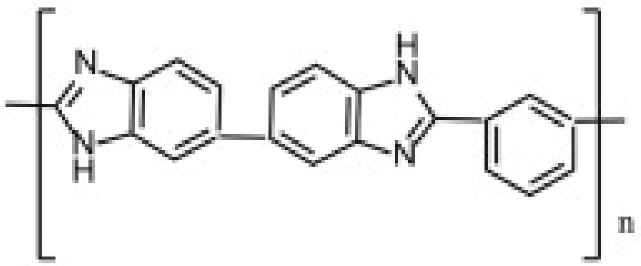
Selective dense layer

PBI

Pebax 1657



PBI (Polybenzimidazole)



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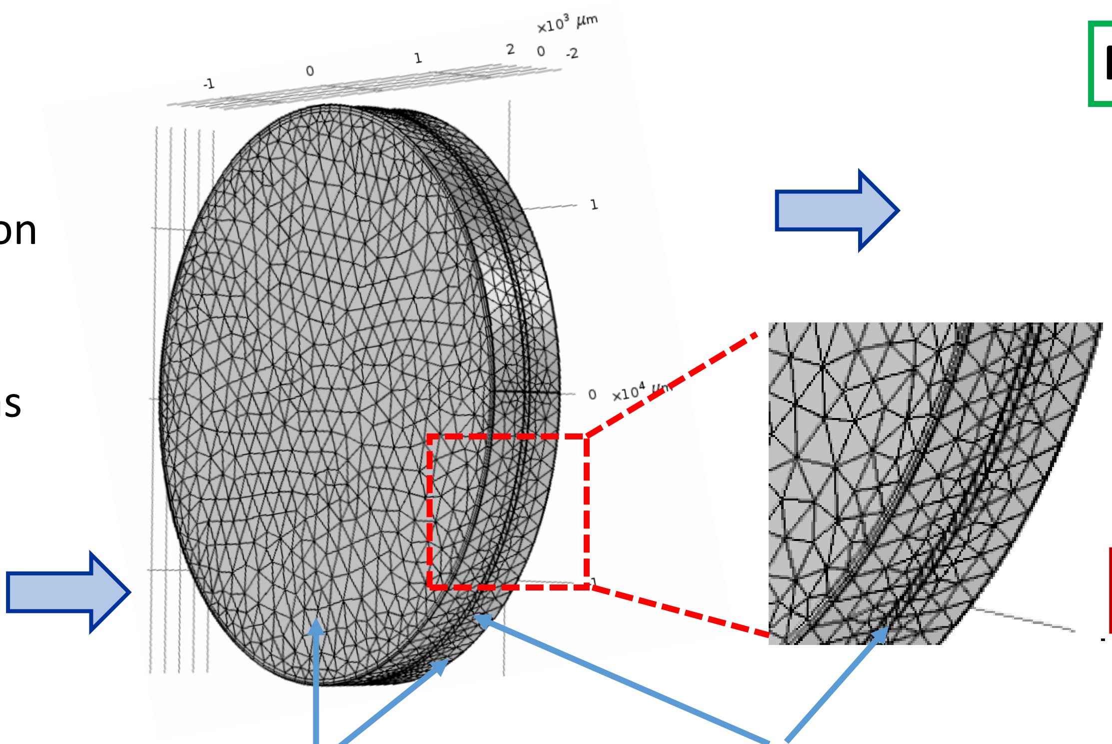
MEMBER

Modelling

COMSOL

Model input

- Input flow
- Inlet concentration
- Pressure
- Temperature
- Diffusivity of a gas in the membrane
- Gas mixture composition



Gas mixture domains (CO_2+N_2)

Membrane

Model output

- Velocity profile
- Pressure
- Concentration profile
- Flux

Model assumptions

- No slip conditions on the walls, **u**=0
- No back-flow permitted
- The flow direction defined as normal to the inlet and outlet
- Atmospheric pressure at the outlet

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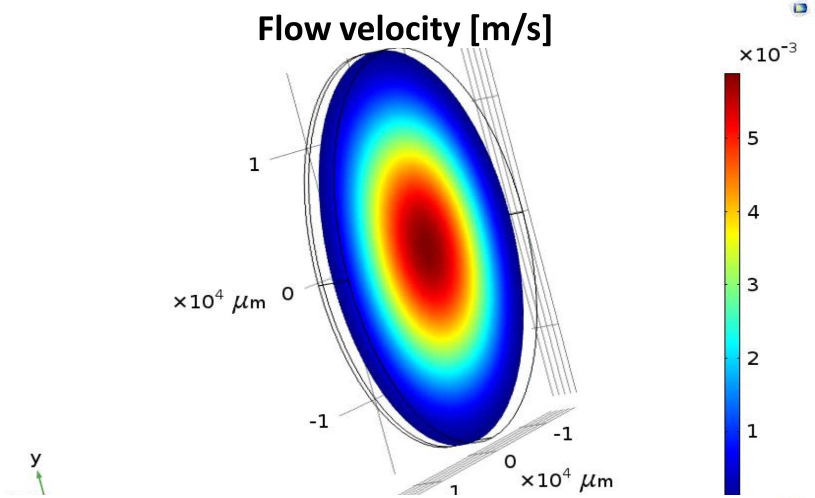
Pre-combustion modelling

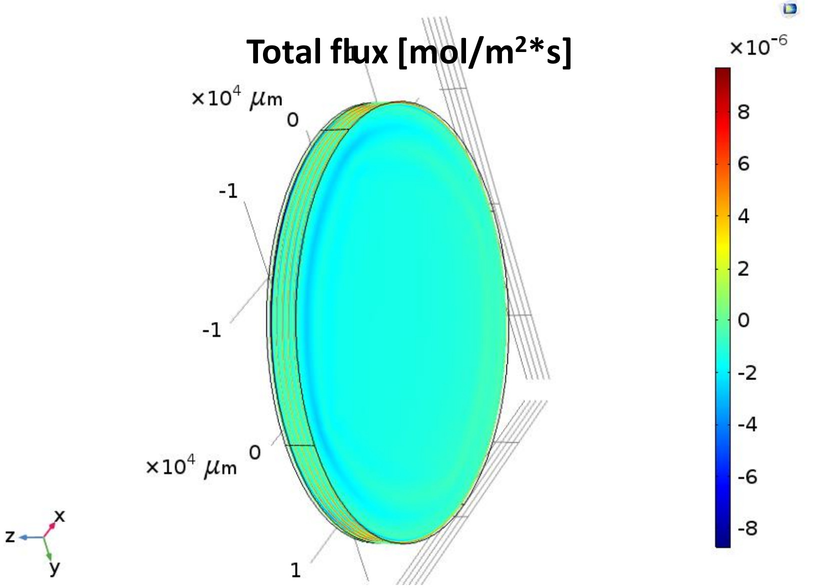
COMSOL

Separation of H_2/CO_2 by flat sheet dense PBI membrane

Flow velocity [m/s]



Total flux [mol/m²*s]



Input	Value
PBI thickness (µm)	30
Feed pressure (bar)	3
Temp (ºC)	150
H_2 (mL/min)	50
CO_2 (mL/min)	50
D_{CO2} (cm^2/s)	$9.45 \cdot 10^5$
D_{H2} (cm^2/s)	$6.87 \cdot 10^6$

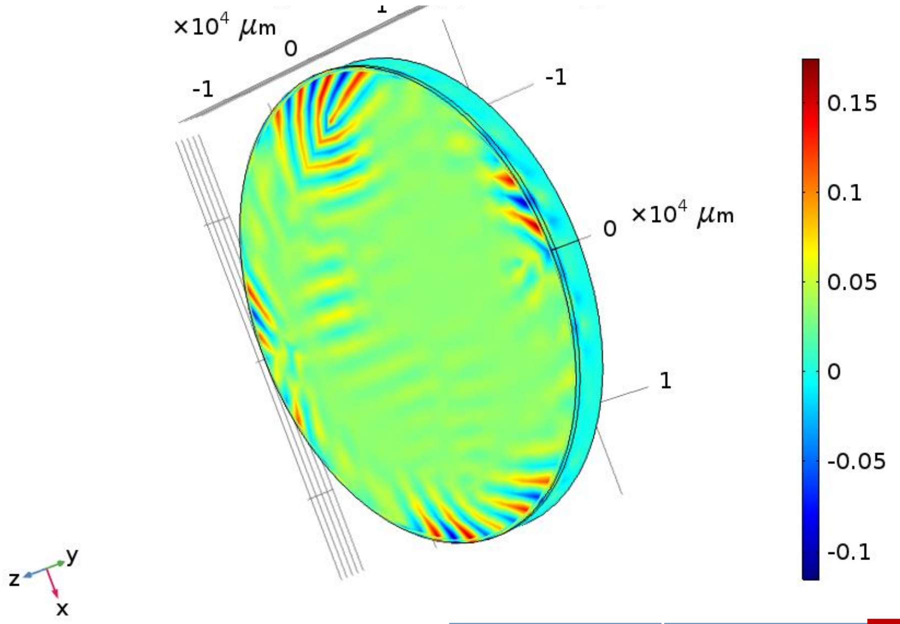
Perm CO_2 (Barrer)	Total flux CO_2 ($mol/m^2.s$)	Perm H_2 (Barrer)	Total flux H_2 ($mol/m^2.s$)	Sel H_2/CO_2	
5.70	$1.18 \cdot 10^{-4}$	33.30	$6.83 \cdot 10^{-4}$	5.79	Gas chromatography
5.79	$1.20 \cdot 10^{-4}$	28.97	$6.00 \cdot 10^{-4}$	5.00	COMSOL

Post-combustion modelling

COMSOL

Separation of CO_2/N_2 by thin film composite Pebax 1657

Total flux [mol/m²*s]



Input	Value
Pebax thickness (μm)	80
PSF thickness (μm)	210
Feed pressure (bar)	3
Temp (°C)	35
CO_2 (mL/min)	15
H_2 (mL/min)	85
D_{CO2} (cm^2/s)	$9.45 \cdot 10^5$
D_{H2} (cm^2/s)	$6.87 \cdot 10^6$

Perm CO_2 (GPU)	Perm CO_2 (Barrer)	Total flux CO_2 ($mol/m^2.s$)	Perm N_2 (GPU)	Perm N_2 (Barrer)	Total flux N_2 ($mol/m^2.s$)	Sel CO_2/N_2	
1.94	87.3	$2.68 \cdot 10^{-5}$	0.06	2.7	$4.69 \cdot 10^{-6}$	32.33	Gas chromatography
2.40	191.4	$3.3 \cdot 10^{-5}$	0.10	6.2	$6.1 \cdot 10^{-6}$	30.66	COMSOL

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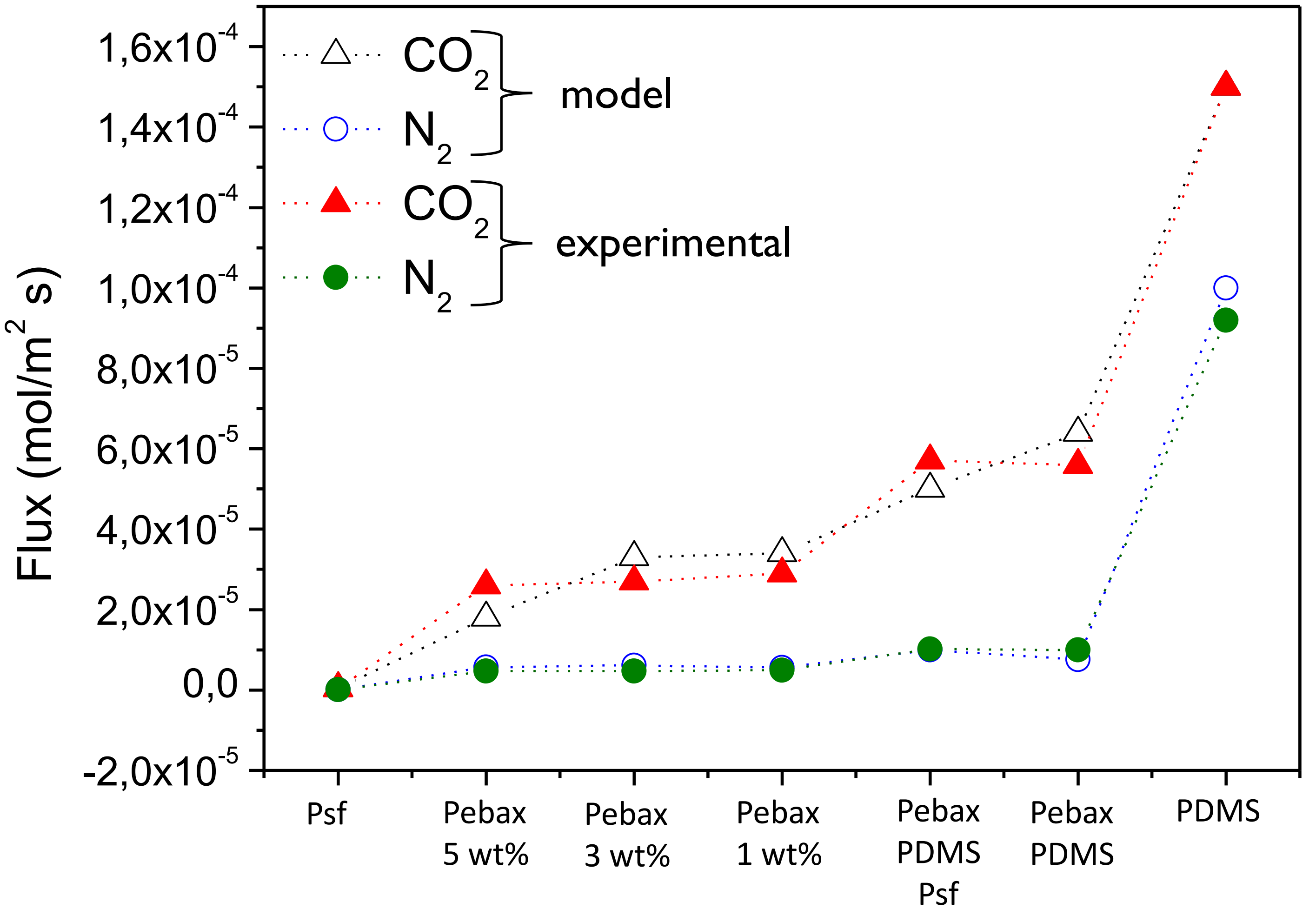
Post-combustion modelling



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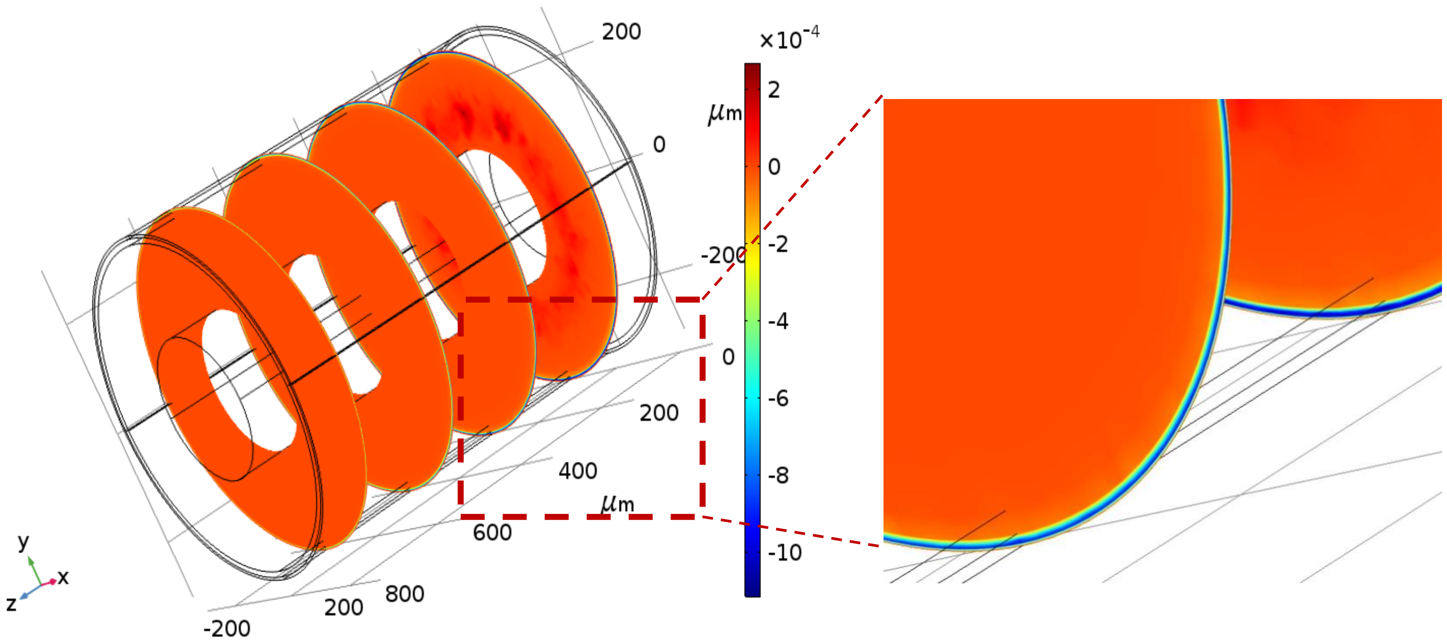
Post-combustion modelling

Separation of CO_2/N_2 by hollow fiber composite Pebax 1657

Model input

Input	Value
Length (cm)	8
PSF thickness (µm)	250
Pebax 1657 thickness (µm)	40
Feed pressure (bar)	3
Temp (ºC)	35
CO_2 (mL/min)	15
N_2 (mL/min)	85

Total flux [mol/m²*s]



Perm CO_2 (Barrer)	Total flux CO_2 (mol/m2.s)	Perm N_2 (Barrer)	Total flux N_2 (mol/m2.s)	Sel CO_2/N_2	
72.5	$2.5 \cdot 10^{-4}$	2.15	$4.21 \cdot 10^{-5}$	33.65	COMSOL

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Conclusion

- The proposed models do not consider **swelling phenomena** and this might be the cause of under-prediction (experimental CO_2 permeance higher than the modelled one)
- The higher the pressure the higher the flux because an increase in free volume due to the gas sorption increases the polymer chain mobility and gas diffusion inside the membrane.
- Simulated values are in agreement with the measured ones
- These simulations can be used to predict the membrane performance and to envision the parameters of the most effective membrane for pre- or post-combustion
- Challenges included:

• High computational time for hollow fiber simulations

• D and S change with temperature – challenging to find these values in the literature for our specific case (time-lag experiments)

Thank you!

2.4. Membrane and system modelling (Hans ten Dam – HYGEAR)

Membrane and system modelling

Pre-combustion and post-combustion CO_2 separation technologies with MMM

Hans ten Dam

Disclaimer: This presentation reflects the author's view and the Commission is not responsible for any use that may be made of the information it contains.
This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 760944

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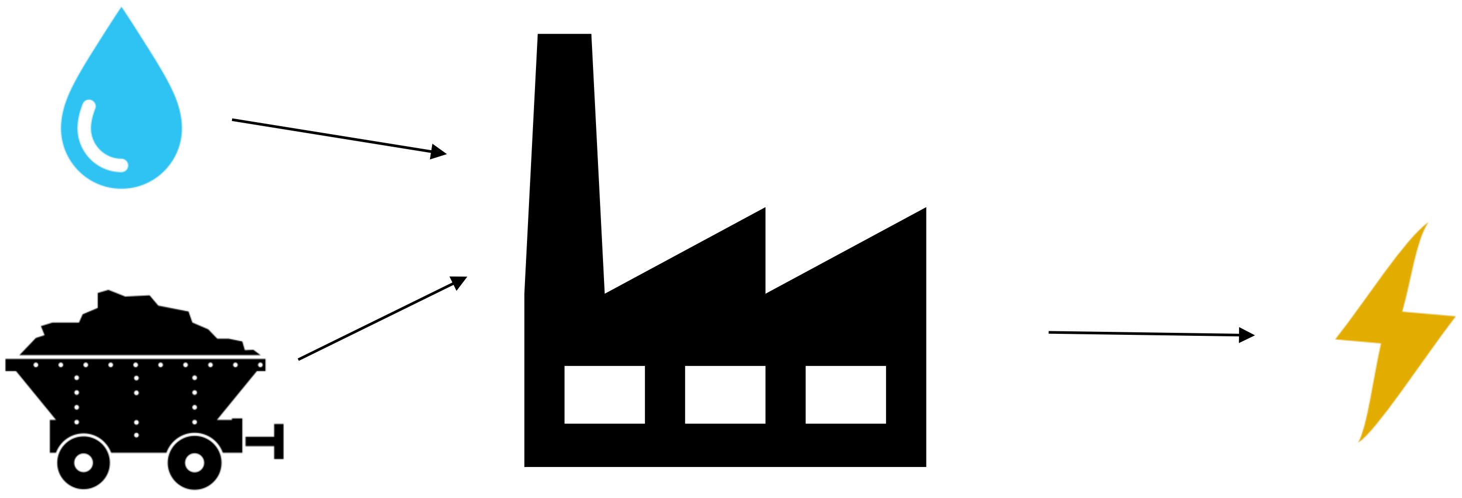
Webinar MEMBER
23-02-2022

Introduction – post combustion



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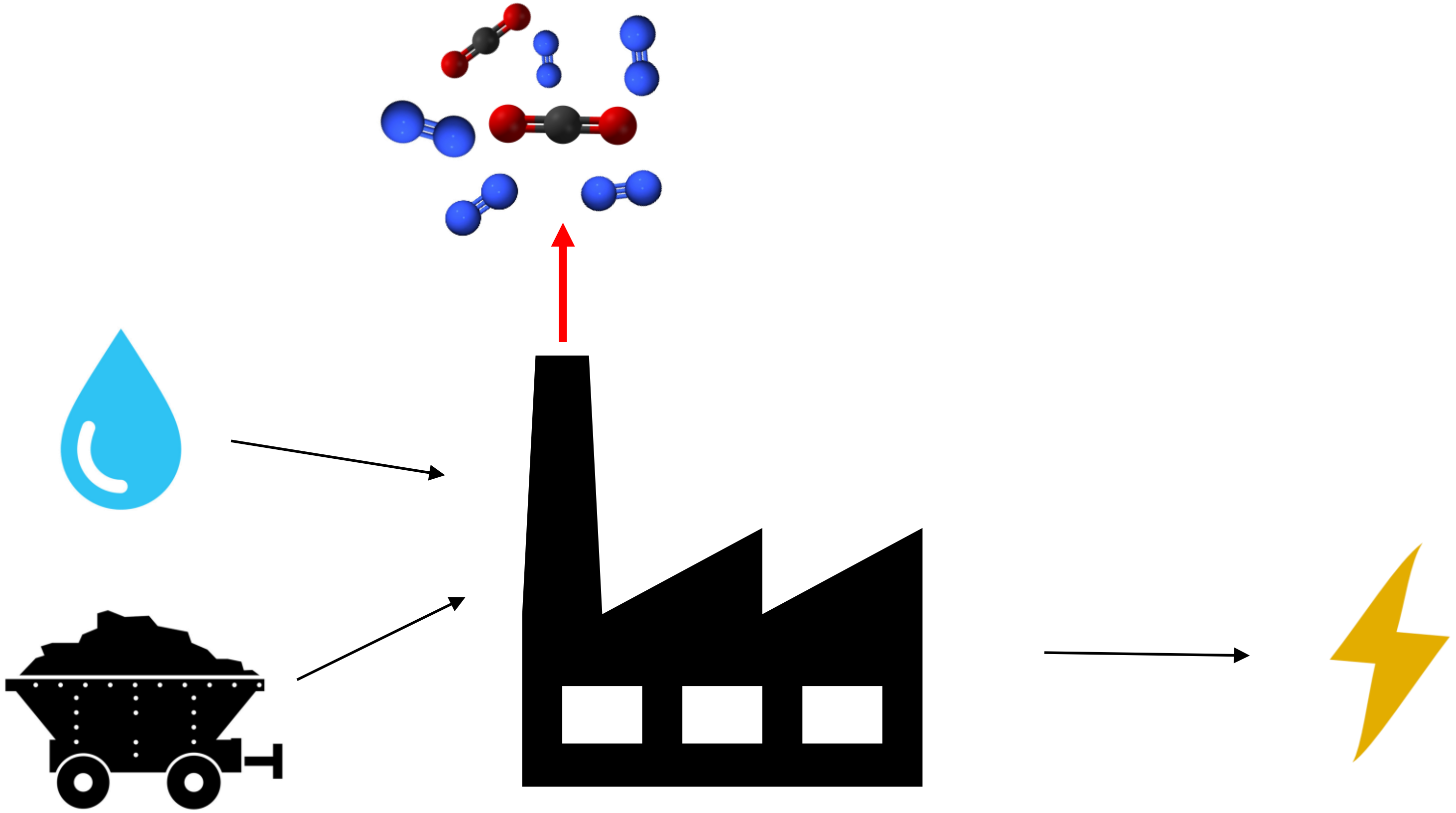

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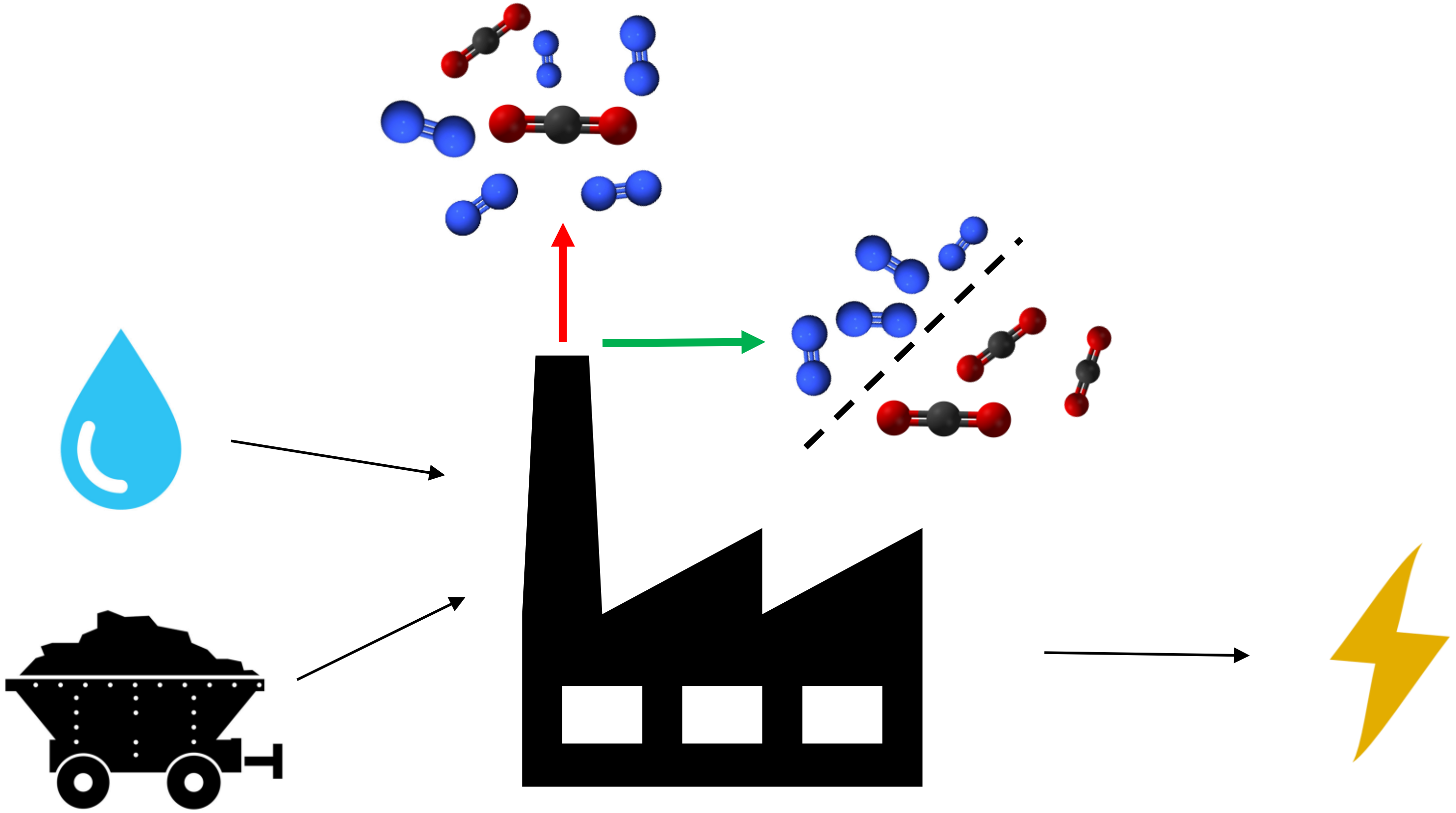

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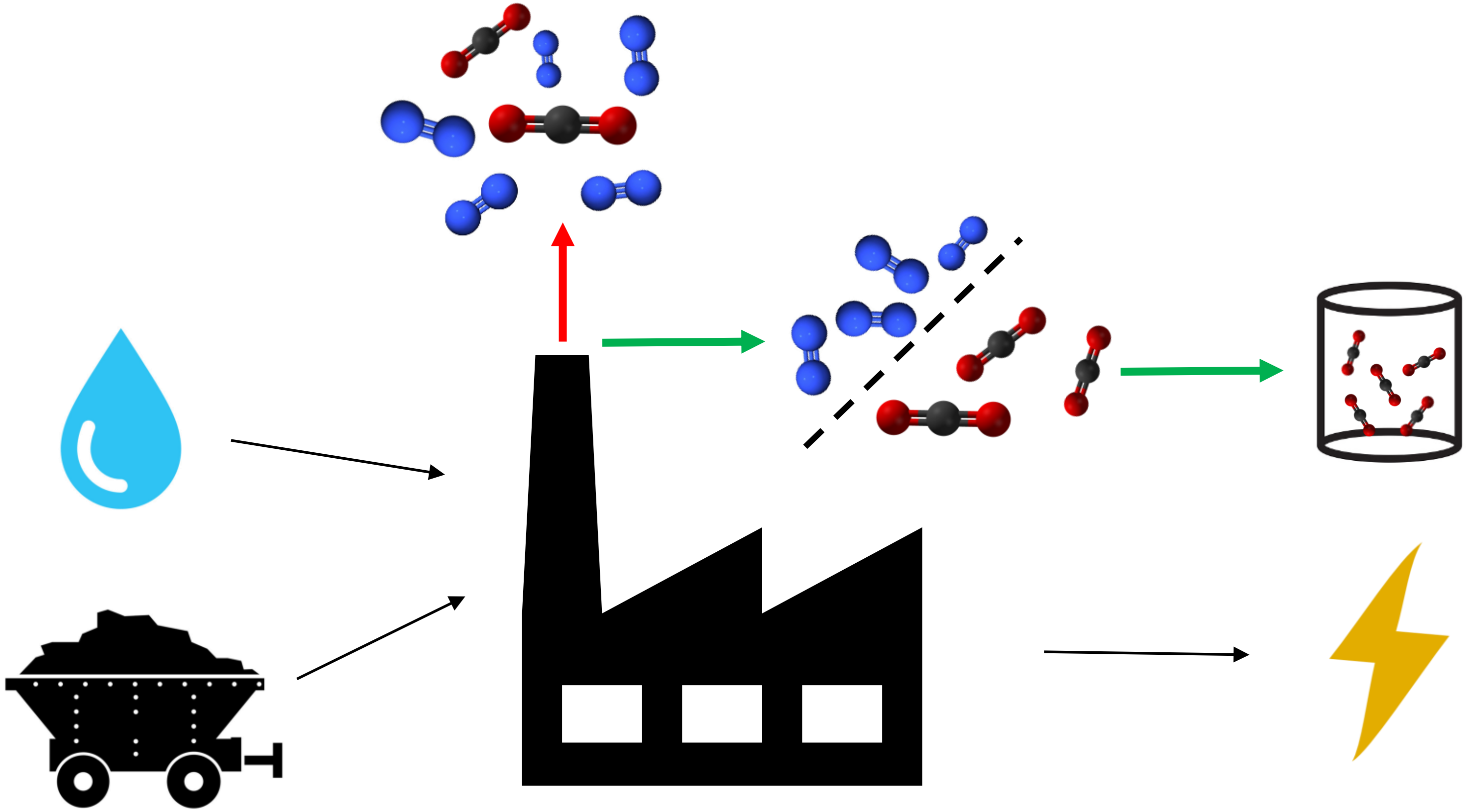
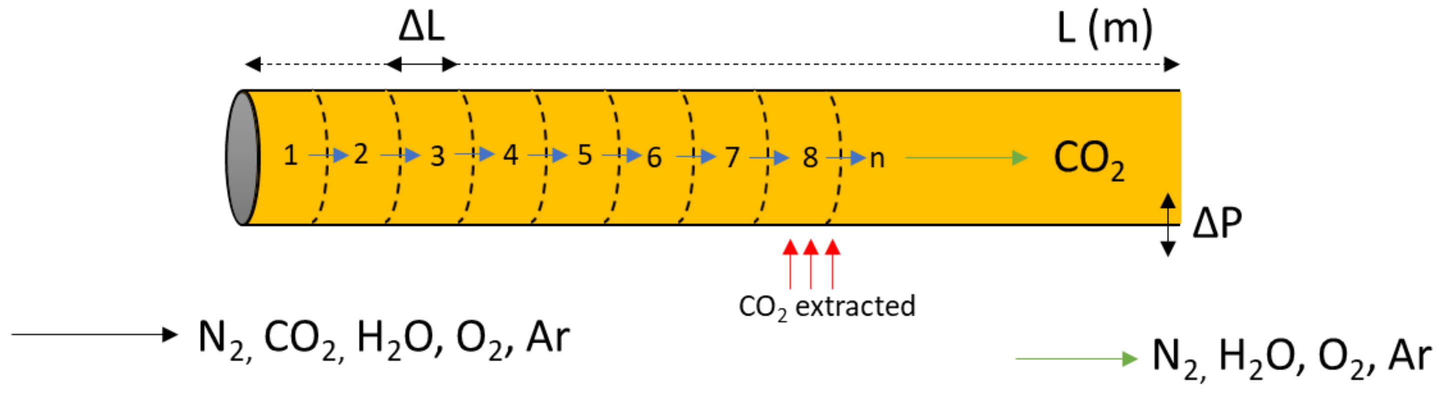


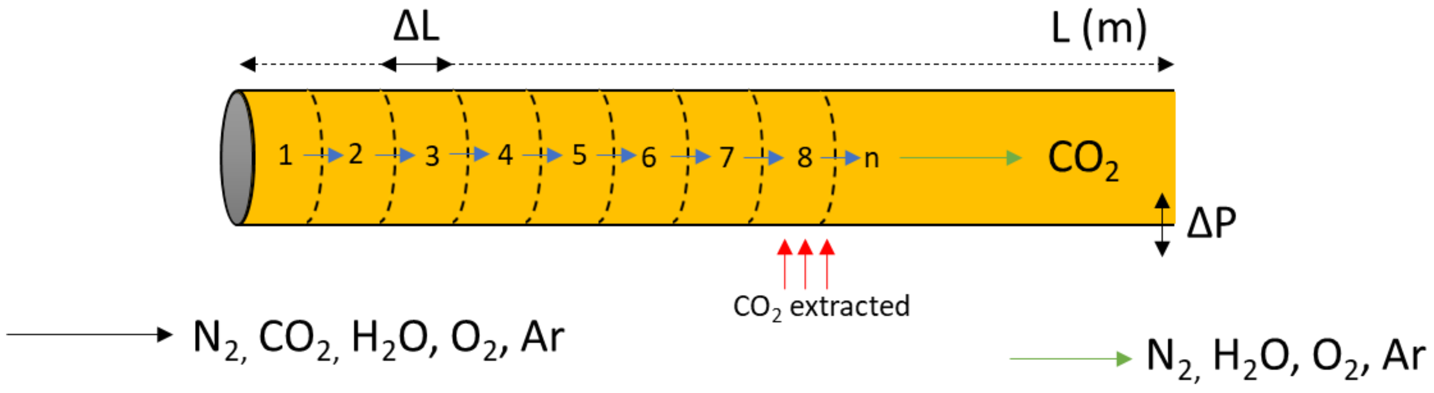
Hollow fiber membranes modelling

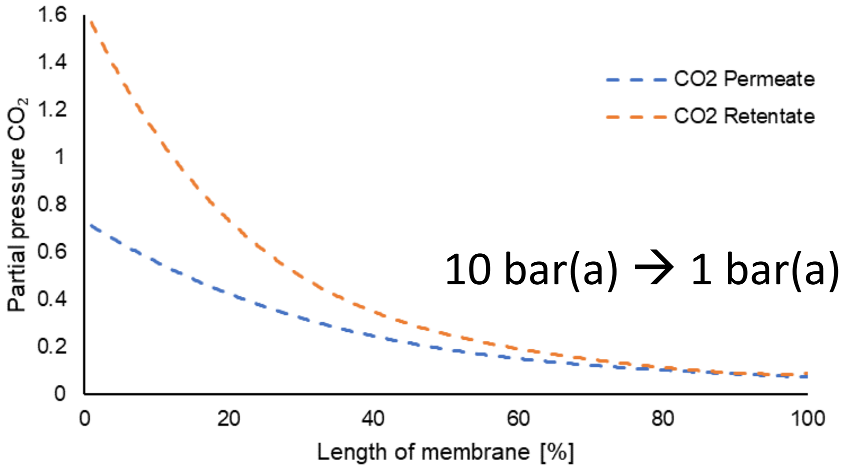


- Selectivity
- Permeability
- Length
- Pressure difference

→ Membrane area

Hollow fiber membranes modelling

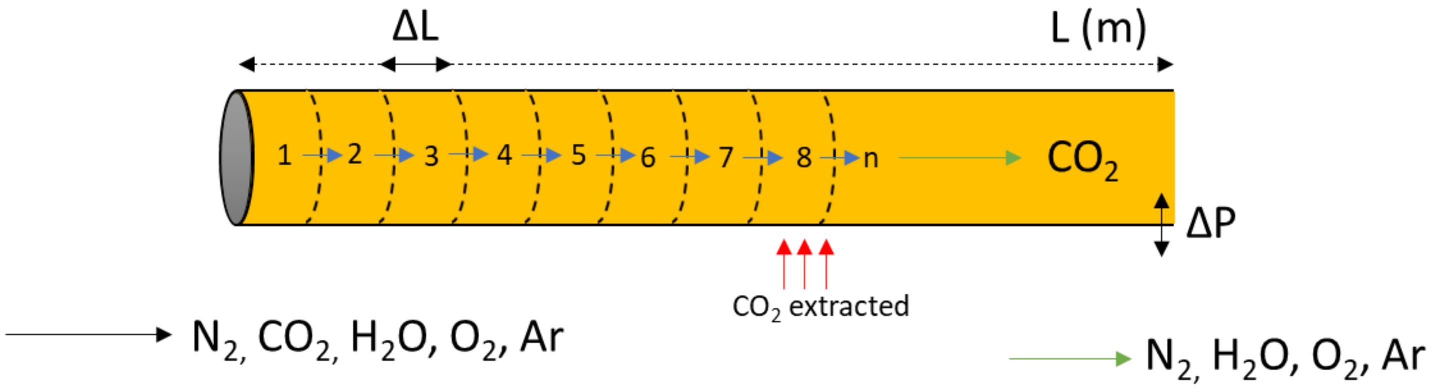


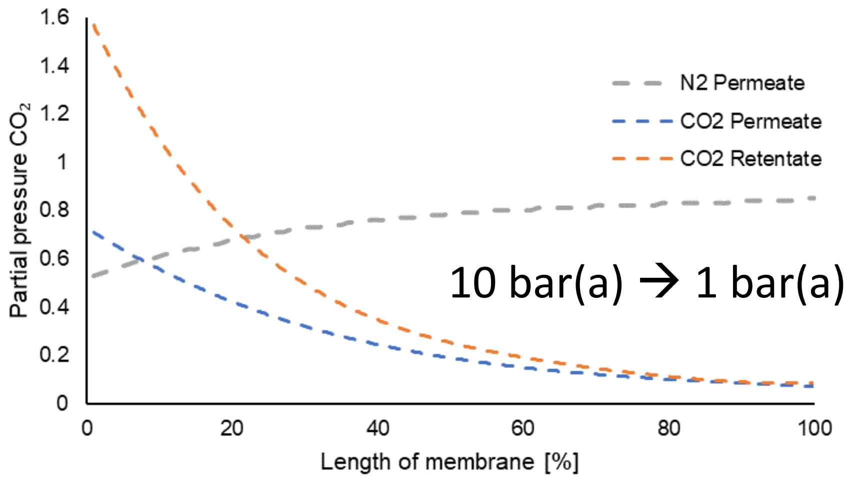


- Selectivity
- Permeability
- Length
- Pressure difference

→ Membrane area

Hollow fiber membranes modelling

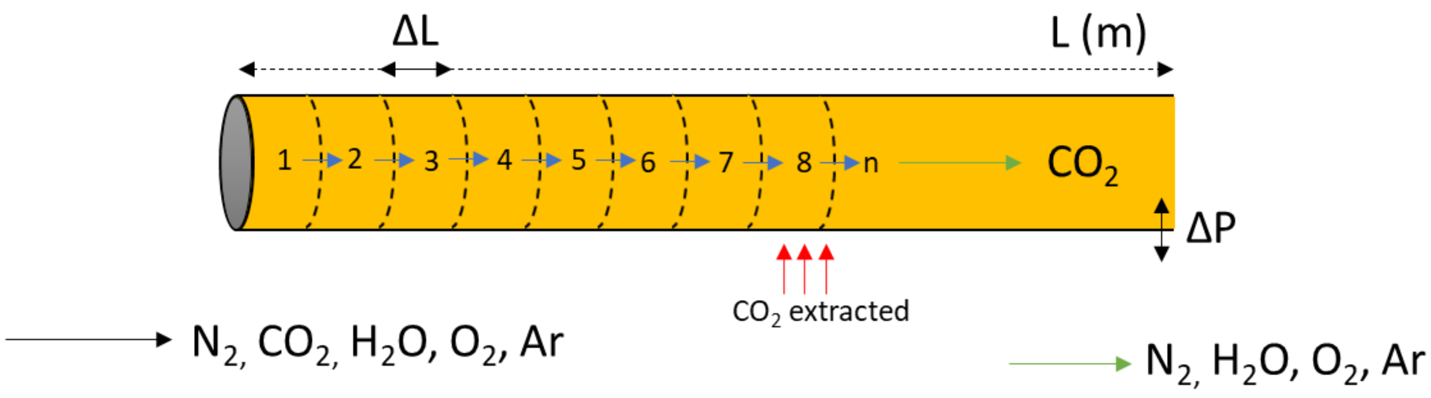


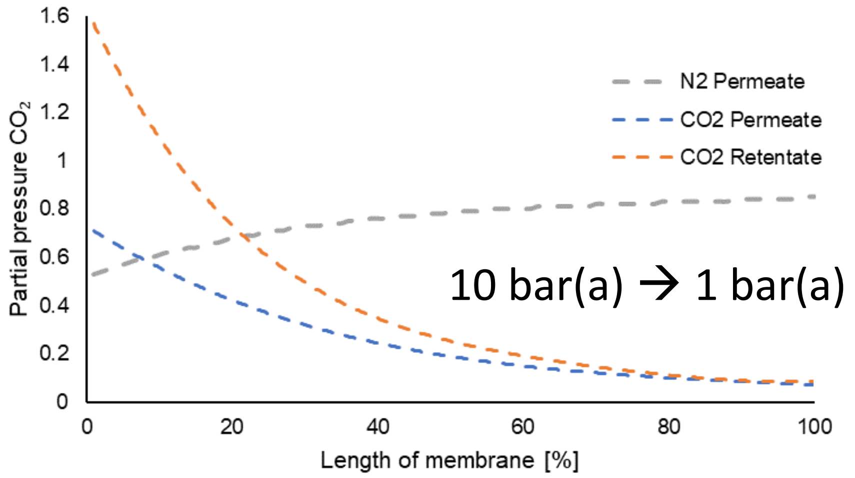


- Selectivity
- Permeability
- Length
- Pressure difference

→ Membrane area

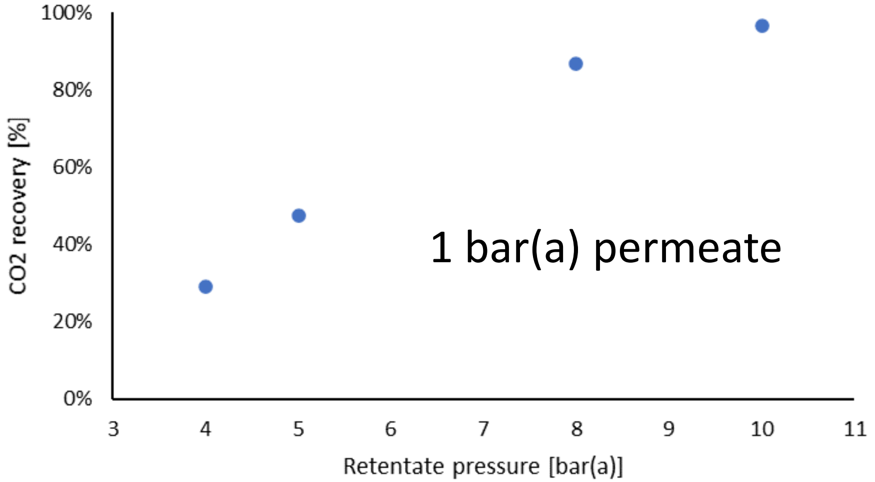
Hollow fiber membranes modelling





- Selectivity
- Permeability
- Length
- Pressure difference

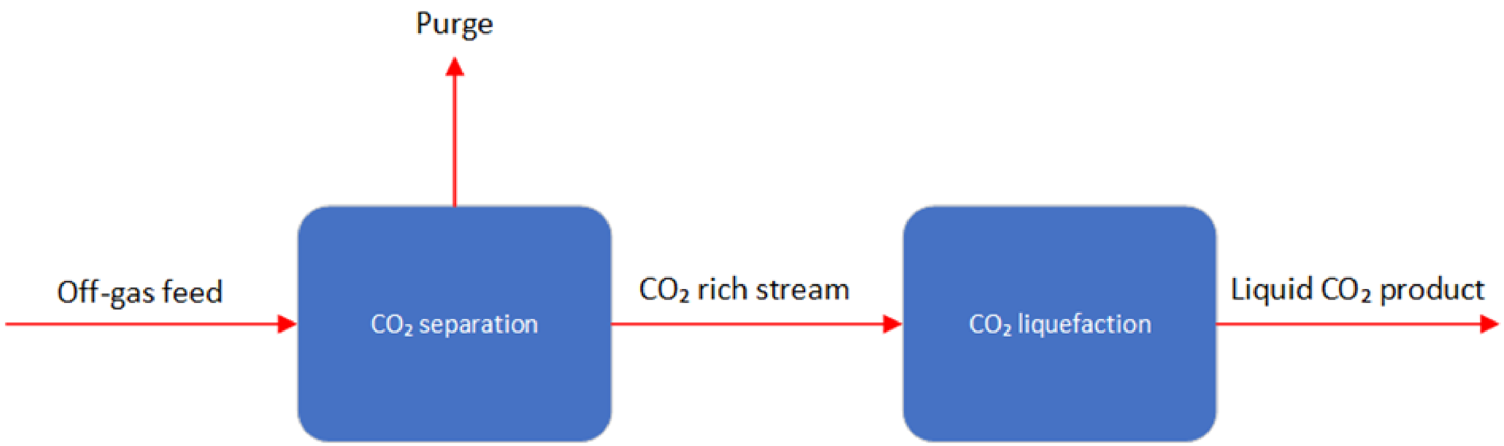
→ Membrane area



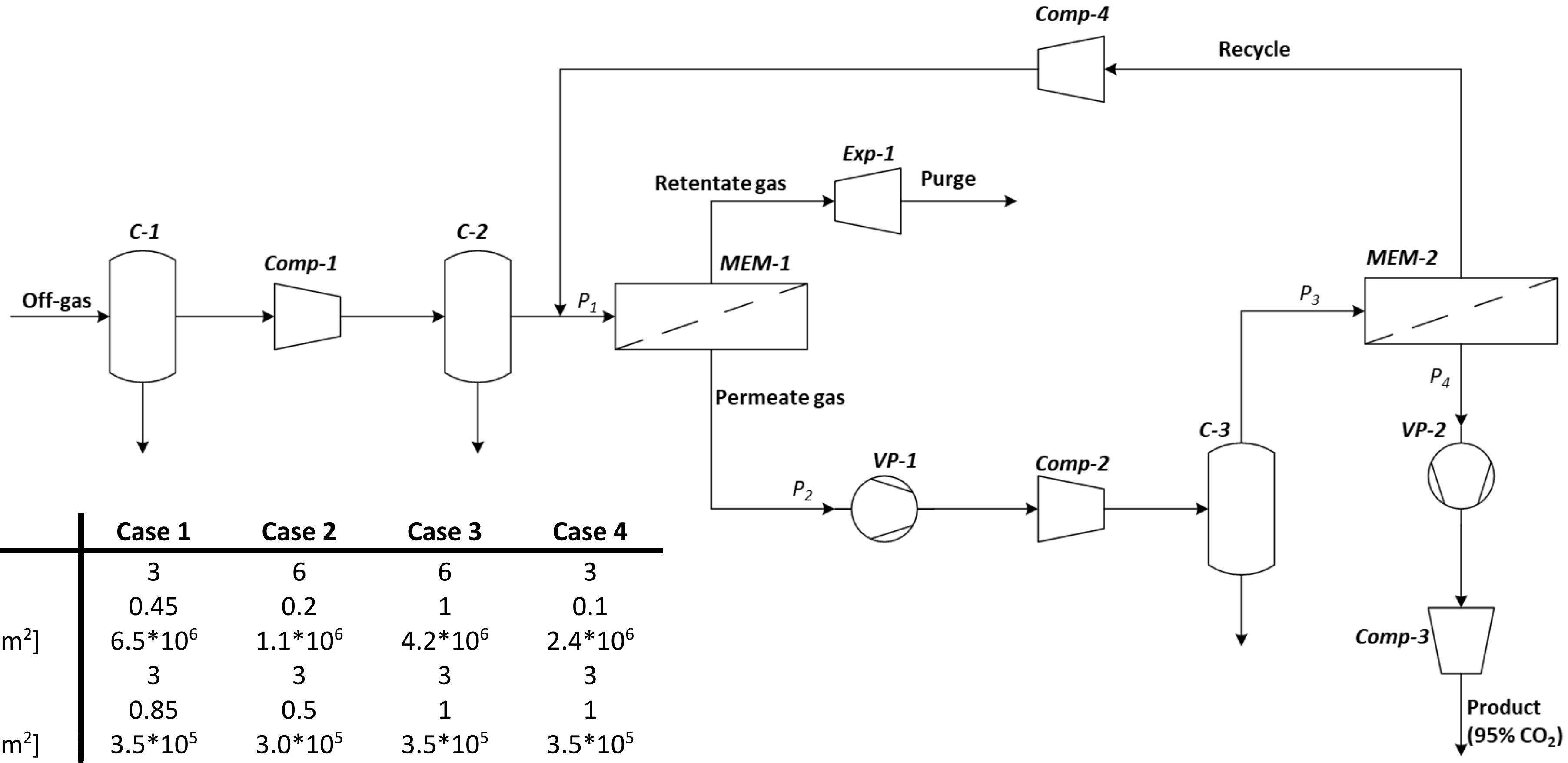
Process functional diagram

- Basis of design
  - MMM in coal fired power plant with net power production 550 MWe
  - 90 % CO_2 recovery & 95 % CO_2 purity

Component	Composition mol %
CO_2	13.5
N_2	68.1
O_2	2.4
H_2O	15.2
Ar	0.8

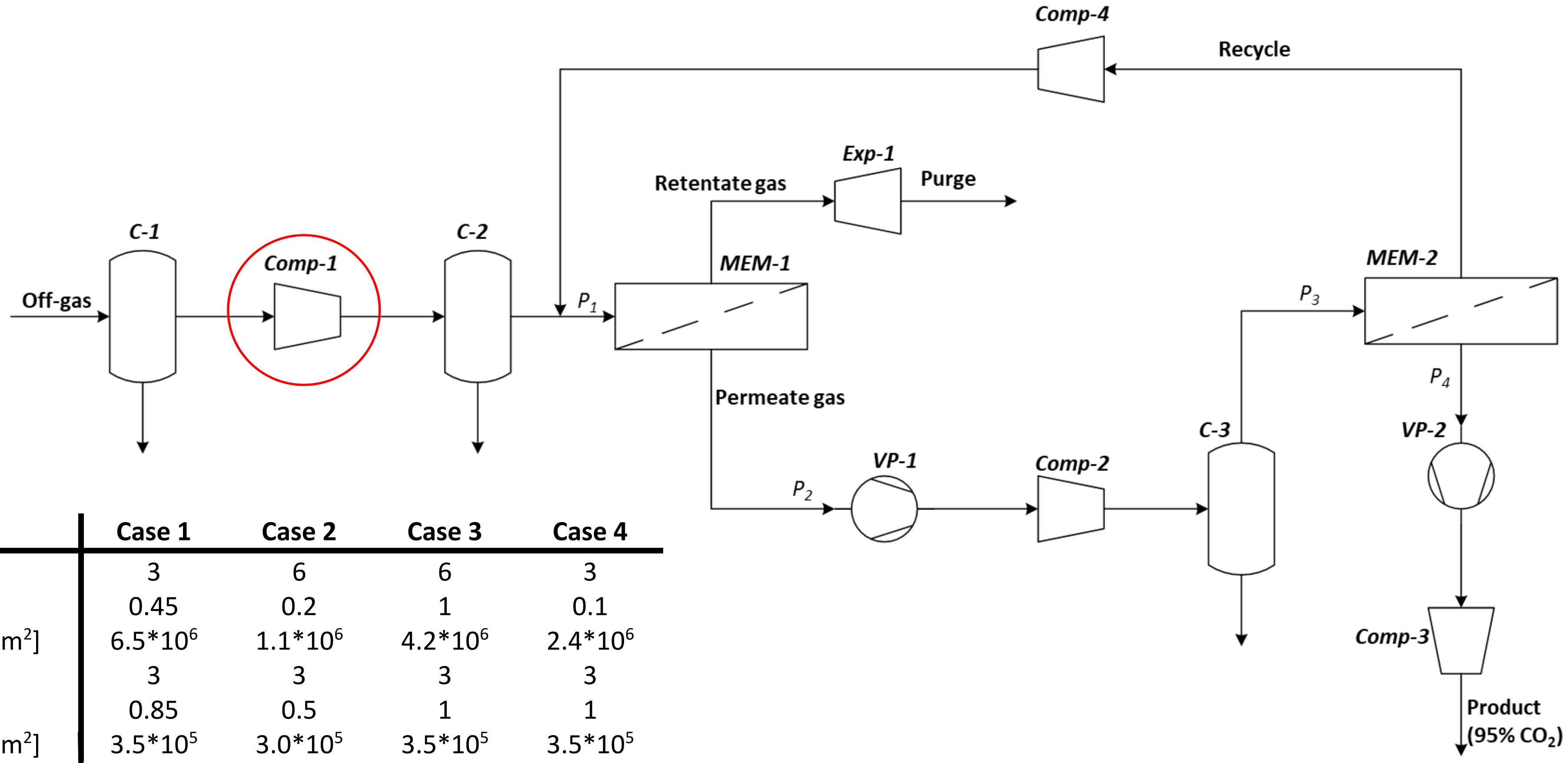


Process flow diagram



Parameter	Case 1	Case 2	Case 3	Case 4
P_1 [bar_a]	3	6	6	3
P_2 [bar_a]	0.45	0.2	1	0.1
Area MEM-1 [m^2]	$6.5*10^6$	$1.1*10^6$	$4.2*10^6$	$2.4*10^6$
P_3 [bar_a]	3	3	3	3
P_4 [bar_a]	0.85	0.5	1	1
Area MEM-2 [m^2]	$3.5*10^5$	$3.0*10^5$	$3.5*10^5$	$3.5*10^5$
E %-net power coal plant	24.6%	27.7%	28.8%	24.9%

Process flow diagram



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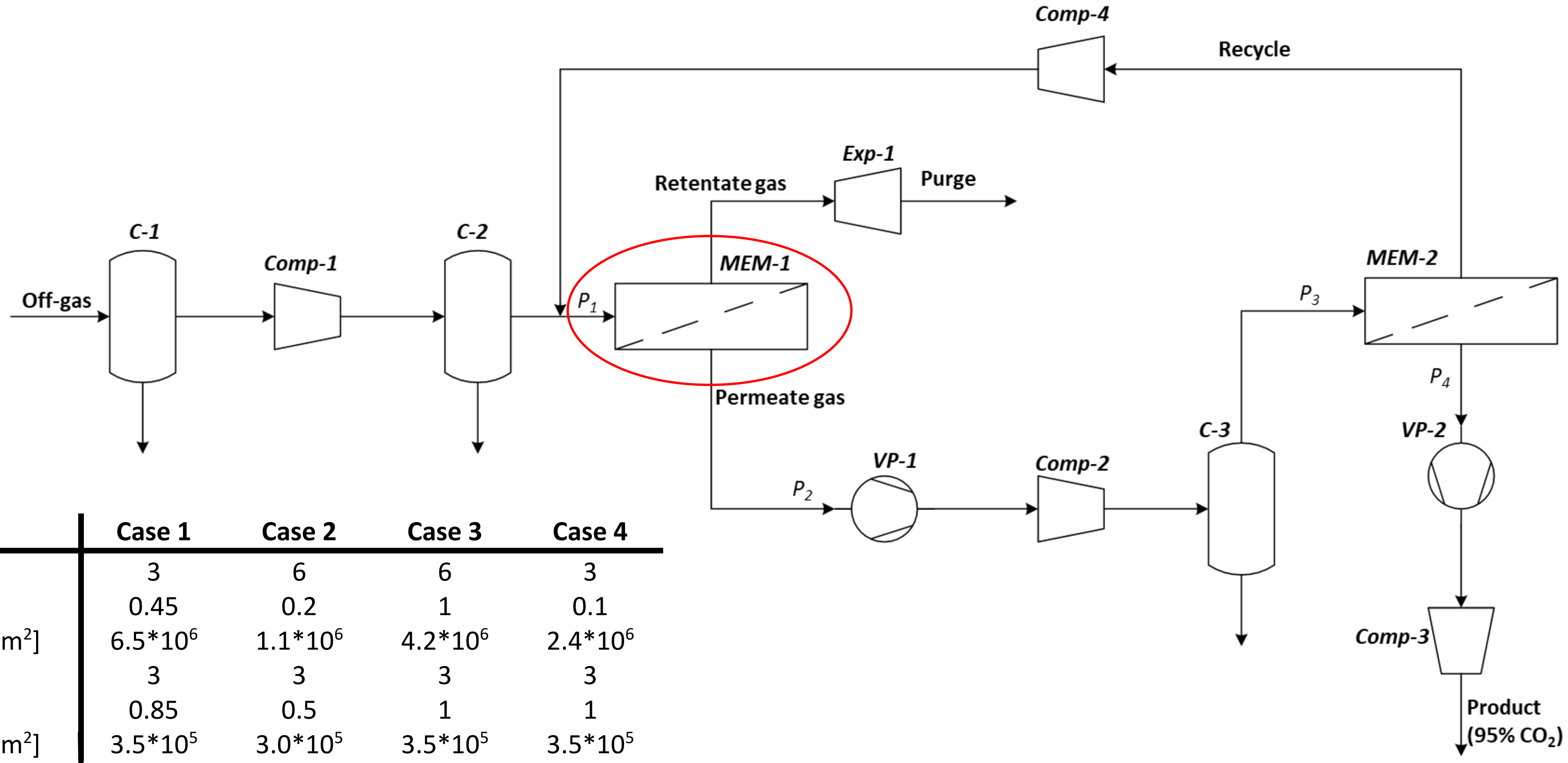

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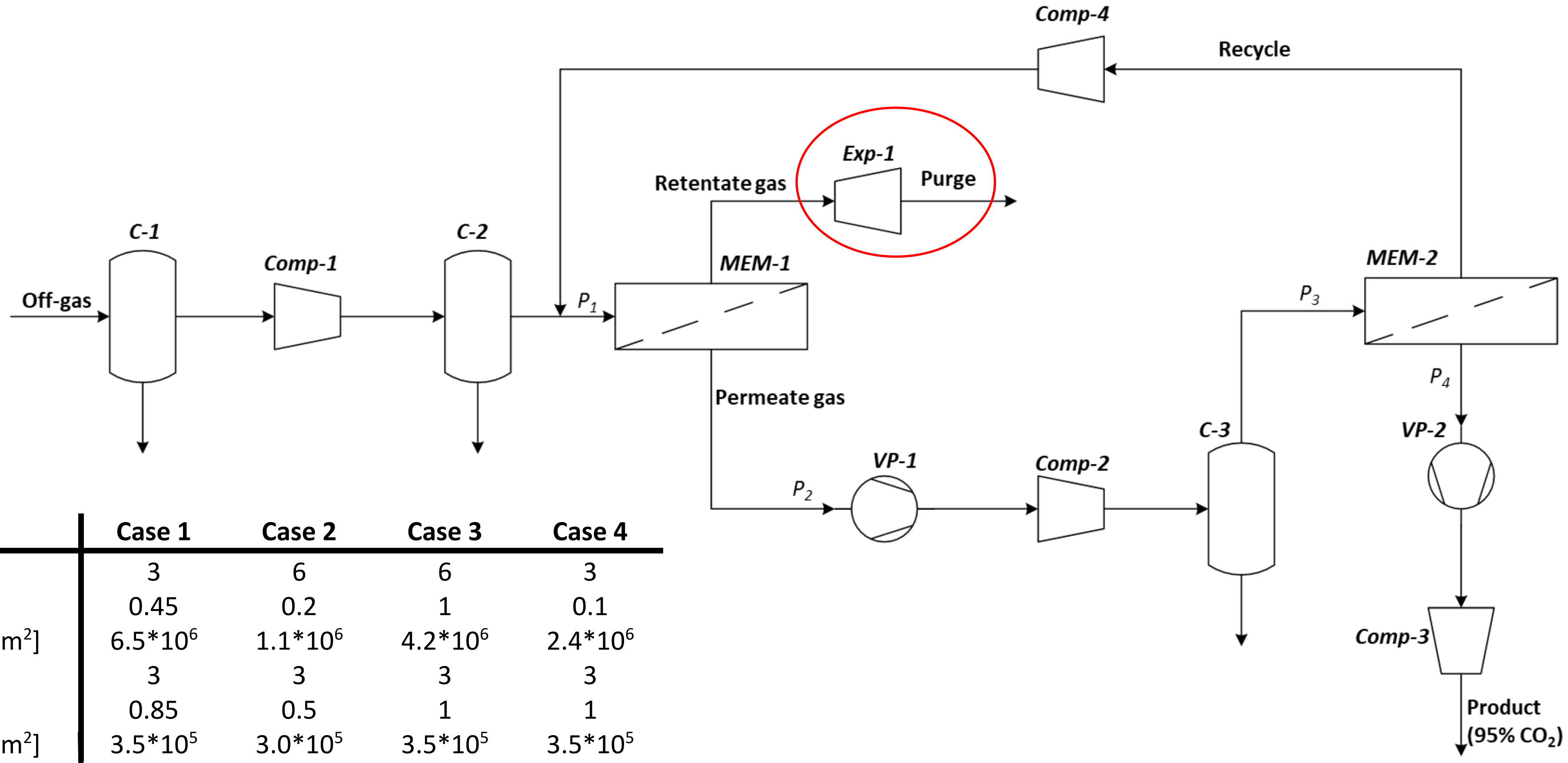

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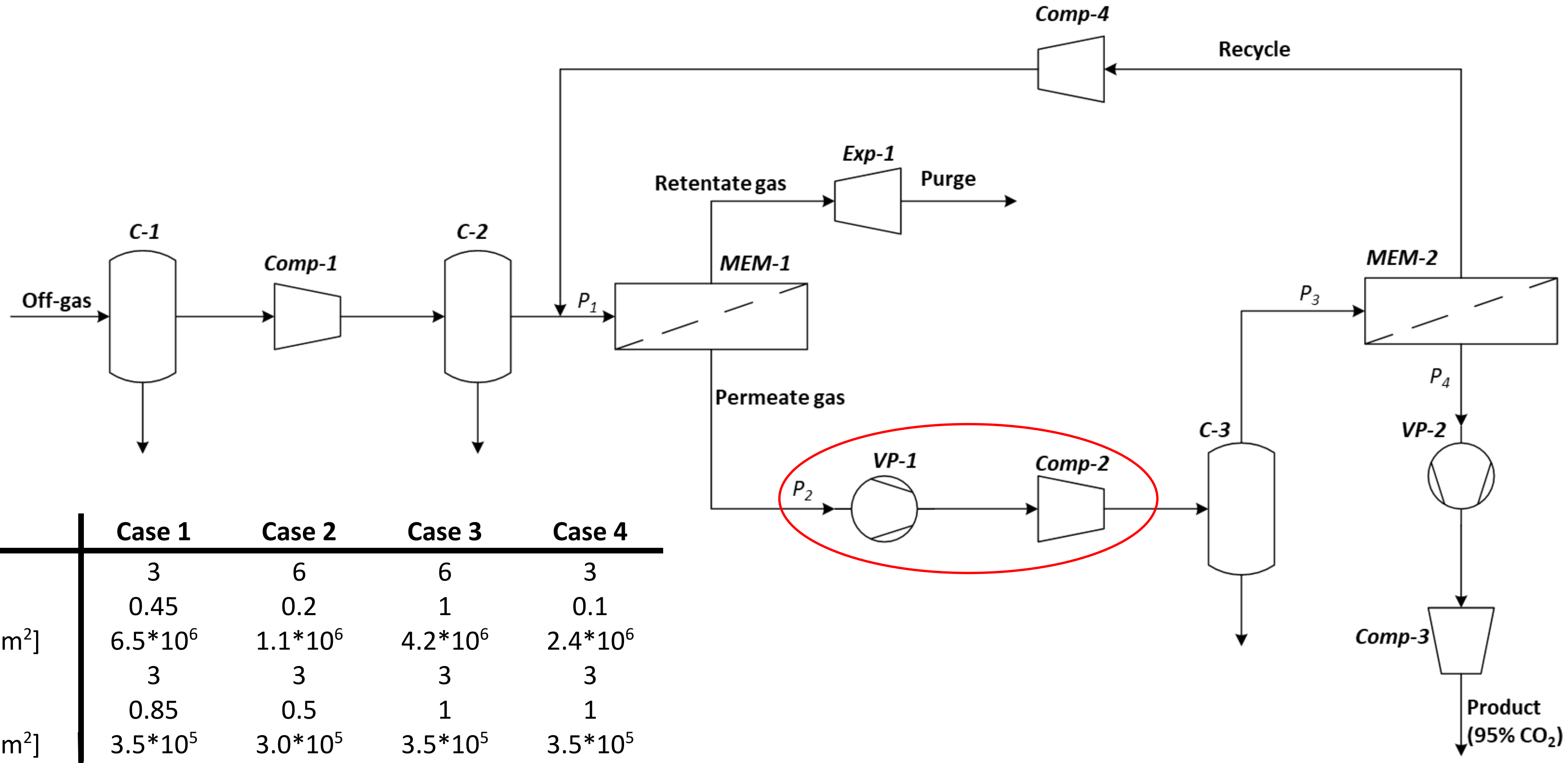

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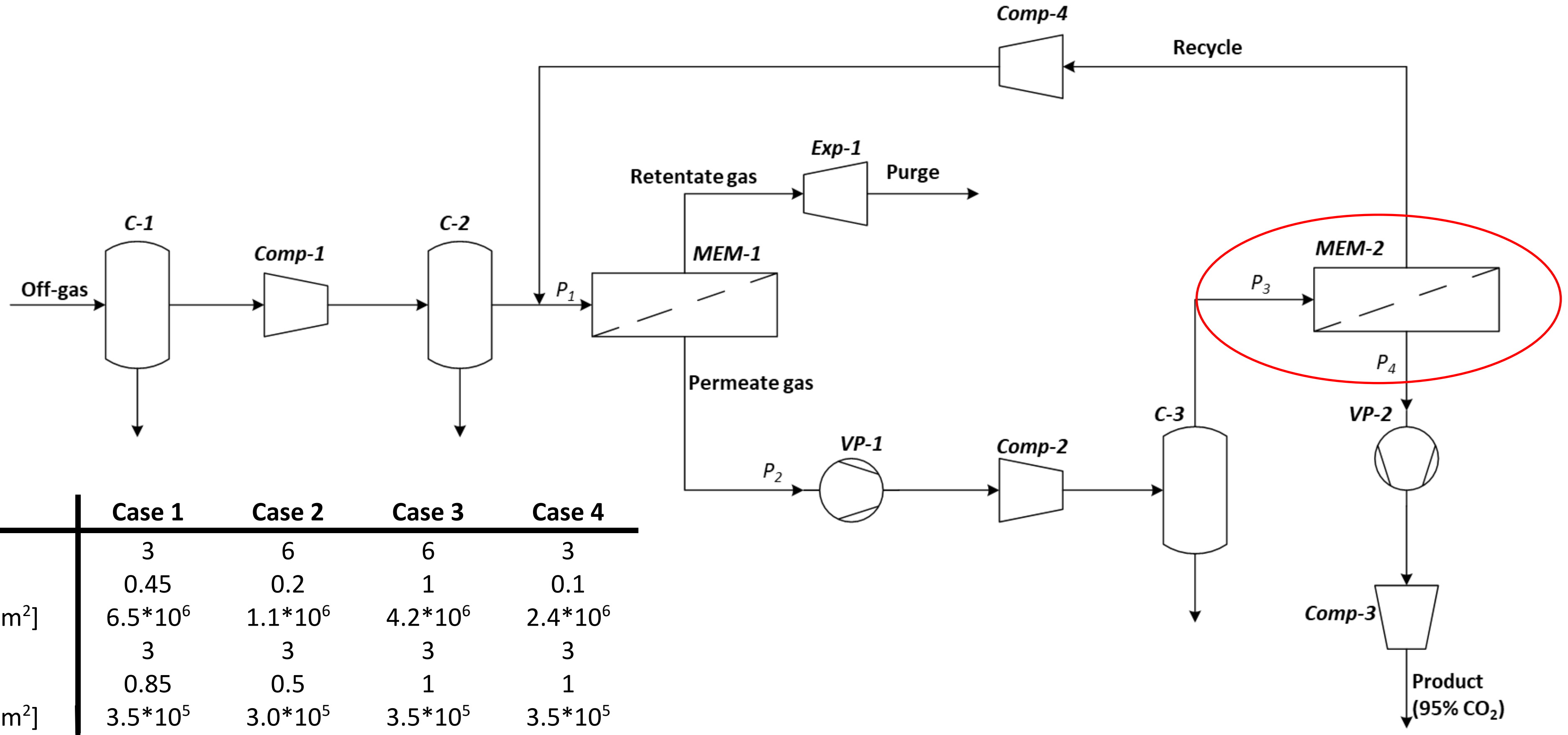

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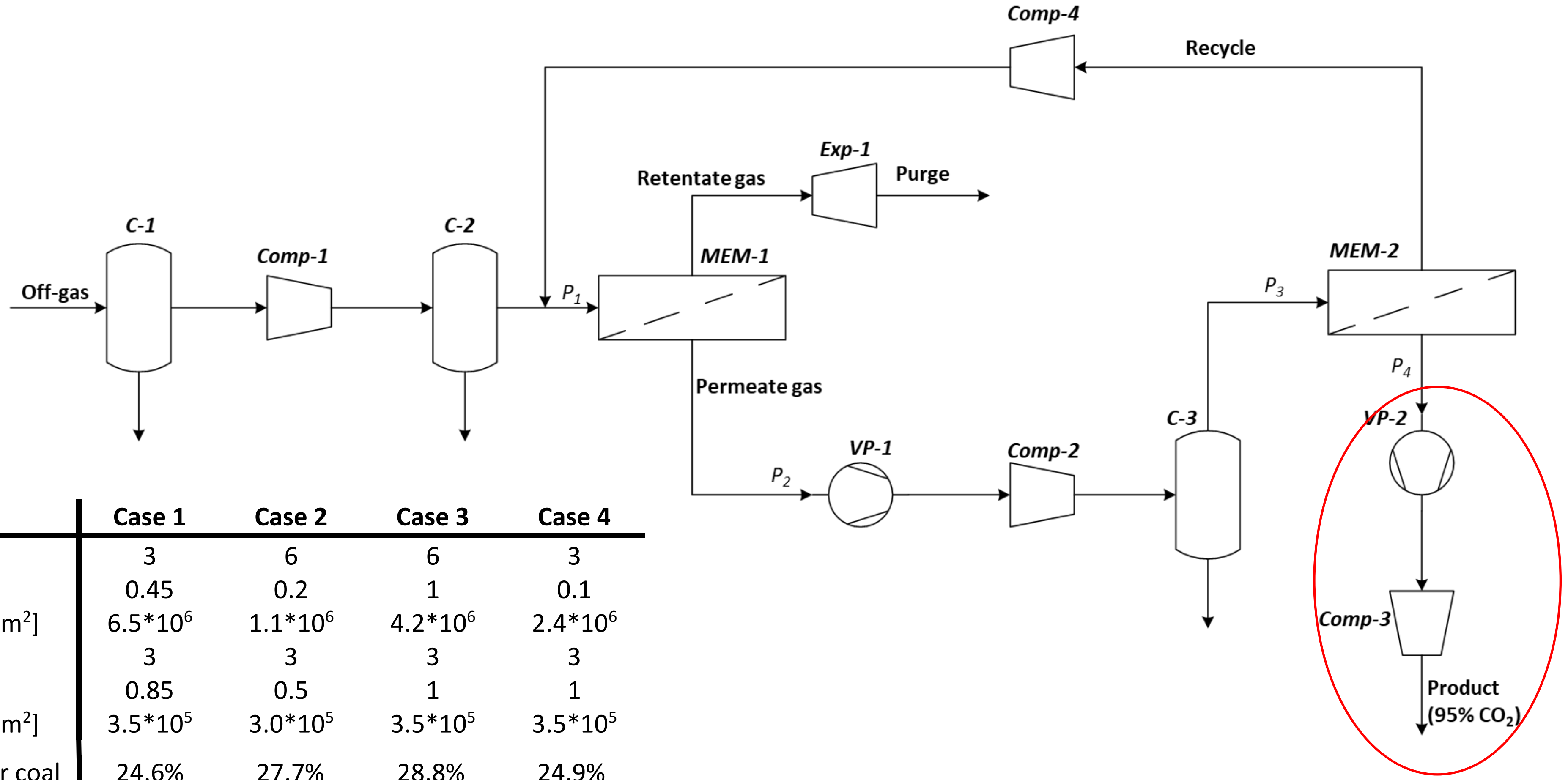

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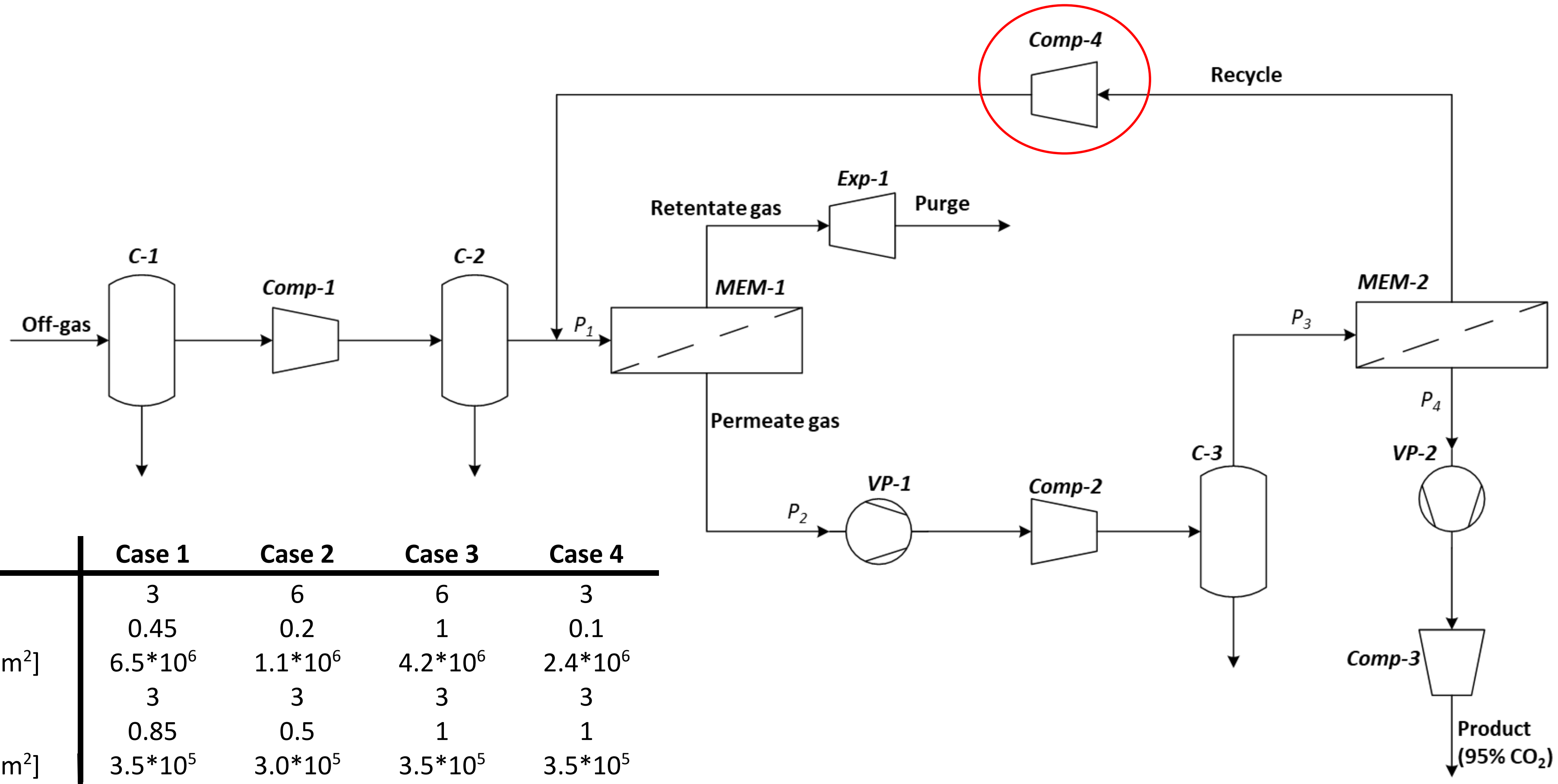

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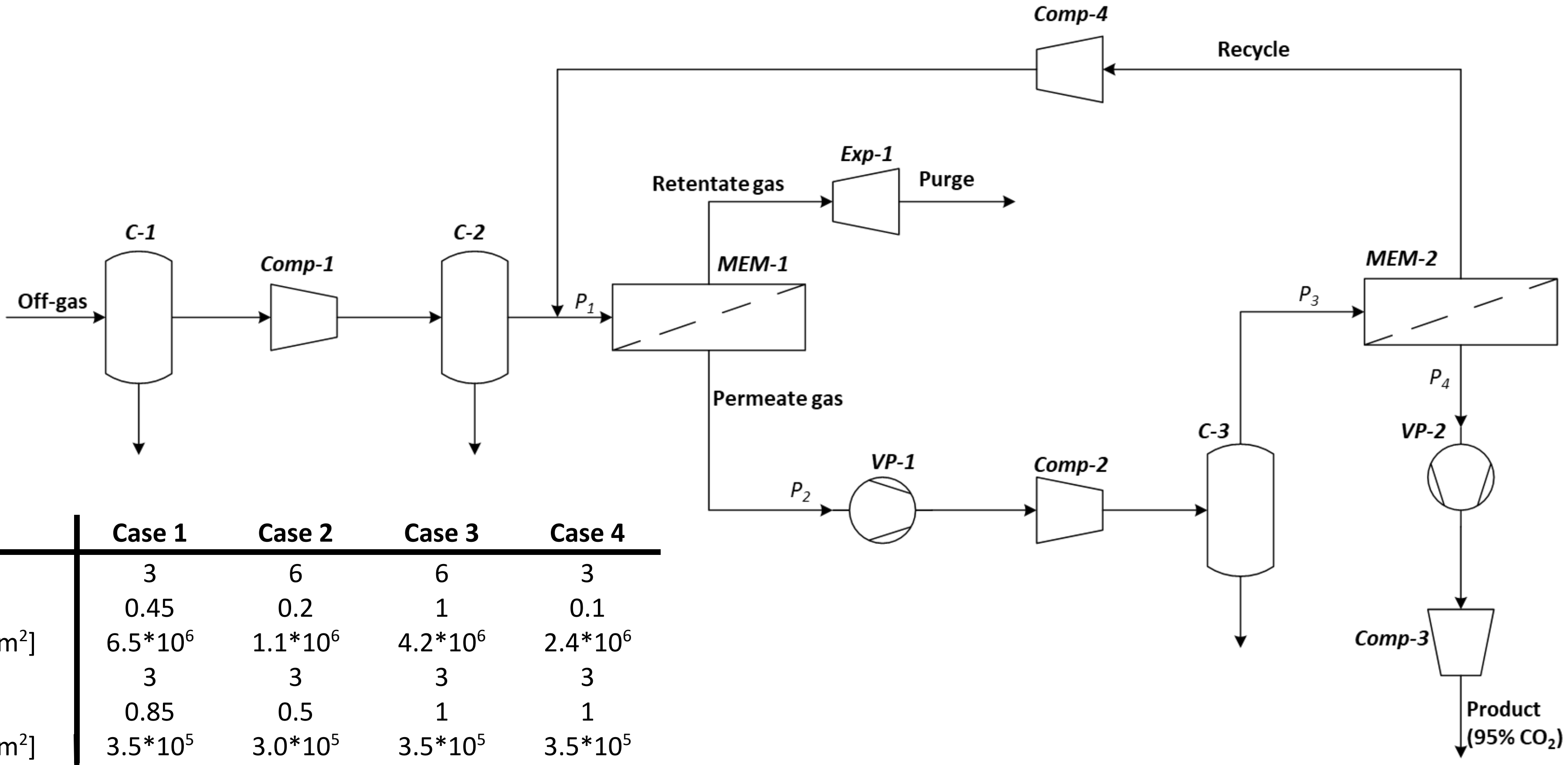

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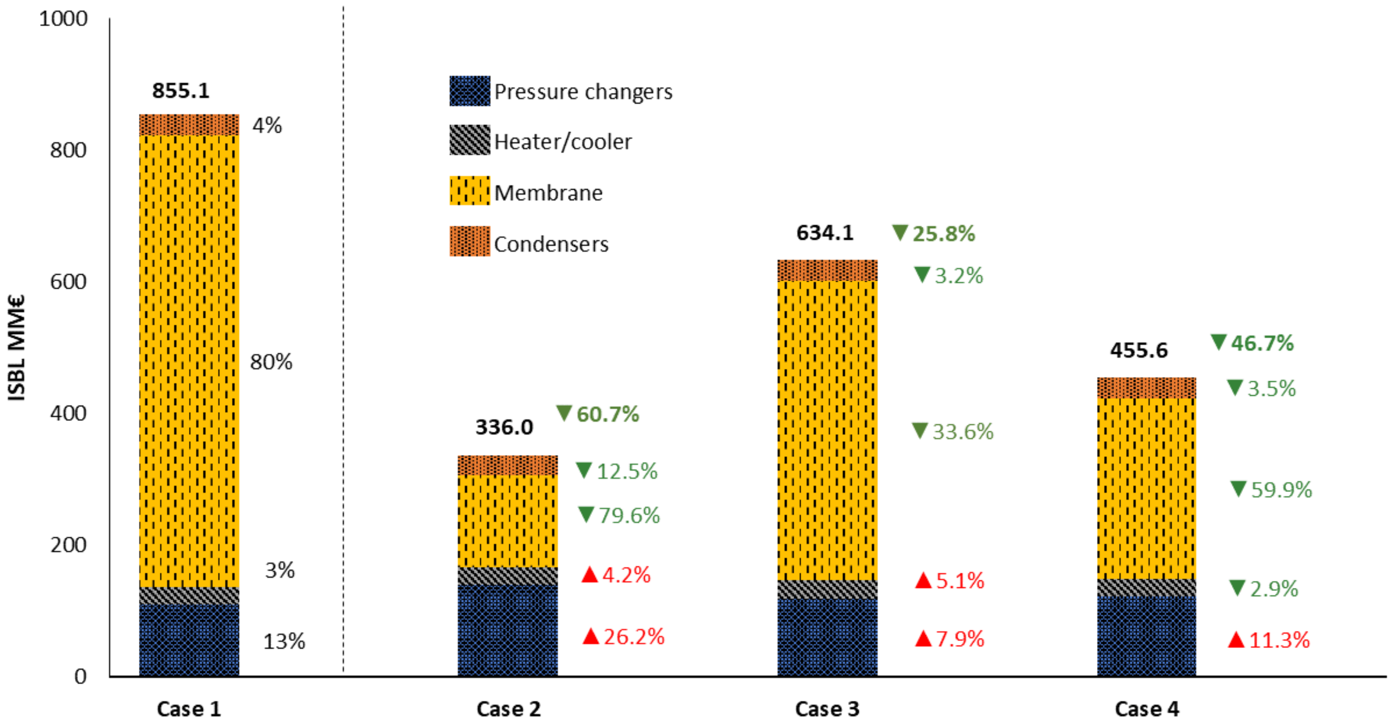
Simulation results (CAPEX)

- Membrane cost → 100 €/m²
- Membrane length → 0.5 m



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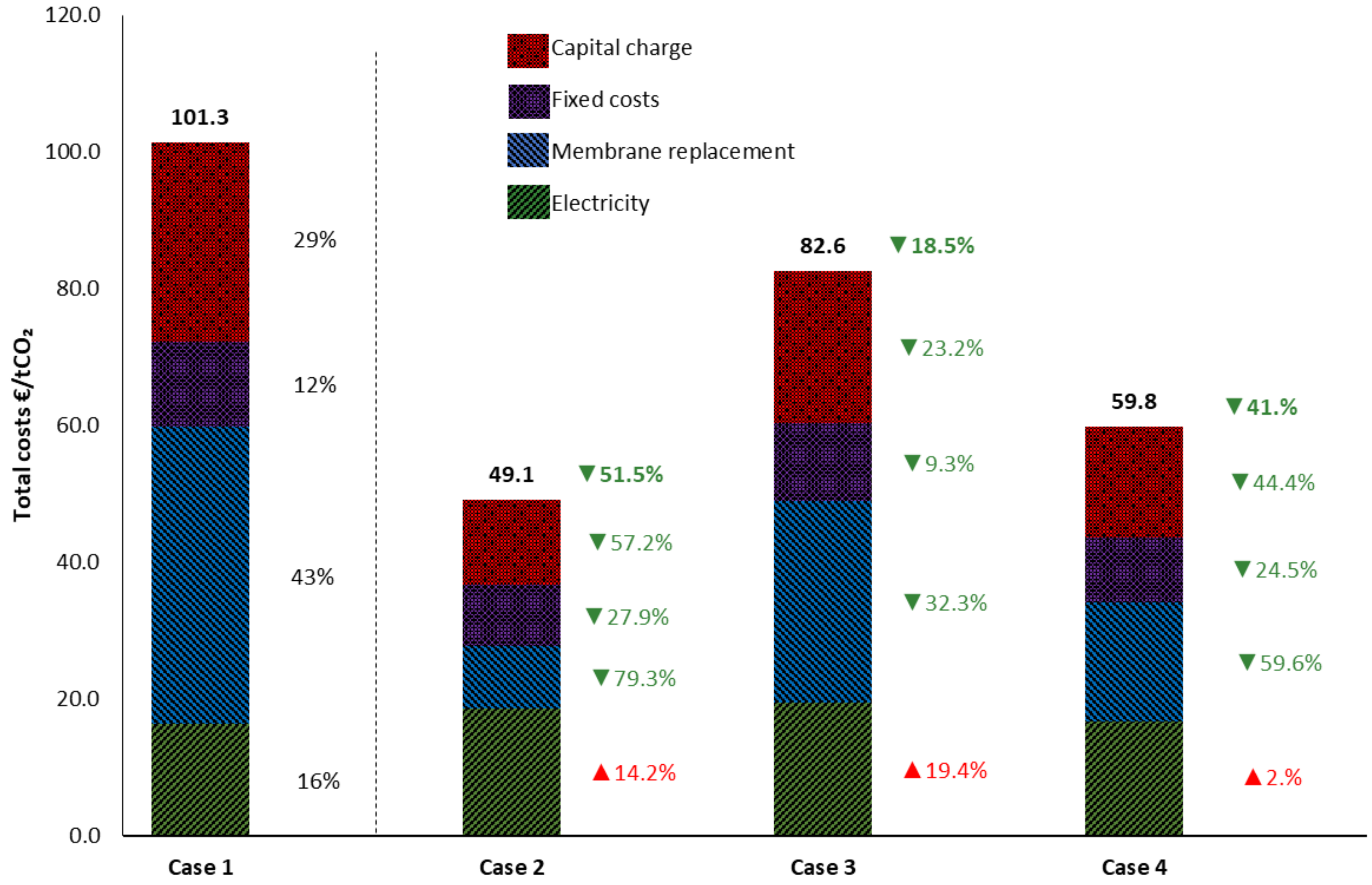
Simulation results (CAPEX + OPEX)

- Replacement → 5 yr
- Electricity → €52/MWh
- Operation → 8000 hr



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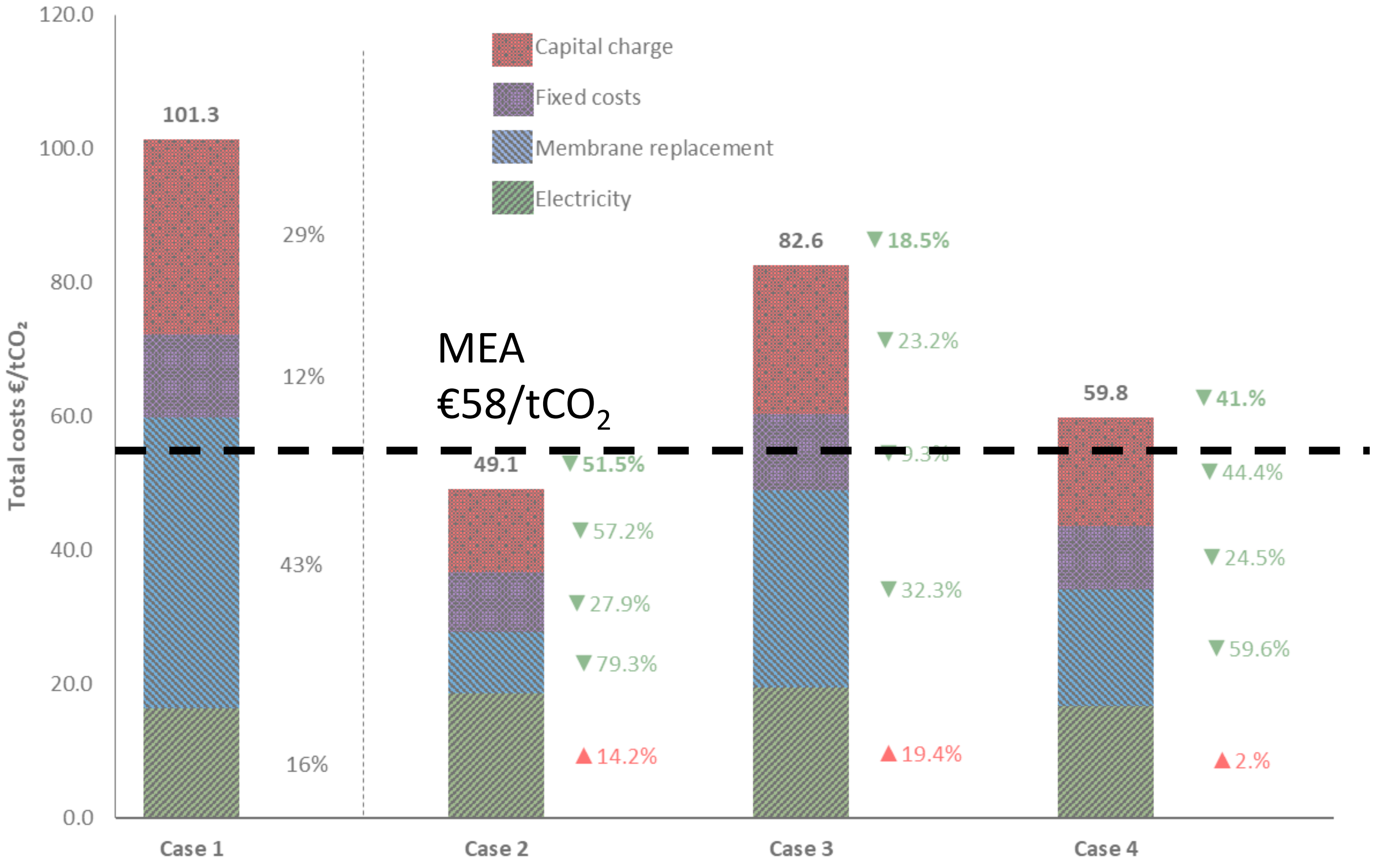

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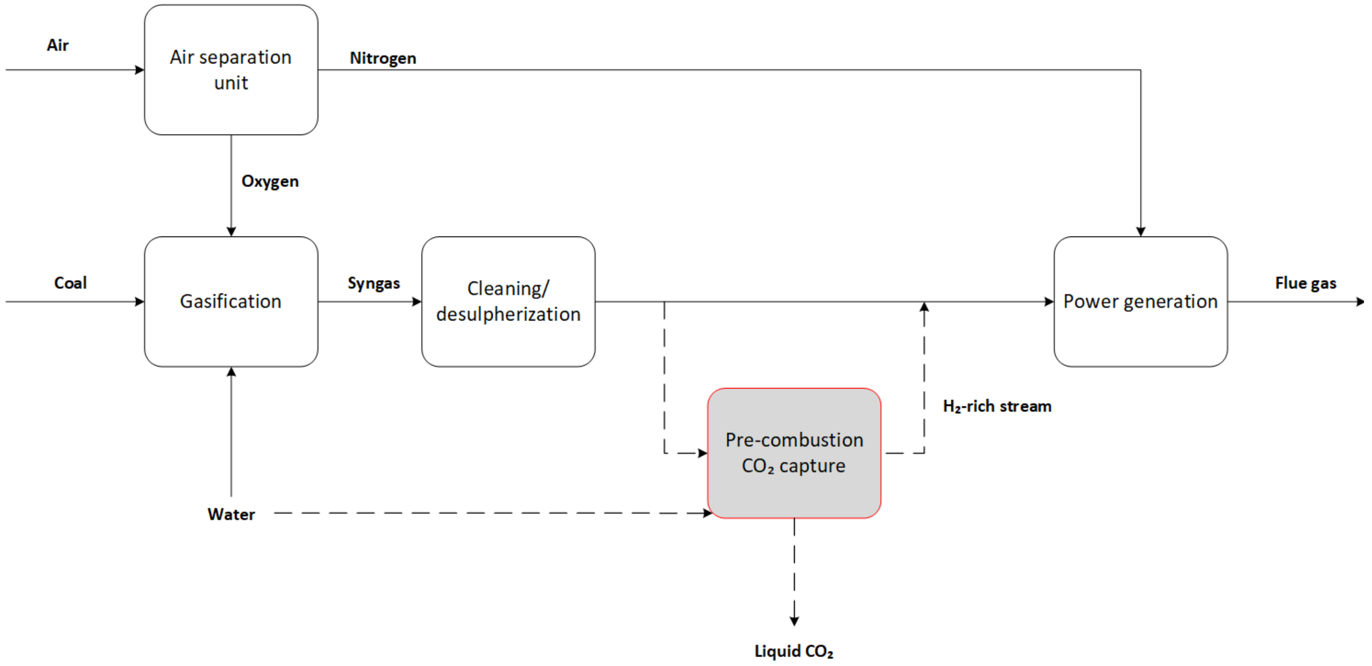
Conclusions and outlook for post-combustion carbon capture

- Cost-competitive with MEA
- Large membrane area

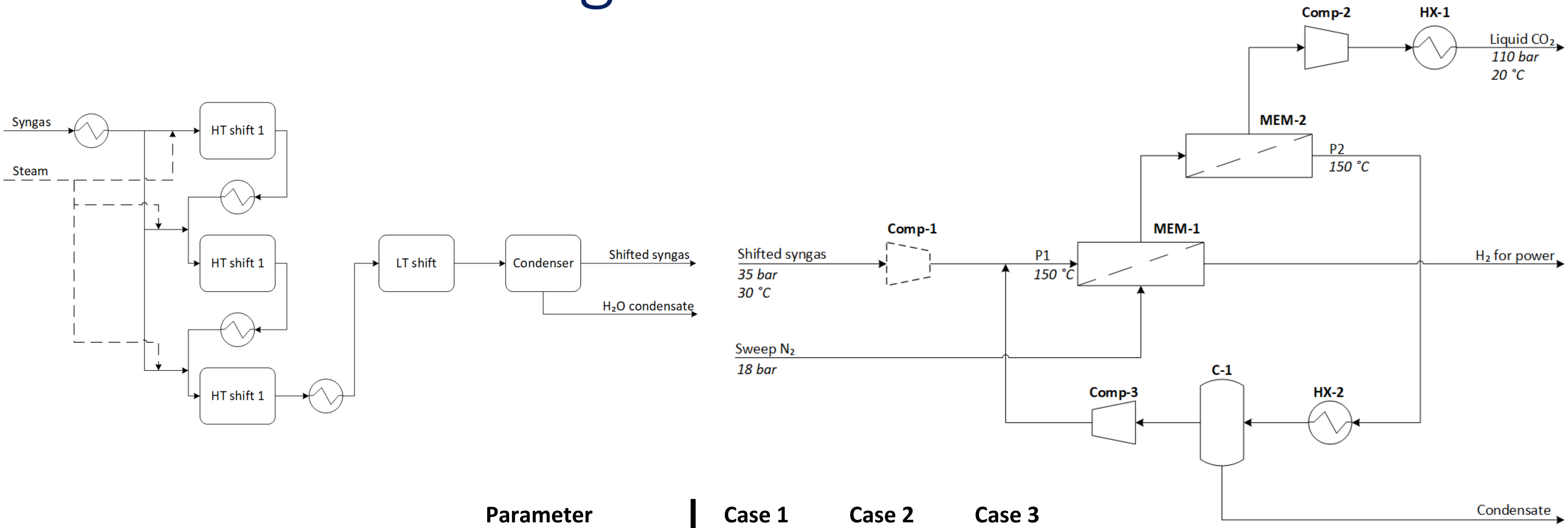
- Module design
- Decreasing membrane area
- Potentially interesting purge stream

Pre-combustion process

- Basis of design
  - MMM in coal fired IGCC with net power production 536 MWe
  - 90 % CO_2 recovery & 95 % CO_2 purity



Process flow diagram



Parameter	Case 1	Case 2	Case 3
P_1 [bar_a]	35	70	110
P_2 [bar_a]	5	10	15
Area MEM-1 [m^2]	110000	35000	20000
Area MEM-2 [m^2]	260000	110000	60000
E %-net power plant	12.4%	9.1%	9.3%

HYGEAR
Member of the xebec group

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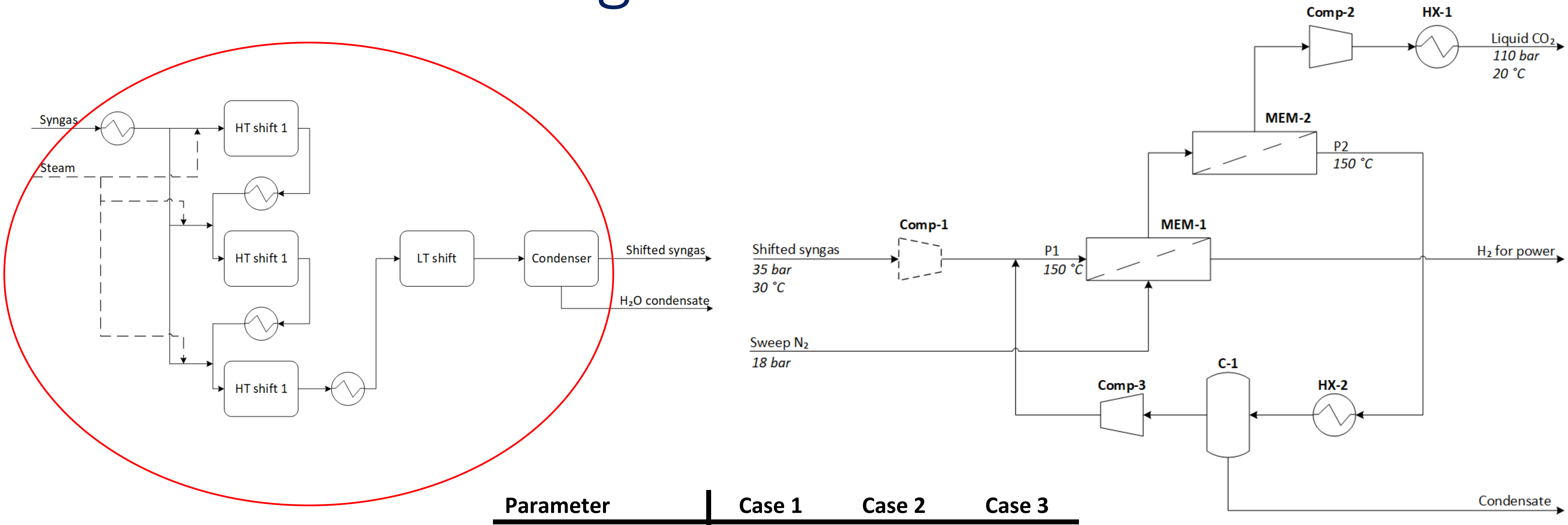
Webinar MEMBER
23-02-2022

Process flow diagram



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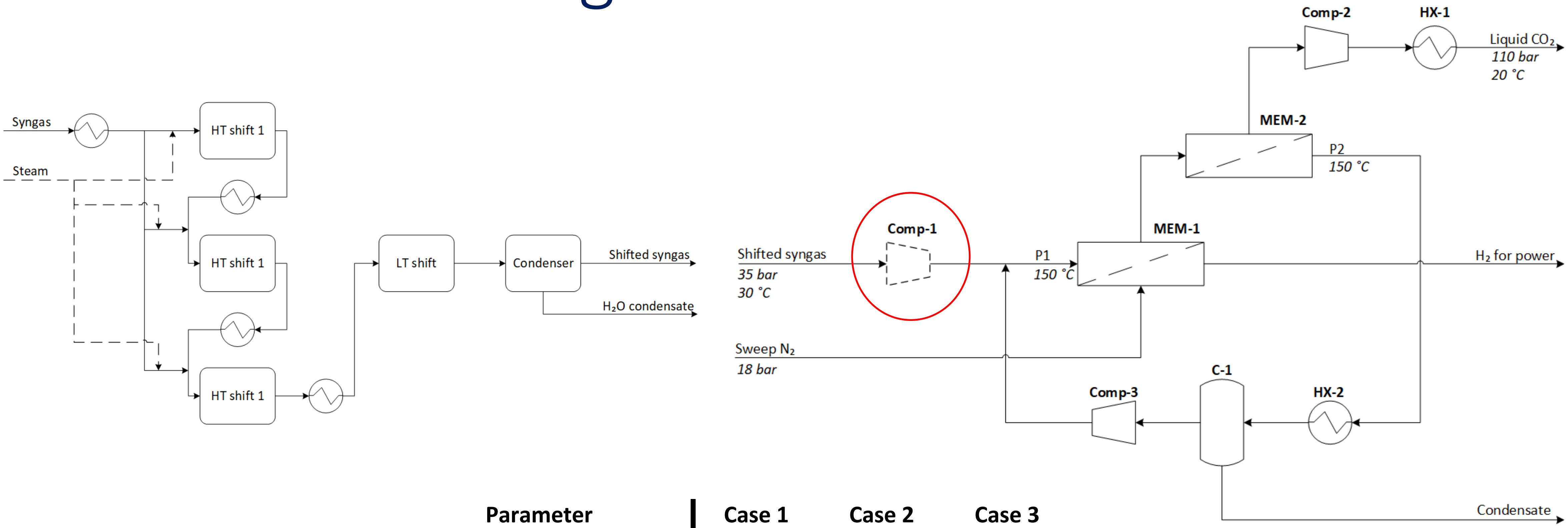

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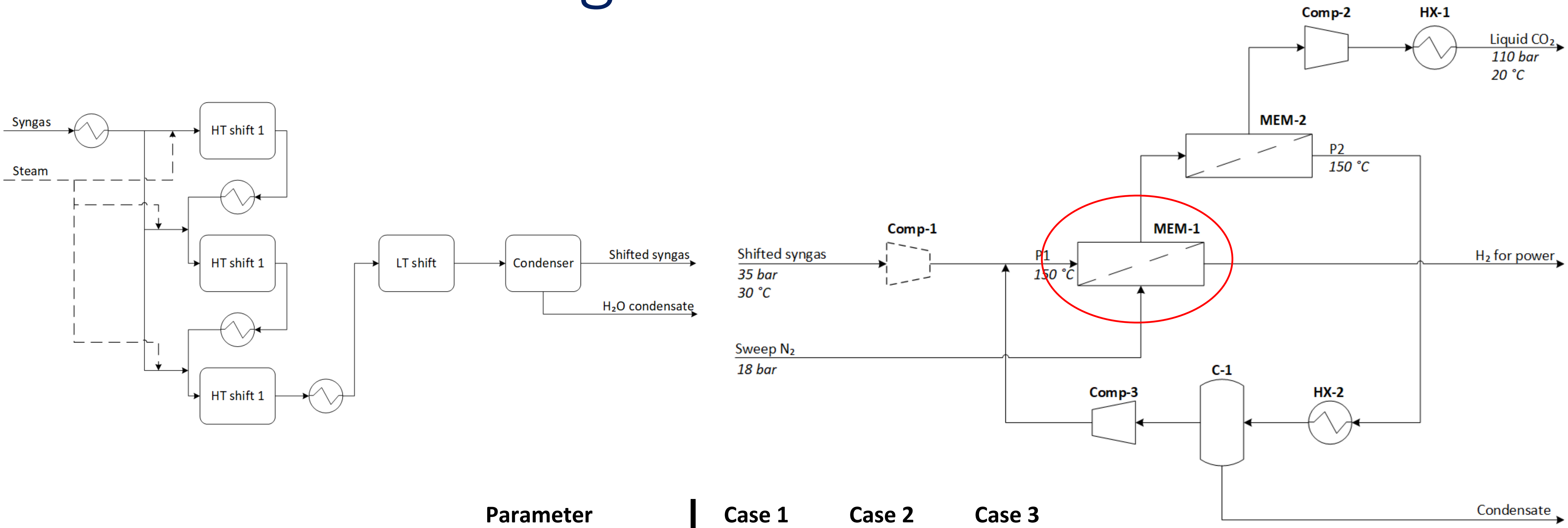
Process flow diagram



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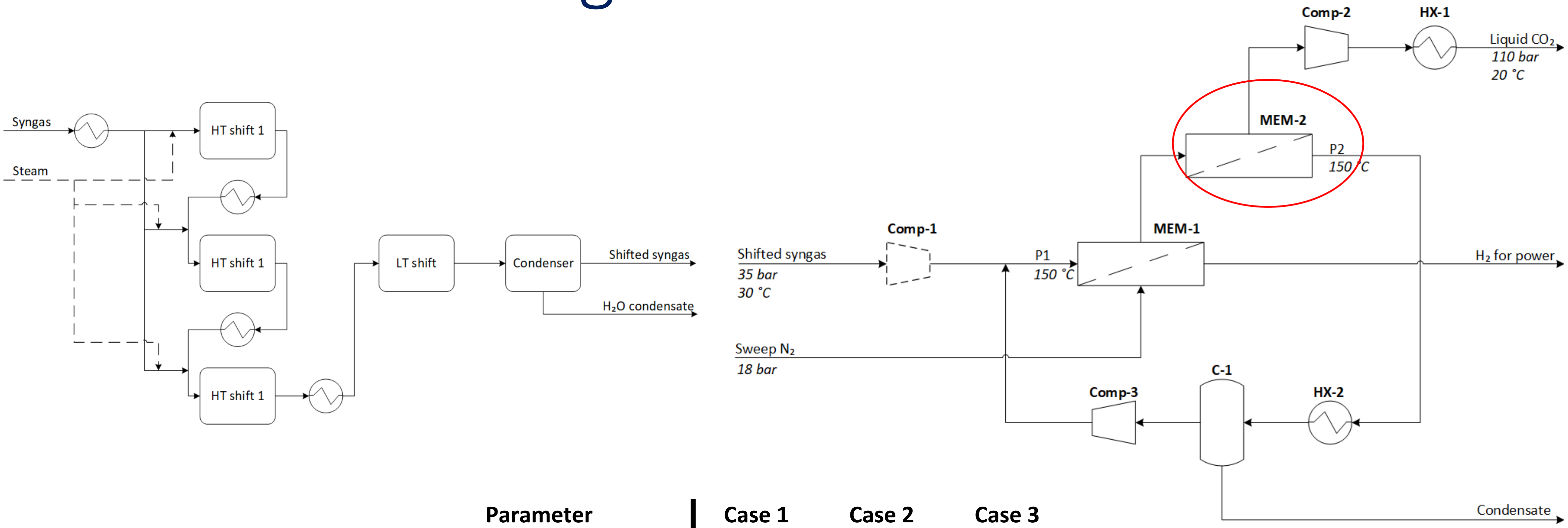
(Confidential & Proprietary)

Process flow diagram



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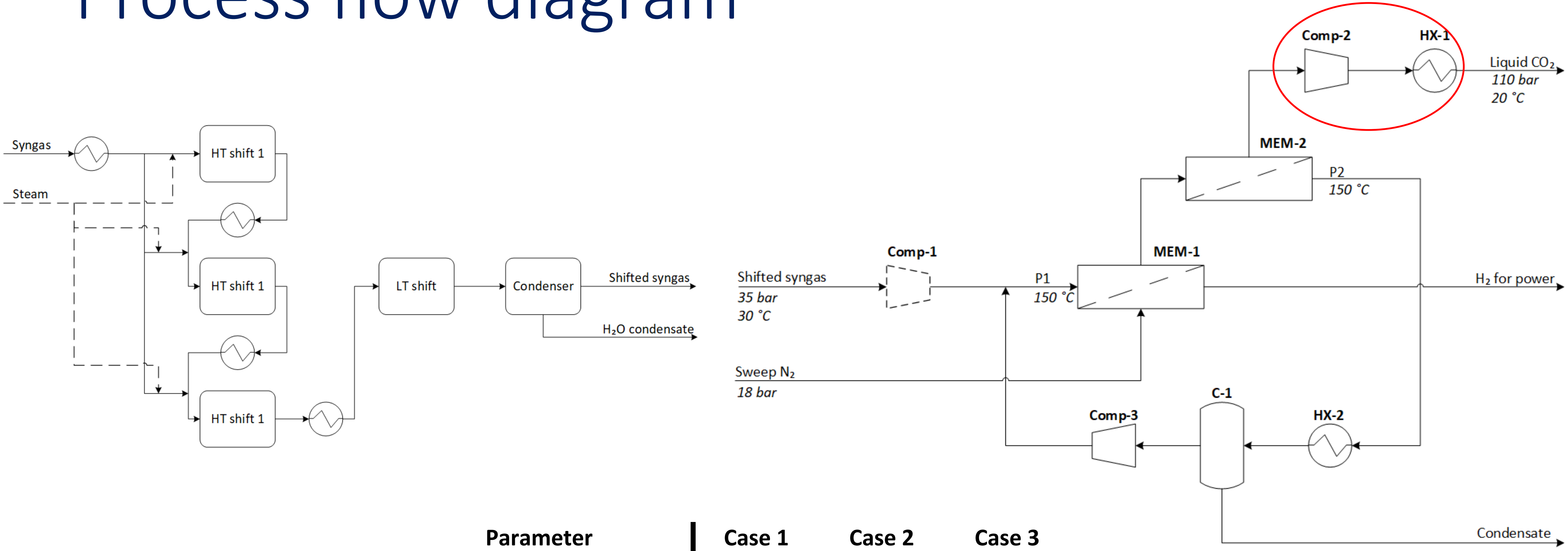

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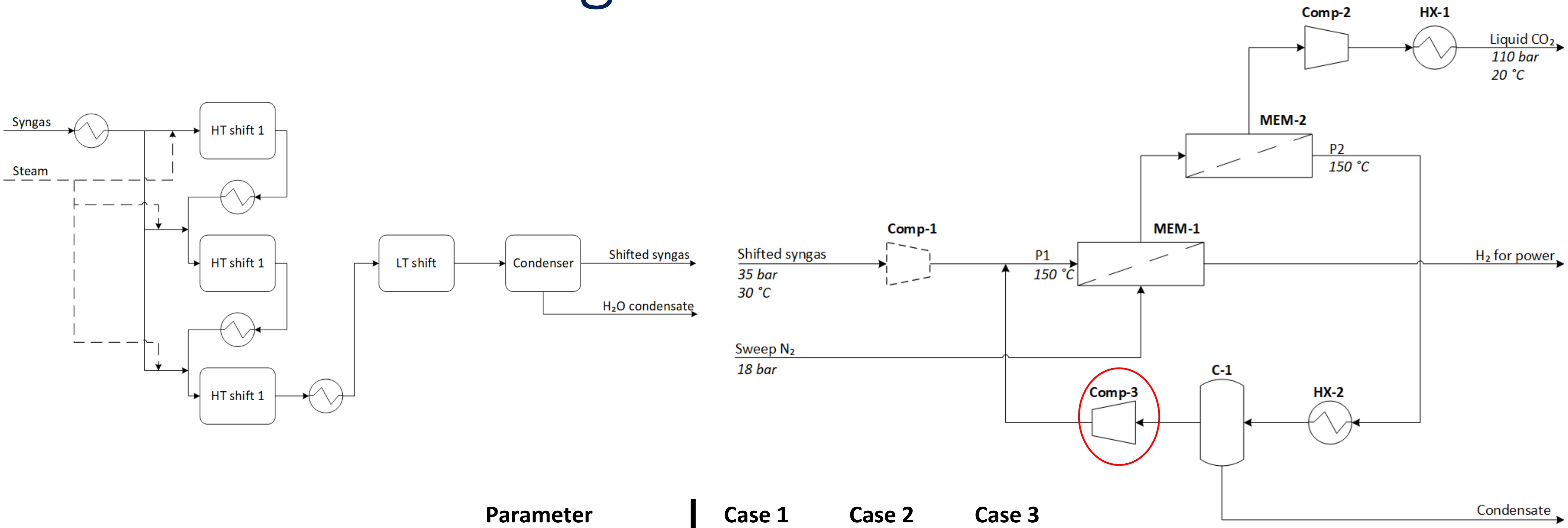

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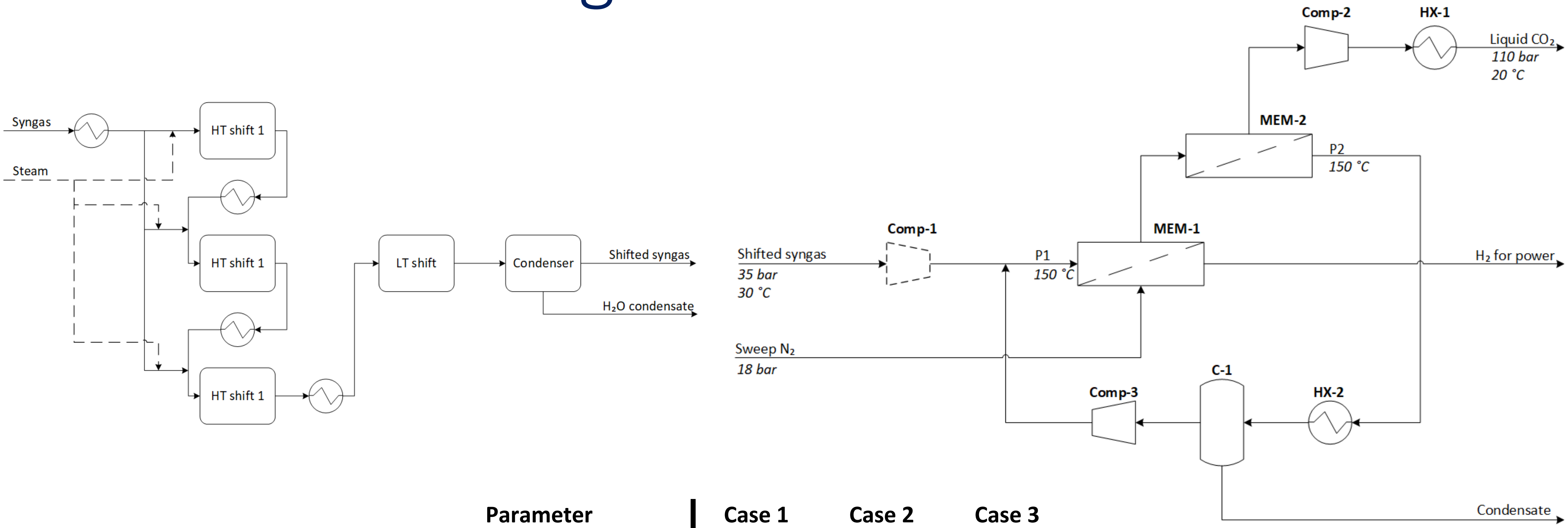
Process flow diagram



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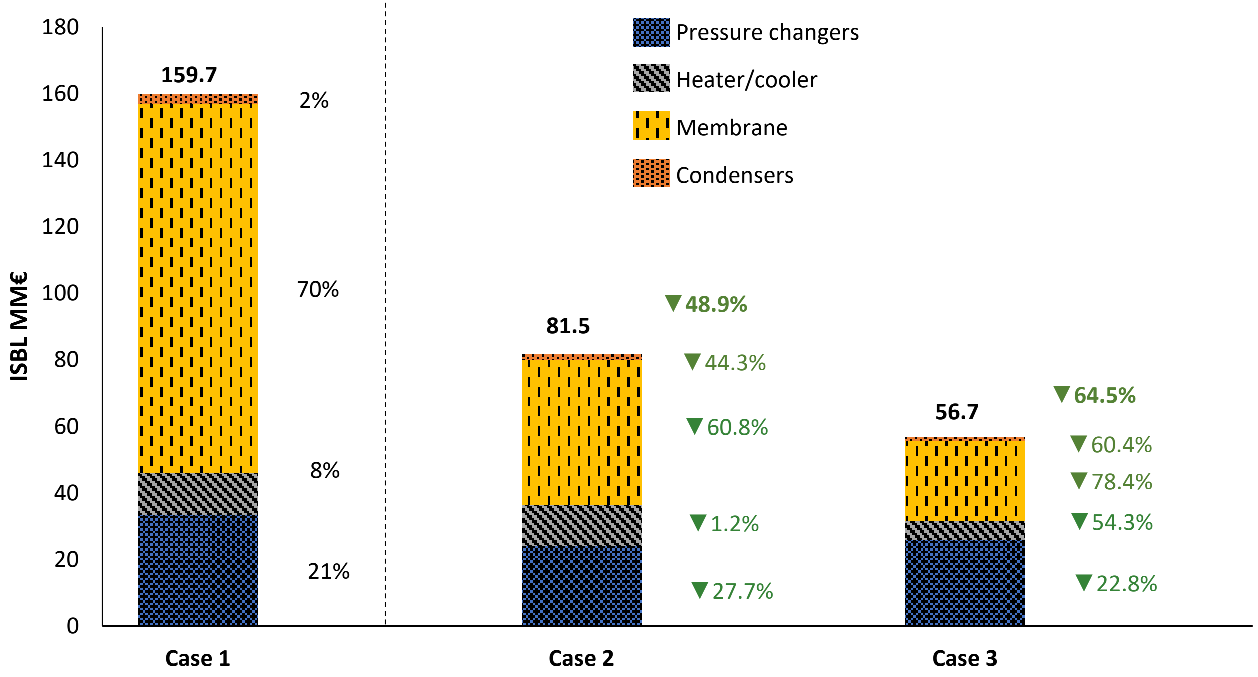
Area MEM-2 [m^2]	260000	110000	60000
E %-net power plant	12.4%	9.1%	9.3%

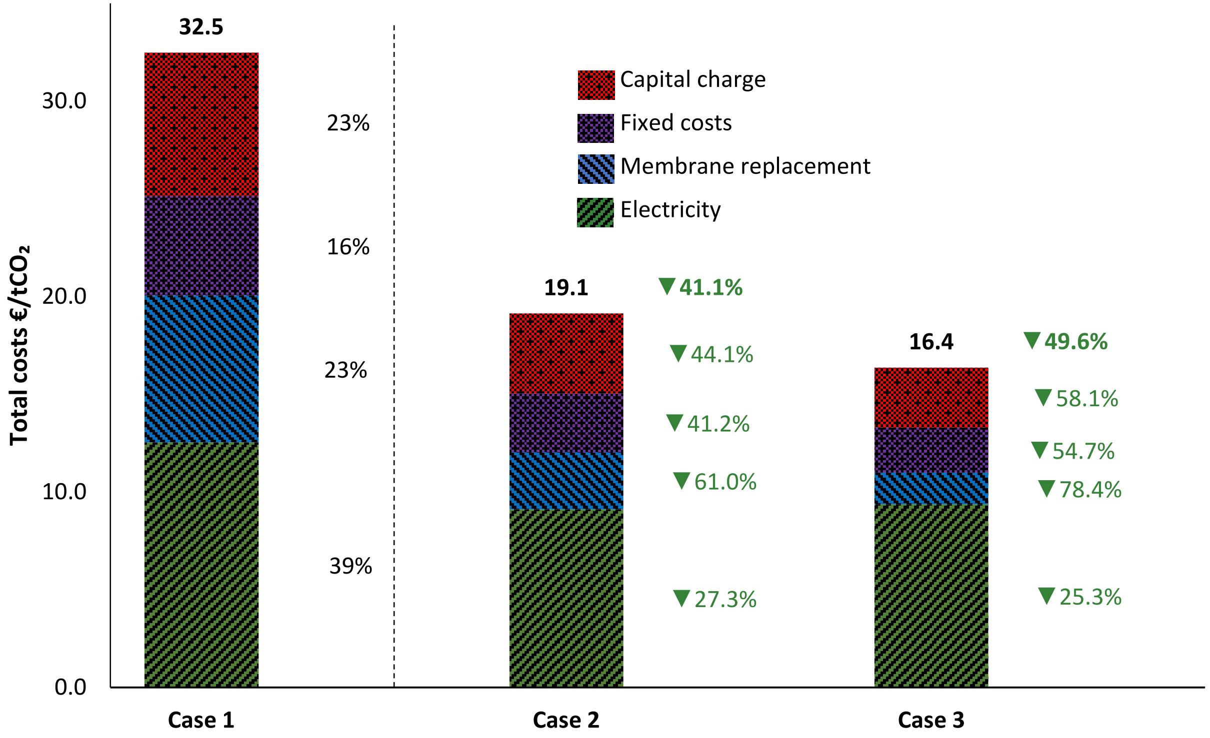
Simulation results (CAPEX)

- Membrane cost → 150 €/m²
- Membrane length → 0.5 m



Simulation results (CAPEX+OPEX)

- Replacement → 2 yr
- Electricity → €68.8/MWh
- Operation → 8000 hr



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Simulation results (CAPEX+OPEX)

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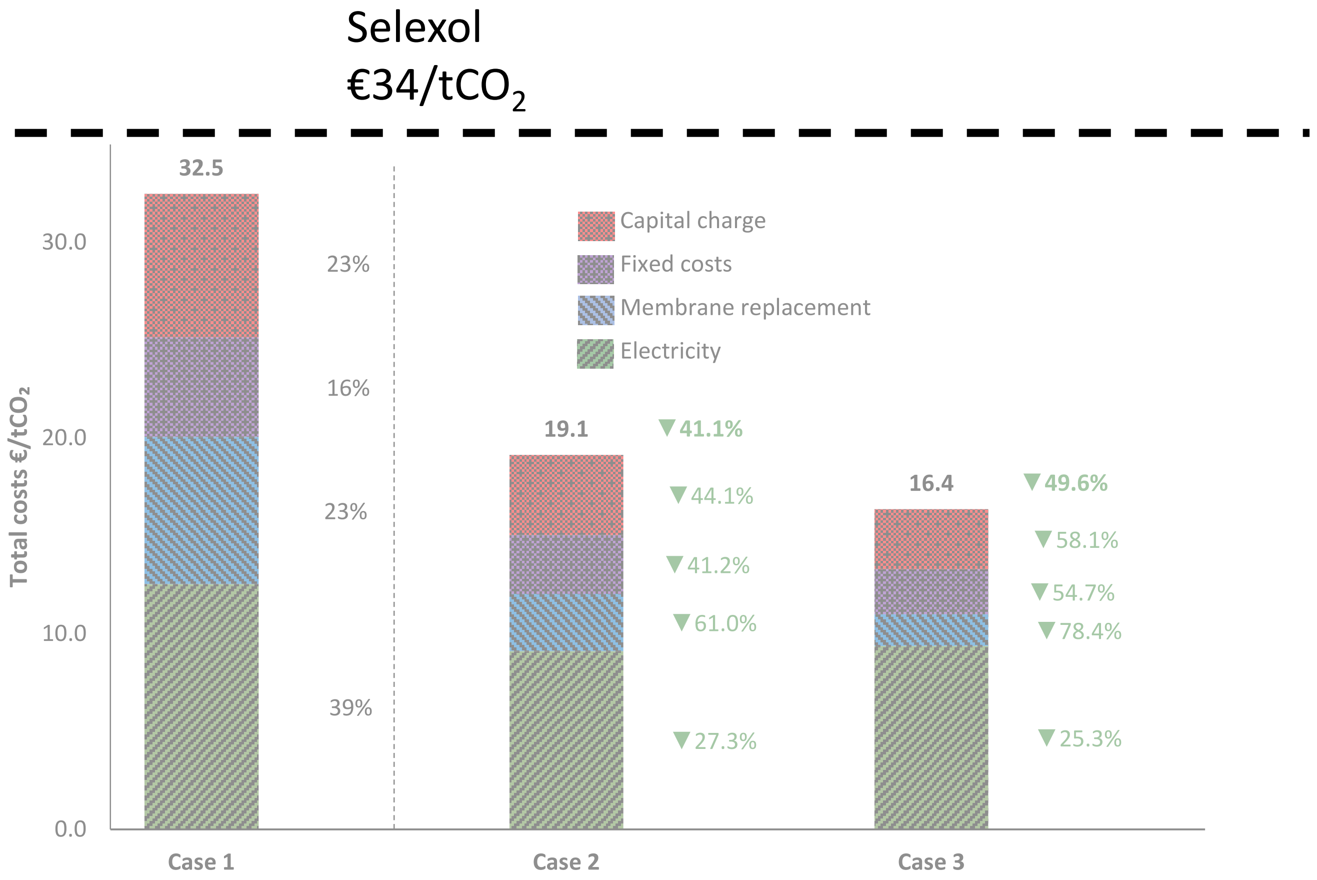

Conclusions and outlook for pre-combustion carbon capture

- Higher feasibility than conventional Selexol
- Relatively low energy consumption

- Module design
- High pressure membranes
- Potential for blue hydrogen production

Overall conclusion

- The use of MMM seems a good fit for pre-combustion carbon capture
- Post-combustion MMM need further development
- Large scale module designs are necessary before further development

Questions

2.5. Modelling of MA-SER reactor for H_2 production with CO_2 capture (Stefan Pouw – TUE)

Modelling of MA-SER reactor for H_2 production with CO_2 capture

by: Stefan Pouw (TU/e)

MEMBER

https://member-co2.com/

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 760944

Contact: s.pouw@tue.nl

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Content

1. Introduction
2. Project Objectives
3. Model approach and methodology
4. Conclusion & outlook

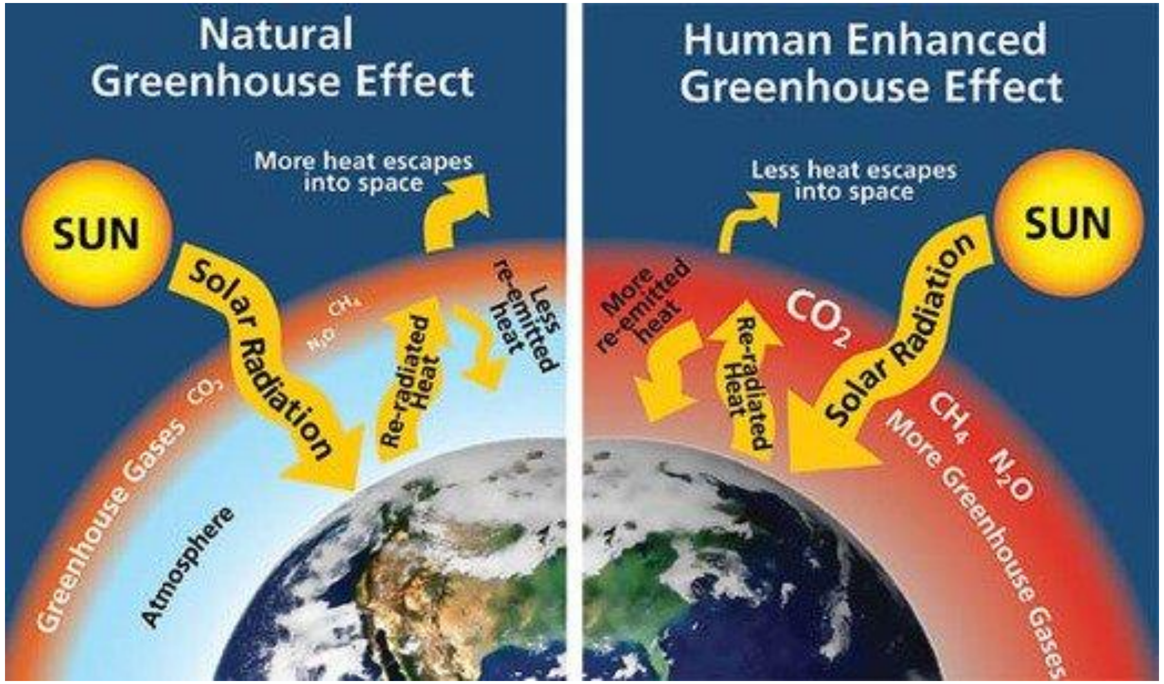
1. Introduction

Energy production 21st century

- Majority from fossil fuel (carbon based)
- CO_2 production through energy evolution

Greenhouse gasses

- Effect
  - Trap IR-radiation (heat)
- Emission points CO_2
  - Natural
  - Human activity
- Cost of CO_2 emissions regulated (ETC)



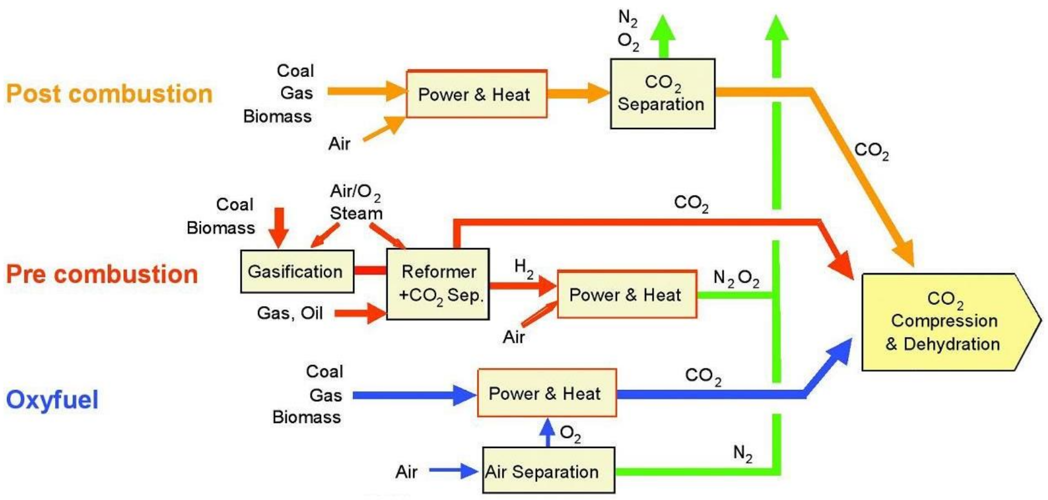
1. Introduction

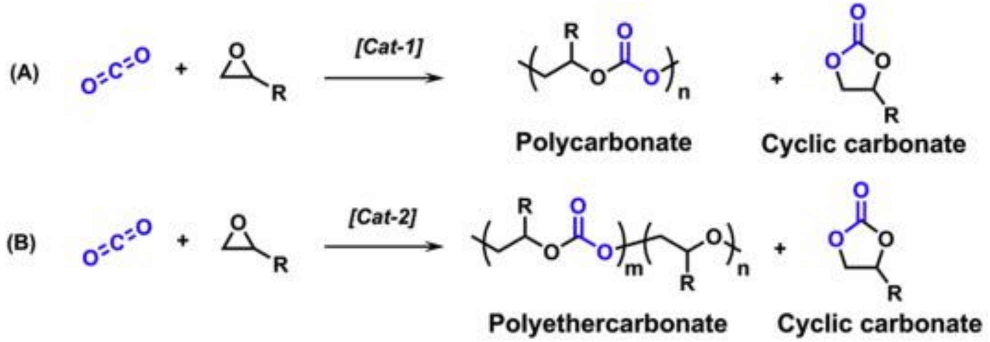
Carbon Capture & Storage techniques: [1]

- Pre-combustion
- Post-combustion
- Oxyfuel combustion

CO_2 for:

- Feedstock for chemicals
    - Fertilizers, polymers [2]
- Solvent extraction
- Carbonation beverages
- Storage (liquid, solid fixation)





$$CO_2 + 2NH_3 \rightarrow H_2N{-}C({=}O){-}NH_2 + H_2O$$

$$CO_2(g) + XO \rightarrow XCO_3(s)$$

[1]: Based on Overview of CO2 capture processes and systems (IPCC, 2005)
[2]: Polymers from carbon dioxide: Polycarbonates, polyurethanes; S.Lui,X Wang (2017)

1. Introduction

Targets

Prototype A

Pre-combustion capture in power plants using MMMs at HYGEAR reforming equipment.

CCR	Capture Cost
> 90%	**< 30 €/ton**

Prototype B

Post-combustion capture in power plants using MMMs at the 8.8 MW CHP facilities of Agroger (GALP, Portugal).

CCR	Capture Cost
> 90%	**< 40 €/ton**

Prototype C

Pure hydrogen production with integrated CO_2 capture using MA-SER at the IFE-HyNor (Norway) under the supervision of ZEG POWER.

CCR	Capture Cost
> 90%	**< 30 €/ton**

2. Project objectives

Objective: Modelling of the MA-SER system to optimize the performance of the reactor with respect to H_2 production, CO_2 capture and material utilization for up-scale process design

3. Model approach & methodology

- Process description
- Define performance indicators
- Material characterization
  - Catalyst
  - Sorbent
  - Membrane module
- MA-SER reactor modelling
- Conclusion and outlook

MA-SER process description

1) Reforming of CH_4 to reformate using catalyst

$CH_4 + H_2O \leftrightarrow CO + 3H_2$

$CO + H_2O \leftrightarrow CO_2 + H_2$

2) Adsorption of CO2 using sorbent

$CO_2 + CaO \rightarrow CaCO_3$

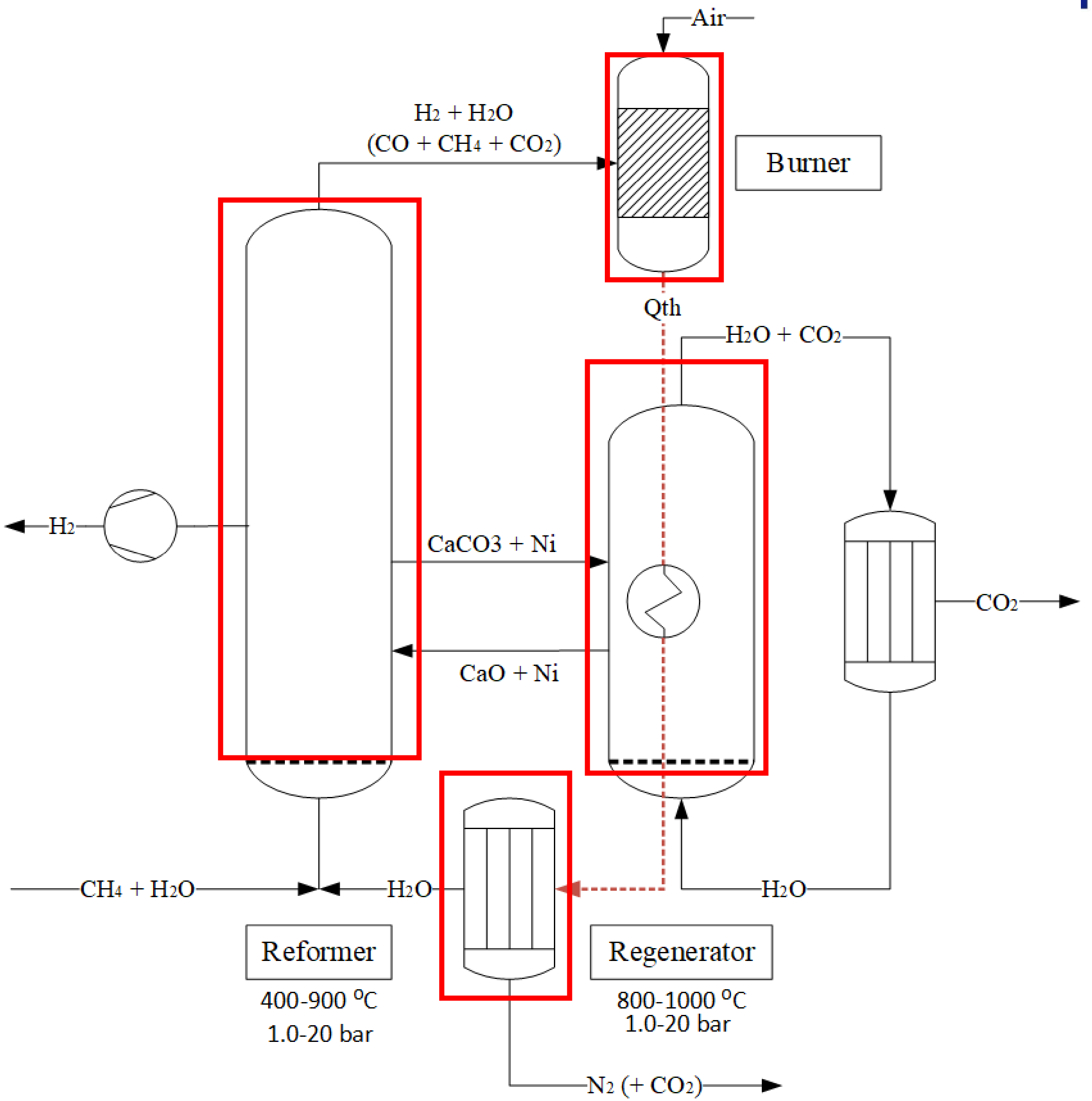
3) Removal of H_2 product using membranes

4) Saturated sorbent send to generator

$CaCO_3 \rightarrow CaO + CO_2$

5) Carbon lean stream combusted to supply energy for calcination reaction regenerator

6) Excess steam recovered by condensation

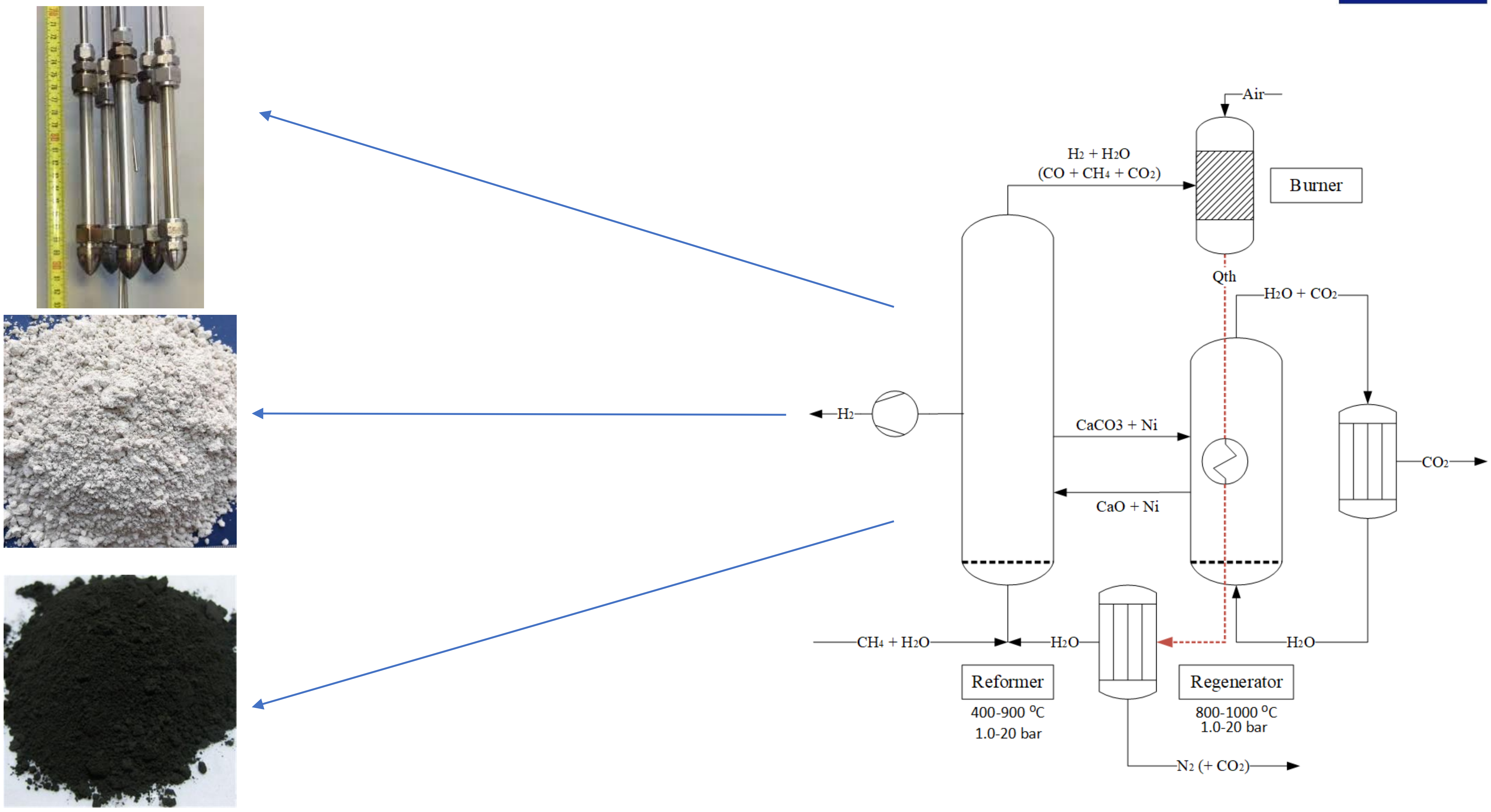


Key performance indicators

Performance indicators

- CH_4 feedstock conversion $$X_{CH4} = 1 - \frac{F_{CH4}|_{Rout}}{F_{CH4}|_{Rin}}$$
- CO_2 capture recovery $$CCR = 1 - \frac{F_{CO2}|_{REG}}{F_{CH4}|_{Rin}}$$
- H_2 product yield $$HRF = \frac{F_{H2}|_{mem}}{4 \cdot F_{CH4}|_{Rin}}$$
- Dimensionless driving force reaction $$\eta_{EQ} = 1 - \frac{1}{K_{eq}} \sum p_i^{\nu}$$

Material characterization



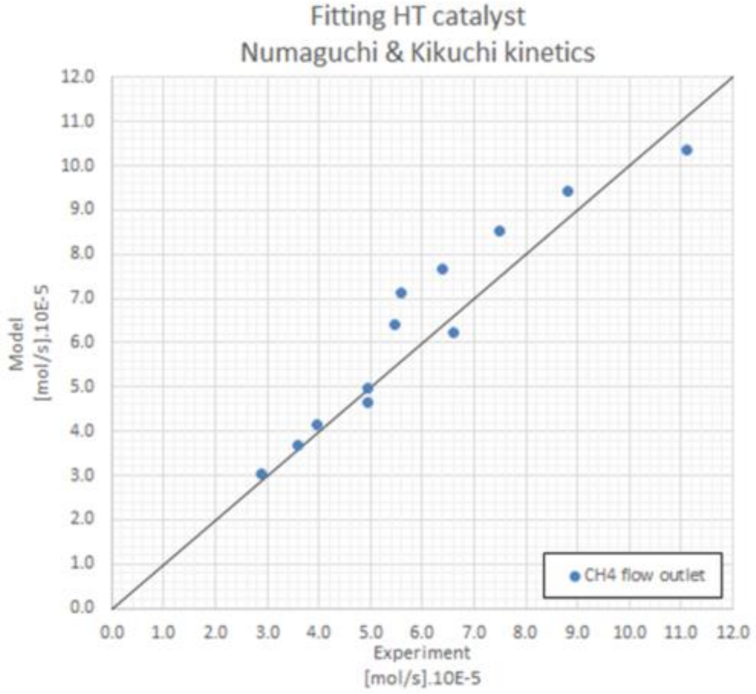
Reforming catalyst

Nickel based catalyst

Kinetics reforming CH_4 using H_2O as oxidizing agent

Researchers	Article	Abr.	H_2O/CH_4	T_R	p_R
			[mol/mol]	[°C]	[bar]
Xu and Froment	1989	XF	3.0 – 5.0	300 – 575	3.0 – 15
Numaguchi and Kikuchi	1988	NK	1.44 – 4.50	400 – 887	1.2 – 25.5
Hou and Hughes	2001	HH	4.0 – 7.0	400 – 550	12 – 60

Experiments C&CS catalyst



Reaction rate expression

fitted using micro fixed bed reactor

Reaction rate SMR, NK $$r_{SMR} = \frac{k_{SMR,NK}}{p_{H2O}^{1.596}}\left[p_{CH4}p_{H2O} - \frac{p_{H2}^{3}p_{CO}}{K_{eq,SMR}}\right] \quad \left[\frac{mol_{CH4}}{kg_{Ni}\cdot s}\right]$$

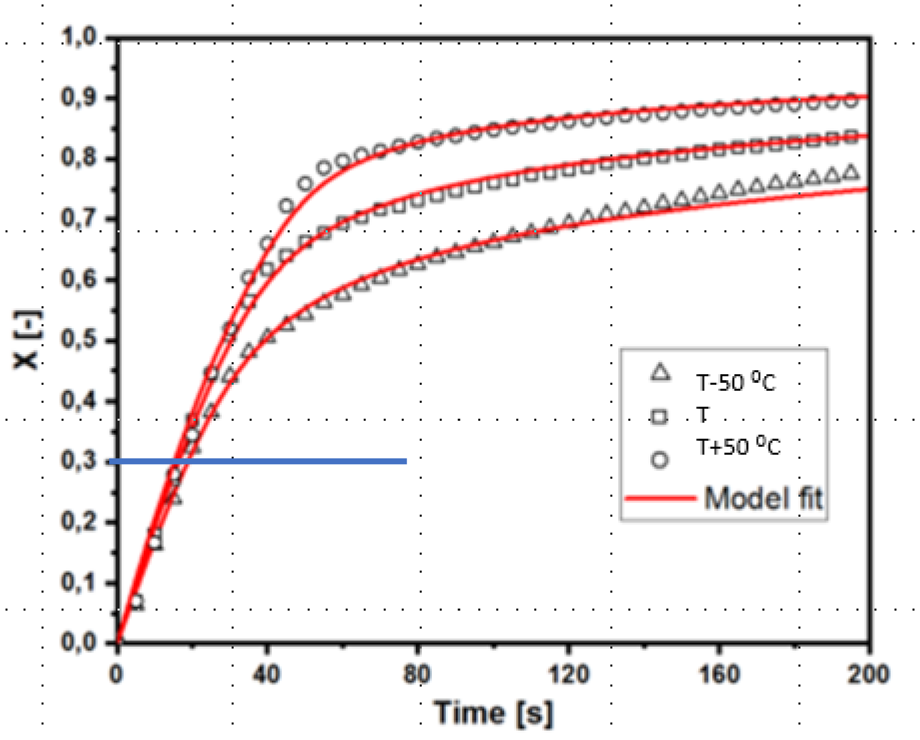
Reaction rate WGS, XF $$r_{WGS} = \frac{k_{WGS,NK}}{p_{H2O}}\left[p_{CH4}p_{H2O} - \frac{p_{H2}^{3}p_{CO}}{K_{eq,WGS}}\right] \quad \left[\frac{mol_{CH4}}{kg_{Ni}\cdot s}\right]$$

Sorbent - Carbonation kinetics

- Sorbent – CaO based
- Sorbent carbonation kinetics, described by particle model with transition kinetic-ion diffusion limiting regimes.
- Kinetics are fitted after restructuring of CaO grains (> 5 cycles)

$$\frac{dX}{dt} = \frac{k_s \sigma^0_{CaO}(1-X)^{2/3}}{1 + \frac{N^0_{CaO} k_s}{2D_{PL}} \delta^0_{CaO} \sqrt[3]{1-X}} \frac{\left(P_{CO_2} - P^{eq}_{CO_2}\right)}{RT}$$

$$D_{PL}(X,T) = D^0_{PL} \exp\left(-aX^{(bT+c)}\right)$$



- Only interested in kinetic limited regime (X_{CaO} < 0.3)

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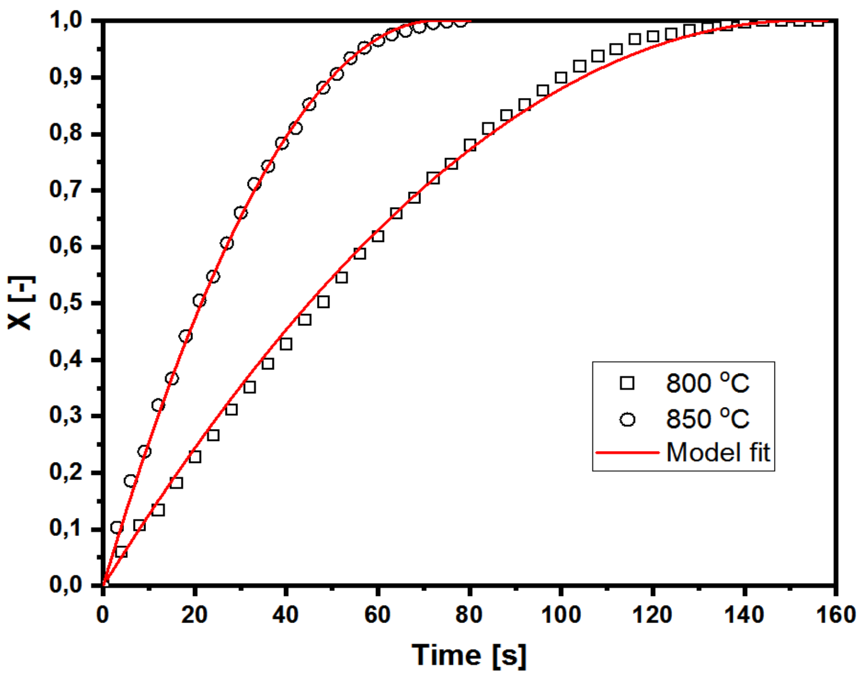
Sorbent - Calcination kinetics

- Sorbent calcination kinetics, described by shrinking core particle model.
- Kinetics are fitted after restructuring of CaO grains (> 5 cycles)

$$\frac{dX}{dt} = k_s^{cal}(1 - X)^{0.5}$$

$$k_s^{cal} = k_{s,0}^{cal} \exp\left(-\frac{E_a^{cal}}{RT_R}\right)$$



- In calciner performance not limited by kinetics, dominated by thermodynamics

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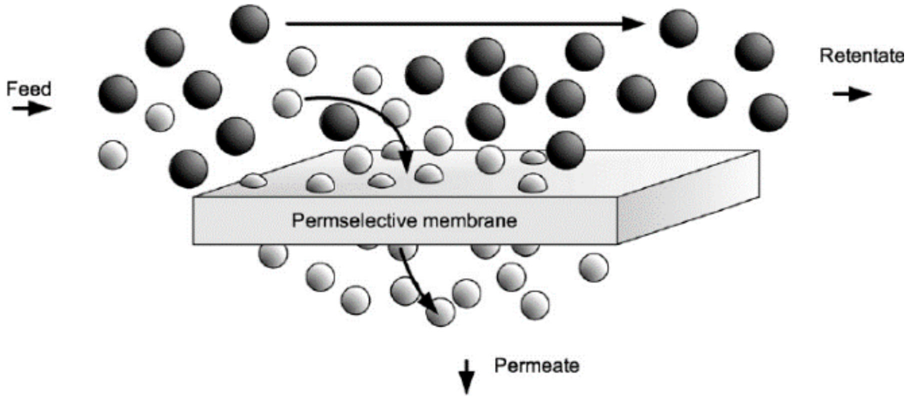
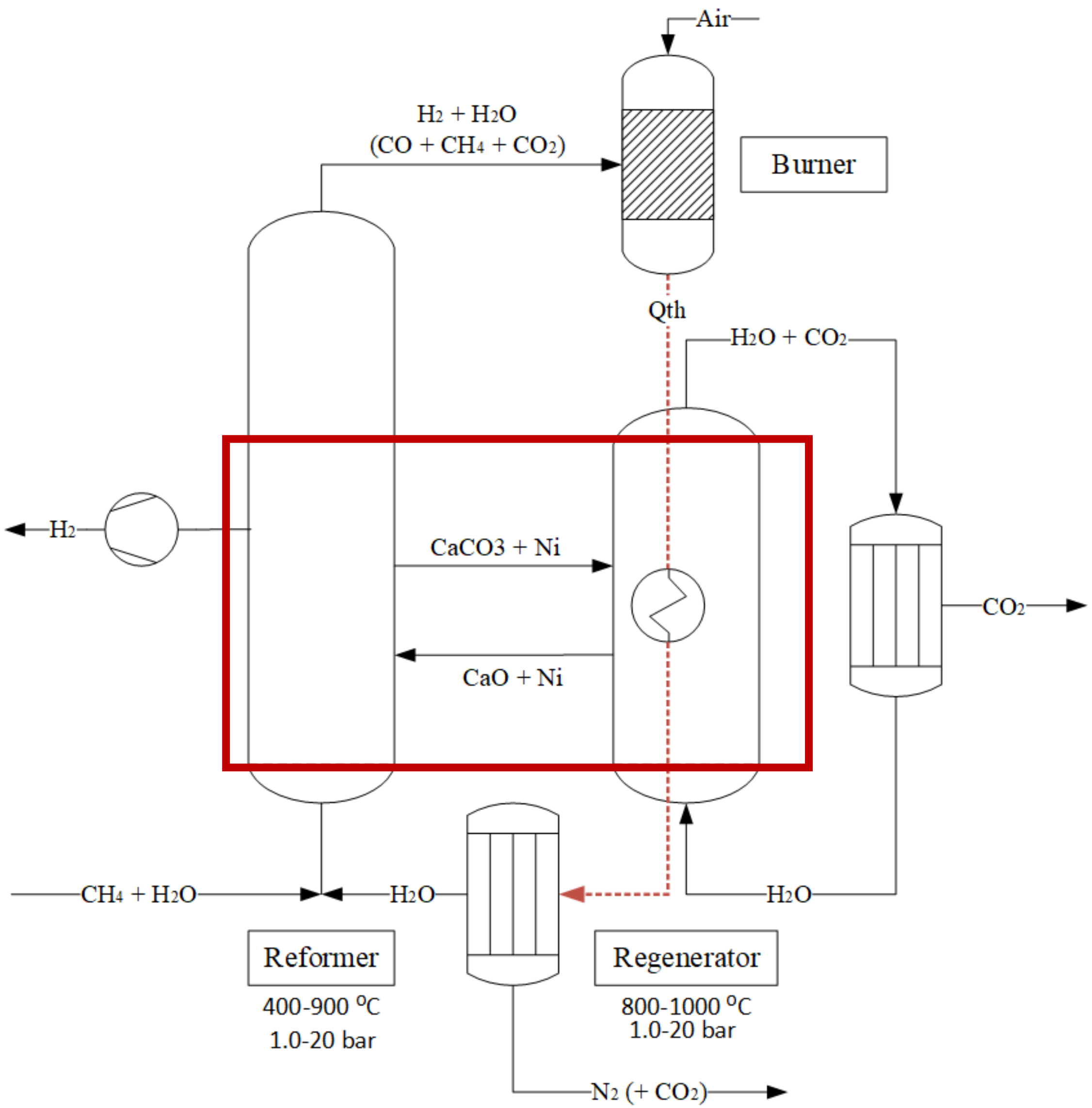
Membrane – H2 recovery

- Hydrogen permeation rate
  - Permeation rate determined by:
    - Surface activity
    - Membrane selectivity
    - External mass transfer limitations



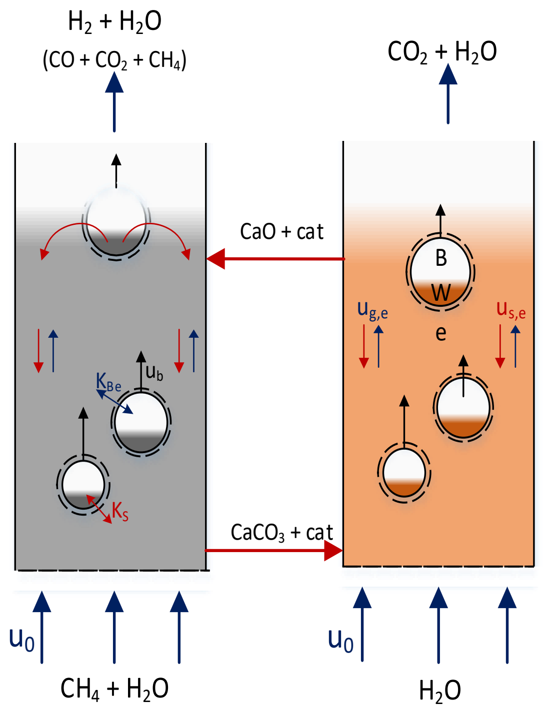
Sherwood correlation in triangular pitch [20]	$Sh_k = \sqrt{f^2 + g^2 Gz^{2/3}}$ $f = \frac{8.92(1+2.82\phi)}{1+6.86\phi^{5/3}}; g = \frac{2.34(1+24\phi)}{(1+36.5\phi^{5/4})[3.464\phi^2 - \pi]^{1/3}}$	[−]
External mass transfer flux	$N_{H2}^{ext} = -\frac{p_R}{RT_R}\frac{ShD_{H2}}{d_h}\frac{\langle y_{H2}\rangle - y_{H2,ret}}{1+\frac{\langle y_{H2}\rangle + y_{H2,ret}}{2}}$	$\left[\frac{mole}{m_{mem}^2 \cdot s}\right]$
Membrane flux	$N_{H2}^{mem} = \frac{P_{H2}}{\delta_{mem}\left[1+\ln\left(\frac{r_{sup}+\delta_{mem}}{r_{sup}}\right)\right]}[p_{H2,ret}^n - p_{H2,perm}^n]$	$\left[\frac{mole}{m_{mem}^2 \cdot s}\right]$
Steady state assumption	$N_{H2}^{mem} = N_{H2}^{ext}$	$\left[\frac{mole}{m_{mem}^2 \cdot s}\right]$

Reformer + regenerator modelling



Modelling of MA-SER reactor

Mathematical description

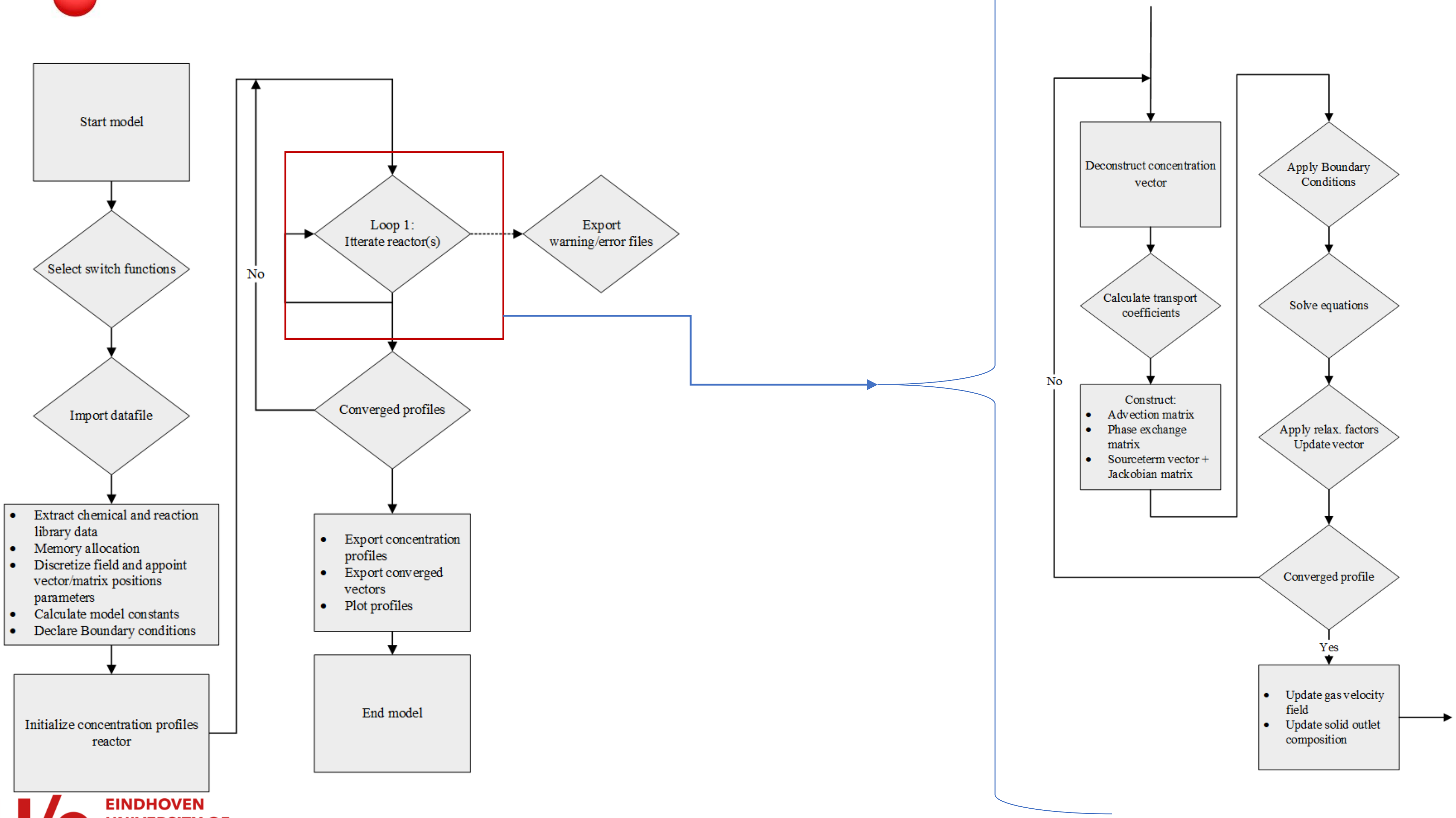


- Modelled the MA-SER reactor system using 1D phenomenological model
- Kunii and Levenspiel 3-phase fluidized bed reactor model
- Discretization of the reactor length into finite mathematical equations describing species composition, phase velocities gas-gas exchange and solid-gas reactions

$$\phi_i^{FBR} = \begin{bmatrix} C_k^{BW} \\ C_k^{e} \\ C_m^{W} \\ C_m^{e} \\ p_R \\ T_R \end{bmatrix}_i ; \phi_i^{CSTR} = \begin{bmatrix} \widehat{C_k} \\ \widehat{C_m} \\ p_R \\ T_R \end{bmatrix}_i ; \phi_i^{FZ} = \begin{bmatrix} \widehat{C_k} \\ p_R \\ T_R \end{bmatrix}_i$$

$$\mathbf{A}\vec{\phi} - \vec{b} = \vec{0}$$

Modelling program structure

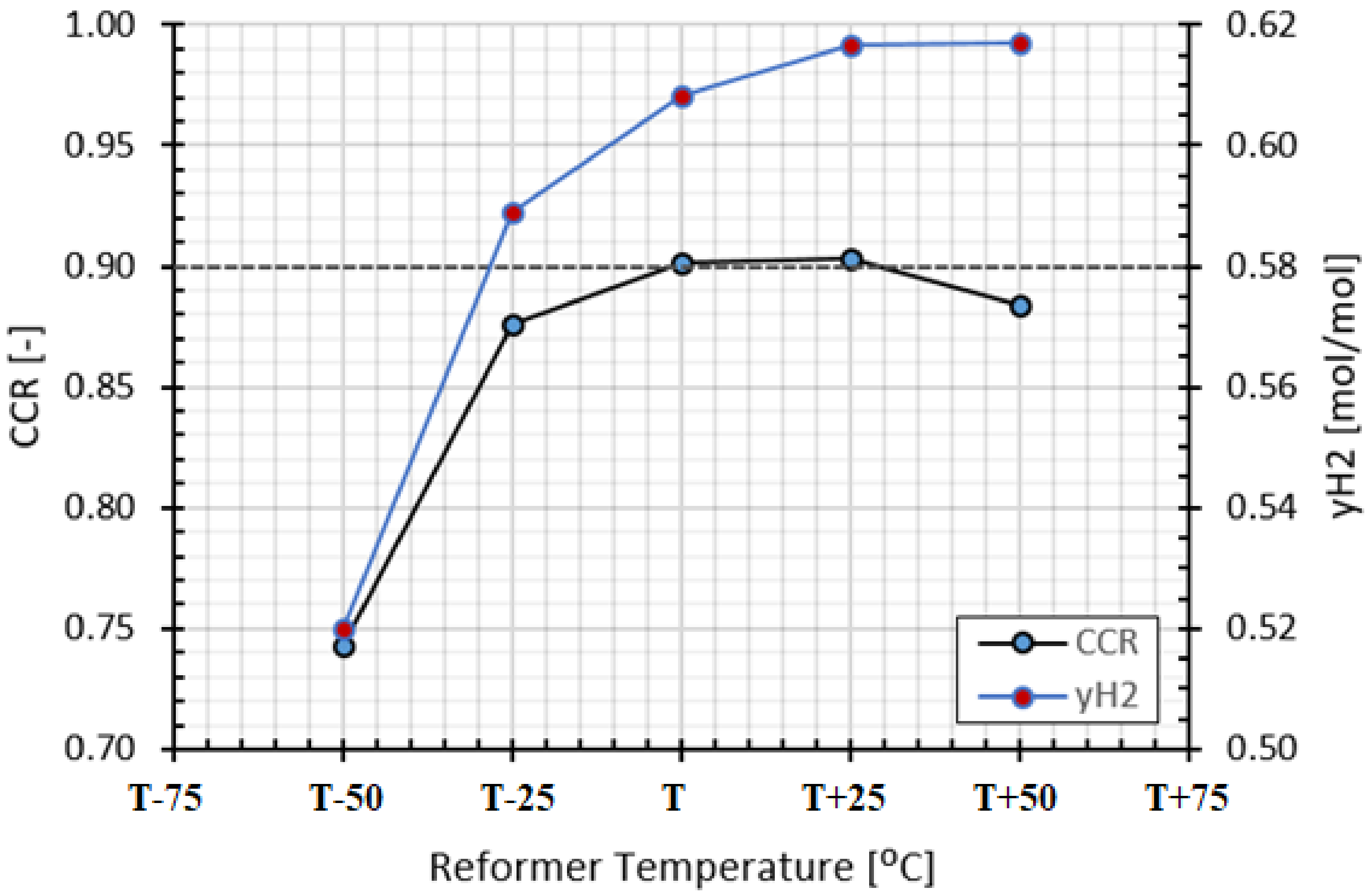


Parametric study on MA-SER reactor

Effect of reformer temperature on KPI

Target performance

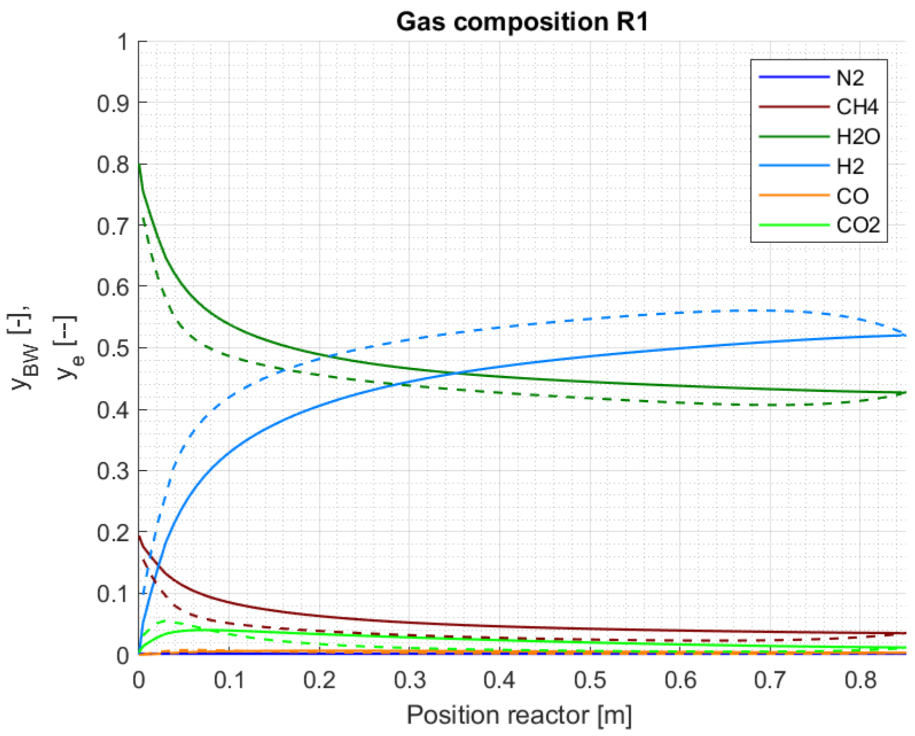
CCR > 90%
yH2 > 0.6

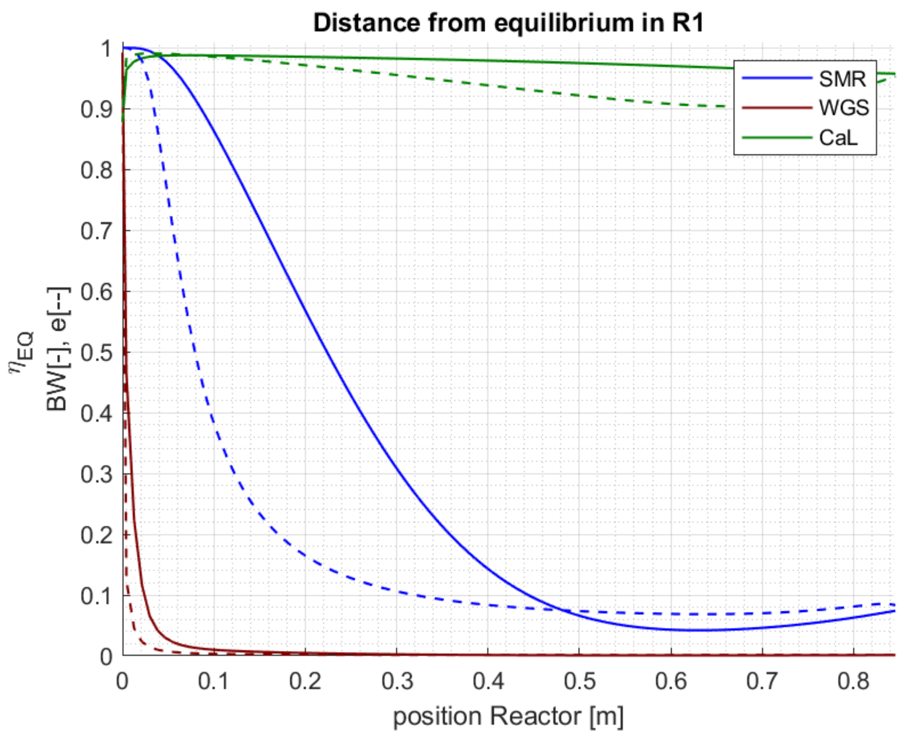


Parametric study on MA-SER reactor

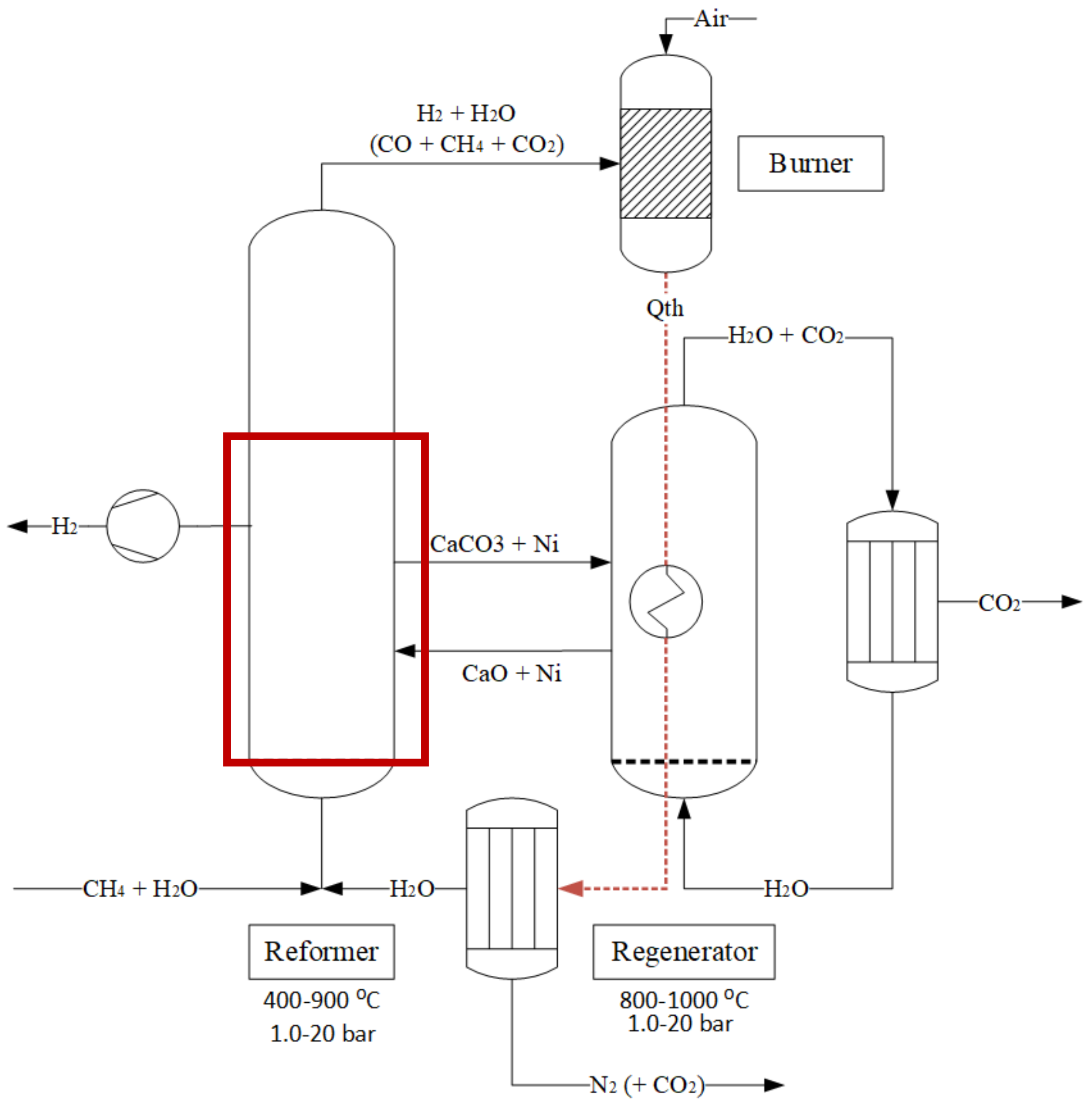
Analysis on performance limiting process step

Target performance
CCR > 90%
yH2 > 0.6



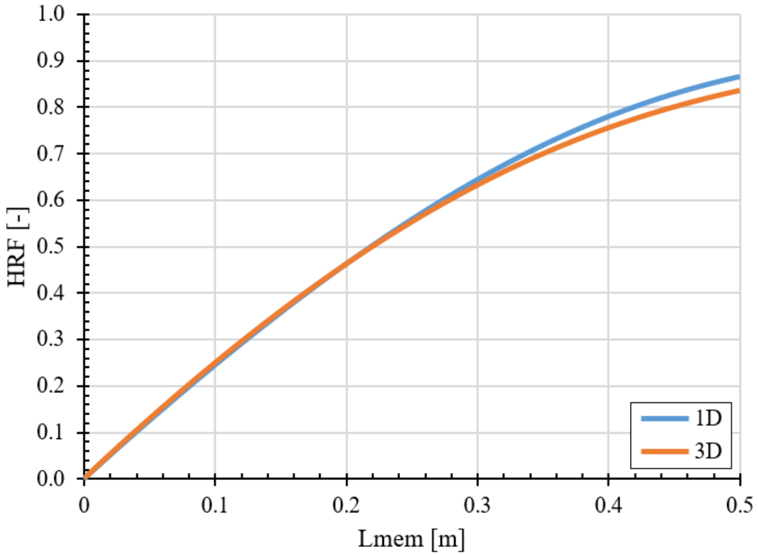


Membrane modelling

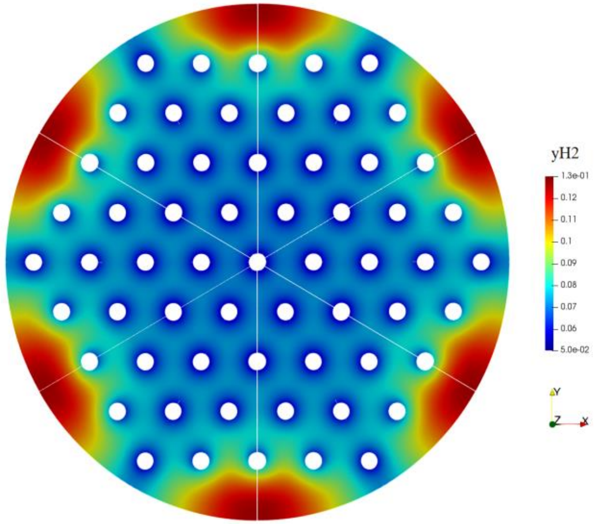


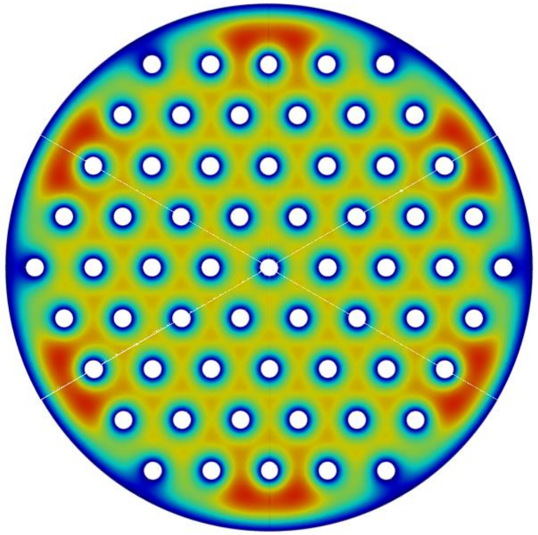
Parametric study on membrane module

- Membrane module design
  - Full 3D simulation of membrane module
  - Comparison with prediction 1D model



  - Hydrogen distribution through module
    - Positioning of membrane important due to concentration polarization





4. Conclusion & outlook

Modelling of the MA-SER system to optimize the performance of the reactor with respect to H2 production, CO2 capture and material utilization for up-scale reactor design

- Dual fluidized bed reactor at bubbling fluidization conditions modelled using 1D phenomenological model
  - Implemented kinetics derived for individual material characterization
- Evaluation of model results
  - Process performance limited by sorbent kinetics
- Evaluation of membrane module
  - 1D model can predict the 3D full scale model CFD simulation
  - Positioning membranes are key for optimal performance

- Model can be used for up-scale reactor design of high-purity hydrogen

Thank you for your attention

https://member-co2.com/

Contact:

joseluis.viviente@tecnalia.com

Acknowledgement: For the CO2 molecule used in the logo:The original uploader was Frederic Marbach at French Wikipedia [GFDL (http://www.gnu.org/copyleft/fdl.html)

Appendix A: model equations 3-phase Fluidized bed reactor model

Table : equations of mass, momentum and thermal energy conservation

Molar gas flow	
$\frac{dF_k}{dV_R} = S_{k,r} \pm S_{k,ph}$	$\frac{mole}{m_R^3 \cdot s}$
Molar solid flow	
$\frac{dF_m}{dV_R} = S_{m,r} \pm S_{m,ph}$	$\frac{mole}{m_R^3 \cdot s}$
Energy balance (thermal)	
$\frac{dU_R}{dV_R} = \frac{d}{dV_R}\left[T_R \sum C_{p,k} F_k + \sum C_{p,m} F_m\right] = S_{H,R}$	$\frac{J}{m_R^3 \cdot s}$
Pressure balance	
$\frac{dp_R}{dV_R} = S_u$	$\frac{Pa}{m_R}$

Sourceterm expressions

Nett reaction rate gas compounds	$S_{k,r} = \sum_{r=1}^{Nr} \theta_{k,r} R_r$
Bubble-emulsion mass transfer	$S_{k,ph} = K_{Be}\left[C_{k,B} - \frac{\psi_e \varepsilon_{mf}}{\psi_B + \psi_W \varepsilon_{mf}} C_{k,e}\right]$
Nett reaction rate solid compounds	$S_{m,r} = \sum_{r=1}^{Nr} \theta_{m,r} R_r$
Wake-emulsion solid exchange	$S_{m,ph} = K_s\left[C_{m,W} - \frac{\psi_e}{\psi_W} C_{m,e}\right]$
Heat of formation reactions	$S_{H,R} = \sum_{r=1}^{Nr} \Delta H_{ref} \theta_{ref,r} R_r$
Pressure drop	$S_u = \frac{150\mu_f}{d_p^2 \phi_p^2} \frac{(1-\varepsilon_{mf})^2}{\varepsilon_{mf}^3} u_{mf} + \frac{1.75\rho_f}{d_p \phi_p} \frac{1-\varepsilon_{mf}}{\varepsilon_{mf}^3} u_{mf}^2$

Discretized mass balances

- Gas balance Bubble+Wake phase

$$(\psi_B + \psi_W \varepsilon_{mf}) C_k^{BW} \Delta V_R = A_R u_B (\psi_B + \psi_W \varepsilon_{mf}) C_k^{BW} + K_{Be}(\psi_B + \psi_W \varepsilon_{mf})[C_k^e - C_k^{BW}] + \Delta V_R \sum R_k^{BW}$$

- Gas balance emulsion phase

$$\psi_e \varepsilon_{mf} C_k^e \Delta V_R = A_R u_e \psi_e \varepsilon_{mf} C_k^{BW} - K_{Be}(\psi_B + \psi_W \varepsilon_{mf})[C_k^e - C_k^{BW}] + \Delta V_R \sum R_k^e$$

- Gas balance in collection cell

$$[\psi_B + (\psi_e + \psi_W)\varepsilon_{mf}]\widehat{C_k} \Delta V_R = \pm u_g A_R \hat{\varepsilon} \Delta V_R \sum \widehat{R_k}$$

- Solid balance per particle in Wake phase

$$\psi_W \varepsilon_p (1 - \varepsilon_{mf}) C_m^W \Delta V_R = A_R u_B \psi_W \varepsilon_p (1 - \varepsilon_{mf}) C_k^{BW} + K_s \varepsilon_p (1 - \varepsilon_{mf})[C_m^e - C_m^W] \Delta V_R + \Delta V_R \sum R_s^W$$

- Solid balance per particle in emulsion phase

$$\psi_e \varepsilon_p (1 - \varepsilon_{mf}) C_m^e \Delta V_R = A_R u_B \psi_W \varepsilon_p (1 - \varepsilon_{mf}) C_m^e - \Delta V_R K_s \varepsilon_p (1 - \varepsilon_{mf})[C_m^W - C_k^e] + \Delta V_R \sum R_s^W$$

- Solid balance in collection cell

$$(\psi_W + \psi_e)\varepsilon_p (1 - \varepsilon_{mf})\widehat{C_m} \Delta V_R = \pm A_R u \psi \varepsilon_p (1 - \varepsilon_{mf})\widehat{C_m} + \Delta V_R \sum \widehat{R_s}$$

2.6. Advances on membrane technologies in hydrocarbon processing industry (Vittoria Cosentino – KT)

Advances on membrane technologies in hydrocarbon processing industry

MEMBER WEBINAR on
Modelling of membranes materials and systems
23-02-2022

Vittoria Cosentino
Contact: v.cosentino@kt-met.it,

Kinetics Technology

The present publication reflects only the author's views. The Commission is not responsible for any use that may be made of the information contained therein.

KT R&D experience on MEMBRANE REACTORS

Industrial Application Sectors

For each application, the industrial feasibility has been assessed with experimental tests at pilot scale

Pure hydrogen production

<u>ITALIAN FISR PROJECT (2005-2010)</u>
«Pure hydrogen from natural gas to total conversion obtained integrating chemical reaction and membrane separation»

<u>EU FP7 COMETHY PROJECT (2011-2015)</u>
«Compact Multifuel-Energy to Hydrogen converter»

Gas-To-Liquid Processes

<u>EU FP7 NEXT-GTL PROJECT (2009-2013)</u>
«Innovative Catalytic Technologies & Materials for Next Gas to Liquid Processes»

Alkane's dehydrogenation

<u>EU FP7 CARENA PROJECT (2011-2015)</u>
«CAtalytic membrane REactors based on New mAterials for C1-C4 valorization»

Bio-hydrogen production

<u>EU HORIZON H2020 (2017-2020, amended 2021)</u>
«Process Intensification through the development of innovative Membranes and Catalysts»

CO_2 capture for pre- & post-combustion and H_2 production

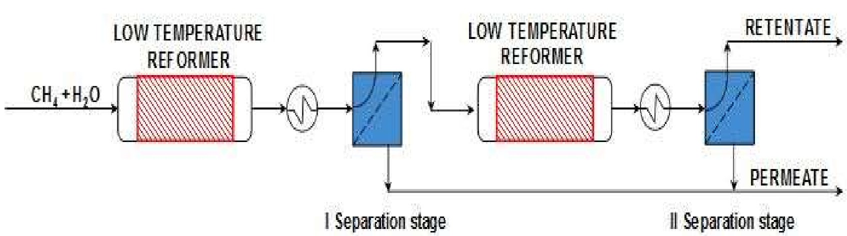
<u>EU HORIZON H2020 (2018-2021, under amend. 2022)</u>
«Advanced Membranes and membrane assisted processes for pre- and post-combustion CO2 capture»

E. Palo, A. Salladini, B. Morico, V. Palma, A. Ricca, G. Iaquaniello, Membranes 8 (2018) 101

TWO INTEGRATION LEVELS CATALYST-MEMBRANE STUDIED

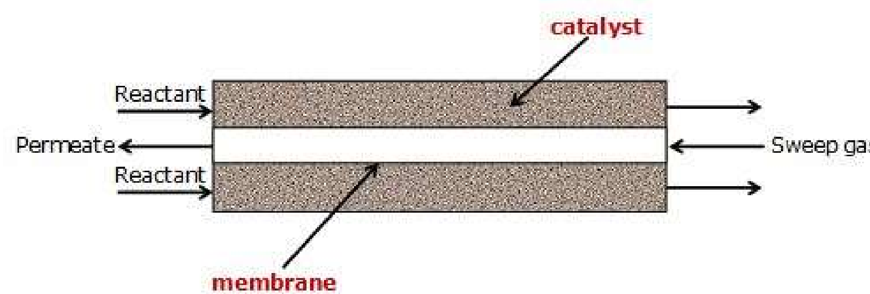
OPEN ARCHITECTURE

- Membrane outside reaction environment
- Sequence of reaction stages and separation ones



CLOSED ARCHITECTURE

- Membrane integrated into the reaction environment
- Membrane reactor assembled as shell and tube heat exchanger



MEMBRANE REACTORS for PURE HYDROGEN PRODUCTION

Methane steam reforming is currently the primary hydrogen production route on industrial scale

This process is highly endothermic and equilibrium limited. To achieve a high conversion of methane, it has to be carried out at high temperature, leading to high energy consumption.

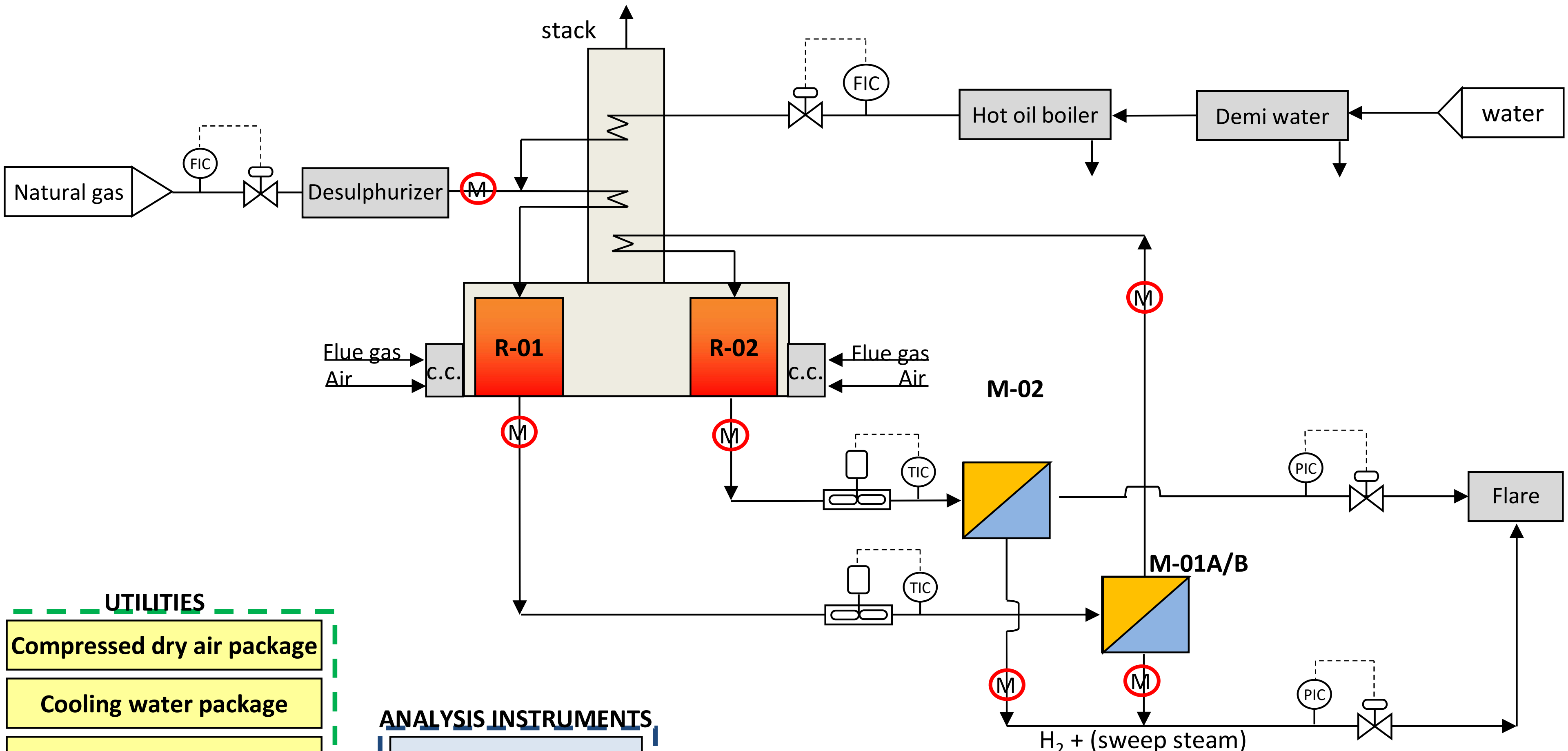
$CH_4 + H_2O \leftrightarrow CO + 3H_2$	Steam reforming reaction, strongly endothermic $\Delta H°_{25°C} = 206$ kJ/mol
$CO + H_2O \leftrightarrow CO_2 + H_2$	Water gas shift reaction, mildly esothermic $\Delta H°_{25°C} = -41$ kJ/mol

Removing hydrogen from the reaction zone allows to shift chemical equilibrium towards products enhancing hydrogen yield at lower temperature

- **USE OF LOW-GRADE HEAT REJECTED BY A BOTTOM PROCESS**
- **USE OF LOWER EXPENSIVE MATERIAL FOR REFORMING TUBE**

MEMBRANE REACTORS for PURE HYDROGEN PRODUCTION

Open Architecture



UTILITIES

- **Compressed dry air package**
- **Cooling water package**
- **Demi water package**
- **Hot oil boiler**

ANALYSIS INSTRUMENTS

- **Gas chromatographer**
- **ABB analyser**

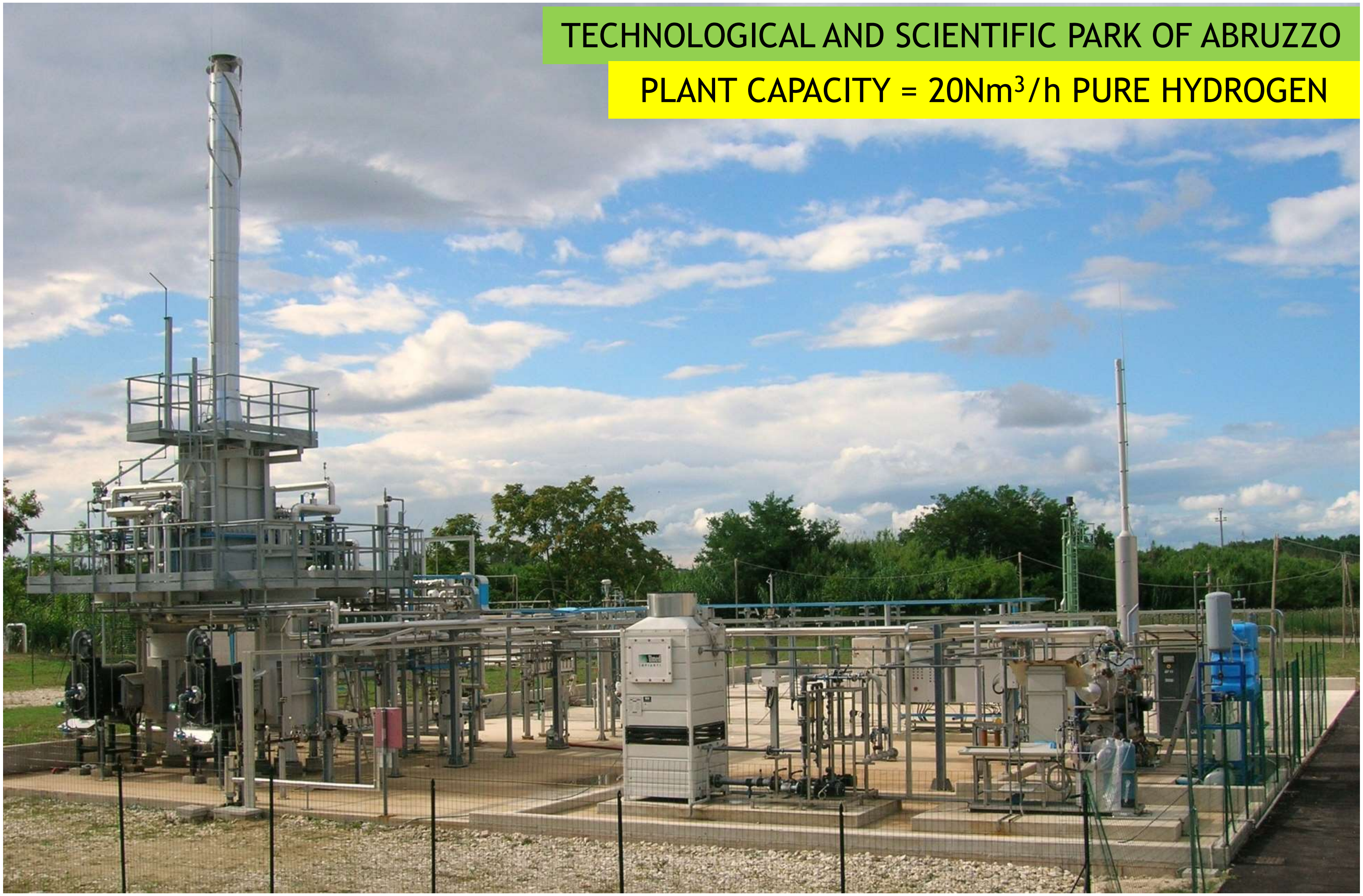
ITALIAN FISR PROJECT (2005-2010)

«Pure hydrogen from natural gas to total conversion obtained integrating chemical reaction and membrane separation»

M. De Falco, G. Iaquaniello, A. Salladini, *J. Membr. Sci.*, 2011, **368**, 264

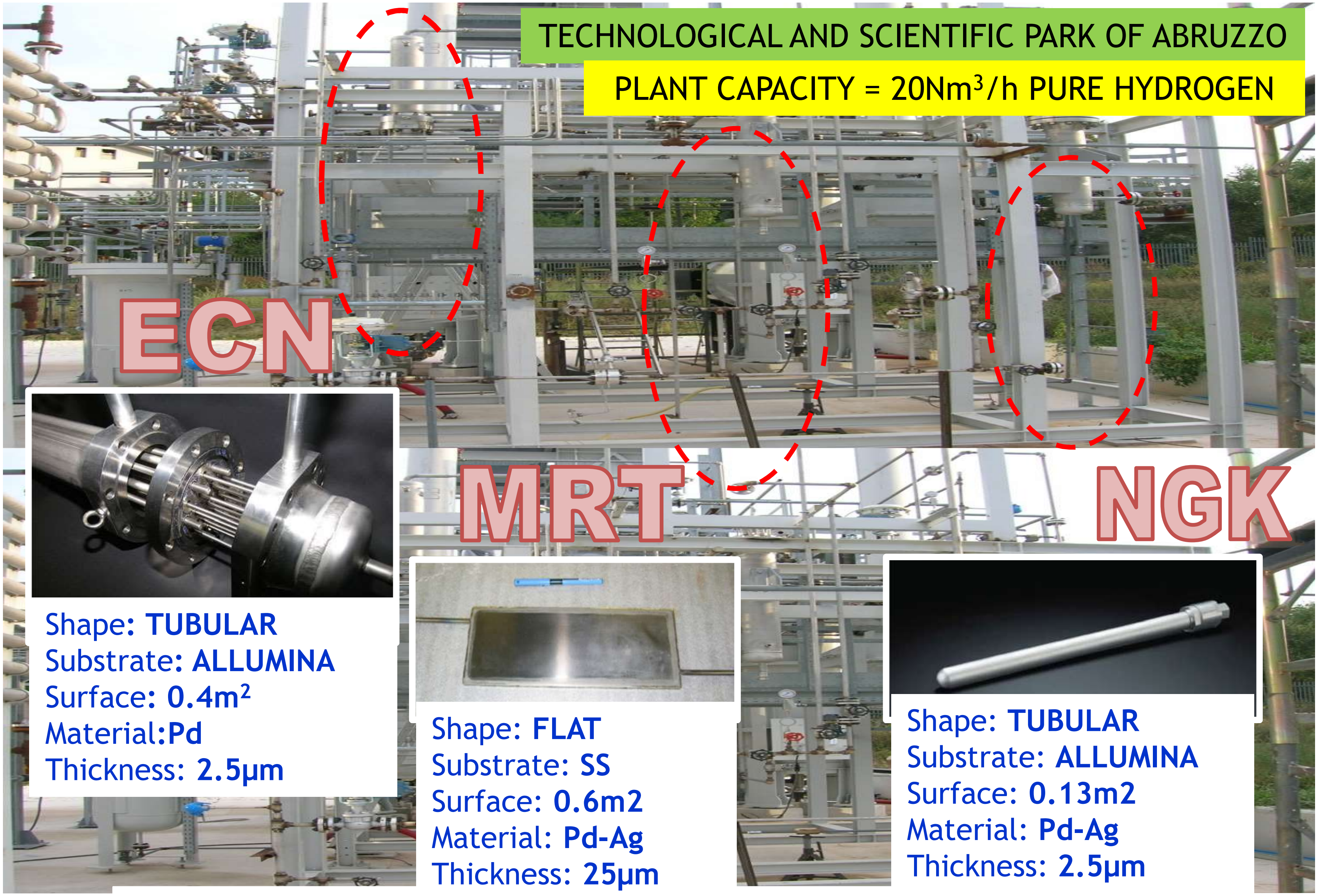
MEMBRANE REACTORS for PURE HYDROGEN PRODUCTION

Open Architecture



MEMBRANE REACTORS for PURE HYDROGEN PRODUCTION

Open Architecture



ECN

Shape: **TUBULAR**
Substrate: **ALLUMINA**
Surface: **$0.4m^2$**
Material:**Pd**
Thickness: **2.5µm**

MRT

Shape: **FLAT**
Substrate: **SS**
Surface: **0.6m2**
Material: **Pd-Ag**
Thickness: **25µm**

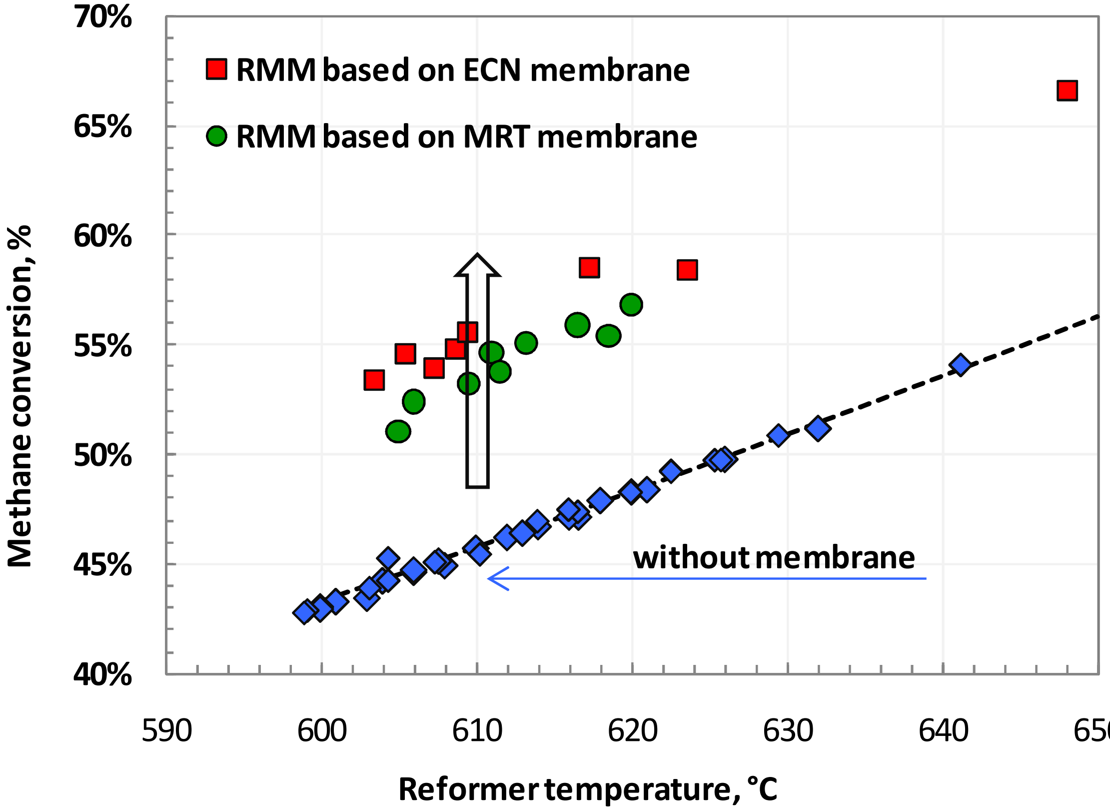
NGK

Shape: **TUBULAR**
Substrate: **ALLUMINA**
Surface: **0.13m2**
Material: **Pd-Ag**
Thickness: **2.5µm**

KT Kinetics Technology

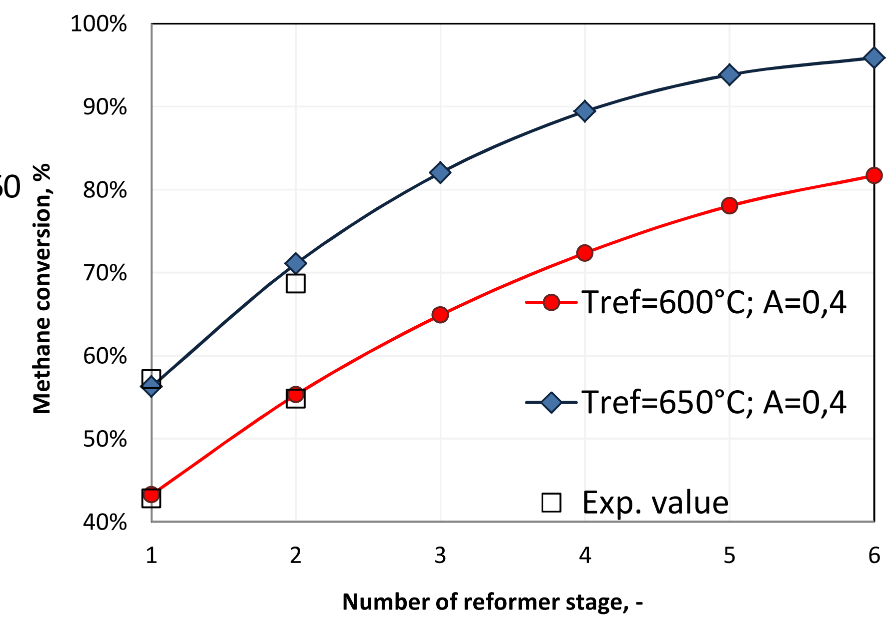
MEMBRANE REACTORS for PURE HYDROGEN PRODUCTION

Open Architecture



Feed Pressure: 10barg
Steam to carbon ratio: 4.8
Membrane Temperature: 400-450° C

An overall feed conversion of 57.3% was achieved at 610° C, about 26% higher than what can be achieved in a conventional reformer at the same temperature.



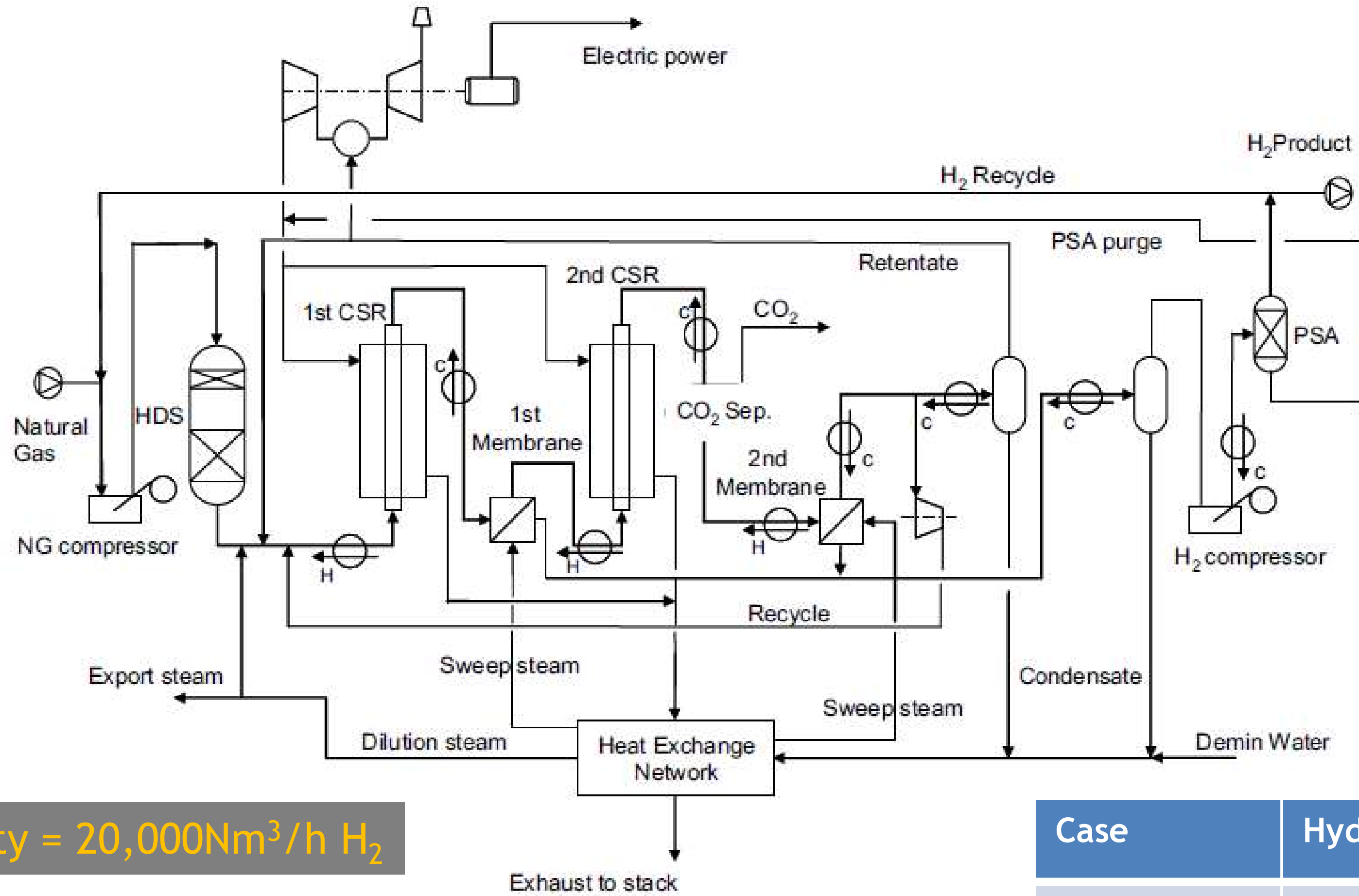
The OPEN architecture performed a methane conversion up to 10-12% higher than equilibrium values

Membrane and catalyst performance stable for up to 3000 hours

E. Palo, A. Salladini, B. Morico, V. Palma, A. Ricca, G. Iaquaniello, Membranes 8 (2018) 101

MEMBRANE REACTORS for PURE HYDROGEN PRODUCTION

Economic analysis



Plant capacity = 20,000Nm^3/h H_2

Hybrid scheme enables for a reduction of COP of around 24%

Case	Hydrogen COP/Nm^3
Conventional	0.1194
Hybrid	0.0911*

*Membrane replacement every three years

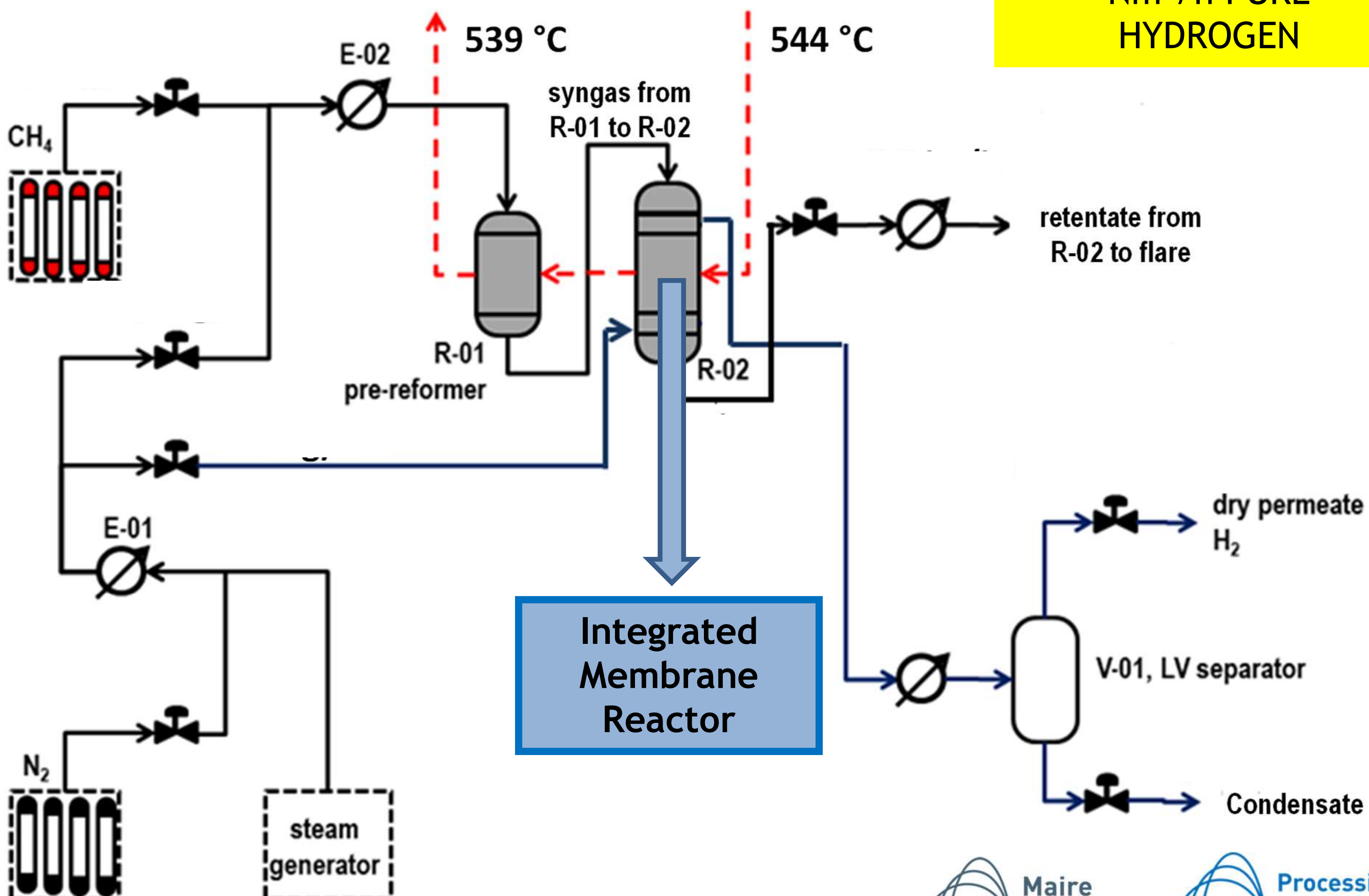
G. Iaquaniello, F. Giacobbe, B. Morico, S. Cosenza, A. Farace, Int.J. Hydrogen Energy 33 (2008) 6595

MEMBRANE REACTORS for PURE HYDROGEN PRODUCTION

Closed Architecture

ENEA, Casaccia

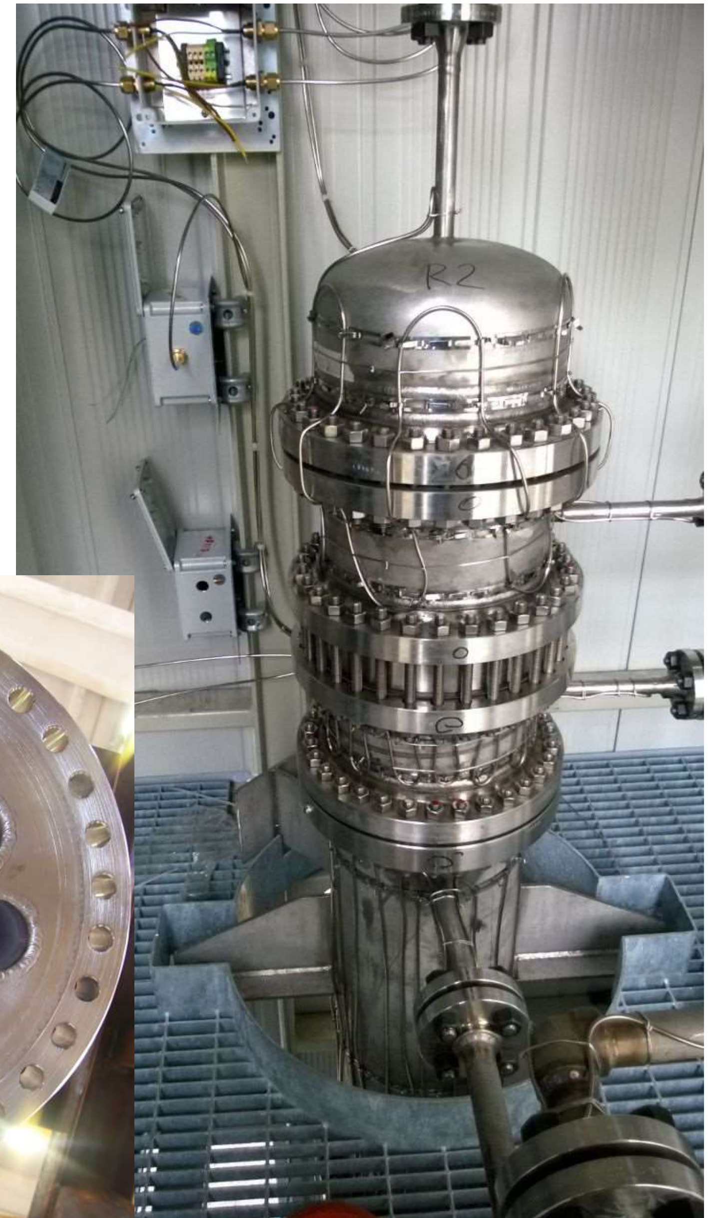
PLANT CAPACITY = 3,5 Nm^3/h PURE HYDROGEN



B. Morico, A. Salladini, E. Palo, G. Iaquaniello, ChemEngineering 3 (2019) 9

MEMBRANE REACTORS for PURE HYDROGEN PRODUCTION

Closed Architecture



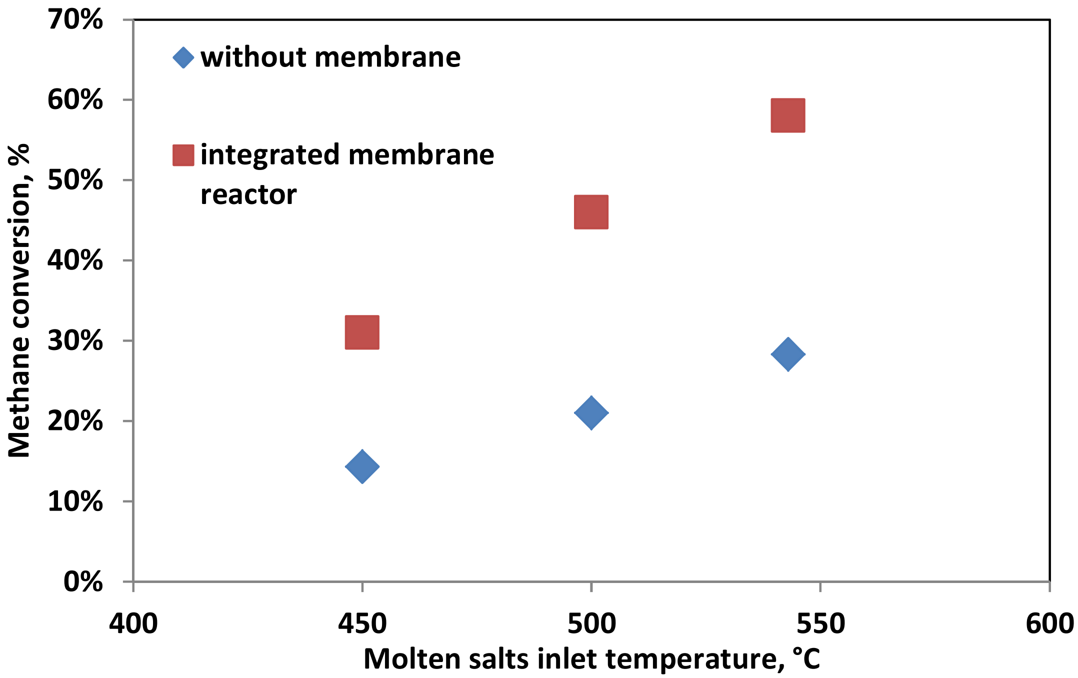
Catalyst

ECN membrane, $0,3 m^2$

B. Morico, A. Salladini, E. Palo, G. Iaquaniello, ChemEngineering 3 (2019) 9

MEMBRANE REACTORS for PURE HYDROGEN PRODUCTION

Closed Architecture



Feed Pressure: **8,5barg**
Steam to carbon ratio: **4**

An overall feed conversion of 58% was achieved at 543° C, doubling the conversion can be achieved in a conventional reformer at the same temperature.

Stable catalyst performance over more than 100 hours of testing

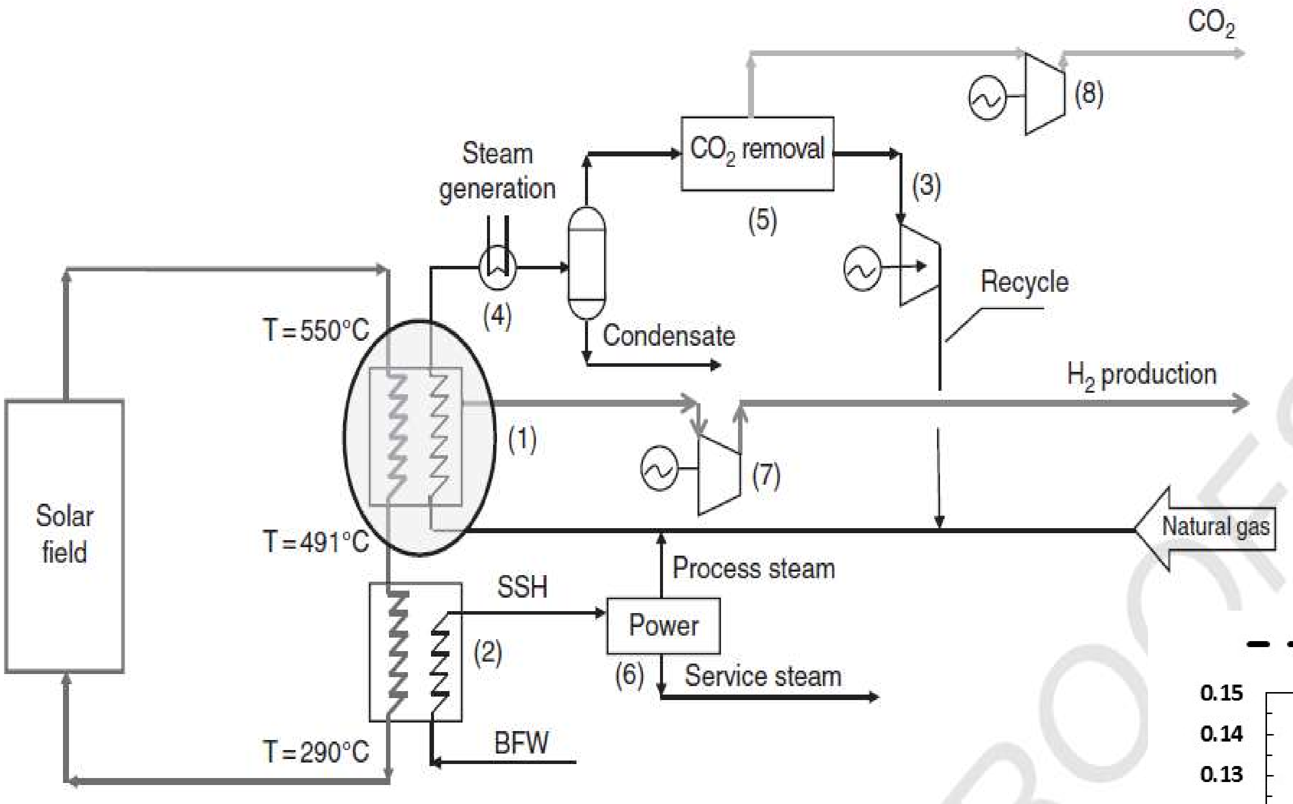
Purity of hydrogen permeate higher than 99.8%

No macroscopical signs of reactor performance loss have been evidenced over the experimental operation period, despite handling of catalysts and membranes and the several switches of operative conditions.

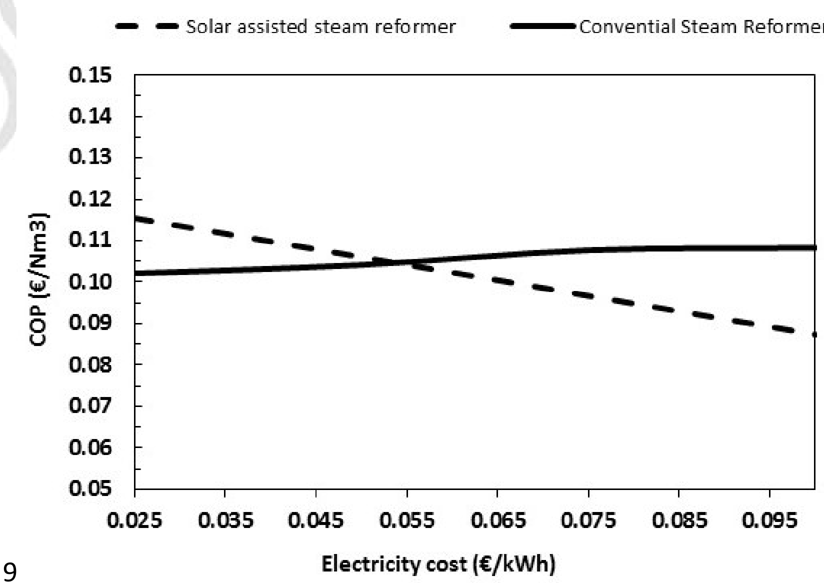
B. Morico, A. Salladini, E. Palo, G. Iaquaniello, ChemEngineering 3 (2019) 9

MEMBRANE REACTORS for PURE HYDROGEN PRODUCTION

Economic analysis



SR reactor powered with a molten salts flow heated with solar energy for 5000 h/y, and in the remaining period, 3400 h/y, molten salts are heated through a process heater where NG is fired.



Plant capacity = 5,000Nm^3/h H_2

Six-step membrane reactor in an open architecture, where reactions stages are followed by membrane stages

B. Morico, A. Salladini, E. Palo, G. Iaquaniello, ChemEngineering 3 (2019) 9

MEMBRANE REACTORS for PROPYLENE PRODUCTION

EU FP7 CARENA PROJECT

«CAtalytic membrane REactors based on New mAterials for C1-C4 valorization»

AIM:
To develop and implement novel nano-structured materials and optimized membrane-reactor based chemical processes to enable the efficient conversion of light alkanes and CO2 into higher valuable chemicals

$C_3H_8 = C_3H_6 + H_2$

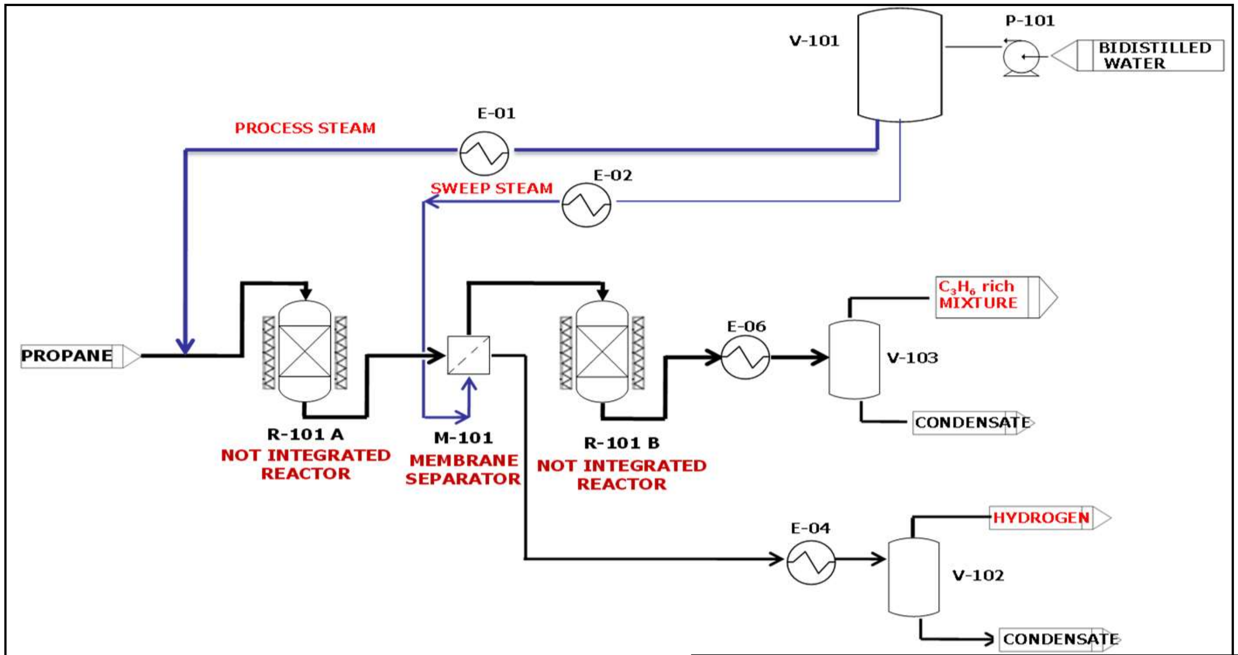
Propane dehydrogenation, strongly endothermic
$\Delta H°_{25°C} = 125$ kJ/mol

High reaction temperature penalises C3H6 selectivity with coke formation on the catalyst

Removing hydrogen from the reaction zone allows to shift chemical equilibrium towards products enhancing hydrogen yield at lower temperature

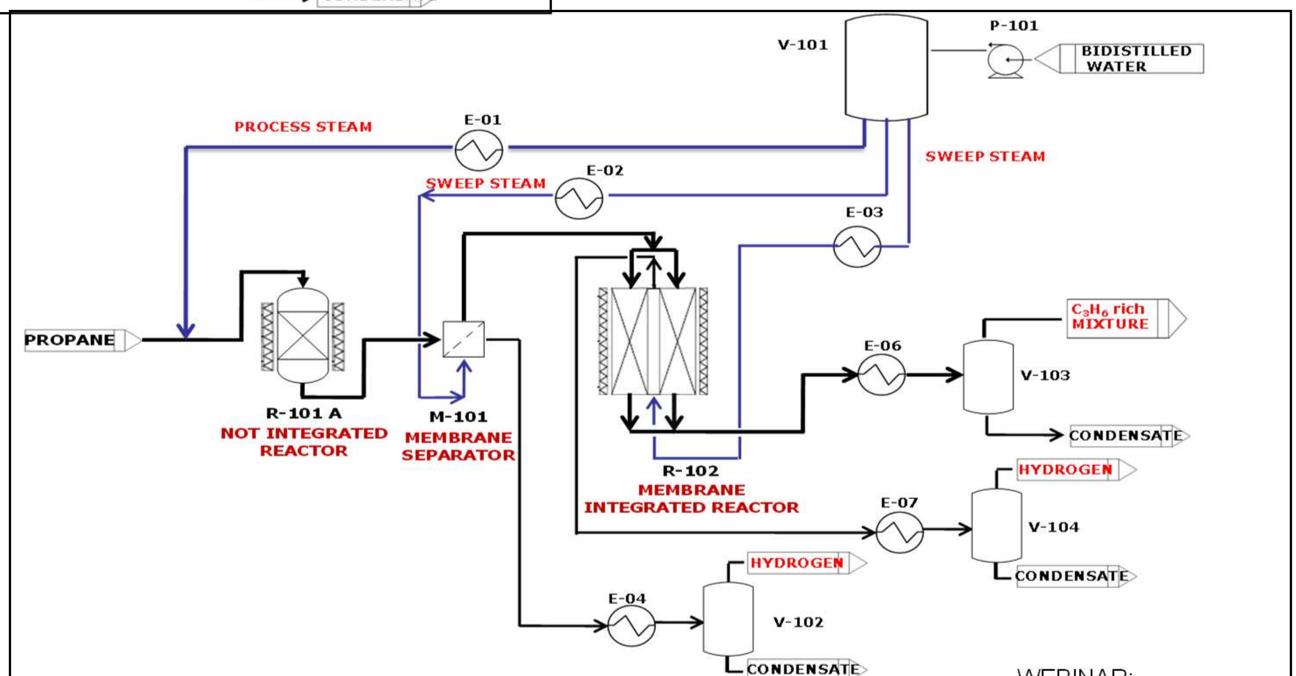
- USE OF LOW-GRADE HEAT REJECTED BY A BOTTOM PROCESS
- REDUCE/AVOID THE CATALYST REGENERATION STEP
- POTENTIAL REDUCTION OF CONVENTIONAL PLANT CAPACITY
- VALORIZATION OF SIDE STREAMS

MEMBRANE REACTORS for PROPYLENE PRODUCTION



OPEN ARCHITECTURE

HYBRID ARCHITECTURE



G. Iaquaniello, E. Palo, PCT /NL2012/050201, March 2012

C. Croppi, F.S. Martorelli, E. Palo, G. Iaquaniello, A. Salladini, PCT/NL/2016/050150, March 2016

MEMBRANE REACTORS for PROPYLENE PRODUCTION

UNIVERSITY OF SALERNO

PLANT CAPACITY = 0,25kg/h PROPANE

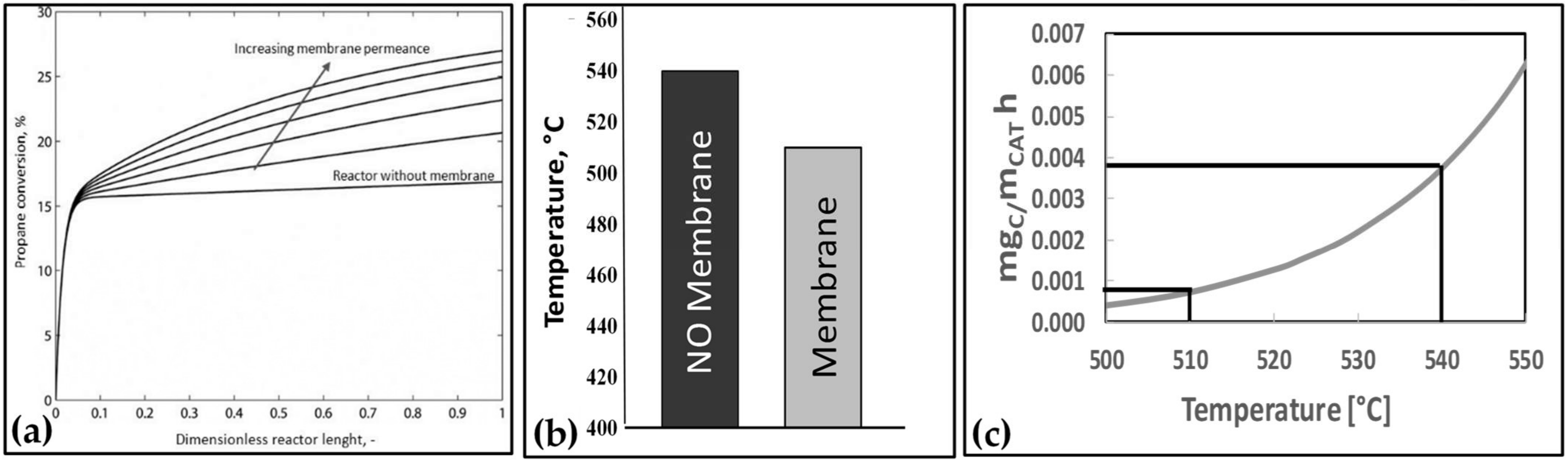
Noble metal based catalyst

Catalytic Reactor

Pd-MEMBRANE, US Company, 101 cm2

Ricca, A.; Montella, F.; Iaquaniello, G.; Palo, E.; Salladini, A.; Palma, V, *Catal. Today* **2018**, in press
Ricca, A.; Palma, V.; Iaquaniello, G.; Palo, E.; Salladini, A. *Chem. Eng. J.* **2017**, *330*, 1119
Ricca, A.; Truda, L.; Iaquaniello, G.; Palo, E.; Palma, V. *Int. J. Mem. Sci. Technol.* **2018**, *5*, 1

MEMBRANE REACTORS for PROPYLENE PRODUCTION



(**a**) numerical simulation of propane conversion at T = 550 °C and different membrane permeances 40–80 $Nm^3/hm^2bar^{0.5}$, (**b**) experimental operating temperature at fixed propane conversion (X_{C3H8} = 10%, 5 barg, S/C3 = 0.25), (**c**) coke amount as a function of the operating temperature

A significant reduction in coke formation can be observed decreasing the operating temperature, as effect of membrane installation in open architecture.
Lack of membrane stability, as reported in the literature

Preliminary economic evaluation in closed architecture show that in the case of a scale down of capacity of a factor 8, a reduction in COP of propylene around 4% can be observed

E. Palo, A. Salladini, B. Morico, V. Palma, A. Ricca, G. Iaquaniello, Membranes 8 (2018) 101

MEMBRANE REACTORS for GAS TO LIQUID PROCESSES

EU FP7 NEXT-GTL PROJECT
«Innovative Catalytic Technologies & Materials for Next Gas to Liquid Processes»

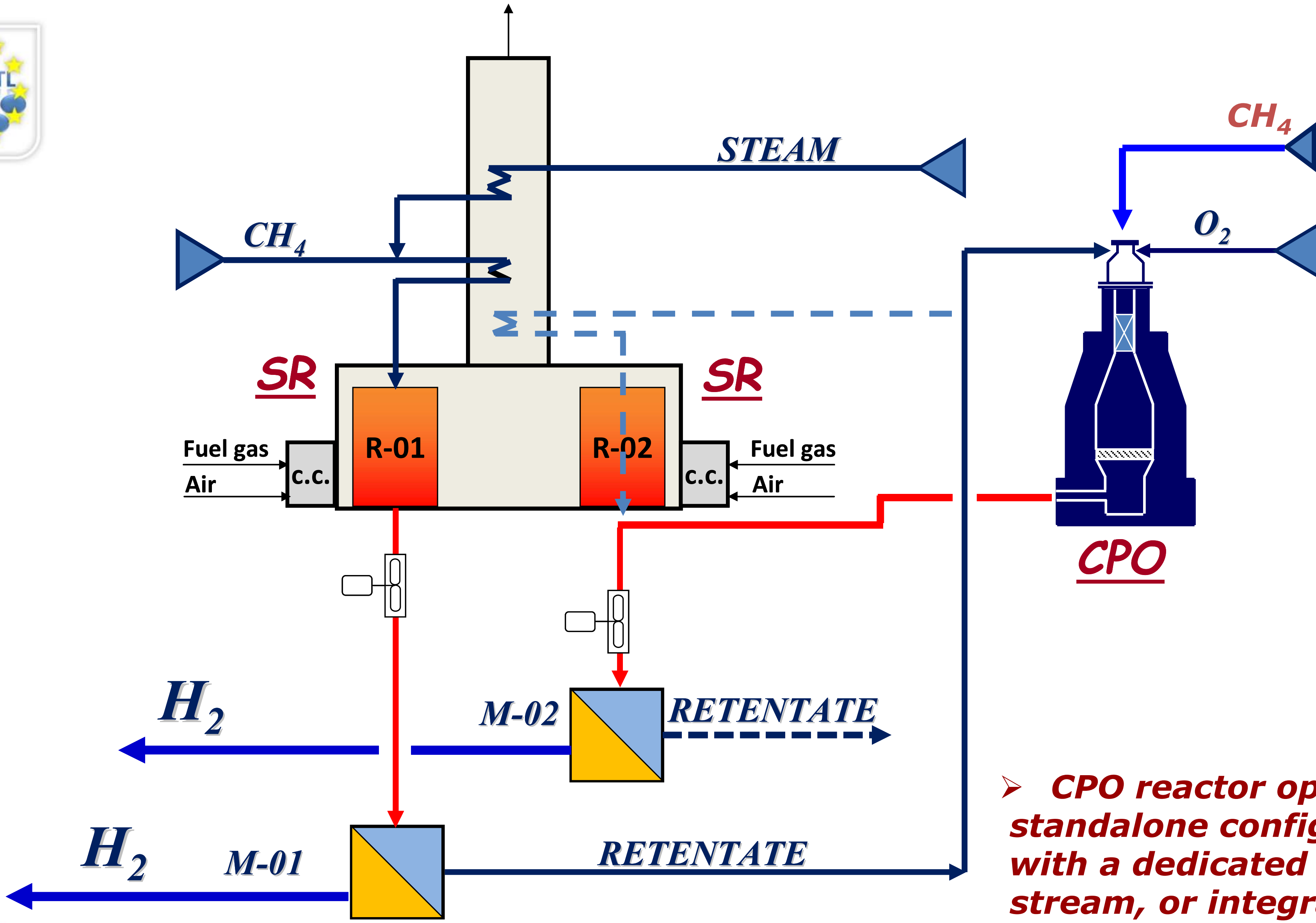
The GTL process has three main steps:

- feedstock preparation and syngas production → **THE MOST EXPENSIVE STEP**
- Fisher Tropsch synthesis
- syncrude upgrading

AIM:

Development of novel process schemes for the production of syngas at lower temperature than the traditional ones, without affecting natural gas conversion and saving the same time in terms of feed consumption and plant complexity, thereby assessing the potentiality of distributed GTL plants

MEMBRANE REACTORS for GAS TO LIQUID PROCESSES



- ***CPO reactor operated in standalone configuration, with a dedicated CH_4 feed stream, or integrated one***

D. Capoferri, B. Cucchiella, A. Mangiapane, S. Abate, G. Centi, *ChemSusChem* 2011, **4**,1787.
G. Iaquaniello, A. Salladini, E. Palo, G. Centi, ChemSusChem, 2015, 8, 717.

MEMBRANE REACTORS for GAS TO LIQUID PROCESSES

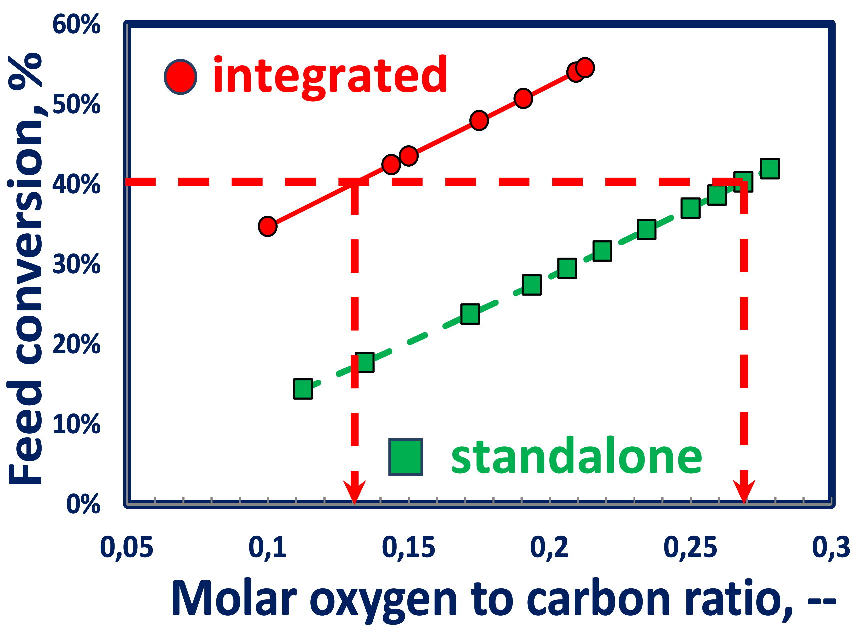
TECHNOLOGICAL AND SCIENTIFIC PARK OF ABRUZZO

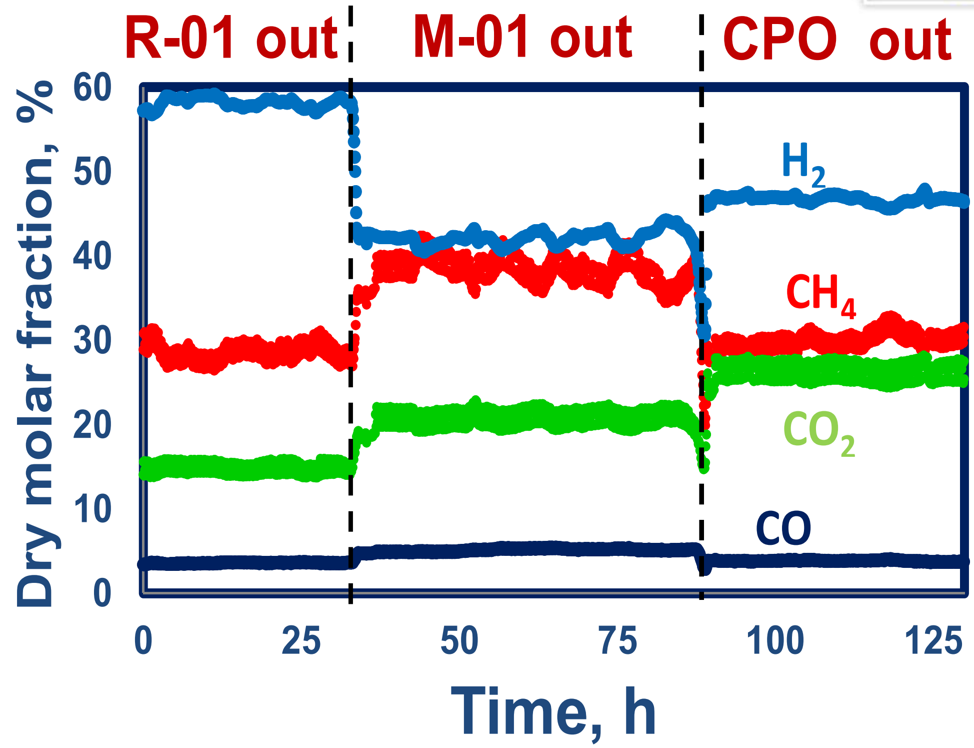
PLANT CAPACITY = 20Nm^3/h PURE HYDROGEN

CPO CATALYSTS

CPO REACTOR

MEMBRANE REACTORS for GAS TO LIQUID PROCESSES





Increase of methane conversion independently from the operating conditions

Overall stable performance in time on stream tests

Reduction in VOC of 10%

MEMBRANE REACTORS for INDUSTRIAL APPLICATION

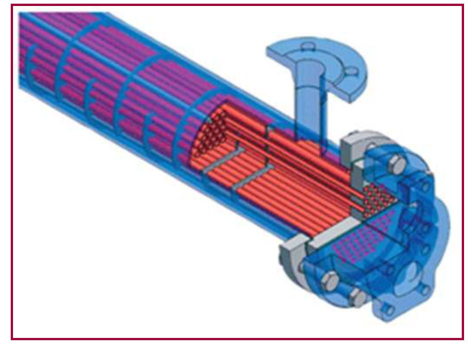
Membrane Recycling

Item	% of total cost
Pressure vessel	20-25
Selective layer deposition	15-20
Pd/Ag alloy	15-25
Ti	-
	30-50
TOTAL	100

Membrane module assumed as heat exchanger shell and tube type

Membrane D = 44 mm
Membrane L = 6 m

Porous stainless-steel support



Minimum target
Recovery of the support not damaged

Identified an optimized leaching treatment for Pd and Ag recovery and undamaged metallic support

Sensible reduction in the membrane Cost of Production

L. Toro, F. Pagnanelli, E. Moscardini, L.M: Baldassari, P. Altimari, E. Palo, A. Salladini, G. Iaquaniello, F. Vegliò, S. Zueva, A. Di Renzo, Italian Patent Application, 27 July 2015

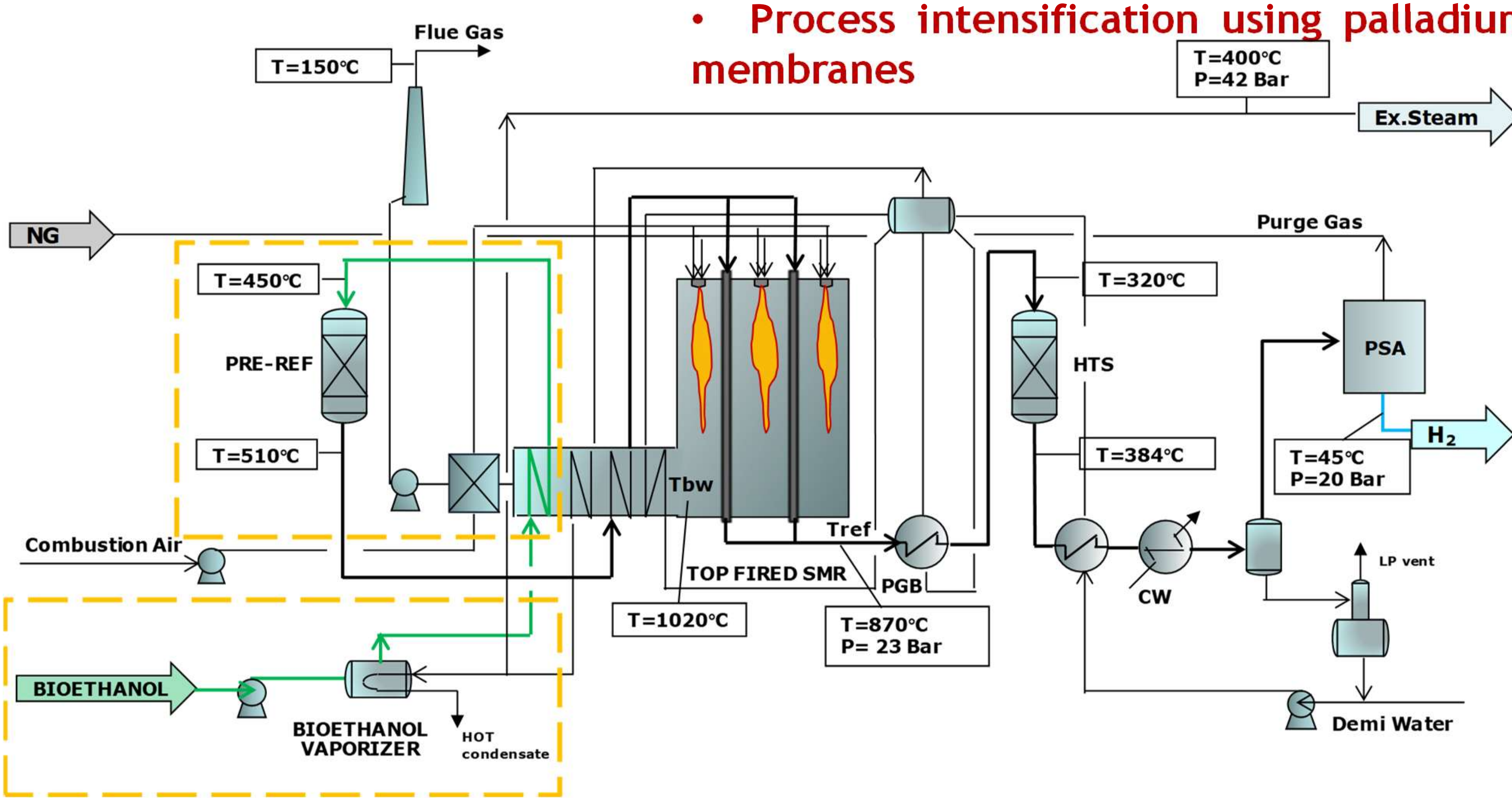
KT Kinetics Technology
ECO Recycling

MEMBRANE REACTORS for BIO-HYDROGEN PRODUCTION

In line with the latest EU roadmap for moving to a competitive low carbon economy, by 2030 to be achieved -40% emission, +27% renewable share, +27% energy efficiency

CENTRALIZED "GREEN" HYDROGEN PRODUCTION

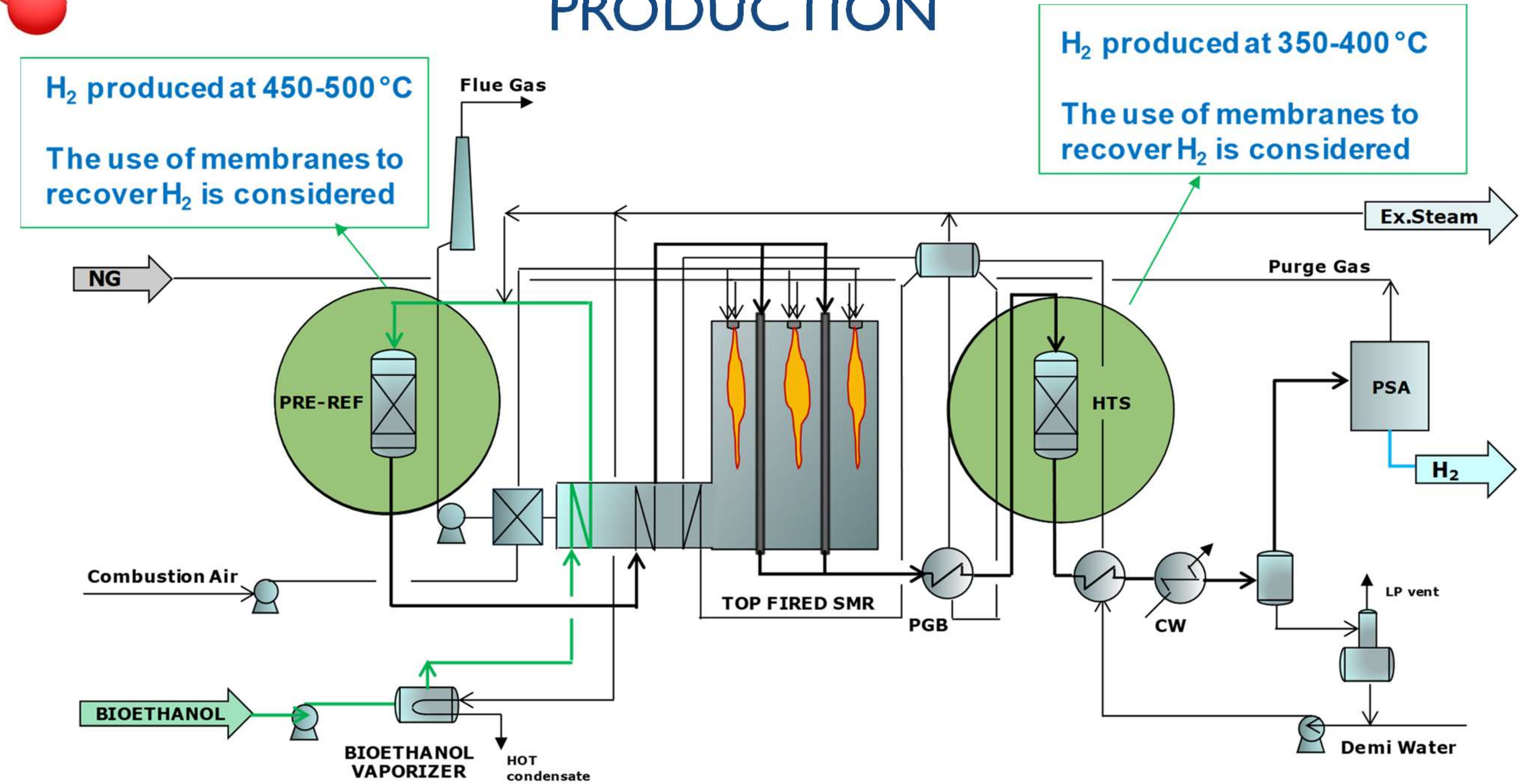
- **Use of bioethanol as feedstock to Steam Reforming Process**
- **Process intensification using palladium-based membranes**



Kinetics Technology · TU/e EINDHOVEN UNIVERSITY OF TECHNOLOGY · PROMECA · MARIE CURIE ACTIONS

WEBINAR:
Modelling of membranes materials and systems

MEMBRANE REACTORS for BIO-HYDROGEN PRODUCTION



- Open and closed architecture have been considered
- The use of bioethanol in H_2 production by Steam Reforming can achieve similar efficiencies as the benchmark technology with NG when membrane technology is integrated in the process
- The use of bioethanol can reduce the carbon footprint up to 67%
- Further studies and process optimization still in progress

MEMBER Project: Novel membrane-based technologies

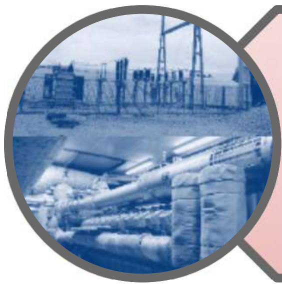
Targets

Prototype A

Pre-combustion capture in power plants using MMMs at HYGEAR reforming equipment.

CCR > 90%

Capture Cost < 30 €/ton



Prototype B

Post-combustion capture in power plants using MMMs at the 8.8 MW CHP facilities of Agroger (GALP, Portugal).

CCR > 90%

Capture Cost < 40 €/ton

Prototype C

Pure hydrogen production with integrated CO_2 capture using MA-SER at the IFE-HyNor (Norway) under the supervision of ZEG POWER.

CCR > 90%

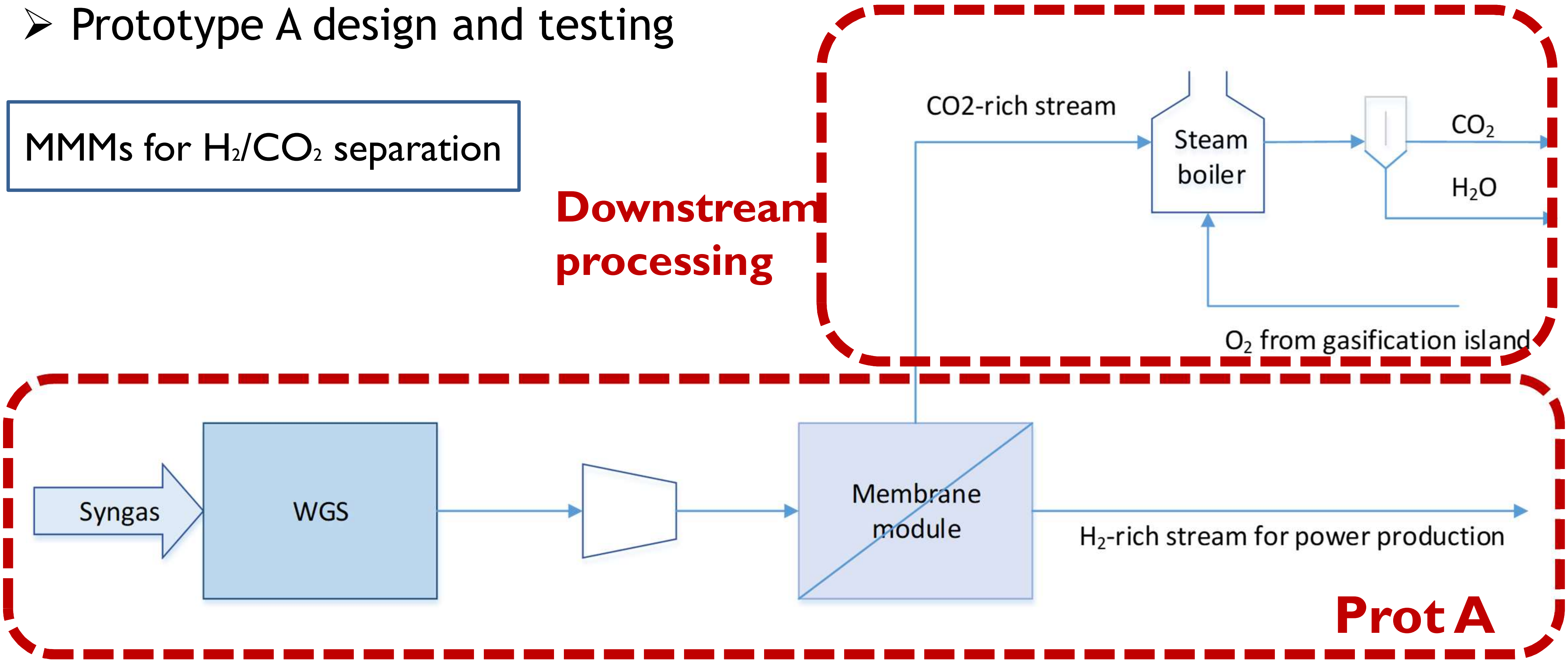
Capture Cost < 30 €/ton

MEMBRANE REACTORS for CO2 CAPTURE

Pre-combustion capture

➢ Prototype A design and testing

MMMs for H_2/CO_2 separation



- CO_2 separation from the shifted syngas after Water Gas Shift reactor
- The heating value contained in the original feedstock is re-allocated in a "decarbonized" fuel → Hydrogen

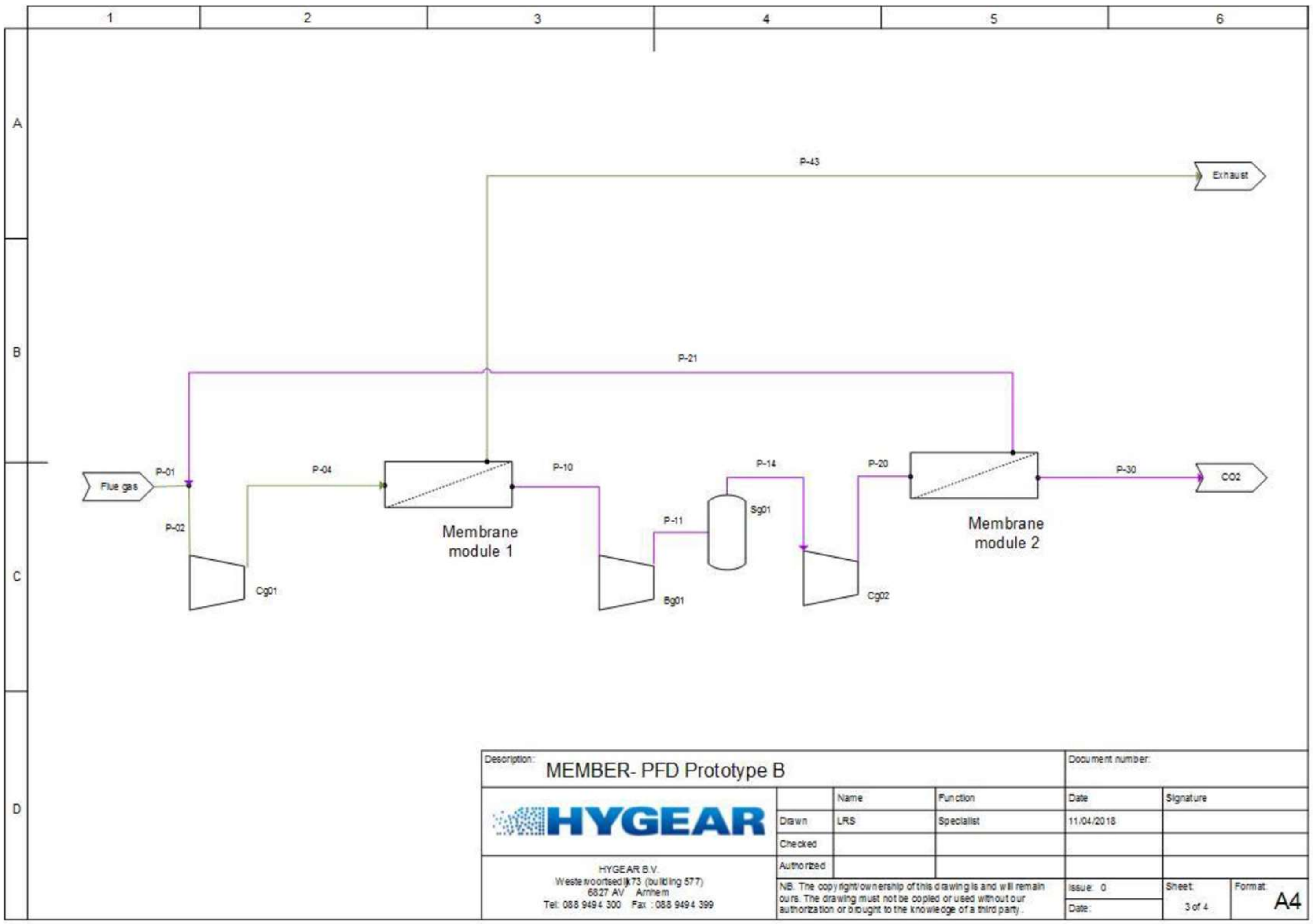
MEMBRANE REACTORS for CO2 CAPTURE

Post-combustion capture

MMMs for CO_2/N_2 separation

- Prototype B design and testing

- CO_2 is separated from the N_2-rich flue gases from a combustion process
- Two membrane modules in series, module 1 larger than module 2



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(Disclosure or reproduction without prohibited permission of MEMBER is prohibited).

WEBINAR:
Modelling of membranes materials and systems

Hydrogen production integrated with CO2 capture

- Prototype C design and testing

Pd-membranes, catalyst and sorbents

IFE HYNOR HYDROGEN TECHNOLOGY CENTRE (NORWAY)

PLANT CAPACITY = 10Nm³/h PURE HYDROGEN

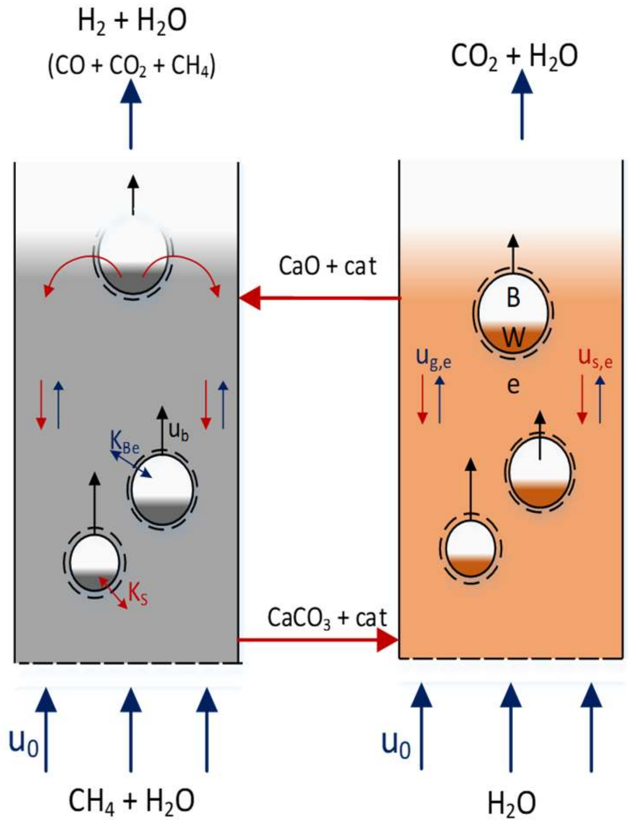
A combination of H_2 membranes, reforming catalyst and CO_2 sorbent into an advanced Membrane Assisted Sorption Enhanced Reforming (MA-SER) process.

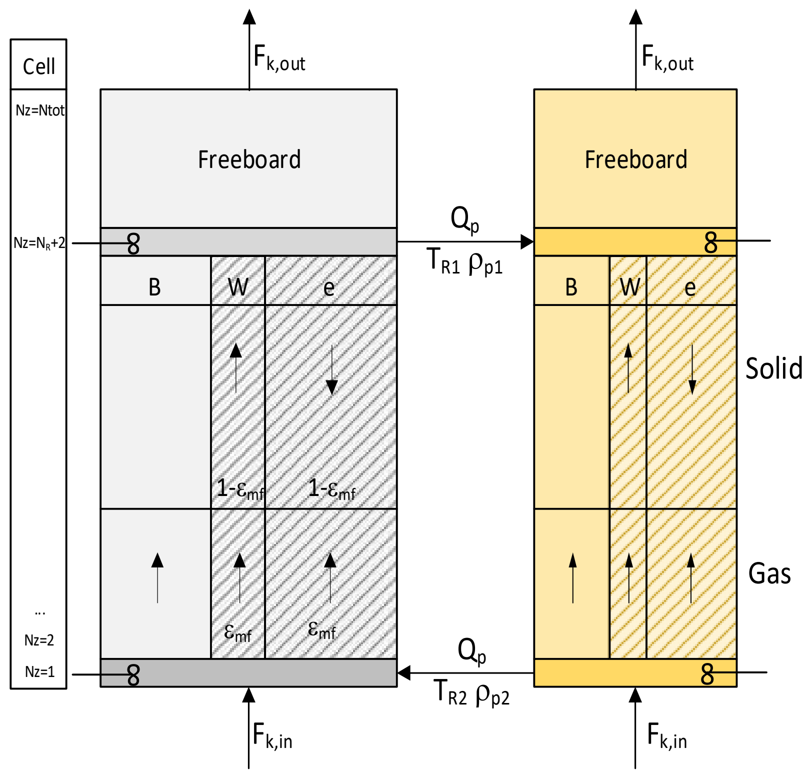
Kinetics Technology
Institutt for energiteknikk

MEMBRANE REACTORS for CO2 CAPTURE

Hydrogen production integrated with CO2 capture

- Increase of Carbon Capture Rate (CCR) of 90%
- The prototype will be demonstrated in an industrially relevant environment, allowing validation of the performance and stability of the technological solutions and materials.





MEMBRANE REACTORS for CO2 CAPTURE

Hydrogen production integrated with CO2 capture

➢ New MEMBER materials for MA-SER line

Pd-based membranes

Ceramic supported thin double skin Pd-based membranes prepared for the prototype

Granulated HTSORB sorbent

Sorbent

Catalyst

An appropriate European patent application EP19201909.9 with the title "Fluidizable steam reforming catalyst and use of a catalyst in methane steam reforming" was filed on October 8, 2019.

CONCLUSION

- Membrane Technology application has been considered and assessed for different processes of industrial interest
- All applications based on syngas production showed very good membrane performance with stable removal activity and very high selectivity
- The application of membrane technology to propane dehydrogenation still needs major improvement in terms of membrane stability
- Recycling of membrane module key elements can contribute to solve the cost issue, at least for membranes with metallic support
- Bioethanol feedstock coupled with membrane reactor can further contribute to the reduction of carbon footprint
- CO_2 capture processes in novel membrane-based technologies can outperform the current technologies for pre- and post-combustion CO_2 capture in power plants as well as H_2 generation with integrated CO_2 capture and can help to meet the targets of the European Green Deal

ACKNOWLEDGMENT

EUROPEAN COMMISSION
IS GRATEFULLY ACKNOWLEDGED
FOR THE FINANCIAL SUPPORT

Advances on membrane technologies in hydrocarbon processing industry

MEMBER WEBINAR on
Modelling of membranes materials and systems
23-02-2022

Thank you for your attention

https://member-co2.com/

Contact:
joseluis.viviente@tecnalia.com

Acknowledgement: The research leading to these results has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement nº760944.

Acknowledgement: For the CO2 molecule used in the logo:The original uploader was Frederic Marbach at French Wikipedia [GFDL (http://www.gnu.org/copyleft/fdl.html)