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

Workshop on "Membrane processes for CO_2 capture Booklet

Topic: NMBP-20-2017: High-performance materials for optimizing carbon dioxide capture
Funding scheme: Innovation action t
Call identifier: H2020-NMBP-2016-2017

Due date of deliverable: -	Actual submission date: 25-02-2020	Reference period: 01-07-2019 – 31-12-2020
Document classification code (*): MEMBER-WP08-D0-Booklet-TECNALIA-25022020-v11.docx		Prepared by (**): TECNALIA

Version	DATE	Changes	CHECKED	APPROVED
v11	25-02-2020	Final version	TECNALIA	J.L. Viviente

Project funded by European Union's Horizon 2020 research and innovation programme (2014-2020)		
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 1st workshop organised by the project MEMBER. The workshop on "Membrane processes for CO_2 capture" was hosted by TUE on January the 15th, 2020. 53 persons attended the workshop. The agenda is shown in the figure hereafter.

Workshop on membrane processes for CO_2 capture

Auditorium 4, Eindhoven University of Technology, January 15th, 2020

Agenda

9:30 - 10:00 Registration/Coffee

10:00 – 10:15 Introduction – Welcome (Fausto Gallucci, José Luis Viviente)

10:15 – 10:45 An overview on MEMBER project (José Luis Viviente – TECNALIA)

10:45 – 11:10 Coffee Break - posters

11:10 - 11:40 Mixed Matrix Membranes for CO_2 capture (Freek Kapteijn – TU Delft)

11:40 - 12:10 High temperature catalysts and sorbents (Julien Meyer – IFE)

12:10 - 12:40 Pd based membranes development (Ekain Fernández – TECNALIA)

12:40 – 13:40 Lunch – posters

13:40 - 14:10 Membrane reactors – current status and perspectives (Fausto Gallucci – TUE)

14:10 - 14:40 Process design for CO_2 capture (Vittoria Cosentino – KT & Leonardo Roses – HYGEAR))

14:40 – 15:10 An overview on BIONICO project (Marco Binotti – POLIMI)

15:10 – 15:40 Environmental aspects of membrane-based CO_2-capture (Mireille Faist – QUANTIS)

15:40 – 16:00 Coffee Break – posters

16:00 - 16:30 An overview on C2FUEL project (Camel Makhlofi – ENGIE)

16:30 – 17:00 Closure of the workshop (Fausto Gallucci, José Luis Viviente)

Figure 1. Agenda of the 1st public workshop organised by MEMBER

2. Presentations

2.1. An overview on MEMBER project (José Luis Viviente – TECNALIA)

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 years. *Starting date: 01 January 2018*

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

Contact: joseluis.viviente@tecnalia.com

Outline

1. Introduction
2. Project Objectives
3. Main goals and S&T objectives
4. Partnership
5. Overall approach and methodology
6. Expected results
7. Prototype status
8. Environmental LCA and economical analysis

1. Introduction

Nowadays, mankind is facing two of the most difficult challenges in its life:

- global warming and

- local pollution of urban areas.

1. Introduction

Energy production 21st century

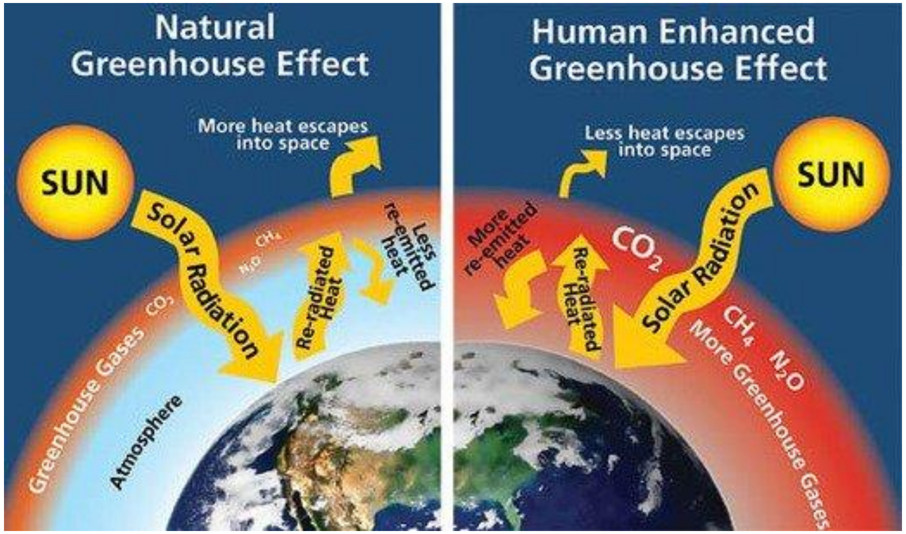
- Majority from fossil fuel derivatives (carbon based): Currently, more than 80% of global primary energy use is fossil based. Over the last decade, 85% of the increase in global use of energy was fossil based.
- CO_2 production

Greenhouse gasses

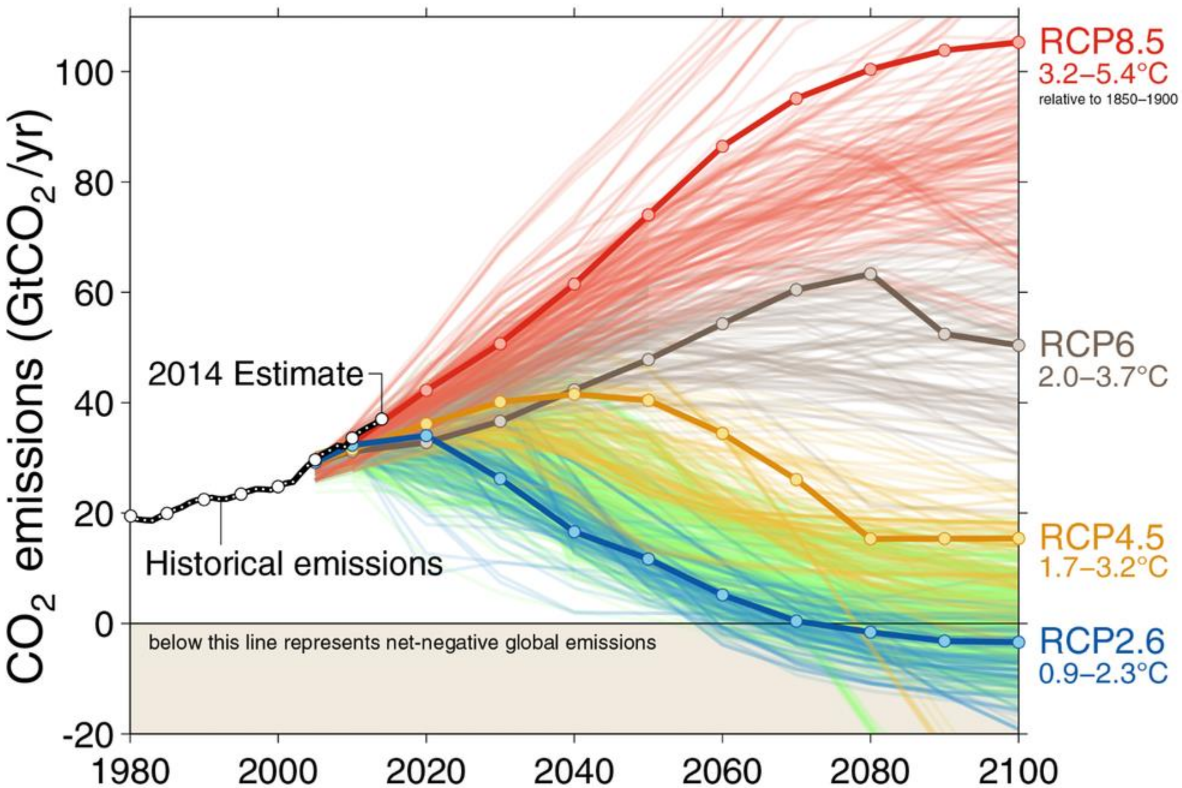
- **Effect**

  Trap IR-radiation (heat)
- **Emission CO_2**

  Natural & human activity



1. Introduction



Global carbon dioxide emissions from human activity, compared to four different possible futures as depicted in IPCC scenarios. Fuss et al. 2014

The EU Commission's Low Carbon Roadmap (and the world climate contract) suggest a reduction of >80% of CO_2 emissions by 2050 compared to levels at the beginning of the 21st century.

2018: 37,1 $GtCO_2$ (www.globalcarbonproject.org)

Transition process requires a new energy system without C at the end with radical technical solutions and infrastructure investments.

1. Introduction

Climate Action in the UN's Sustainable Development Goals (SDGs):
Limiting global warming to 1.5°C (https://www.ipcc.ch/sr15/)

Greenhouse gasses

- **Reduce emission to environment**

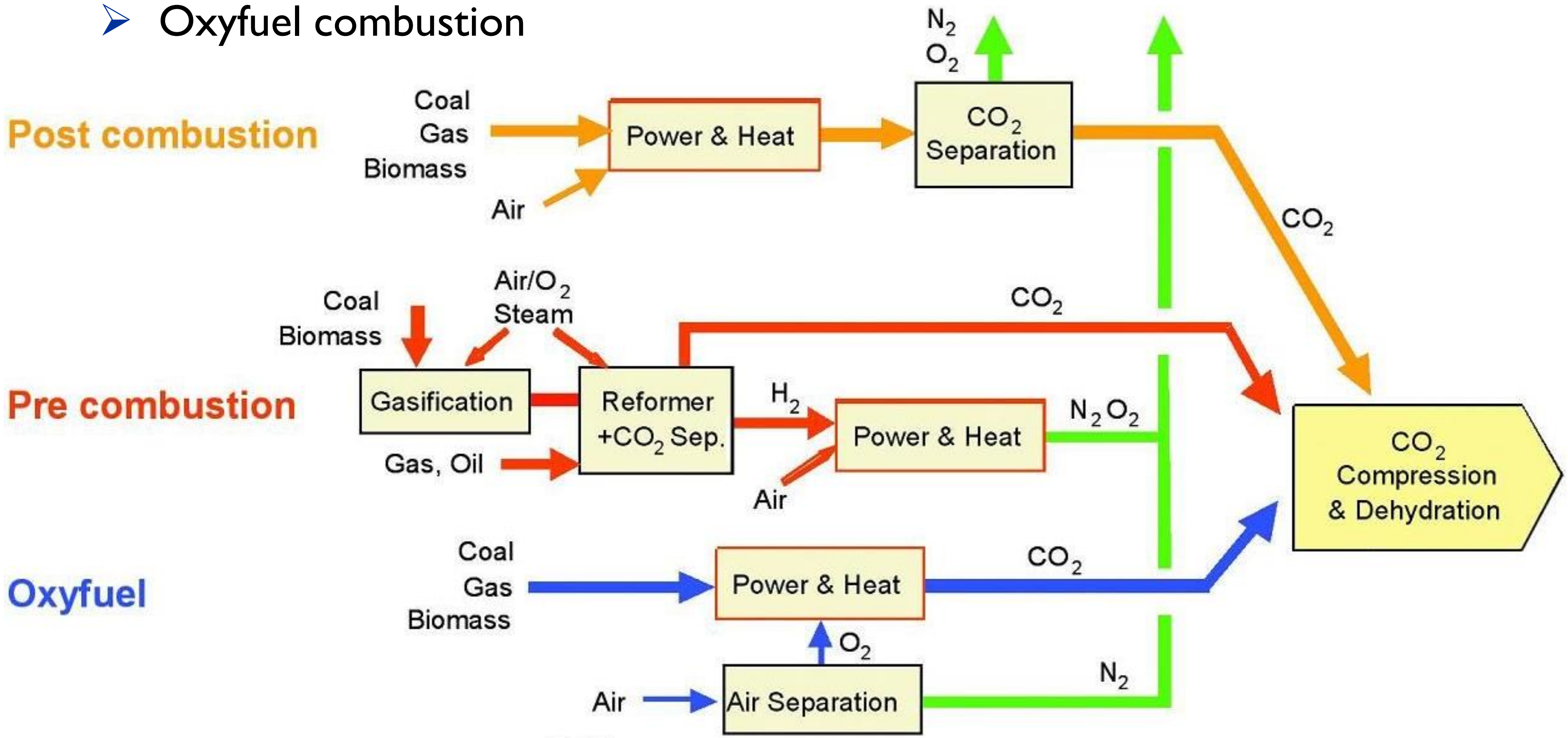
  Increasing Energy efficiency;
  Low carbon processes
  Net-negative global emission
  Search for renewable energy carrier: Hydrogen,
  ….

- **Cost of CO_2 emission (ETC)**
- **Carbon Capture, Utilization and Storage**

  In the transition to a fully low-carbon economy, the CCUS is key to reconcile the demand for fossil fuels, with the need to reduce greenhouse gas emissions and fight climate change.

Carbon Capture & Storage techniques

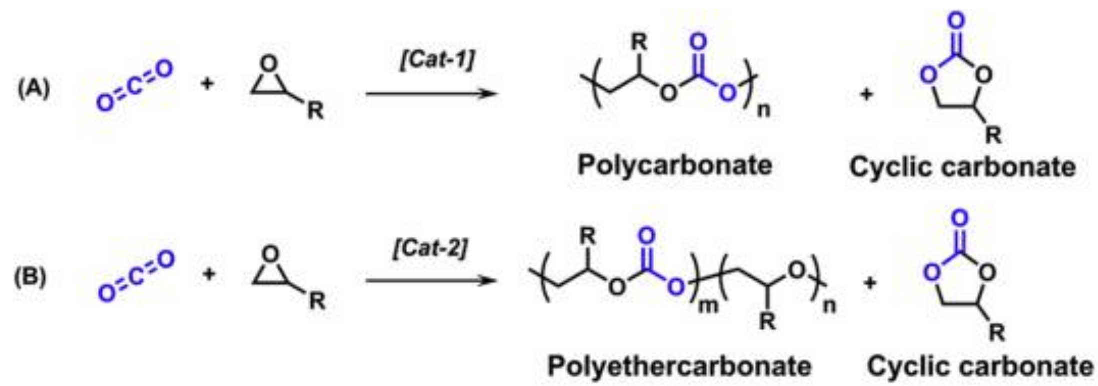
- Pre-combustion
- Post-combustion
- Oxyfuel combustion

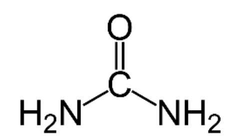


1. Introduction: CCS/CCU techniques

Carbondioxide for:

- Feedstock of chemicals:
  - Fertilizer, polymers
- Solvent
- Carbonation beverages
- Synthetic fuels
- Horticulture
- Construction materials: aggregates and concrete
- Storage (liquid, fixation)
- EOR



$CO_2 + 2NH_3 \rightarrow$  $+ H_2O$

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

1. Introduction

MEMBER project aims to reduce the cost of the Carbon Dioxide capture technologies to fight against the climate change.

MEMBER has been built on the basis of the best materials and technologies developed in three former FP7 projects:

- M^4CO_2 (Energy efficient MOF-based Mixed Matrix Membranes for CO_2 Capture),
- FluidCELL (Advanced m-CHP fuel CELL system based on a novel bio-ethanol Fluidized bed membrane reformer),
- ASCENT (Advanced Solid Cycles with Efficient Novel Technologies)

H2020 – Topic addressed:

NMBP-20-2017: High-performance materials for optimizing carbon dioxide capture

2. Objectives

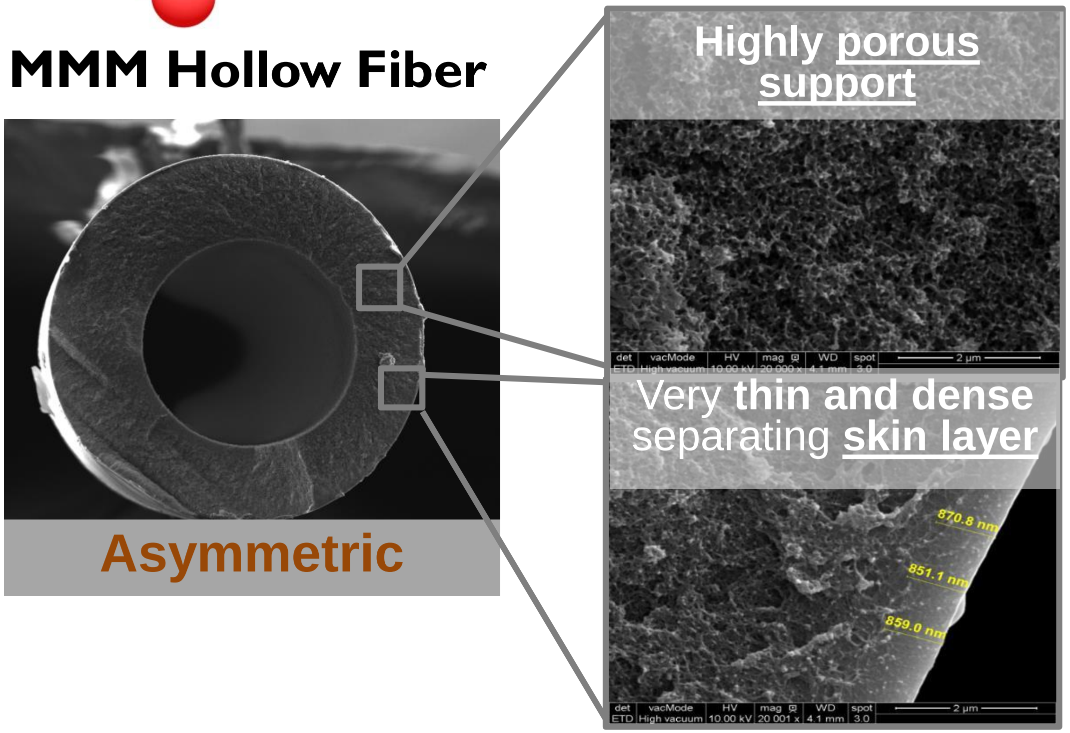
The key objective of MEMBER is to demonstrate state-of-the-art CO_2 capture technologies in an industrially relevant environment. To achieve this, MEMBER will **scale-up and manufacture advanced materials** and prove their added value in terms of sustainability and **performance at TRL 6** in novel **membrane based technologies** for **pre- and post-combustion CO_2 capture in power plants** as well as **in H_2 generation systems with integrated CO_2 capture** and meet the targets of the European SET plan.

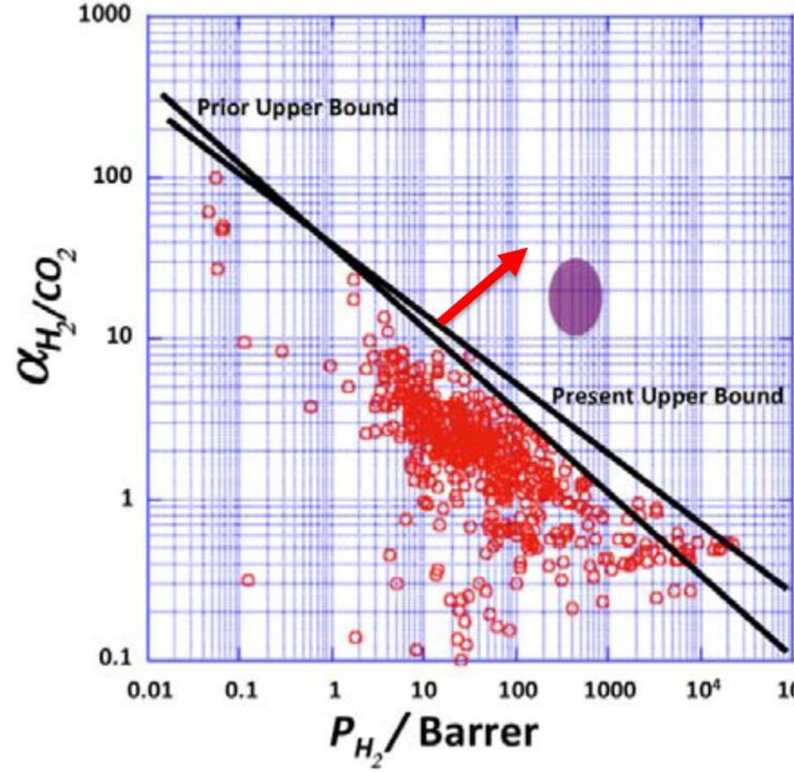
Two different technological solutions involving advanced materials will be developed and demonstrated at three different end user's facilities:

- 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.

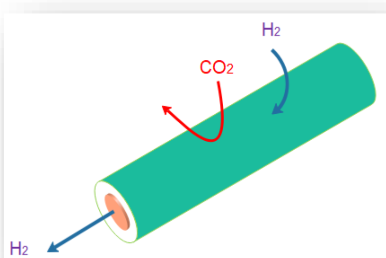
2. Objectives: MMMs concept

MMM Hollow Fiber

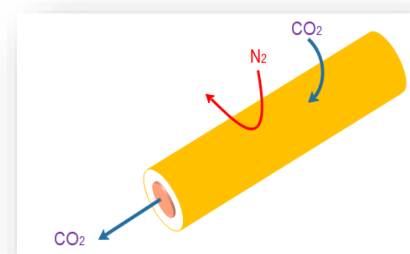




Pre - combustion membrane for H_2/CO_2 separtion



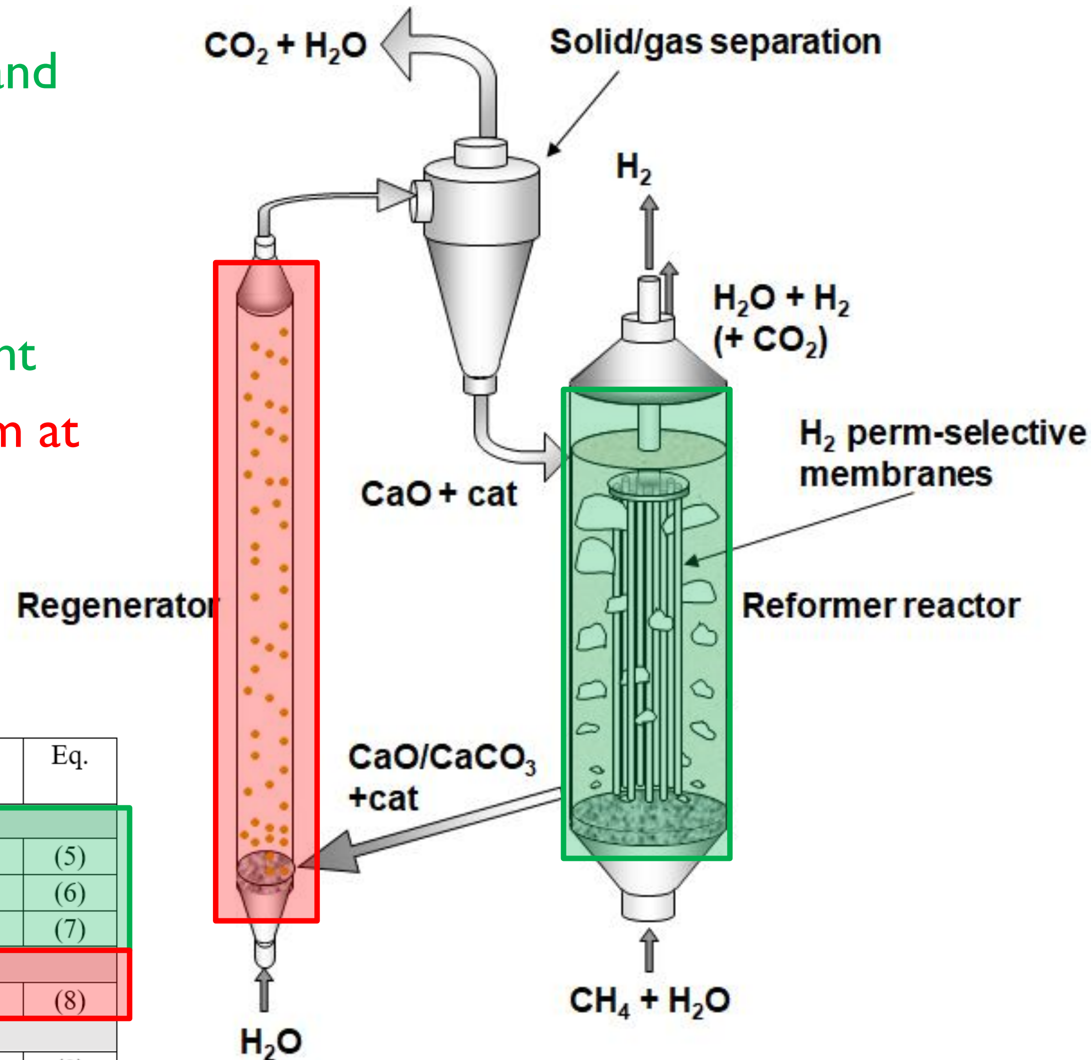
Post - combustion membrane for CO_2/N_2 separation



2. Objectives: MA-SER concept

Three main components:

1. H_2 production with in situ CO_2 and H_2 removal
   - ➢ Hydrogen purification through membranes
   - ➢ Capture of CO_2 by CaO sorbent
2. Regeneration sorbent with steam at elevated temperatures
3. Supply heat by reformate combustion of carbon lean, hydrogen rich stream



Abr.	Reaction	ΔH_r^0 [kJ/mol]	Ref. comp.	Eq.
Reformer				
SMR	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	+206	CH_4	(5)
WGS	$CO + H_2O \leftrightarrow CO_2 + H_2$	−41.1	CO	(6)
Car	$CaO + CO_2 \leftrightarrow CaCO_3$	−178	CaO	(7)
Regenerator				
Cal	$CaCO_3 \leftrightarrow CaO + CO_2$	+178	$CaCO_3$	(8)
Burner				
HC	$2H_2 + O_2 \rightarrow 2H_2O$	–	H_2	(9)
CC	$CO + O_2 \rightarrow CO_2 + H_2O$	–	CO	(10)
MC	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	–	CH_4	(11)

2. Project Objectives

- Prototype A, targeted for **pre-combustion capture in power plants** using MMMs at the 2MWth biomass gasifier of **CENER (Spain) aimed for BIO-CCS demonstration.**
- Prototype B targeted for **post-combustion capture in power plants** using MMM at the 8.8MW CHP facilities of **Agroger (GALP, Portugal).**
- Prototype C targeted for **pure hydrogen production with integrated CO_2 capture** using MA-SER at the **IFE-HyNor Hydrogen Technology Centre (Norway)** under the supervision of ZEG POWER.

Main operation conditions & performance targets for the MEMBER prototypes.

	Technology	CO_2 Capture [%]	Capture cost [€/ton]	Demo site
Pre-comb. Power (IGCC)	MMM	> 90	< 30	CENER
Post-comb. Power (Coal)	MMM	> 90	< 40	GALP
H_2 with integrated CO_2 capture	MA-SER	> 90	< 30	IFE-HYNOR

3. Main Goals and S&T objectives

OBJ. 1: MARKET & BUSINESS OBJECTIVES

- To overcome CCS market barriers with an ambitious set of CCS solutions.
- To take European industrial companies (Materials manufacturers, engineering companies and end users) to a leading position in the CCS market, generating economic growth and job opportunities.

OBJ. 2: ECONOMIC OBJECTIVES

- Compliance with strict cost-effectiveness and performance targets:
  - Pre-combustion Mixed Matrix Membrane system for Power generation
  - Post-combustion Mixed Matrix Membrane system for Power generation
  - Mixed Matrix Membrane materials for MEMBER
  - MA-SER system for pure hydrogen production with integrated CO_2 capture
  - MA-SER materials for MEMBER

3. Main Goals and S&T objectives

OBJ. 3: TECHNICAL OBJECTIVES

- To take to manufacturing development stage (from MRL 4-5 to MRL 6) a portfolio of materials and membranes of MMM technology:
  - Process optimization on pilot production lines (Polymers and MOFs).
  - Scaling production lines for the fine-tuned core material: MOF > 1kg/batch;
  - Scaling up the production of hollow fibres MMMs to >10.000 hollow fibers / batch
  - Scale up the membrane module size to >10 m^2
  - Manufacturing of MMM modules for the pre- and post-combustion CO_2 capture in Power Plants
  - ……
- Move from MRL 4-5 to MRL 6 a portfolio of materials of MA-SER technology:
  - Scale up production for core material: Sorbents: 50-100 kg/day; catalyst: 50 kg/batch;
  - Scaling up the production of Pd-based H_2 membranes to 8 membranes / batch
  - Lifetime Analysis of MA-SER at TRL6
  - Demonstration of compliance with CCS codes and standards. Installations in experimental demo plants to support and provide additional information on product characterization from qualification testing.

MEMBER Workshop, Jan. 15, 2020; TUE, Eindhoven – The Netherlands

3. Main Goals and S&T objectives

OBJ. 3: TECHNICAL OBJECTIVES

- Development of a software tool to simulate MEMBER components and CO_2 capture energy performance from the earliest design phases:
  - Module/reactor design and process simulation (at large scale) for full integration of the MMM systems for pre- and post-combustion, and for MA-SER for pure H_2 production with integrated CO_2 capture
  - Development of a model of the MA-SER reformer
  - Validation of the models through demonstration in relevant conditions (demo site)

OBJ. 4: DEMONSTRATION OBJECTIVES

- Demonstration of MEMBER systems and related business models in 3 representative demonstration sites across Europe, covering different sectors, membrane based technologies and CO_2 containing streams

3. Main Goals and S&T objectives

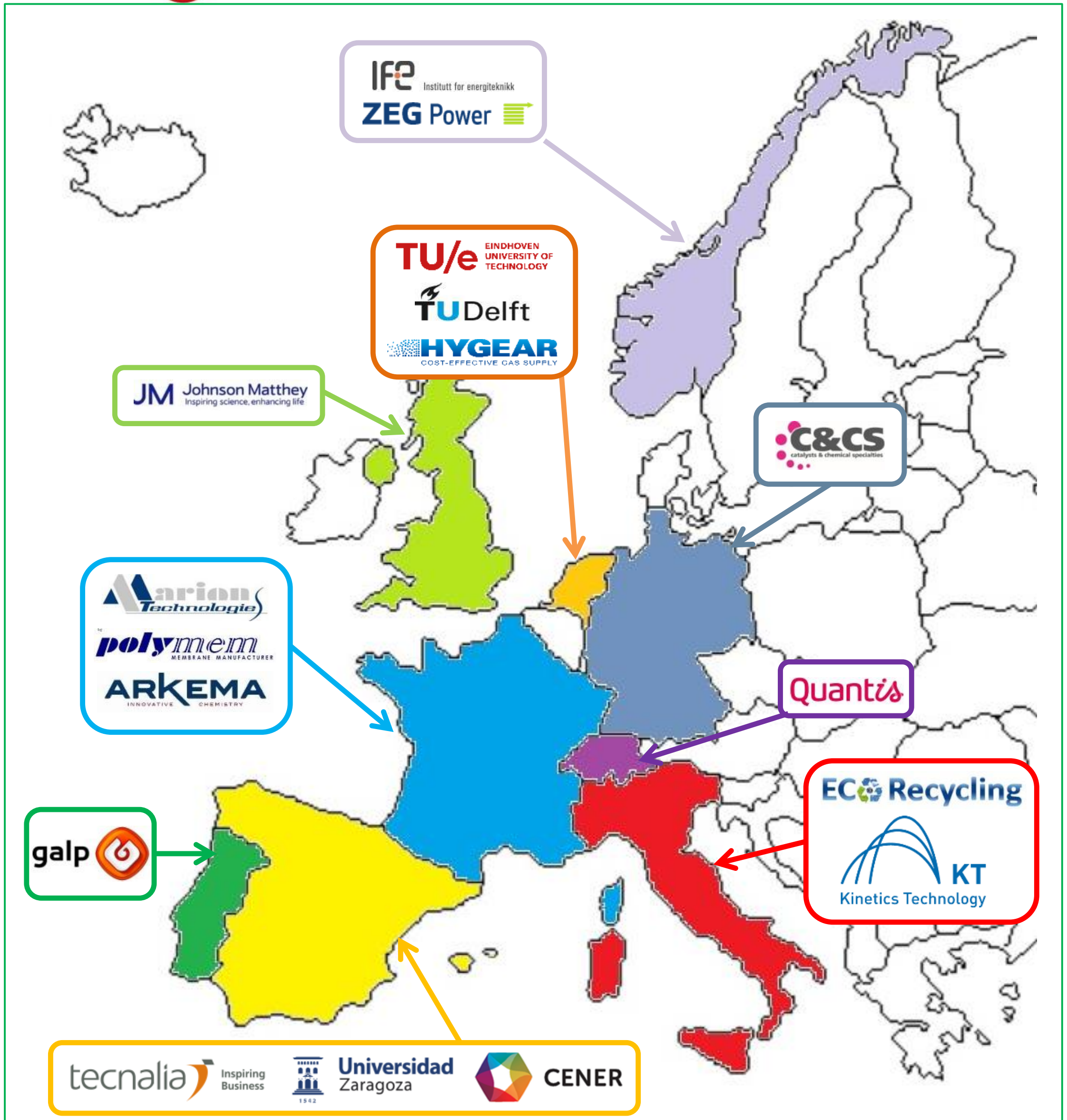
OBJ. 5: ENVIRONMENTAL OBJECTIVES

- To quantify the environmental impacts of the proposed holistic solutions through life cycle assessment based on 3 case studies throughout Europe

OBJ. 6: SOCIAL OBJECTIVES

- Job creation and increase awareness and involvement within the whole social & industrial chain: plant owners, manufacturers, installers, authorities, students, CCS organizations, general public, etc.

4. Partnership

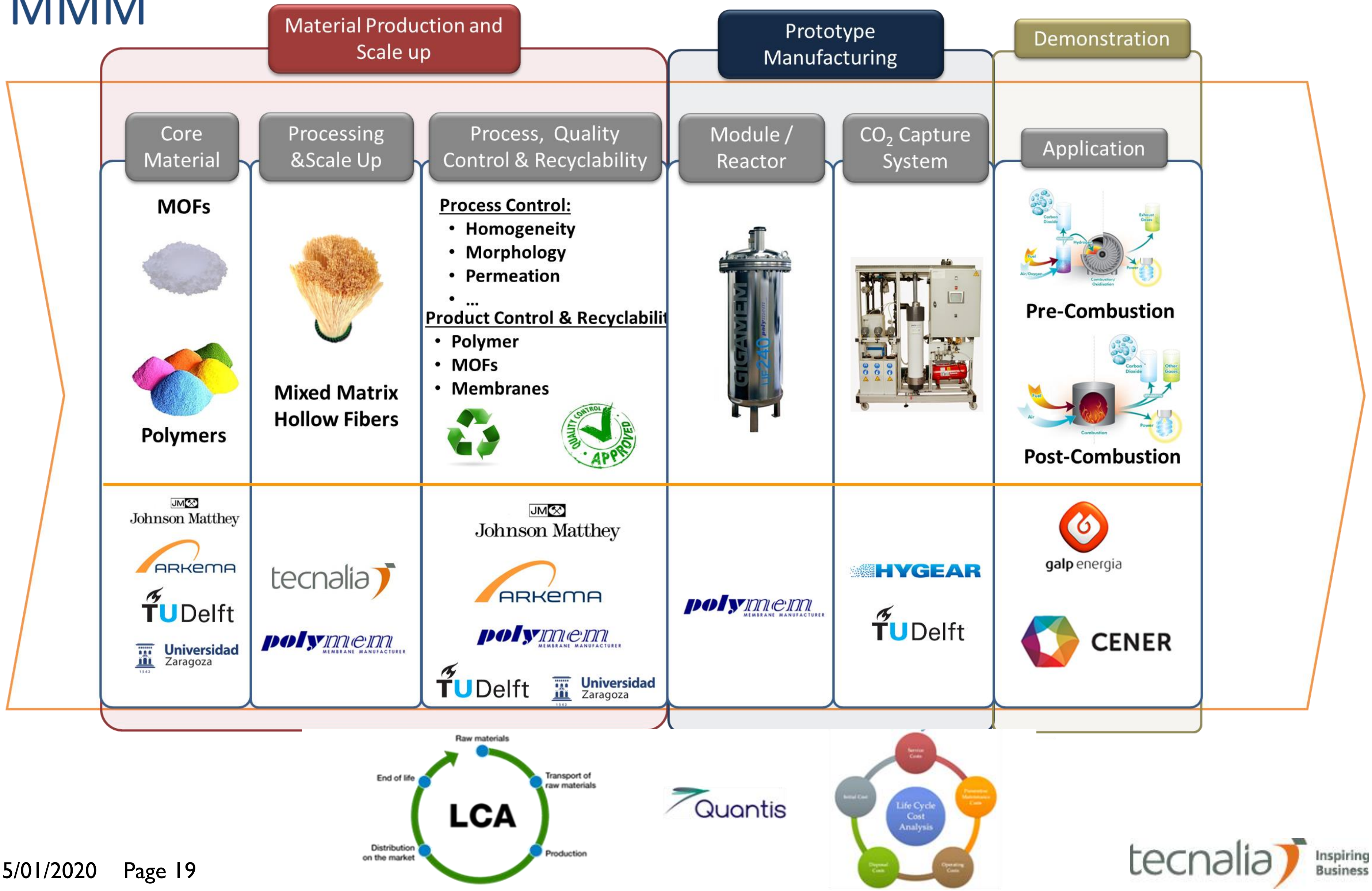


- Multidisciplinary and complementary team.
- 17 partners from 9 countries.
- Industrial oriented (65%):

  11 SME/IND + 6 RTO/HES
- 7 SMEs (41%) & 4 IND (24%)

5. Overall approach and methodology

MMM



tecnalia Inspiring Business

5. Overall approach and methodology

MEMBER

MA-SER

Material Production and Scale up | **Prototype Manufacturing** | **Demonstration**

Core Material Manufacturing & Scale up

Sorbents

Membranes

Catalyst

Partners: Marion Technologie, tecnalia, C&CS catalysts & chemical specialities, IFE

Process, Quality Control & Recyclability

Process Control:
- Homogeneity
- Morphology
- Permeation
- …

Product Control & Recyclability
- Catalyst
- Sorbents
- Membranes

Partners: Marion Technologie, tecnalia, C&CS catalysts & chemical specialities, ECO Recycling

Module / Reactor

Partners: KT Kinetics Technology, TU/e Eindhoven University of Technology

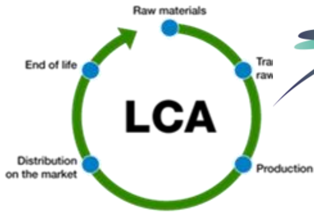
CO_2 Capture System

Partners: KT Kinetics Technology, TU/e Eindhoven University of Technology, IFE

Application

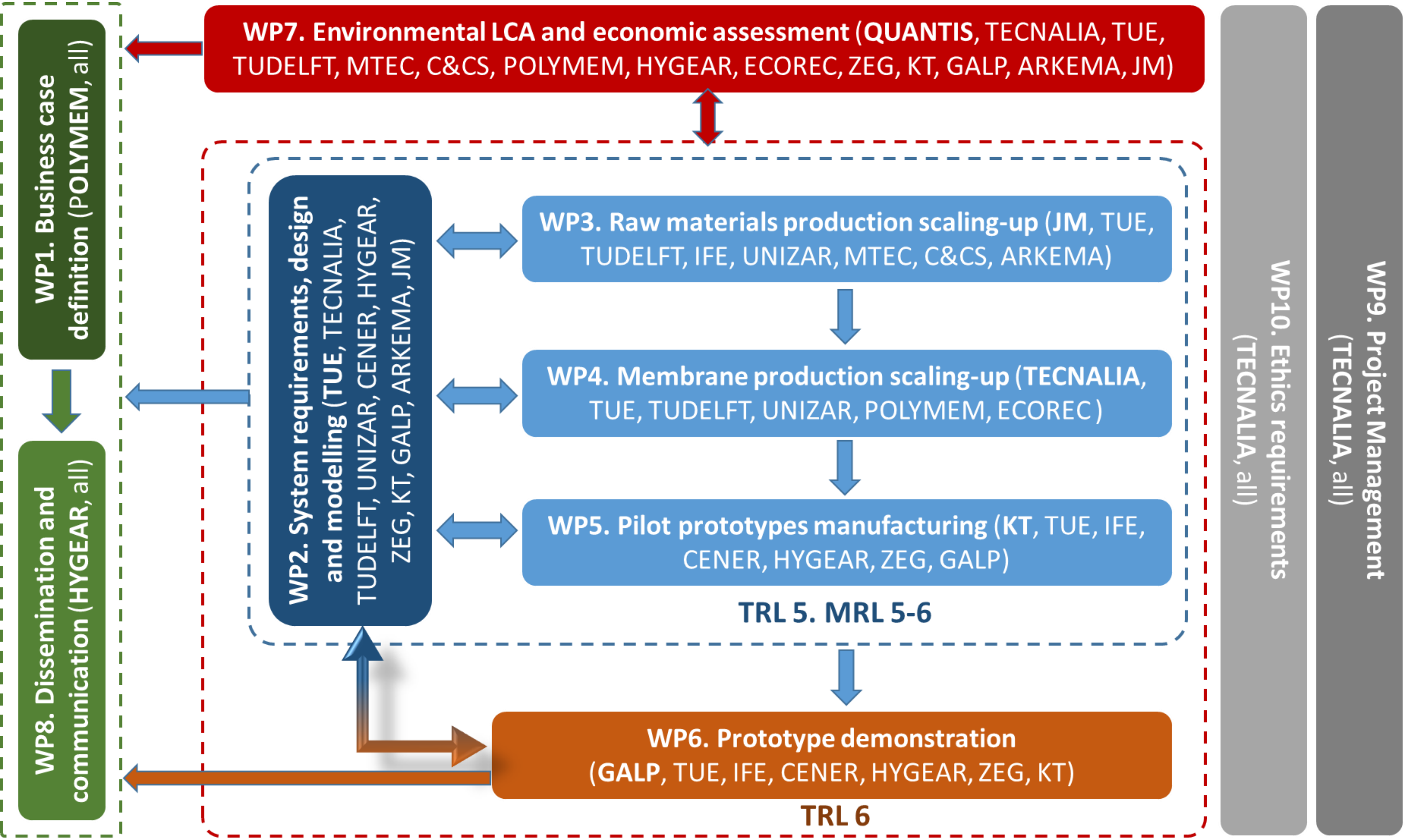
Hydrogen production with integrated CO_2 capture for industrial sectors

Partners: Hynor Lillestrøm, IFE, ZEG Power



Quantis

tecnalia Inspiring Business



WP7. Environmental LCA and economic assessment (QUANTIS, TECNALIA, TUE, TUDELFT, MTEC, C&CS, POLYMEM, HYGEAR, ECOREC, ZEG, KT, GALP, ARKEMA, JM)
WP1. Business case definition (POLYMEM, all)
WP8. Dissemination and communication (HYGEAR, all)
WP2. System requirements, design and modelling (TUE, TECNALIA, TUDELFT, UNIZAR, CENER, HYGEAR, ZEG, KT, GALP, ARKEMA, JM)
WP3. Raw materials production scaling-up (JM, TUE, TUDELFT, IFE, UNIZAR, MTEC, C&CS, ARKEMA)
WP4. Membrane production scaling-up (TECNALIA, TUE, TUDELFT, UNIZAR, POLYMEM, ECOREC)
WP5. Pilot prototypes manufacturing (KT, TUE, IFE, CENER, HYGEAR, ZEG, GALP)
TRL 5. MRL 5-6
WP6. Prototype demonstration (GALP, TUE, IFE, CENER, HYGEAR, ZEG, KT)
TRL 6
WP10. Ethics requirements (TECNALIA, all)
WP9. Project Management (TECNALIA, all)

6. 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

7. Prototype status: Prototype A

- System layout selected
  - 1 membrane module system, operating at 4.5 bar
    Recovery rate 88%; Purity: 98.3%.
  - Multi-module systems enhance the hydrogen recovery: 73% (1 stage) to 86% (2 stages)
  - Lower Permeance reduces the hydrogen separation
  - Reduced Selectivity reduces the CO_2 recovery
- System states defined
  - Start-up sequence, normal operation, stand-by, controlled shut-down and emergency shut-down described
- P&ID made
  - Interfaces with gas cleaning system and gasifier defined
  - Power consumption estimated
- Information documented in Process Book Prototype A

7. Prototype status: Prototype B

- System layout selected
  - 2 membrane module system, operating at 8 bar_a
    Membrane area 10 m^2 and 0.7 m^2 respectively for module 1 and 2
    Recovery rate >90%; Purity: >90%.
  - Reduced Permeance lowers the recovery while purity is not affected
    An increase in operation pressure can counteract the effect
  - Lower Selectivity lowers the CO_2 purity
- System states defined
  - Start-up sequence, normal operation, stand-by, controlled shut-down and emergency shut-down described
- P&ID made
  - Interfaces with the 8.8 MW CHP facility of Agroger defined
  - Power consumption estimated
- Information documented in Process Book Prototype B

7. Prototype status: Prototype C

- Process scheme
  - The process scheme has been finalised in order to integrate the MA-SER reactor in existing facility at IFE-HyNor premises
- MA-SER reactor
  - The design of MA-SER reactor has been addressed in order to address the project objective of pure H_2 production with integrated CO_2 capture
- Piping & Instrumentation Diagrams
  - Interfaces with the existing facility at IFE-Hynor premises defined
- Information documented in Process Book Prototype C

8. Environmental LCA and economical analysis

Reference Systems, to which MEMBER systems are compared

	Without capture	With capture
Pre-combustion	IGCC power plant	IGCC power plant with Selexol absorption
Post-combustion	Coal Power Plant	Coal Power Plant with MEA absorption
Integrated H_2 production	Steam reforming process (biomass based scenario)	Steam reforming process with MDEA absorption

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)

2.2. Mixed Matrix Membranes for CO2 capture (Freek Kapteijn – TU Delft)

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

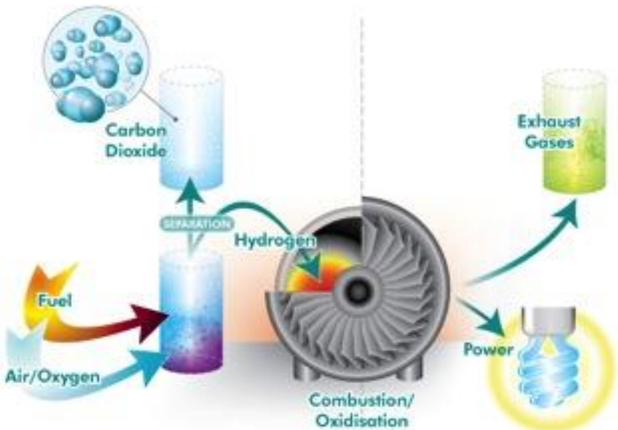
Delft University of Technology

What you can expect.....

- Goal
- Basics
  - Definitions
  - Membrane types
- Experimental
  - Steady state, transient techniques
  - Data interpretation aspects
- Modelling
- Take home message

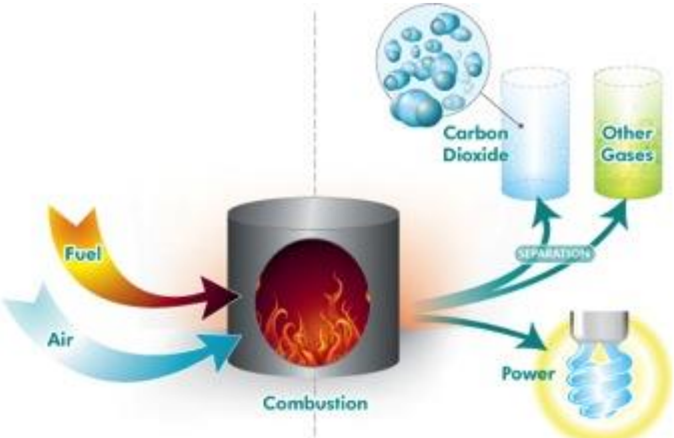
Membrane separation ≡ Energy efficiency

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

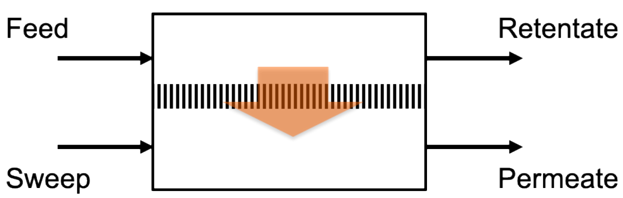
H_2 selective membranes

CO_2 selective membranes

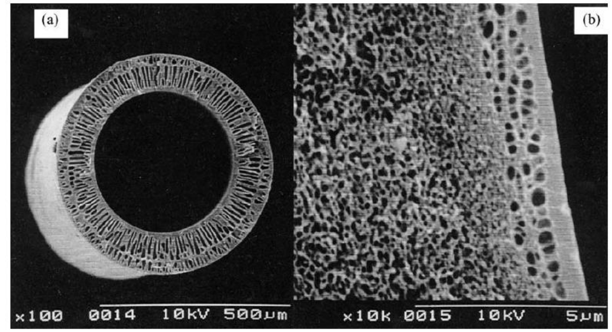
Delft University of Technology

Membrane performance testing

- 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 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)

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

- Permeance
  - Gas Permeation Unit $GPU = 10^{-6} \dfrac{cm^3_{STP}}{s \cdot cm^2 \cdot cm\,Hg}$ $\quad 3.346 \cdot 10^{-10} \dfrac{mol}{s \cdot m^2 \cdot Pa}$

- Permeability
  - Barrer $Barrer = 10^{-10} \dfrac{cm^3_{STP} \cdot cm}{s \cdot cm^2 \cdot cm\,Hg}$ $\quad 3.346 \cdot 10^{-16} \dfrac{mol \cdot m}{s \cdot m^2 \cdot Pa}$

Units interconversion - relation

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

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

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

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

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

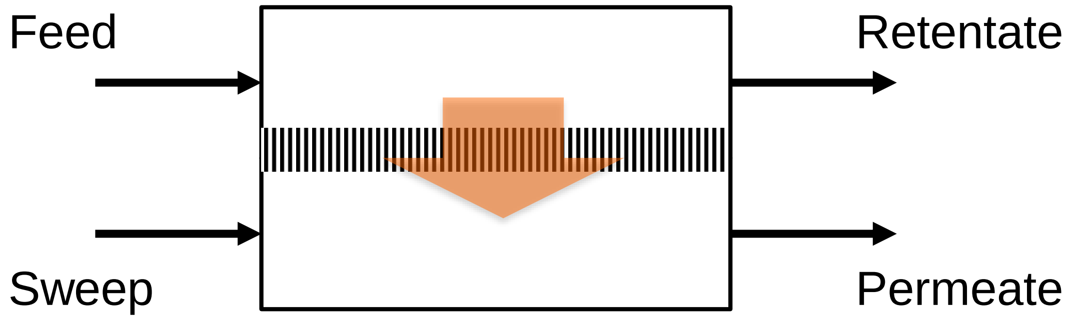
GPU

thickness 0.3 μm (3.10^{-5} cm)

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

$$\frac{1\ \text{Barrer}}{3\times10^{-5}\ \text{cm}} = 10^{-10}\frac{\text{cm}^3_{STP}\times\text{cm}}{\text{s}\times\text{cm}^2\times\text{cm Hg}}\times\frac{10^5}{3}\ \text{cm}^{-1} = 3.3\times10^{-6}\frac{\text{cm}^3_{STP}}{\text{s}\times\text{cm}^2\times\text{cm Hg}} = 3.3\ \text{GPU}$$

Other nomenclature membranes



- Separation factor

  mixed gas selectivity

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

- Ideal separation factor

  ideal selectivity, pure gases

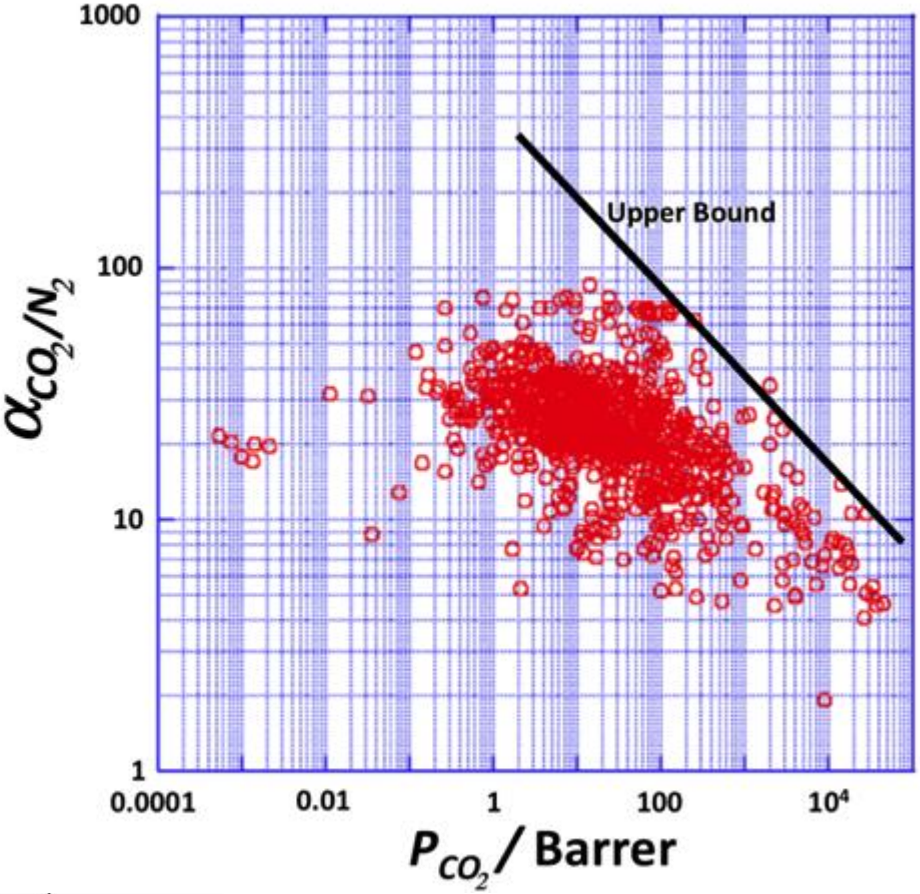
$$ideal\ S_F(AB) = \frac{P_A}{P_B}$$

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

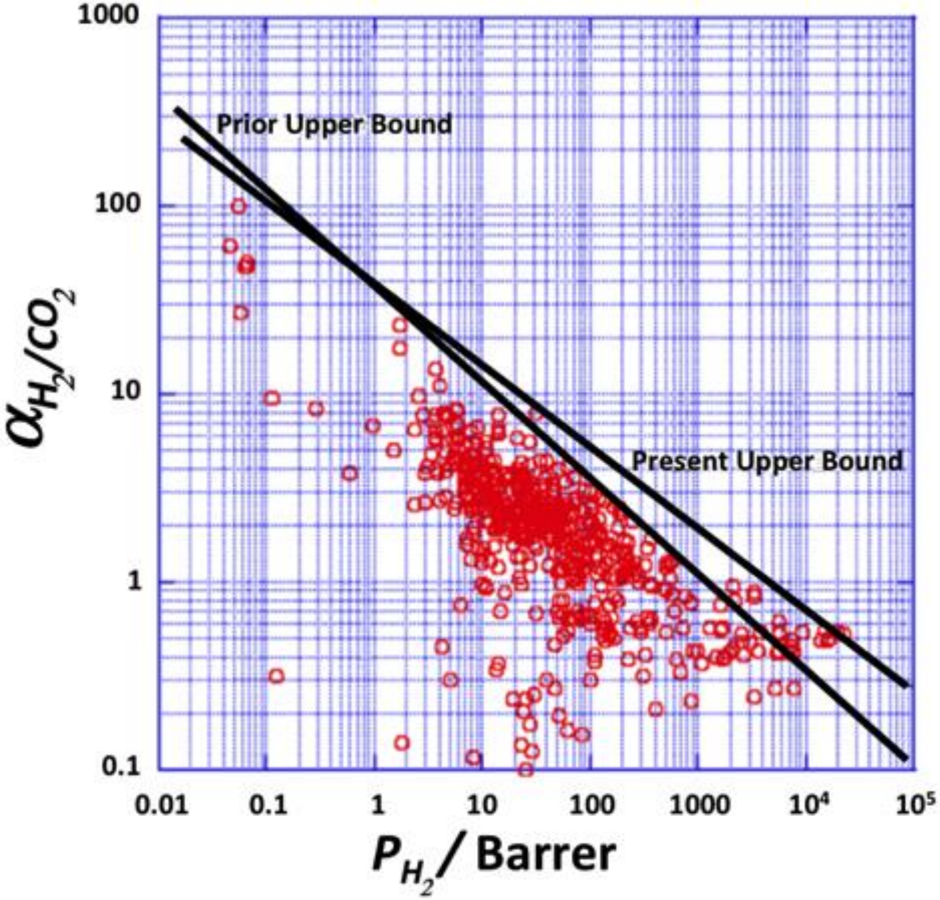
Membrane performances - polymers

Robeson upper bounds

Post-combustion

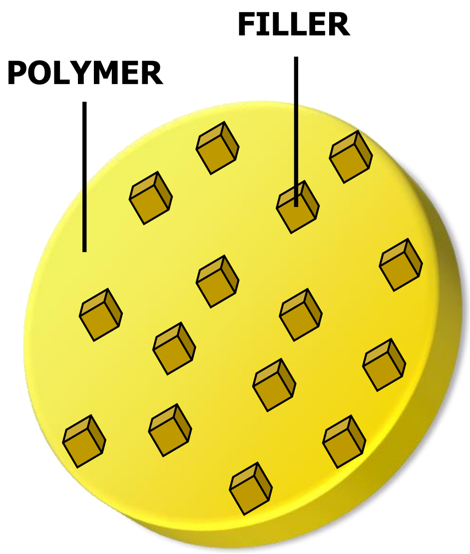


Pre-combustion



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

What is a Mixed-Matrix Membrane?



- Silica, Alumina
- Carbon, CMS
- Clays
- Zeolites
- CNT

Polymeric membrane
(continuous phase)

containing an inorganic '**Filler**'

Combination is expected
to exhibit an improved *performance:*

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

Mixed Matrix Membranes (MMMs)

Polymeric Membranes

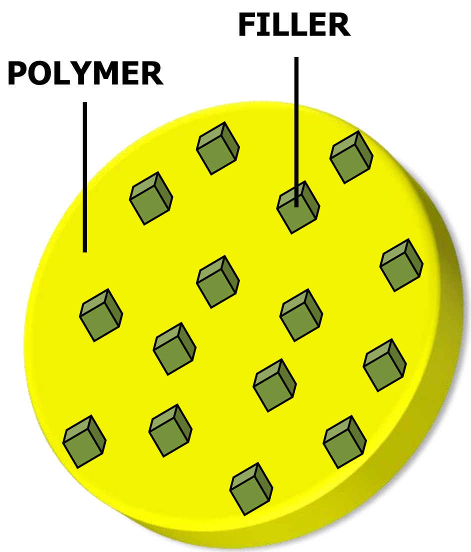
- Mechanical stability
- Easy processing and low price

- Thermal and chemical stability
- Low permeability

Inorganic Membranes

- Chemical stability
- Gas sieving properties

- Mechanical stability (brittle)
- Complex processing and expensive



Mixed Matrix Membranes

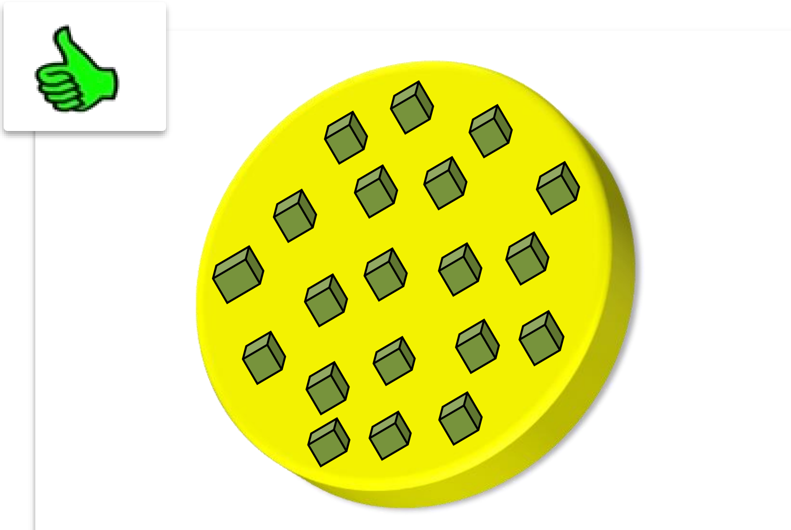
Filler (Molecular sieve)
+
Matrix (Polymer)

- Mechanical stability
- Easy processing and low price

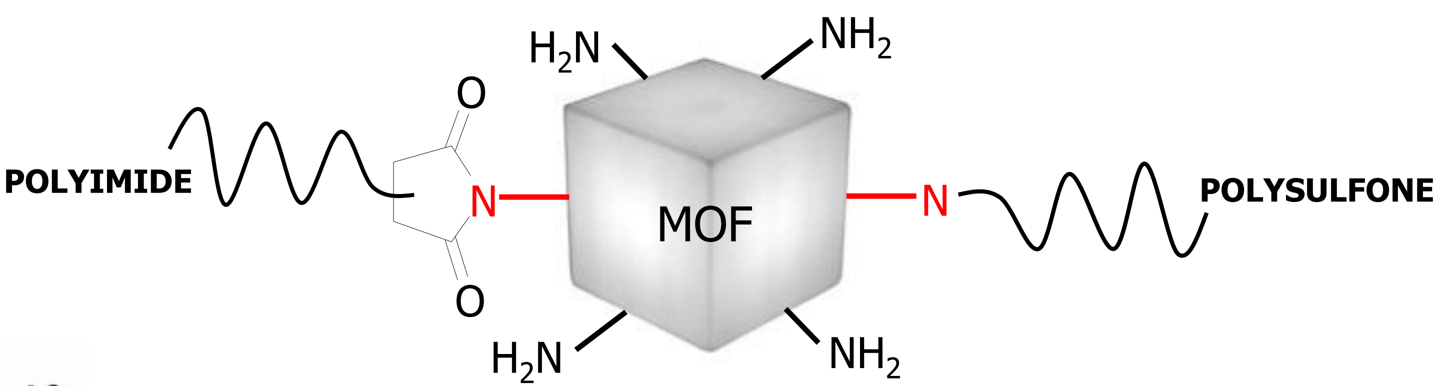
- Chemical stability
- Gas sieving properties

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.

MOF-based Mixed Matrix Membranes



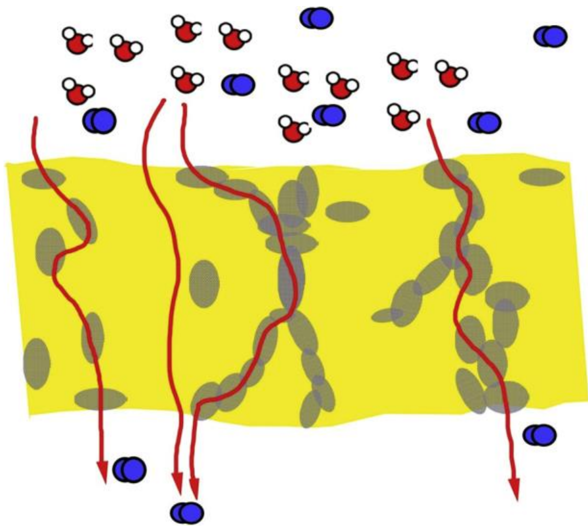
Good match between filler and matrix required



Mahajan, R.; Koros, W. J., *Ind. Eng. Chem. Res.* 39 **(2000)** 2692-2696.

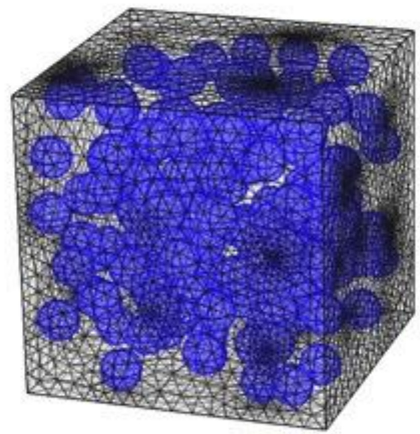
Gascon, J.; Aktay, U.; Hernandez-Alonso, M. D.; van Klink, G. P. M.; Kapteijn, F., *J. Catal.* 261 **(2009)** 75-87.

Transport modeling - sorption and diffusion



$$P_i \approx D_i \times S_i$$

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



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)

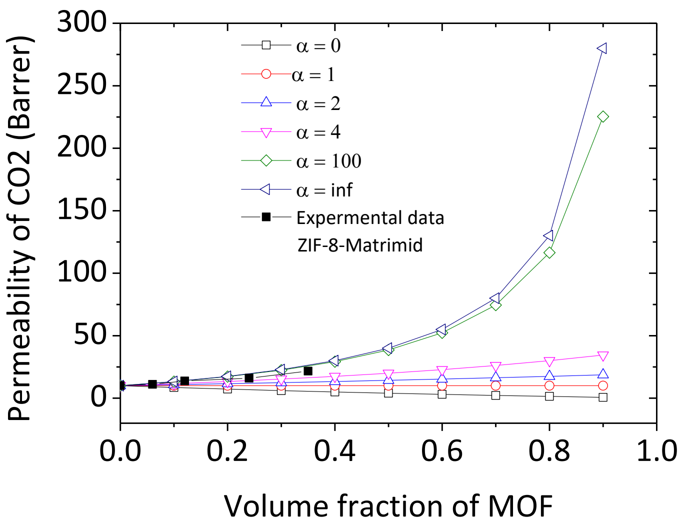
Maxwell model - effect filler on permeability

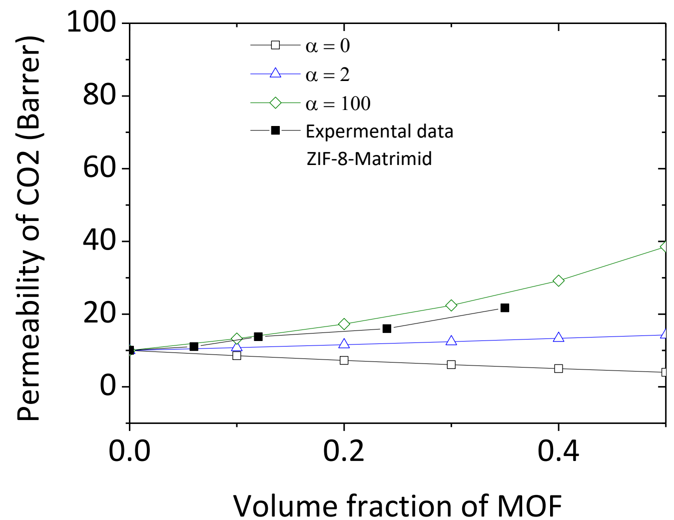
Maxwell model

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

α is the permeability ratio, P_d/P_c

System	Permeability (Barrer)
ZIF-8	1192
Matrimid	10



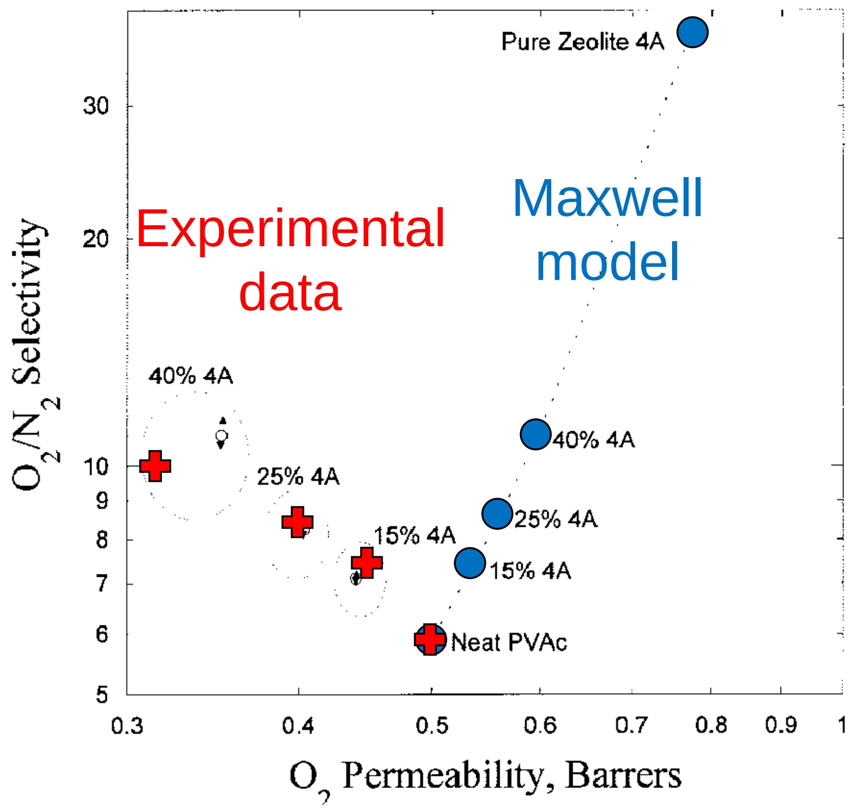


Permeability ratios > ~100 no further improvement

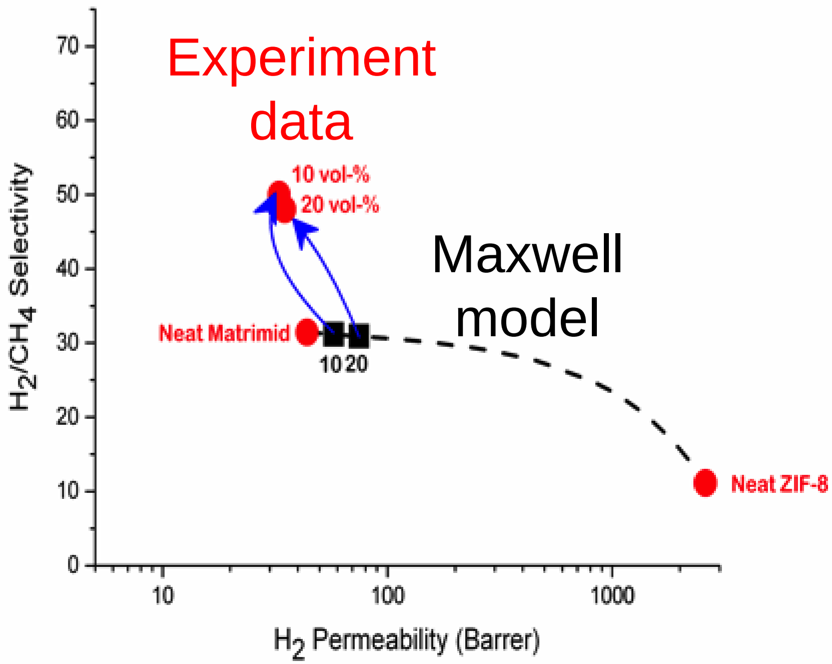
H. Bux et al., J. Am.Chem. Soc., 131 (2009) 16000–16003
S. Shahid et al., J. Membr. Sci., 470 (2014) 166-177

Modelling – predictive?

zeolite 4A filled PVAc at 35°C



ZIF-8@Matrimid®

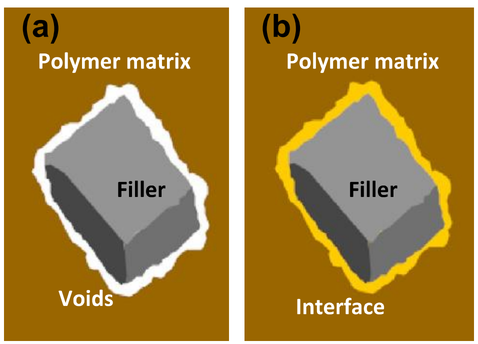


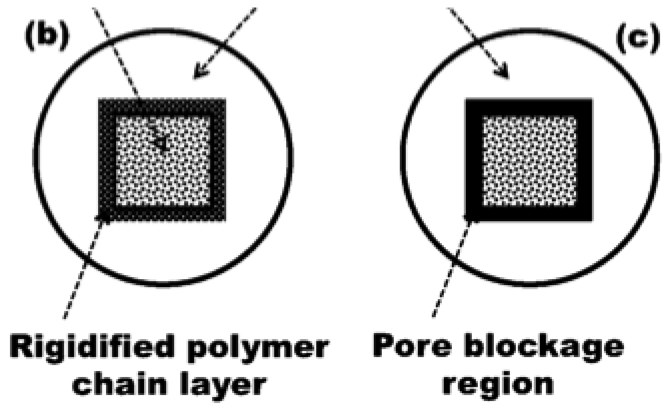
- *Adapted models*
- *Non-predictive*
- *Fundamental insight needed*

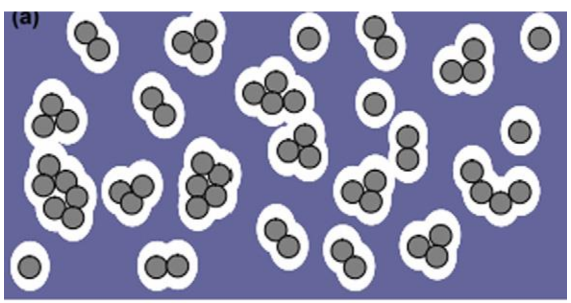
Moore, et al., *AIChE Journal* **2004,** *50* (2) 311
Diestel, et al. *Journal of Membrane Science* **2015,** *492*, 181

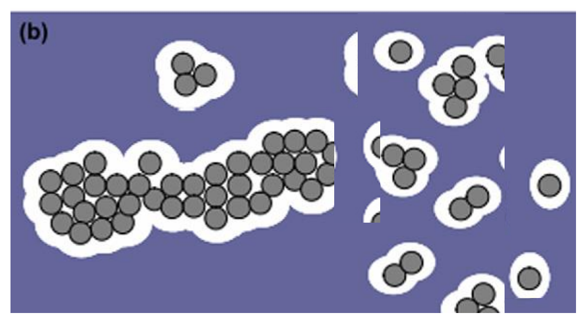
General observations

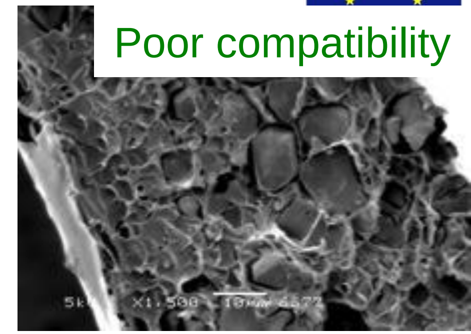
Deviations from ideal membrane system

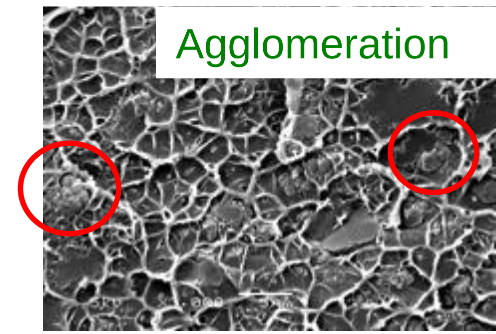


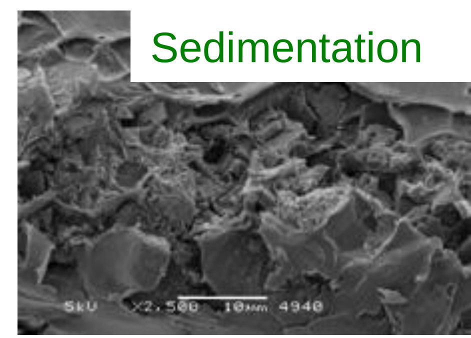












S.A. Hashemifard et al., Chemical Engineering Journal 172 (2011) 581
P.S. Goh et al., Separation and Purification Technology 81 (2011) 243
Vinh-Thang, & Kaliaguine, *Chemical reviews* **2013,** *113* (7) 498

General observations

- Voids
  - Poor adherence filler-polymer
  - Agglomeration filler
  - Sedimentation

Faster transport
No selectivity

Percolation danger

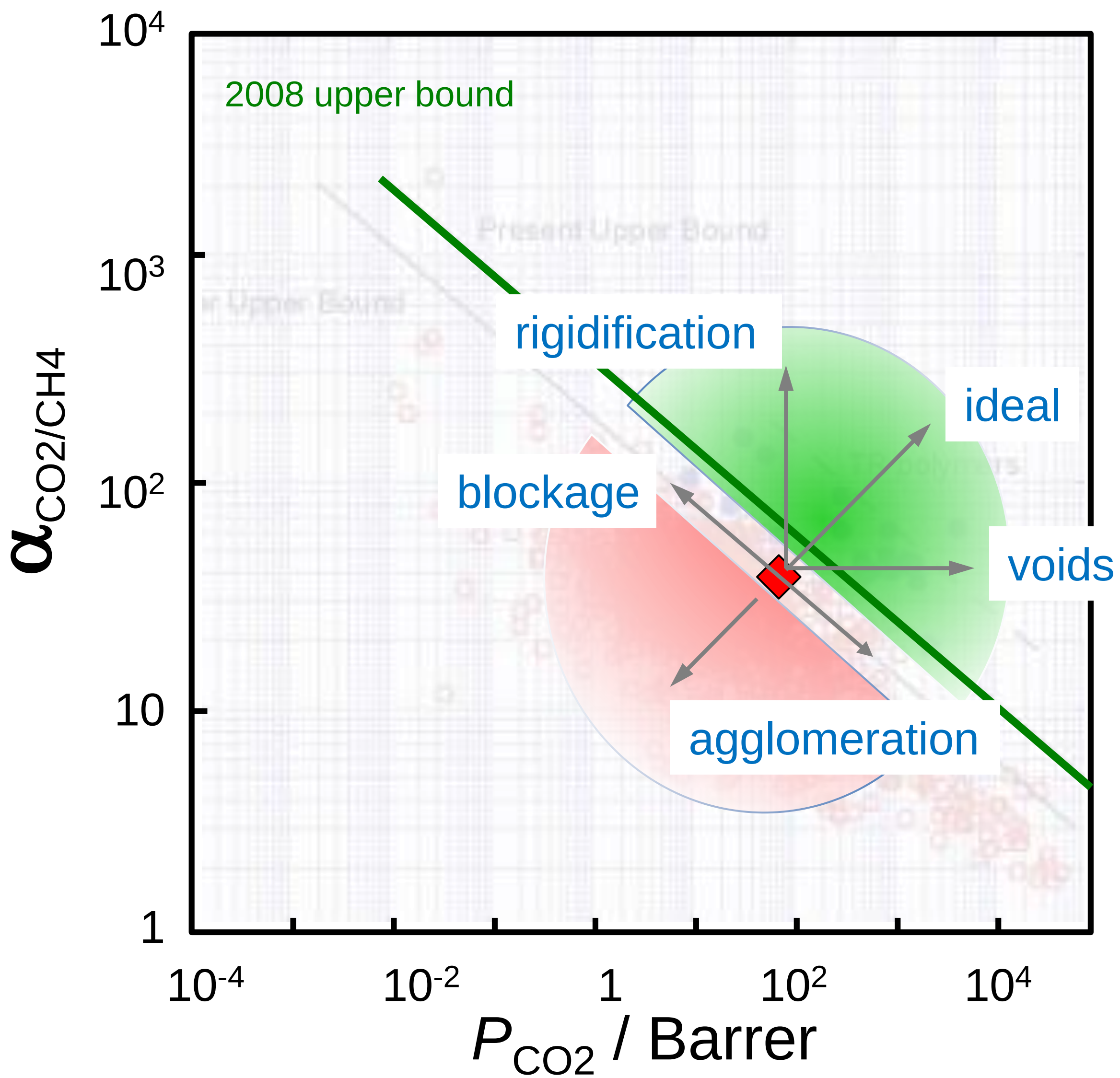
- Rigidification, chain orientation
- Pore blocking

Changing properties: + or -

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

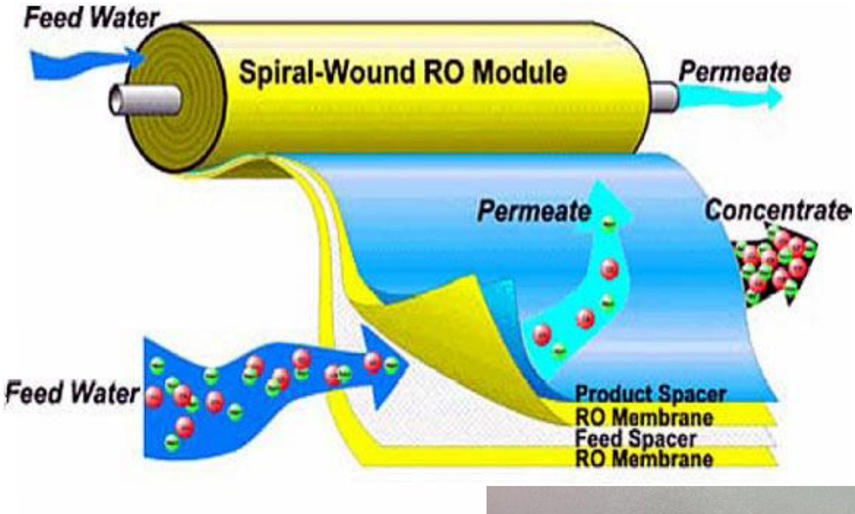
T.T. Moore, W.J. Koros / Journal of Molecular Structure 739 (2005) 87
S.A. Hashemifard et al., Chemical Engineering Journal 172 (2011) 581

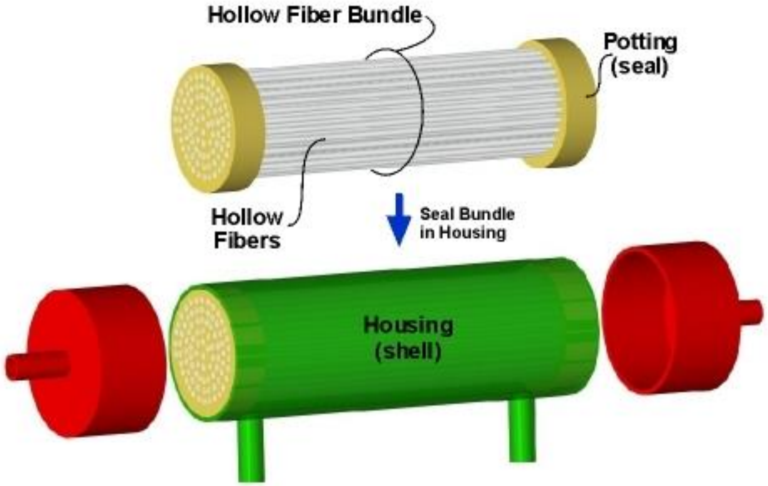
Robeson plot – effect of filler

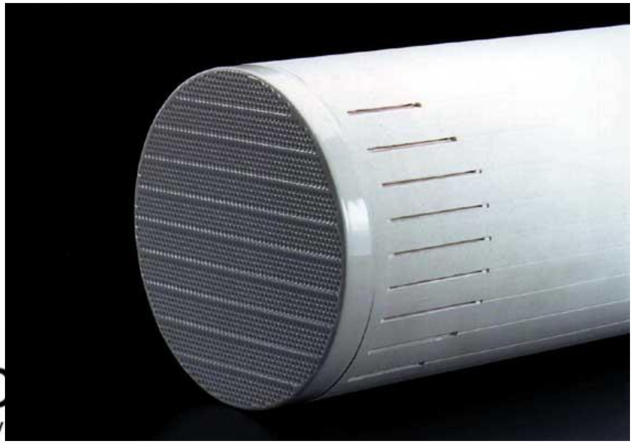


Experimental aspects

Examples of membrane modules







Module operation configurations

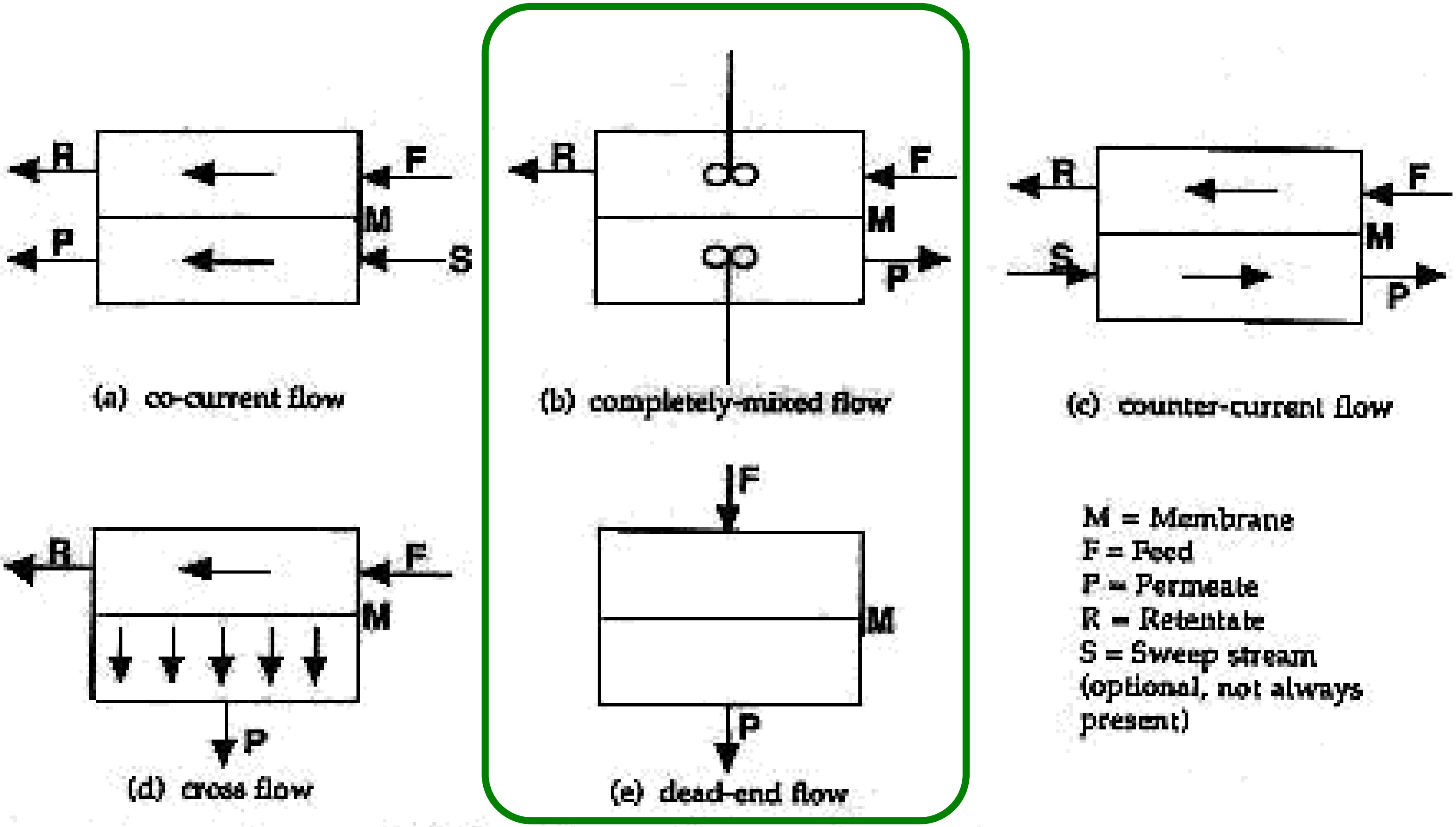
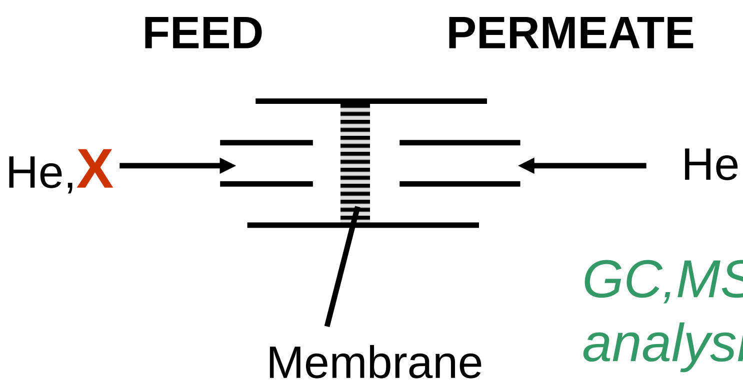


Figure 1: Types of ideal continuous flows used in membrane-based separations

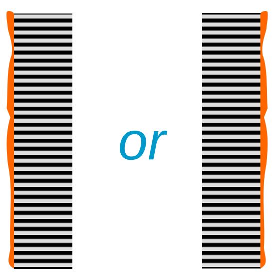
PureApplChem 68(1996)1479-1489 IUPAC-Membranes

Experimental methods

Wicke-Kallenbach

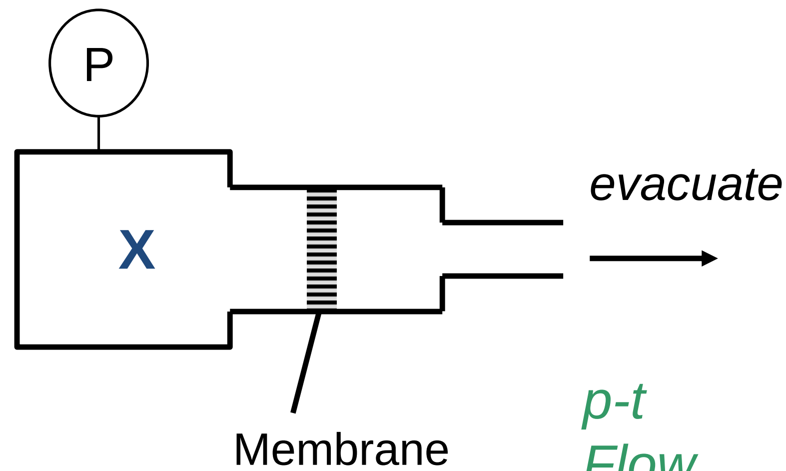


GC,MS analysis

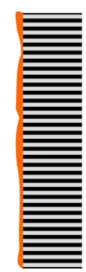


'unary' & mixtures

Batch method



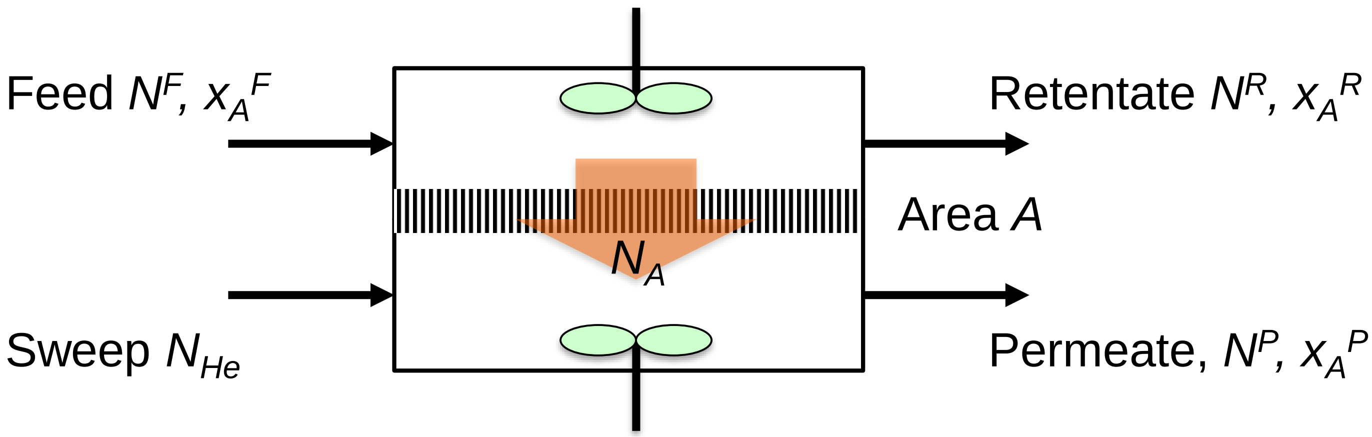
p-t Flow



unary

Membrane testing – module assumptions

Single component



$$N_A = \left(N^F \cdot x_A^F - N^R \cdot x_A^R\right) = \left(N^P \cdot x_A^P\right)$$ mol/s

- Well mixed volumes
- Local conditions identical
- No sweep permeation

Pure feed:

$$N_A = \left(N^F - N^R\right) = \left(N^P \cdot x_A^P\right) \approx \left(N^{sweep} \cdot x_A^P\right)$$

$$N_A \ll N^{sweep}$$

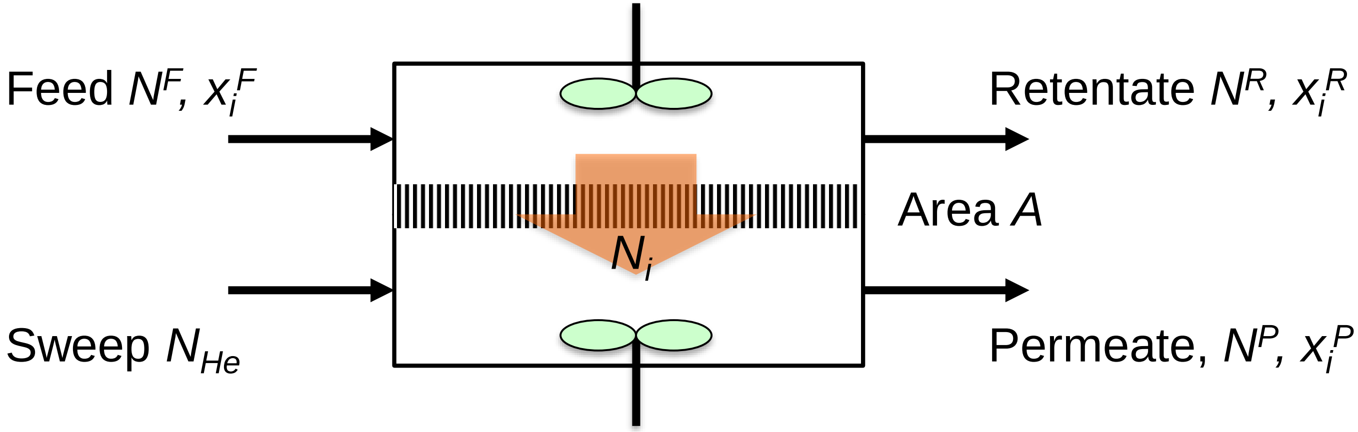
Mixed feed:

$$N_A \approx N^F \cdot \left(x_A^F - x_A^R\right) \approx \left(N^{sweep} \cdot x_A^P\right)$$

$$if: \; N^R \approx N^F$$

Membrane testing – module assumptions

Mixtures



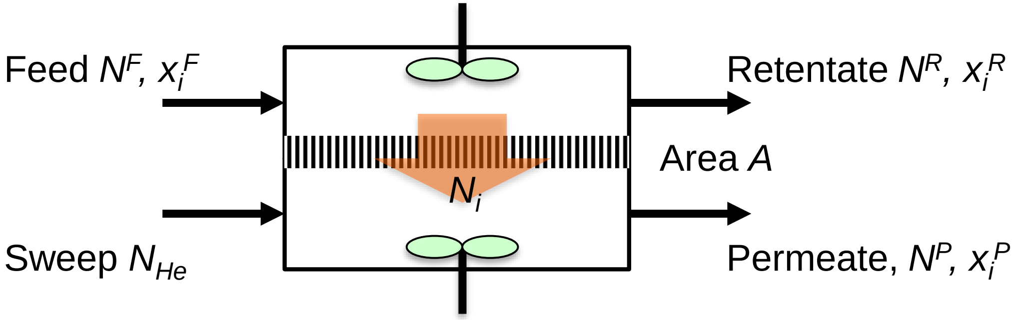
$$N_i \approx \left(N^{sweep} \times x_i^P\right) \qquad N_A \ll N^{sweep}$$

- Well mixed volumes
- Local conditions identical
- No sweep permeation

$$a_{ij} = \frac{\left(x_i / x_j\right)_{permeate}}{\left(x_i / x_j\right)_{retentate}}$$

What if sweep gas back-permeates?

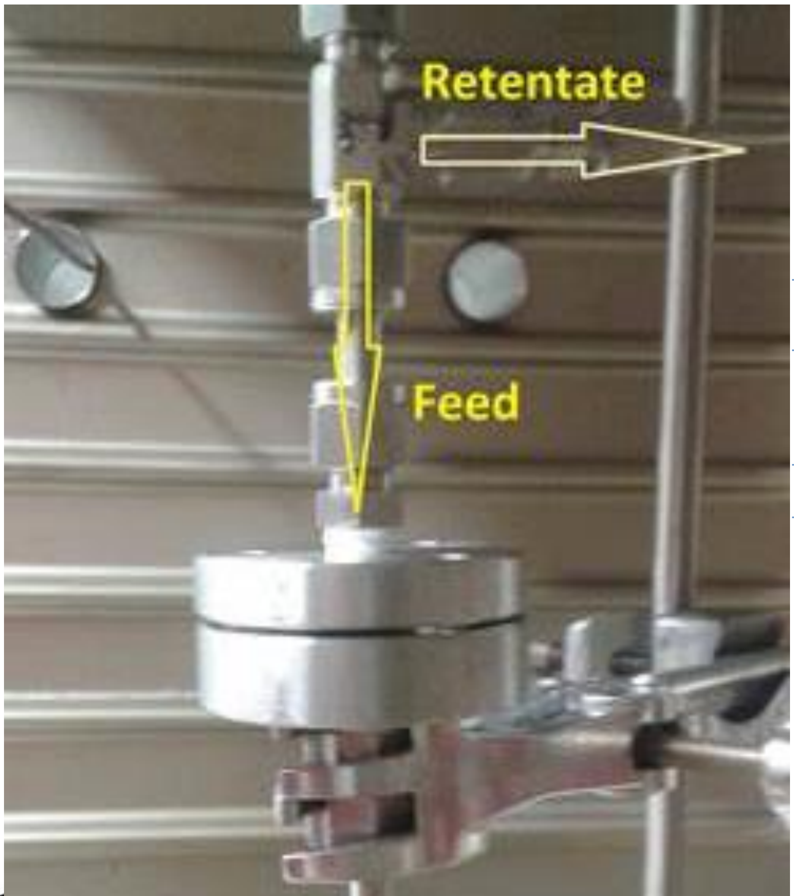
- Round Robin experiments
  - Feed gas CO_2/N_2
  - Sweep 3 ml_{STP} /min He

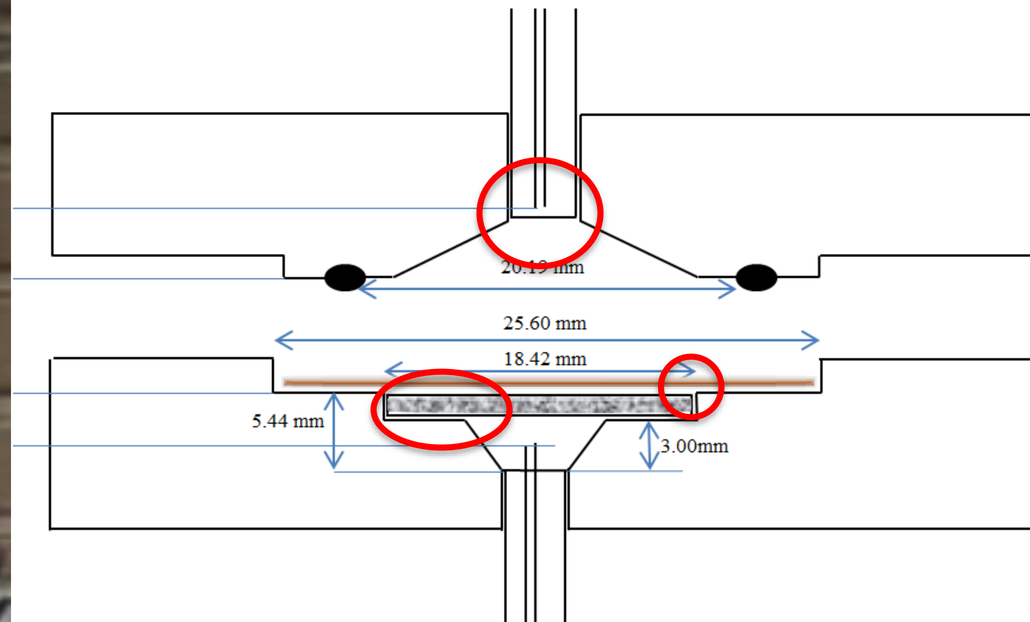


- Pure gas measurement
  - Permeation 1 ml_{STP} /min He

Higher concentration in Permeate
Too high flux calculated?
Hindrance of permeation?

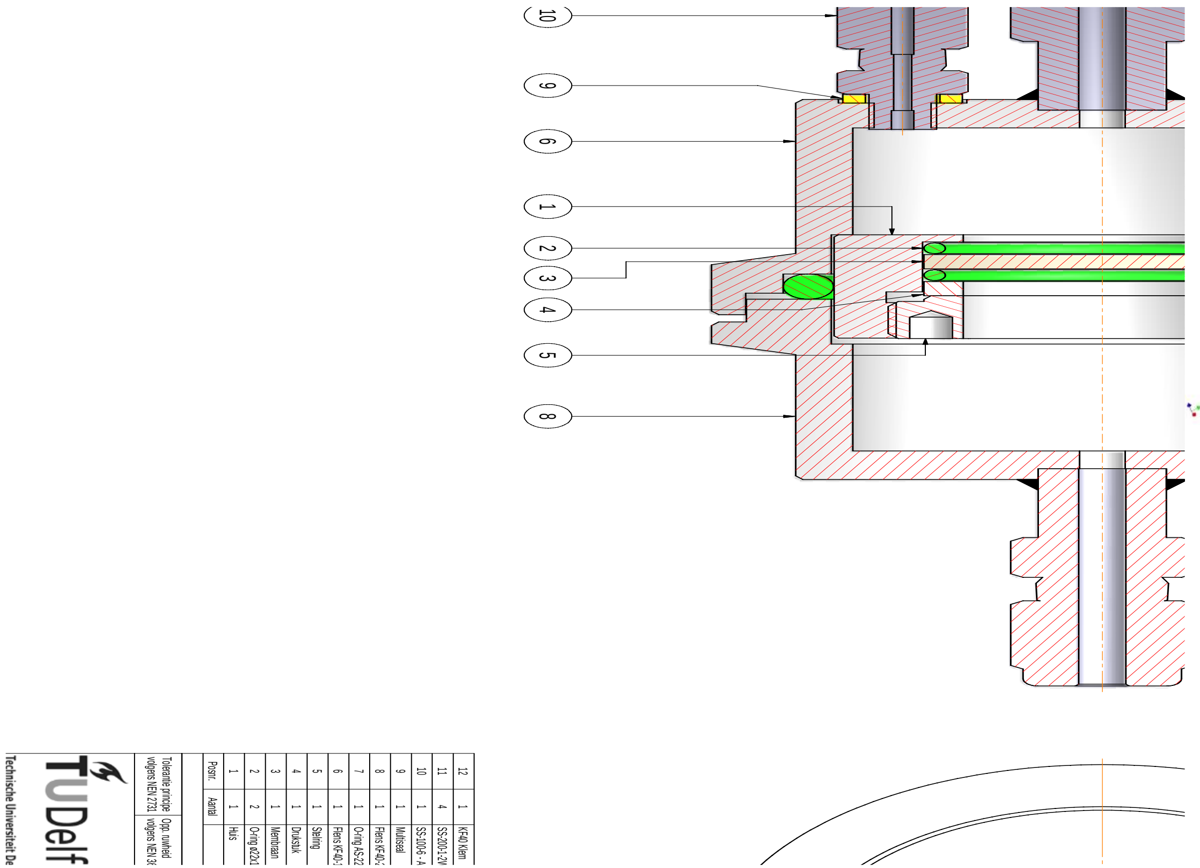
Do assumptions hold?

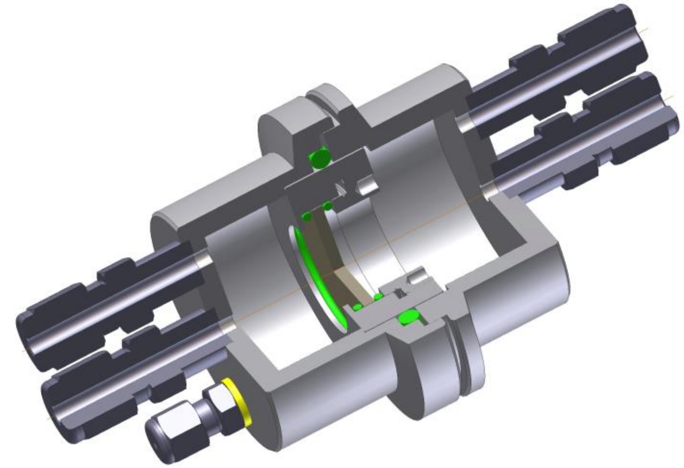




Carefully consider configuration

Do assumptions hold?

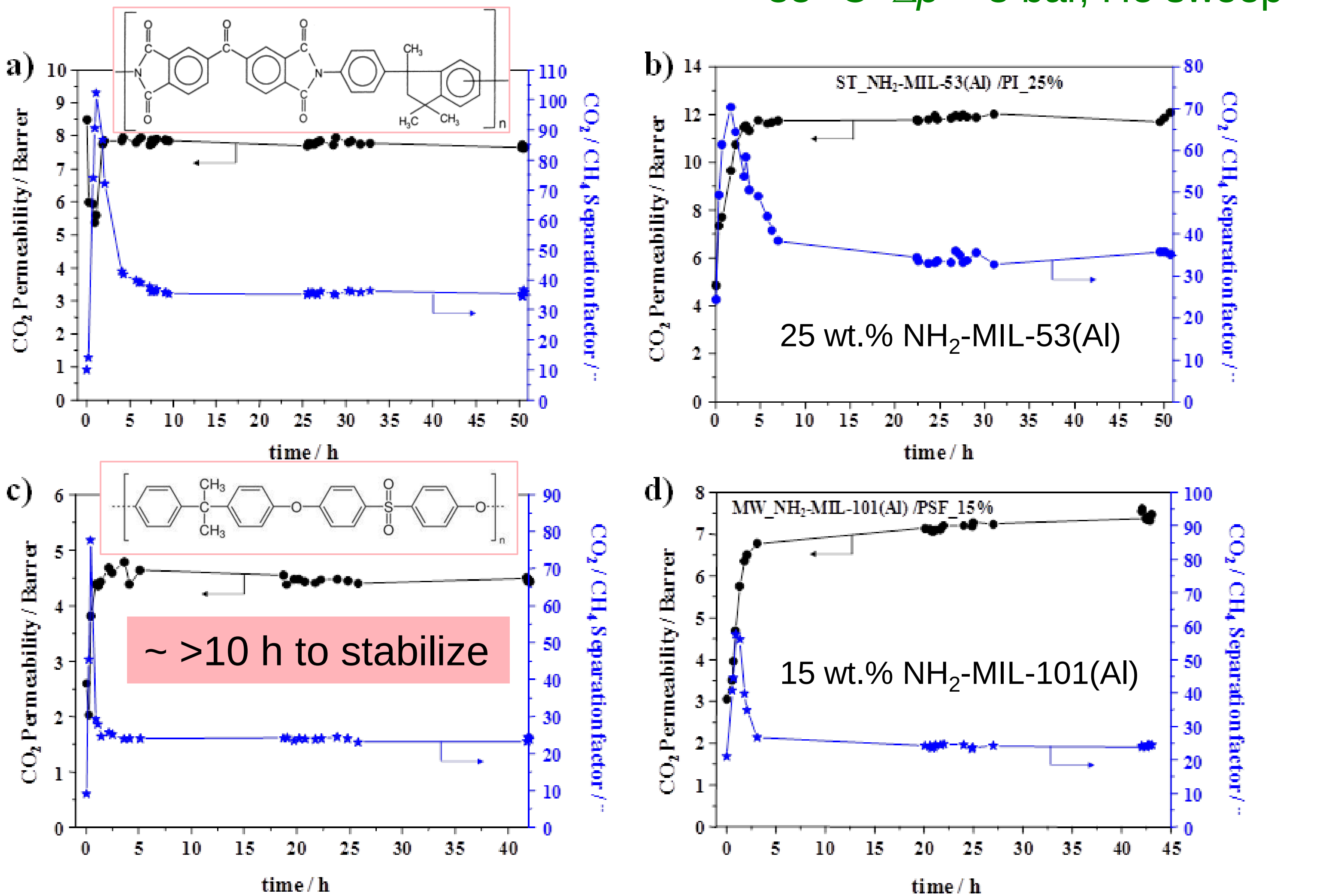




How to test for CSTR behaviour?

Stabilization time?

equimolar CO_2/CH_4 mixture
35 ^oC Δp = 3 bar, He sweep



T. Rodenas et al., Microporous Mesoporous Mater., 2014, 192, 35–42.

Can we rationalize this time needed?

- Permeability 2 – 8 Barrer
- Thickness 70 μm
- Pressure 4 and 1 bar (abs)
- CO_2 adsorption
  - 200-400 ml_{STP}/g MIL-101 (15 wt%)
  - 50 ml_{STP}/g MIL-53 (25 wt.%)

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

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

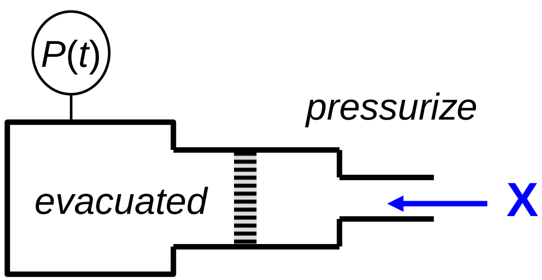
$$\mathcal{P}_i = P_i \cdot d \qquad \frac{\mathrm{mol} \cdot \mathrm{m}}{\mathrm{s} \cdot \mathrm{m}^2 \cdot \mathrm{Pa}}$$

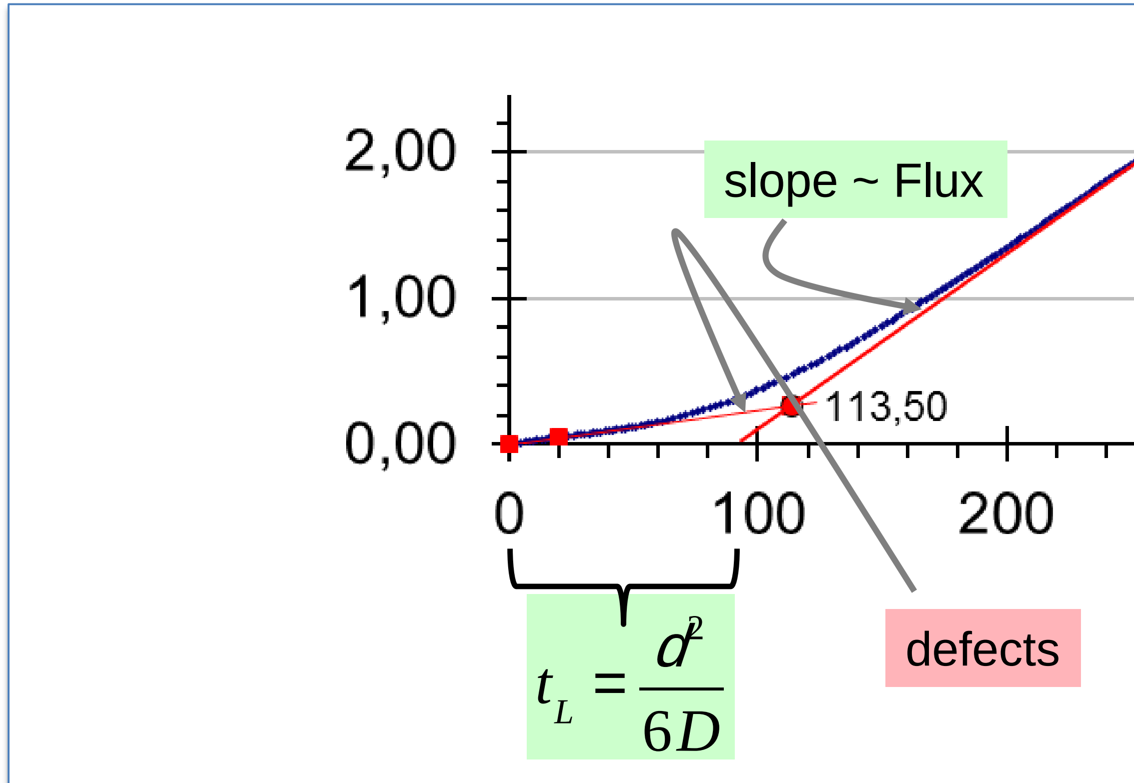
Estimate time it takes to 'fill' the membrane

$$1\ \mathrm{Barrer} = 3.346 \cdot 10^{-16}\ \frac{\mathrm{mol} \cdot \mathrm{m}}{\mathrm{s} \cdot \mathrm{m}^2 \cdot \mathrm{Pa}}$$

Transient operation

- How ?
  - **Time–lag technique**
  - Single component
  - Constant diffusivity



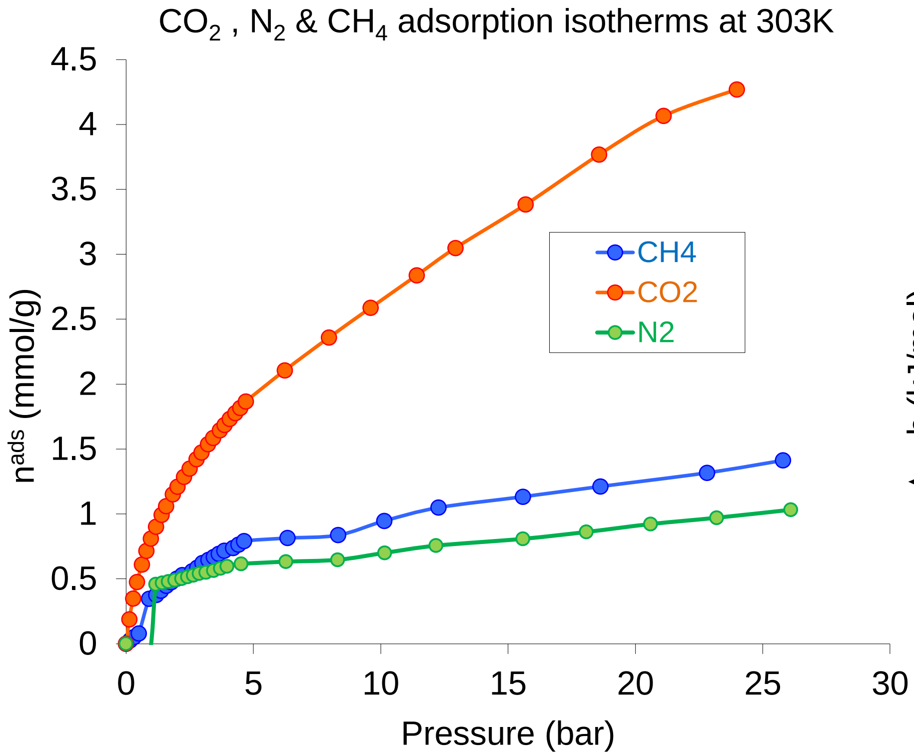


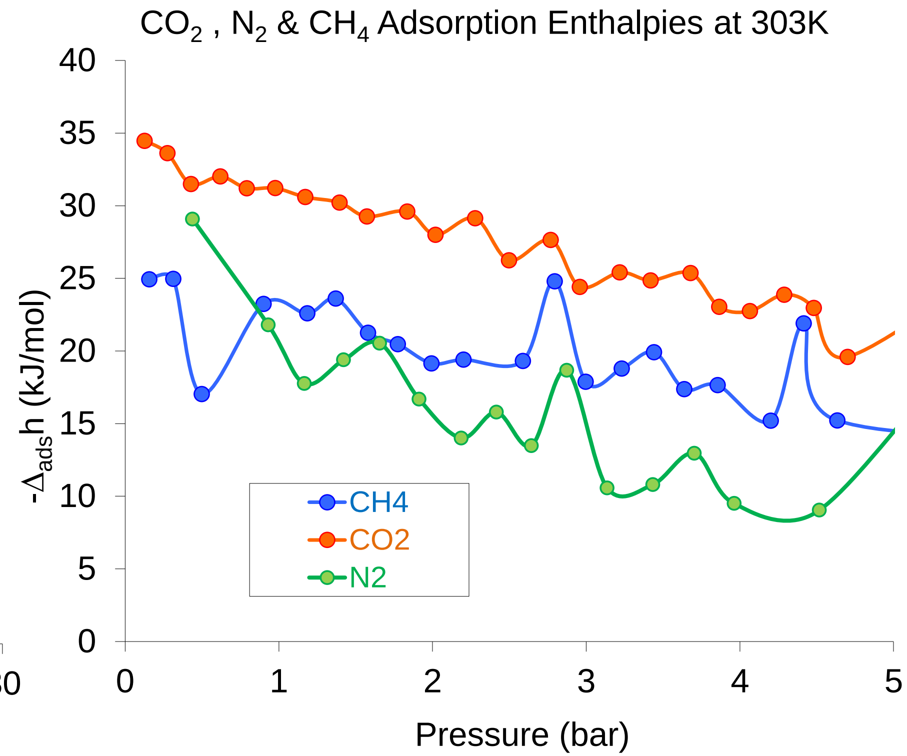
- What information?
  - Permeability *P = flux*δ/Δp*
  - Diffusivity - Wide window
  - Solubility - *S = P/D*

J.C. Jansen, Polymer (2007)

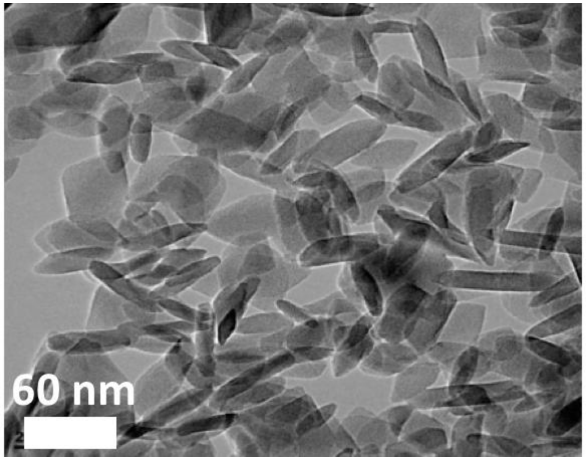
6FDA-DAM

CO_2, CH_4 & N_2 adsorption isotherms and enthalpies

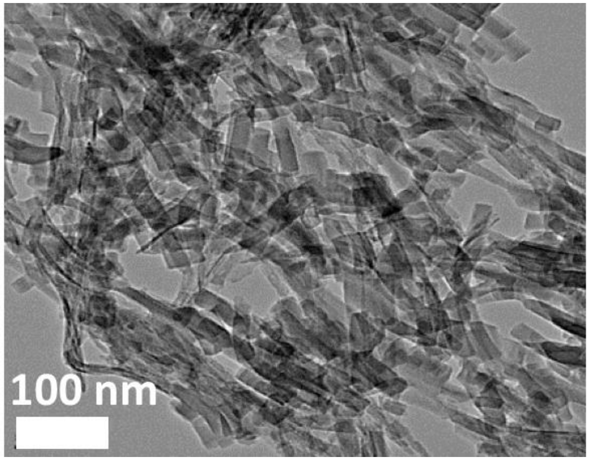




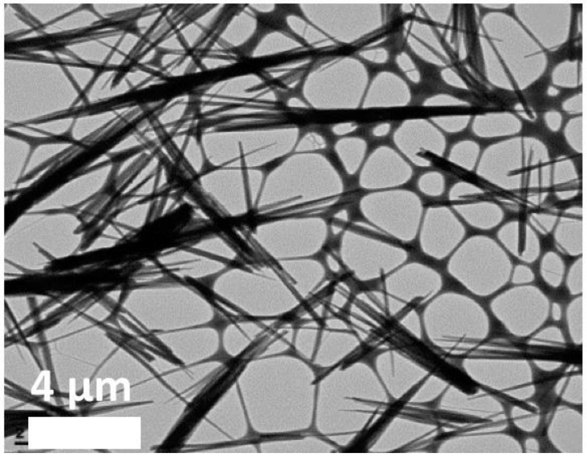
Morphology variation NH_2-MIL-53(Al)



Nanoparticles



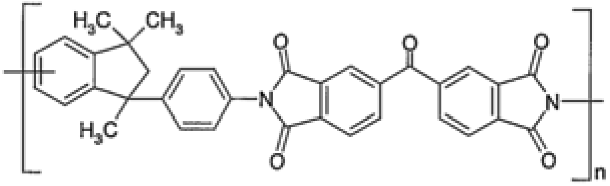
Nanorods

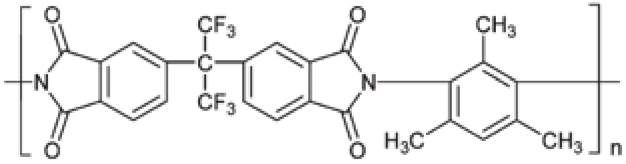


Microneedles

High-flux polymer 6FDA-DAM

Low-flux Matrimid





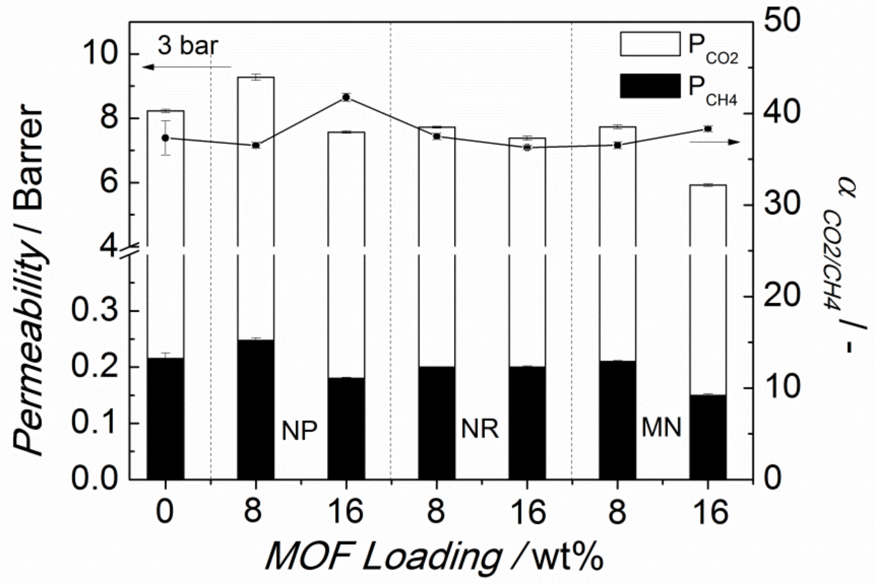
A. Sabetghadam *et al. Adv. Funct. Mater. 2016, 26, 3154–3163*

Morphology & loading variation NH_2-MIL-53(Al)

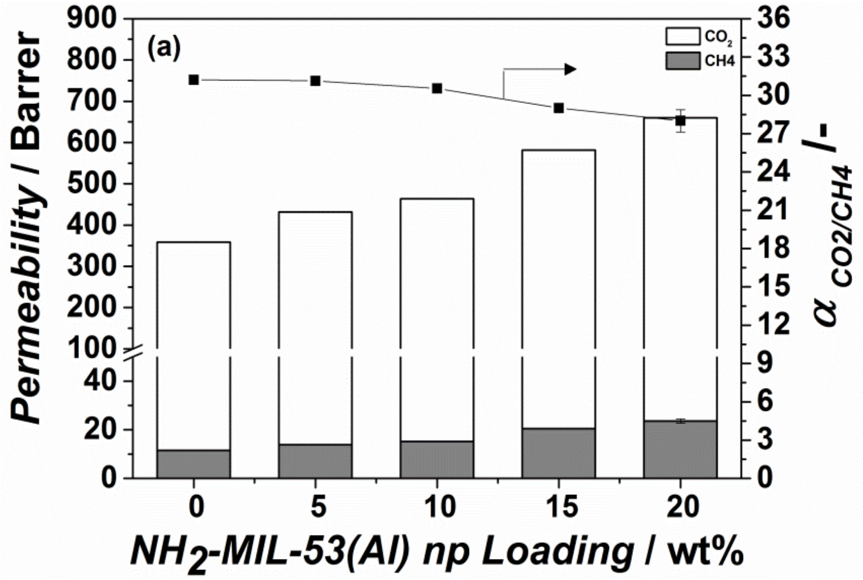
polymer permeability

CO_2:CH_4 = 1:1; ΔP = 3 bar; T = 298 K

Matrimid – low permeability



6FDA-DAM – high permeability

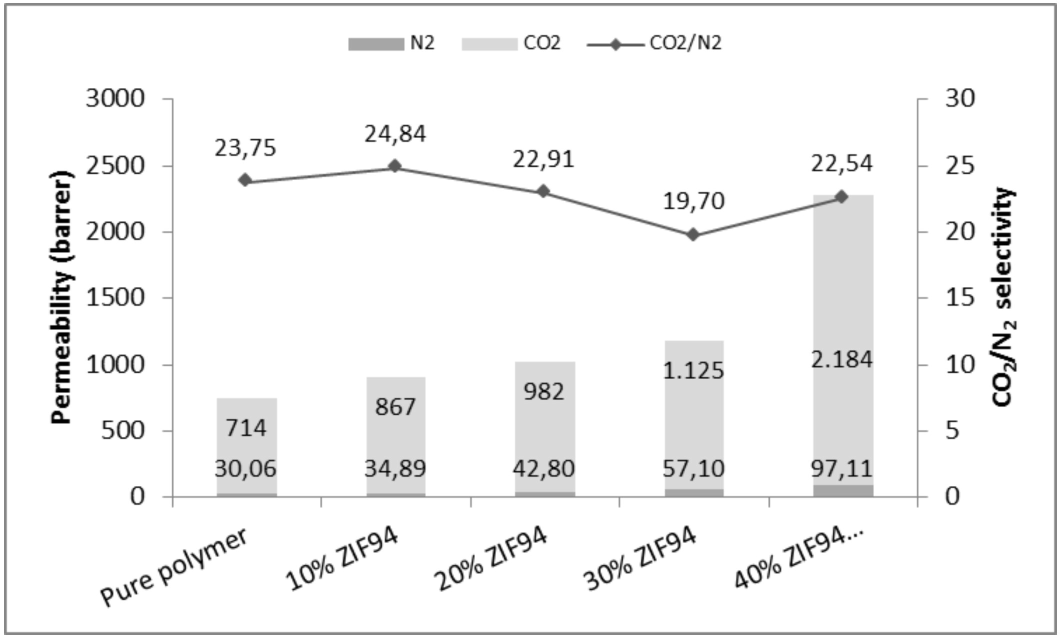


- little effect permeability and selectivity

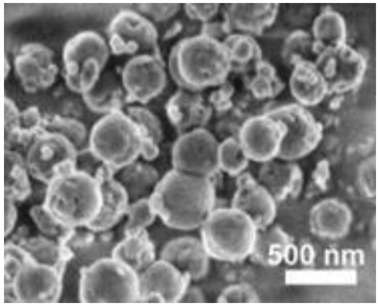
- doubling permeability
- selectivity little effect

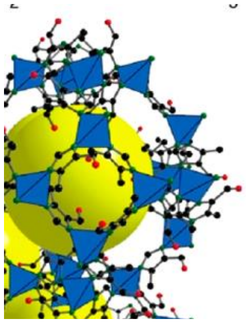
A. Sabetghadam *et al. Adv. Funct. Mater. 2016, 26, 3154–3163*

CO_2/N_2 separation – ZIF-94/6FDA-DAM



15% CO_2/85% N_2
25 °C
2 bar
~25 μm





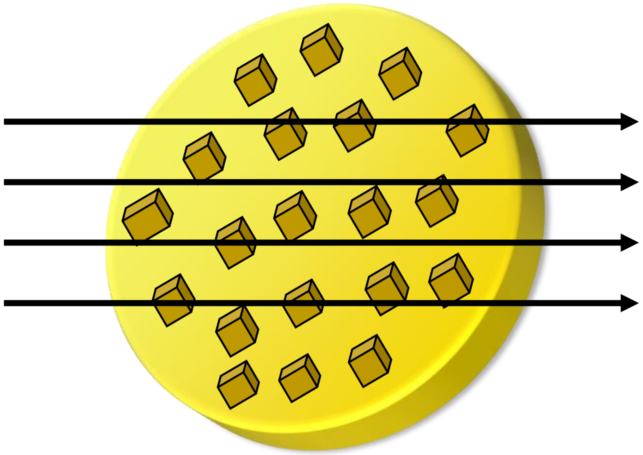
ZIF-94

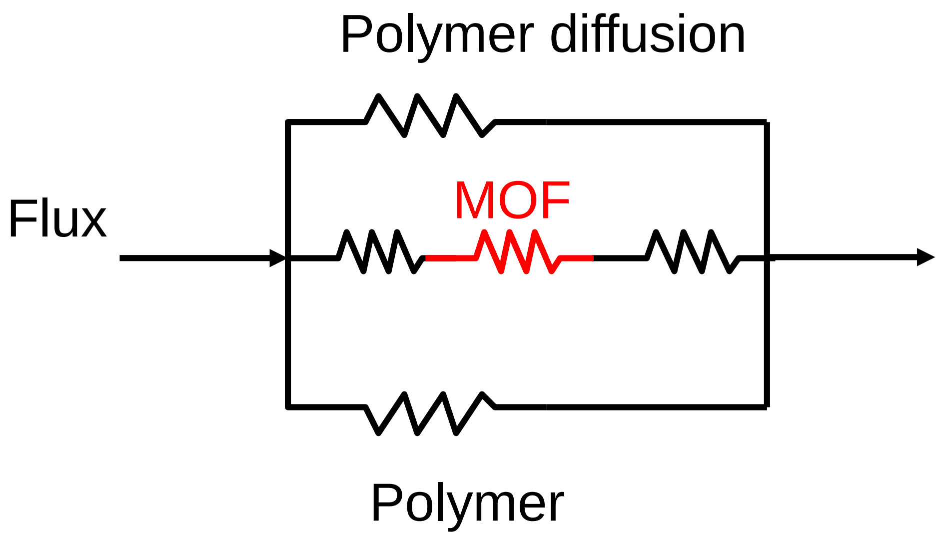
- *Permeability increased with loading*
- *Selectivity hardly affected*

Etxeberria et al. *Journal of Membrane Science* **2018,** *550*, 198-207

MOF-based mixed matrix membranes

- Polymer continuous phase
- MOF filler, below percolation

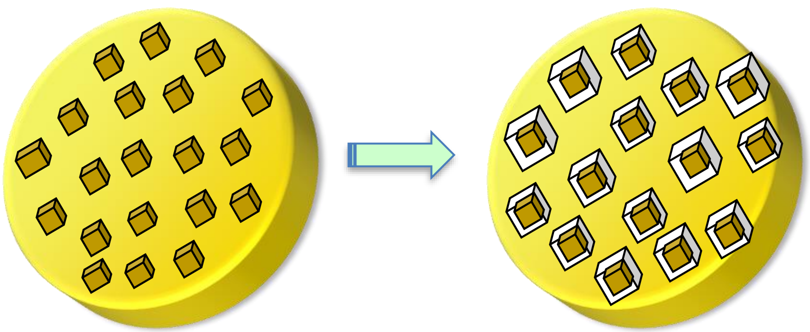




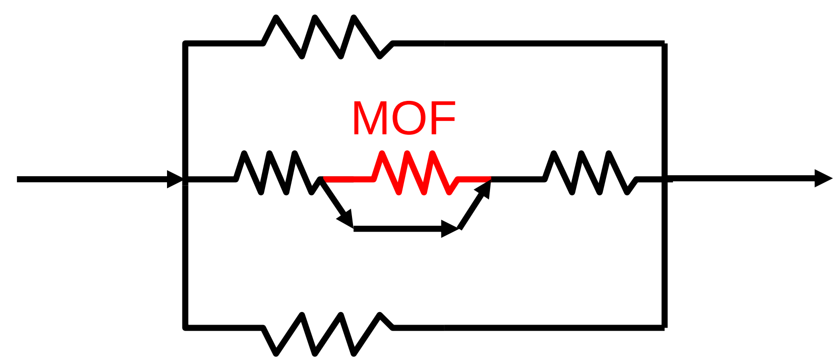
MOF-based mixed matrix membranes

What if?

- Polymer continuous phase
- MOF filler surrounded by gaps



Knudsen diffusion ?

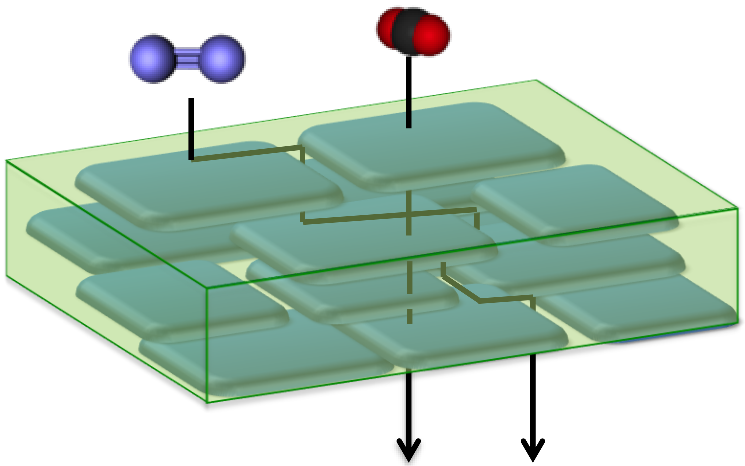


- Bypassing
  - higher flux
  - same selectivity

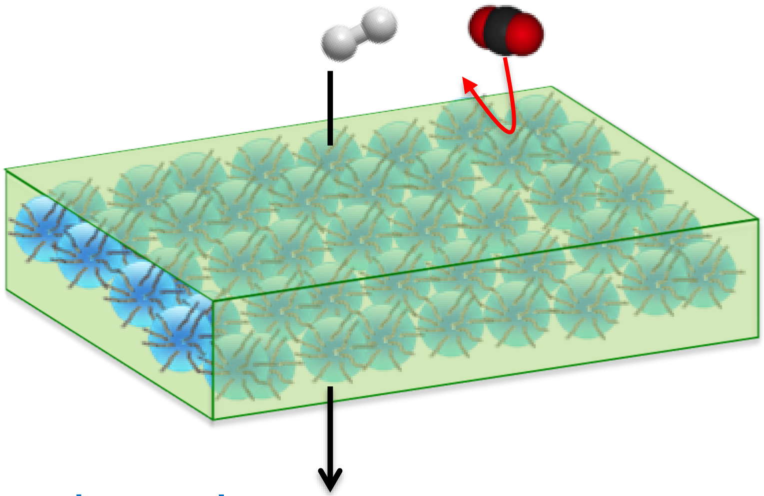
What M^4 configuration do we want? What properties of materials?

- Models don't capture performance
  - Volume fraction filler important parameter - loading
  - Control transport pathways
- 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

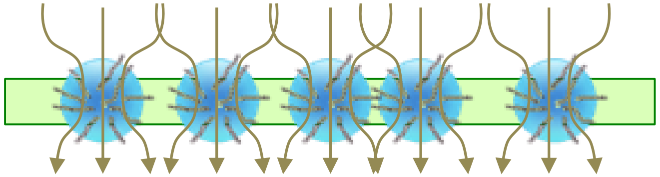
Flux - Selectivity improvements



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



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



- Percolation membranes

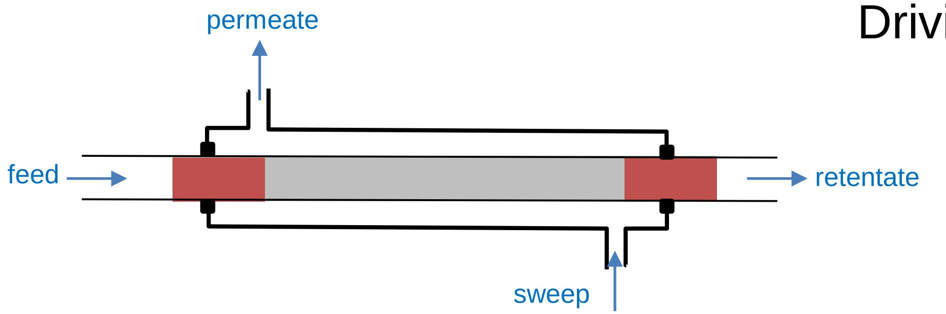
TU Delft
Delft University of Technology

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

Take home message

- Experimentation
  - Check assumptions – are these obeyed?
    - Module design important
  - Beware of sweep gas back permeation – Ar as sweep better?
  - Estimate uncertainty in selectivity
  - Verify mass balances
- Important characteristics materials (MOF and polymer)
  - Adsorption isotherms, temperature dependency
  - Diffusivities – different transport mechanisms, not constant
    - Swelling, aging, dual mode,…
- Modelling
  - Predictive models do not exist, simulations important
  - A posteriori model description

Tubular membrane testing



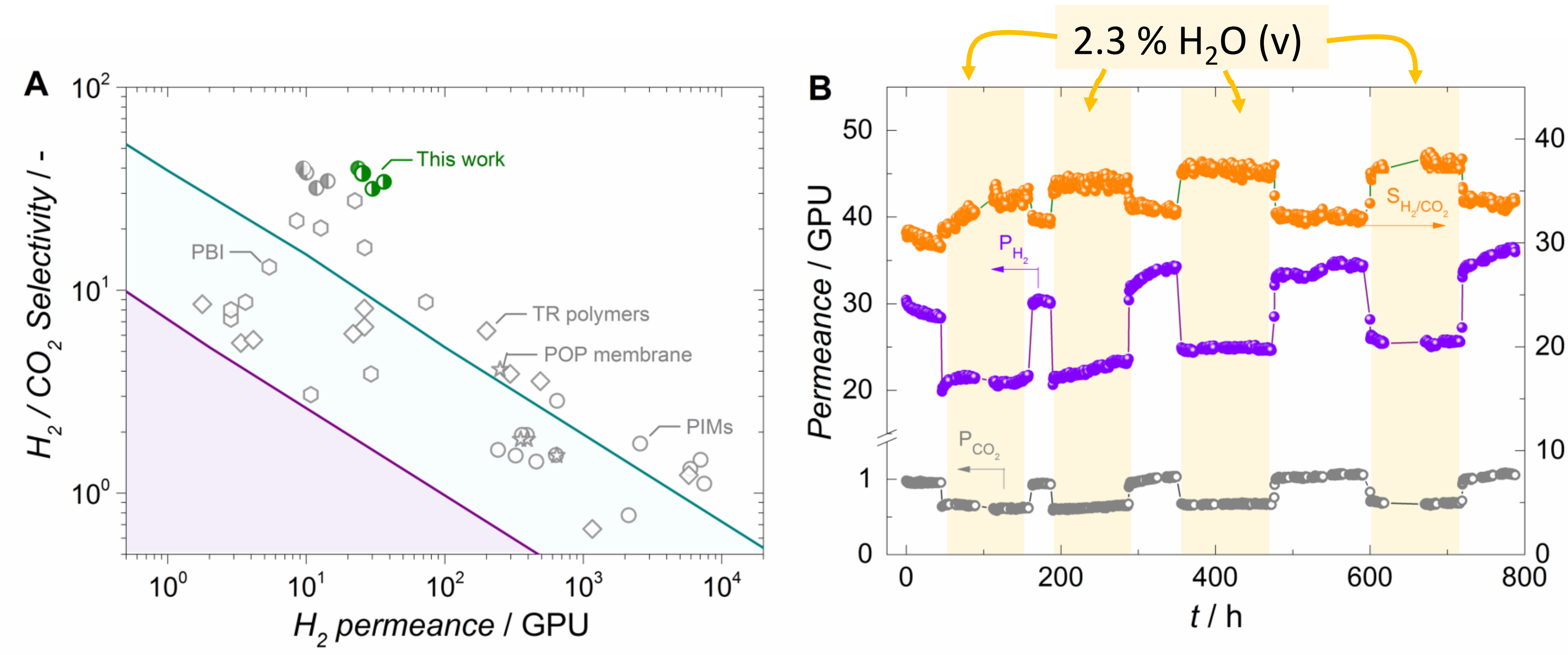
Driving pressure gradient:

$$\left(\Delta p_i\right)_{\ln} = \frac{\left(p_i^{feed} - p_i^{perm}\right) - \left(p_i^{ret} - p_i^{sweep}\right)}{\ln\left(\frac{\left(p_i^{feed} - p_i^{perm}\right)}{\left(p_i^{ret} - p_i^{sweep}\right)}\right)}$$

- Concentrations change along length (non-differential)
- Analogies with heat exchanger
  - co-, counter-, cross-current
  - Use logarithmically averaged pressure/concentration difference

BILP-101x membrane performance

H_2/CO_2 mixture (1:1) separation
423 K, He sweep



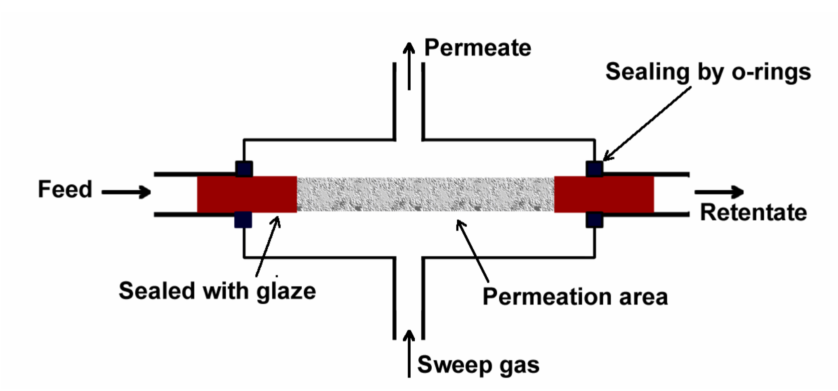
H_2/N_2 mixture (1:1)
$S_{H2/N2}$ = 75-93

- High selectivity, moderate permeance
- Long term stability @ 423 K >800 h
- Water tolerant, pressure stable (>10 bar)

What about (pure) MOF membranes?

- Available literature
  - Like zeolite membranes hard to make
  - Gas permeation data shows similarity with zeolites
  - Separation more fuzzy than zeolites
    - (local) Flexibility of structure
    - Less clear distinction between molecular size
    - Adsorption effects sometimes visible

Tubular membrane testing



Driving pressure gradient:

$$\left(\Delta p_i\right)_{\ln} = \frac{\left(p_i^{feed} - p_i^{perm}\right) - \left(p_i^{ret} - p_i^{perm}\right)}{\ln\left(\dfrac{\left(p_i^{feed} - p_i^{perm}\right)}{\left(p_i^{ret} - p_i^{perm}\right)}\right)}$$

- Concentrations change along length
- Analogies with heat exchanger
  - co-, counter-, cross-current
  - Use logarithmically averaged pressure/concentration difference

2.3. High temperature catalysts and sorbents (Julien Meyer – IFE)

MEMBER workshop, TU/e, Eindhoven, 15.01.2020

High temperature sorbent development for pre-combustion CO_2 capture via Sorption-Enhanced Reforming

Julien Meyer

Department of Environmental Industrial Processes

Institute for Energy Technology (IFE)

- IFE R&D is organized in 3 different sectors
- R&D in a broad scope of energy technology

Flow Technology and Environmental Analyses

Material and Process Technology

Digital systems

- Neutron Material Characterization
- Environmental Industrial Processes
- Material Processing
- Renewable Energy Systems
- Battery Technology
- Solar Energy

H_2 production and CO_2 capture activities

National Center of Excellence
Zero Emission Transport (MoZEES)

National Center of Excellence
PV Technology (SuSolTech)

Dep. of Environmental Industrial Processes at IFE

- RD&D in the field of **power and hydrogen production with integrated CO_2-capture**, with a special focus on the development of:
  - sorption-enhanced processes
  - novel high temperature CO_2 solid sorbents
  - novel oxygen carriers for chemical looping processes

Autoclaves

Granulators

- The research group has expertise in:
  - process intensification
  - gas-solid catalytic and non-catalytic reactions
  - advanced material science
  - fluidized bed reactor technology
  - process modelling and simulation

TGAs

Reactor rigs

Solid sorbents for CO_2 capture

Required sorbent properties

- High absorption capacity
- High reaction rate
- Low energy requirement for desorption
- Chemical stability (reversible CO_2 sorption/desorption)
- Mechanical stability
- Long term multi-cycle use
- Availability / abundance of raw materials
- Acceptable price

Sorption mechanisms, cycling principle, process types

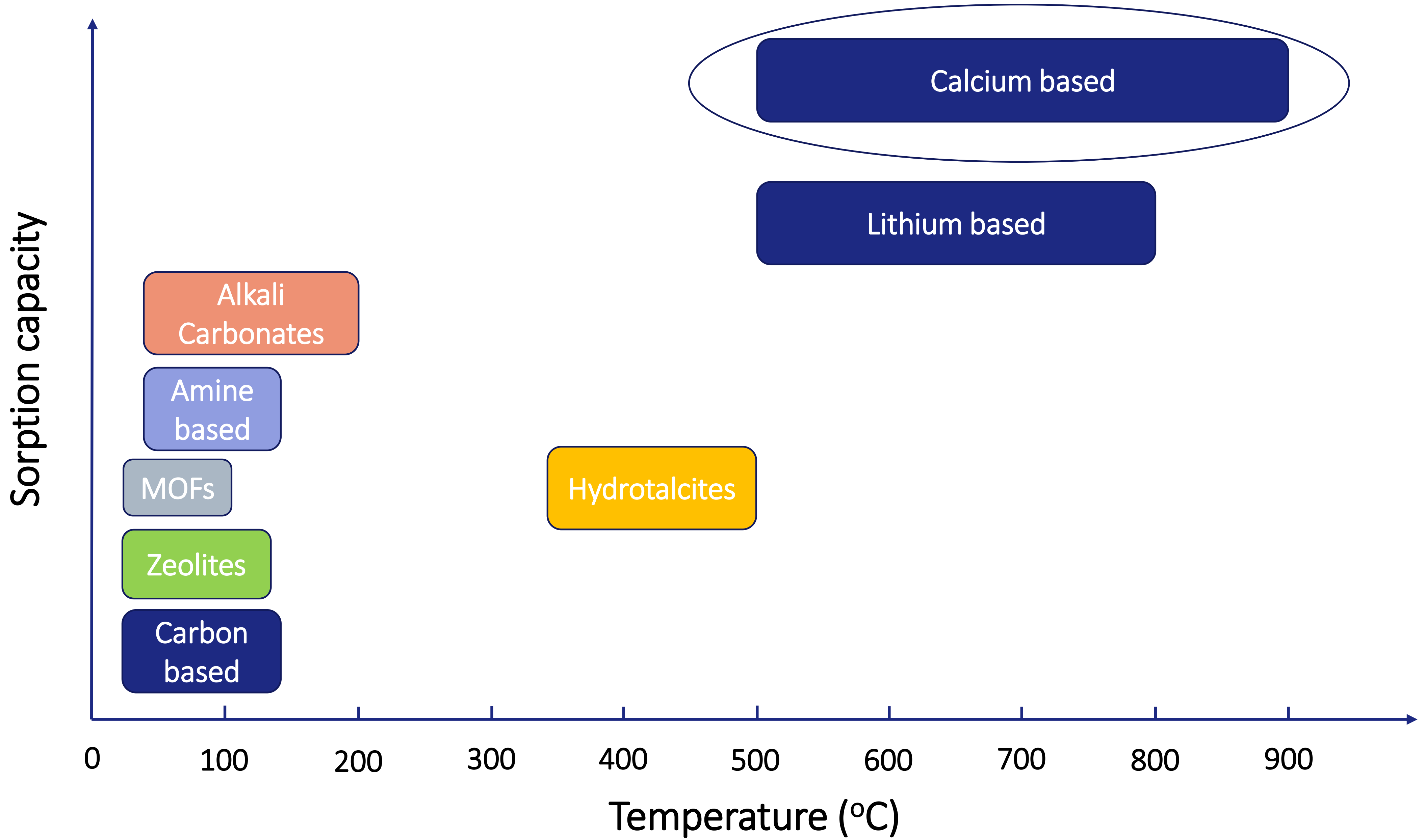
- Adsorption / chemisorption
- Absorption / chemical reaction

- Temperature and/or pressure swing processes
  - Low temperature difference between sorption and desorption is advantageous
  - Pressure swing at high temperature is challenging

- Batch or continuous processes
  - Batch processes usually operated with packed bed reactors
    - Synchronization, number/size of reactors, valve operation can be challenging

  - Continuous process usually operated with fluidized/moving bed reactors
    - Attrition and material consumption can be challenging

Type of CO_2 solid sorbents for different temperature range



Type of solid sorbents and sorption principles

- Sodium/potassium carbonates
  - Based on a carbonate-bicarbonate cycle
  - 60-200°C range
  - Developed for post-combustion capture
  - Operated in circulating fluidized bed systems, developed by KIER and KEPCO (South-Korea)

- Hydrotalcites (double layered hydroxide, usually Mg- and Al-based)
  - Anion-exchange, adsorption mechanism
  - 350-500°C range
  - Developed for pre-combustion capture (Sorption-Enhanced Water Gas Shift)
  - Operated as PSA system in multiple packed bed reactors, developed by ECN/TNO (Netherlands)

- Calcium based sorbents
  - Based on oxide-carbonate cycle
  - 500-900°C
  - Developed for post and pre-combustion capture (Calcium Looping and Sorption-Enhanced Reforming)
  - Circulating fluidized bed systems developed by several groups in Europe

CaO-based solid sorbents for high temperature CO_2 capture via sorption-enhanced reforming

Sorption-Enhanced Reforming (SER)

Emerging reforming technology with integrated CO_2 capture

Reforming

$CH_4\,(g) + H_2O\,(g) \rightarrow CO\,(g) + 3H_2\,(g)$

Water gas shift

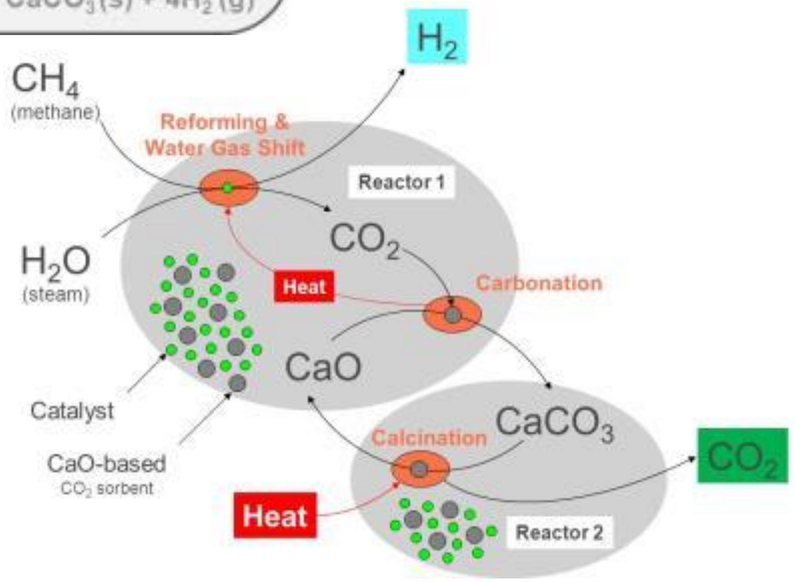
$CO\,(g) + H_2O\,(g) \rightarrow CO_2\,(g) + H_2\,(g)$

Carbonation

$CaO\,(s) + CO_2\,(g) \rightarrow CaCO_3\,(s)$

Total reaction (SER)

$CaO\,(s) + CH_4\,(g) + 2H_2O\,(g) \rightarrow CaCO_3\,(s) + 4H_2\,(g)$



Calcination (regeneration)

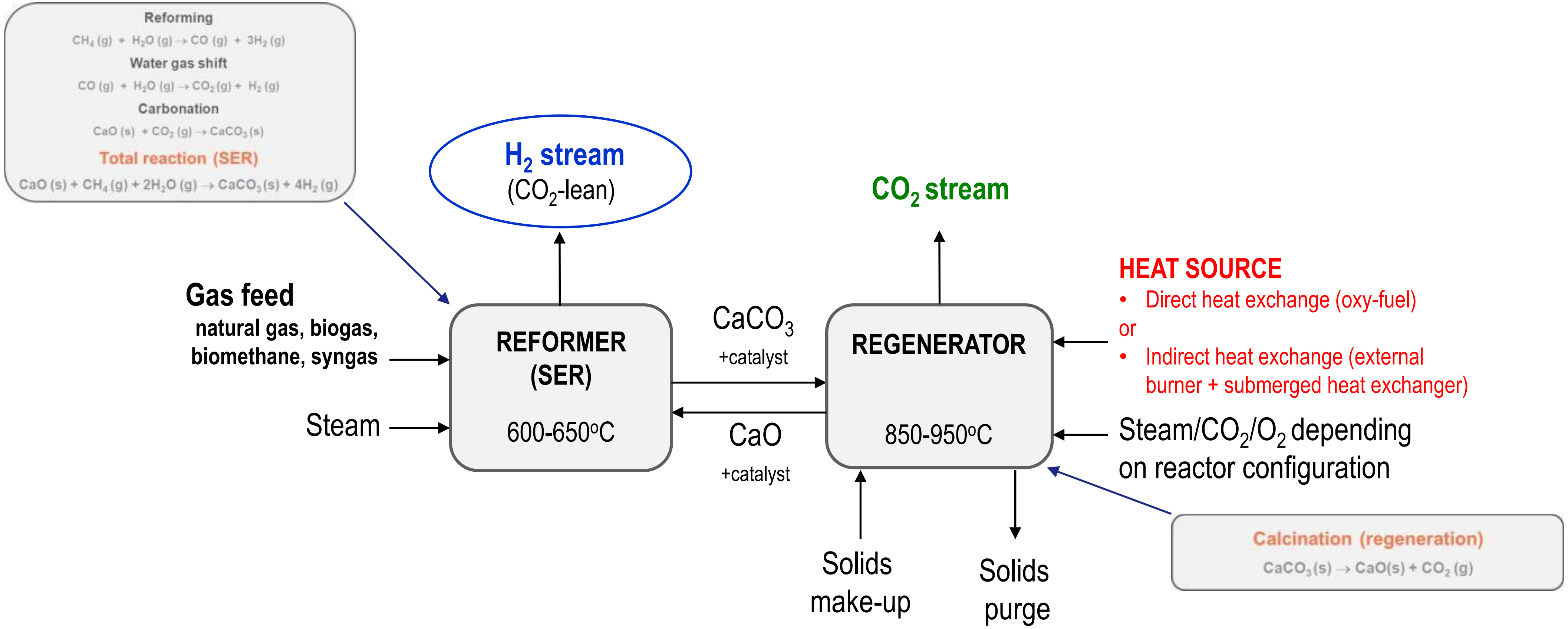
$CaCO_3\,(s) \rightarrow CaO(s) + CO_2\,(g)$

- Hydrogen production in one single step made possible by the addition of a CaO-based solid sorbent and a carbonation-calcination loop

- Combination of
    - Steam reforming
    - Water gas shift
    - In-situ Carbonation

- Regeneration of the CO_2 sorbent by decomposition of the $CaCO_3$ formed (calcination)

Sorption-Enhanced Reforming process



- 2 reactors instead of 6 in the conventional reforming process with CO_2 capture
- Heat supplied to the reformer by hot solids and carbonation reaction
- Suited for continuous operation in fluidized bed reactor system

Sorption-Enhanced Reforming SER

- Advantages
  - Higher H_2-yields (95 vol% +) than in conventional SMR, in one single step, and at lower temperature (600-650°C), due to “Le Chatelier’s principle”
  - In-situ CO_2 capture included in the process
  - No need for pre-reformer and shift catalysts
  - Simplified process layout and **process intensification**
- Performance
  - Potential for lower production costs and energy savings
    - Up to 30% reduction of energy intensity
    - Saving in capital and investment cost between 20-30%
  - Efficiency of 70% including
    - CO_2 capture rate of 90%
    - CO_2 compression to 120 bar and H_2 compression to 60 bar

Why CaO-based sorbents?

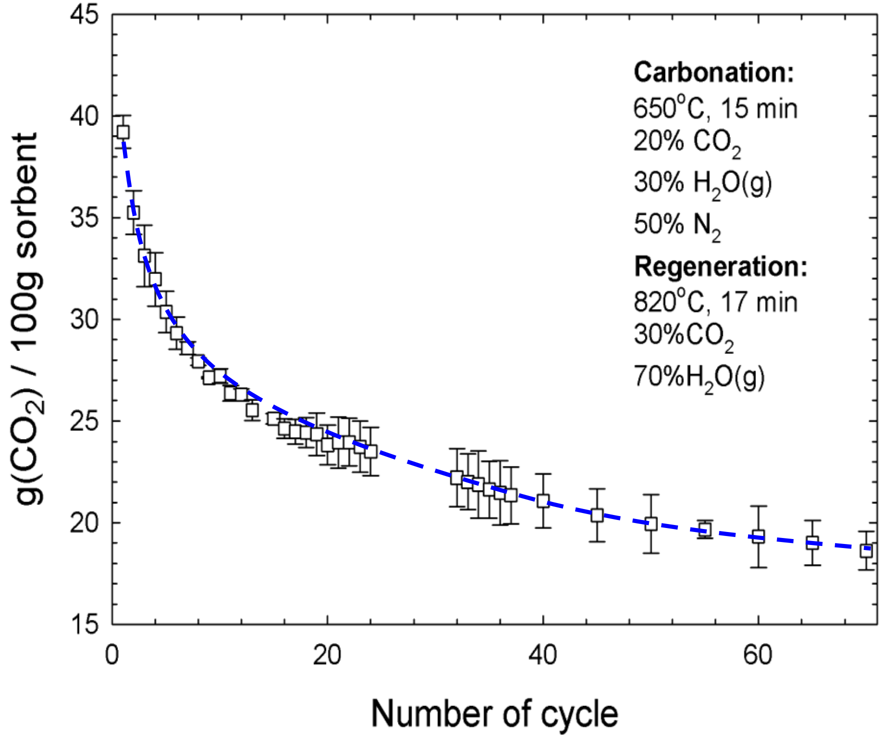
- Carbonation temperature matches reforming/shift temperatures +
- High absorption capacity +
- High reaction rate +
  - carbonation is a fast reaction
- Availability / abundance of raw materials +
- Acceptable price +
- **High temperature capture range**
  - **Potential for high efficiency** +
  - **Material stability challenges** −

Natural calcium-based sorbents: calcite and dolomite

- Calcined limestone and dolomite show
  - Good availability
  - Low cost
  - High sorption capacity
  - Fast kinetics

- However, they suffer from
  - Rapid loss of sorption capacity during multi-cycling due to pore closure and sintering
  - Relatively poor mechanical stability
  - Can contain impurities like Sulphur that can contaminate catalysts

- Synthetic CaO-based sorbents can solve the challenges of natural CaO-based sorbents by controlling the chemistry and the particle production process
  - ➢ increase sorption capacity
  - ➢ obtain a stable sorption capacity with increasing number of cycles
  - ➢ increase the mechanical stability for use in fluidized bed systems

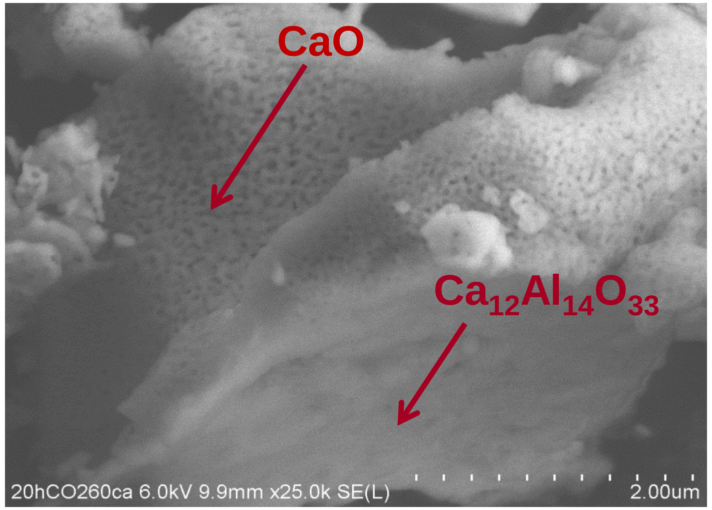


Methodology for the development of the sorbent production method
HTSORB material

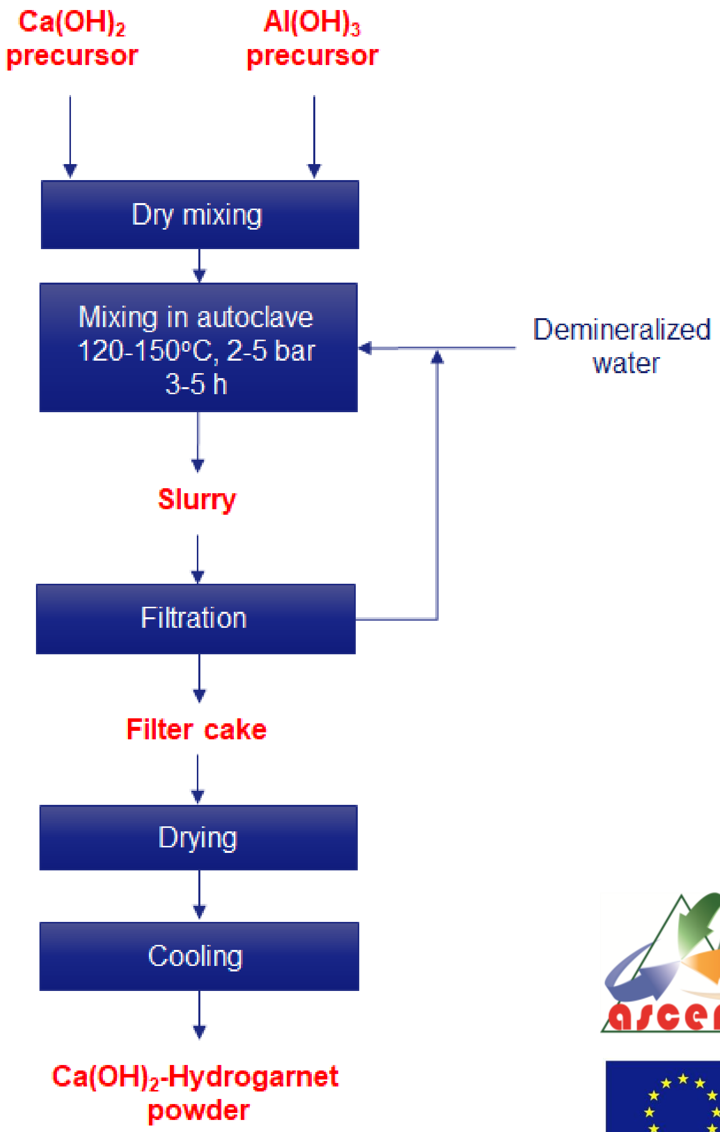
- The sorbent material developed uses a mayenite support ($Ca_{12}Al_{14}O_{33}$)
  - Mayenite has revealed to be a suited **stable support** for CaO-based sorbent materials and operations up to 925°C
- The sorbent material is based on a **hydrothermal synthesis route**
- Sorbent granules are produced by **high shear granulation**

Production of the sorbent micro-powder

- Hydrothermal synthesis
  - Production of calcium hydroxide/calcium aluminium hydroxide powder (hydrogarnet $Ca_3Al_2[(OH)_4]_3$)
  - Low cost, largely available hydroxide precursors
    - From limestone and bauxite
  - Simple and easily reproducible

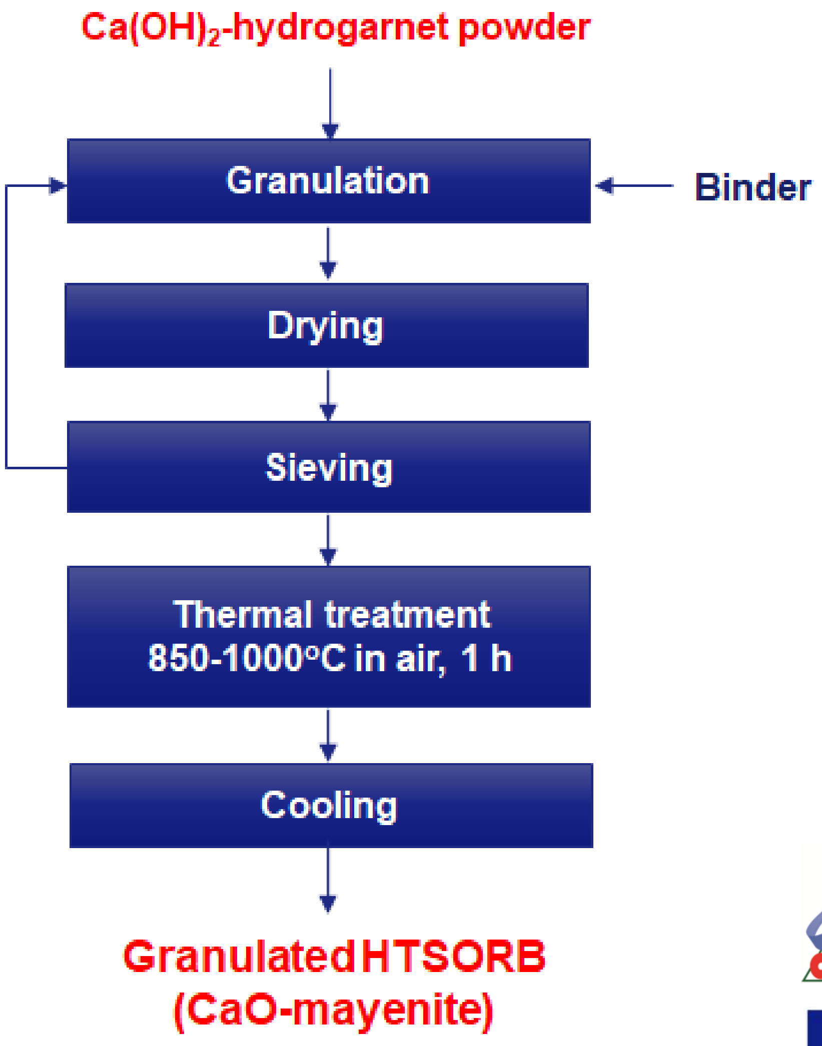


$Ca(OH)_2$-hydrogarnet powder



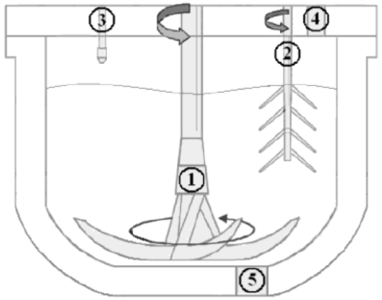
Production of granulated sorbent (HTSORB)

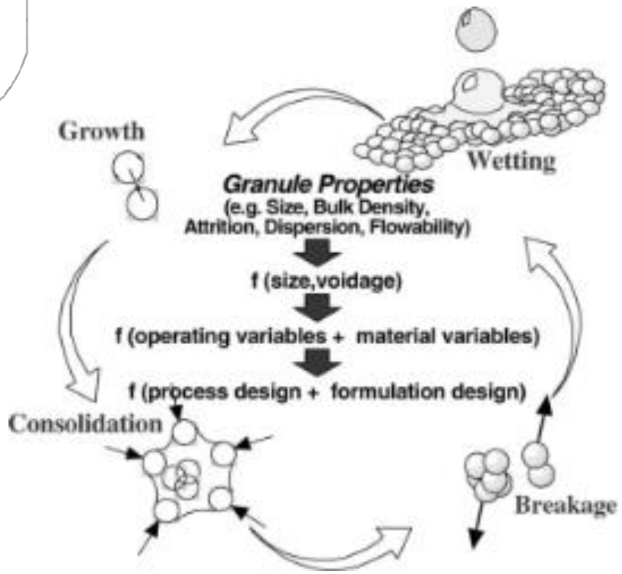
- Thermal treatment
  - Removal of water and binder
  - Conversion of $Ca(OH)_2$-hydrogarnet to CaO-mayenite
  - Partial sintering to give mechanical strength



Production of granulated HTSORB

- High shear granulation method
  - Dense granules with good mechanical properties
  - Widely industrially used
  - Scalable up to typically 500 kg/batch

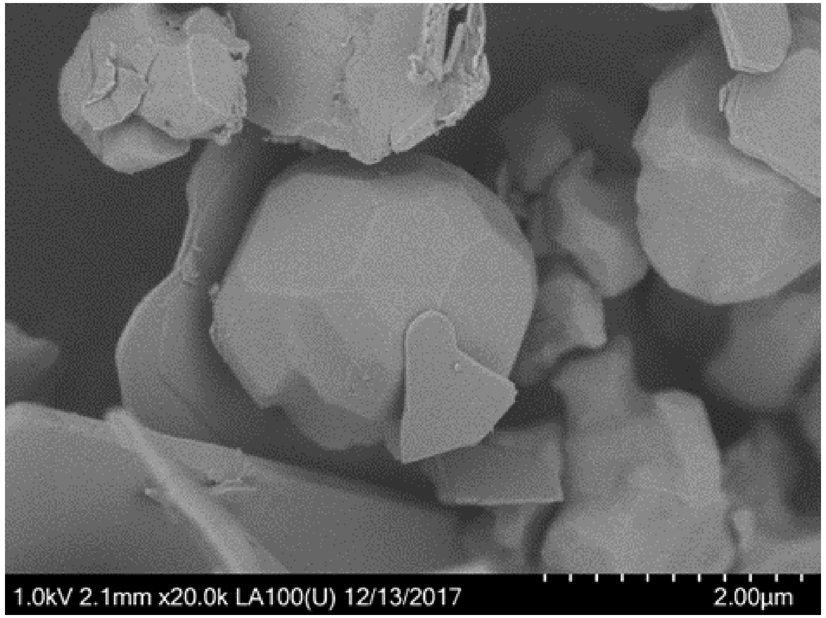




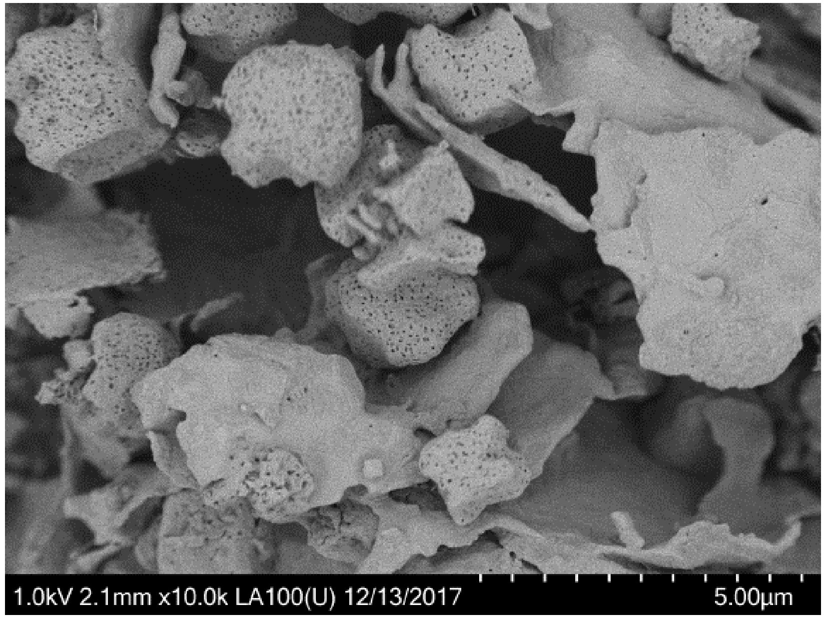
From lab to large scale

HTSORB texture analysis

- Micro-porosity formed during the decomposition of the $Ca(OH)_2$-hydrogarnet
- Good macro-porosity of the granules

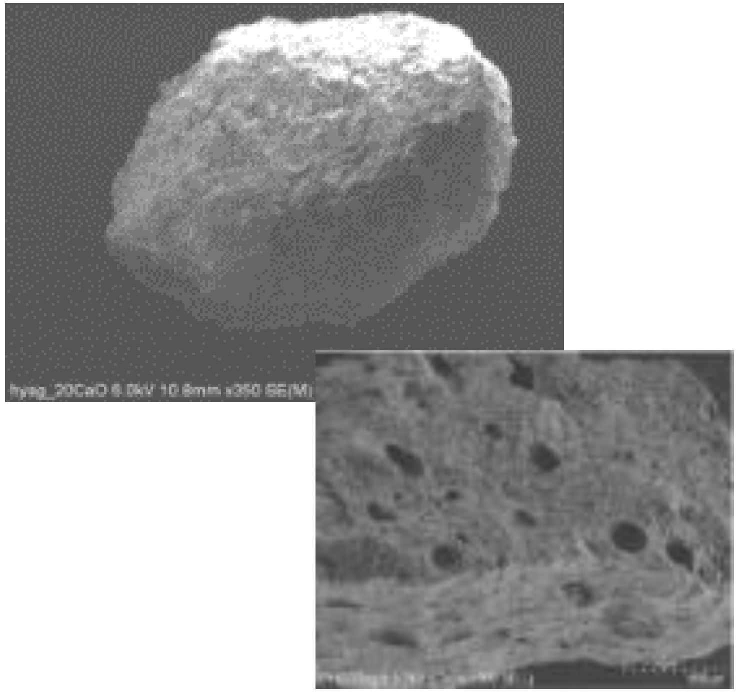


$Ca(OH)_2$, $Ca_3Al_2(OH)_{12}$ after synthesis



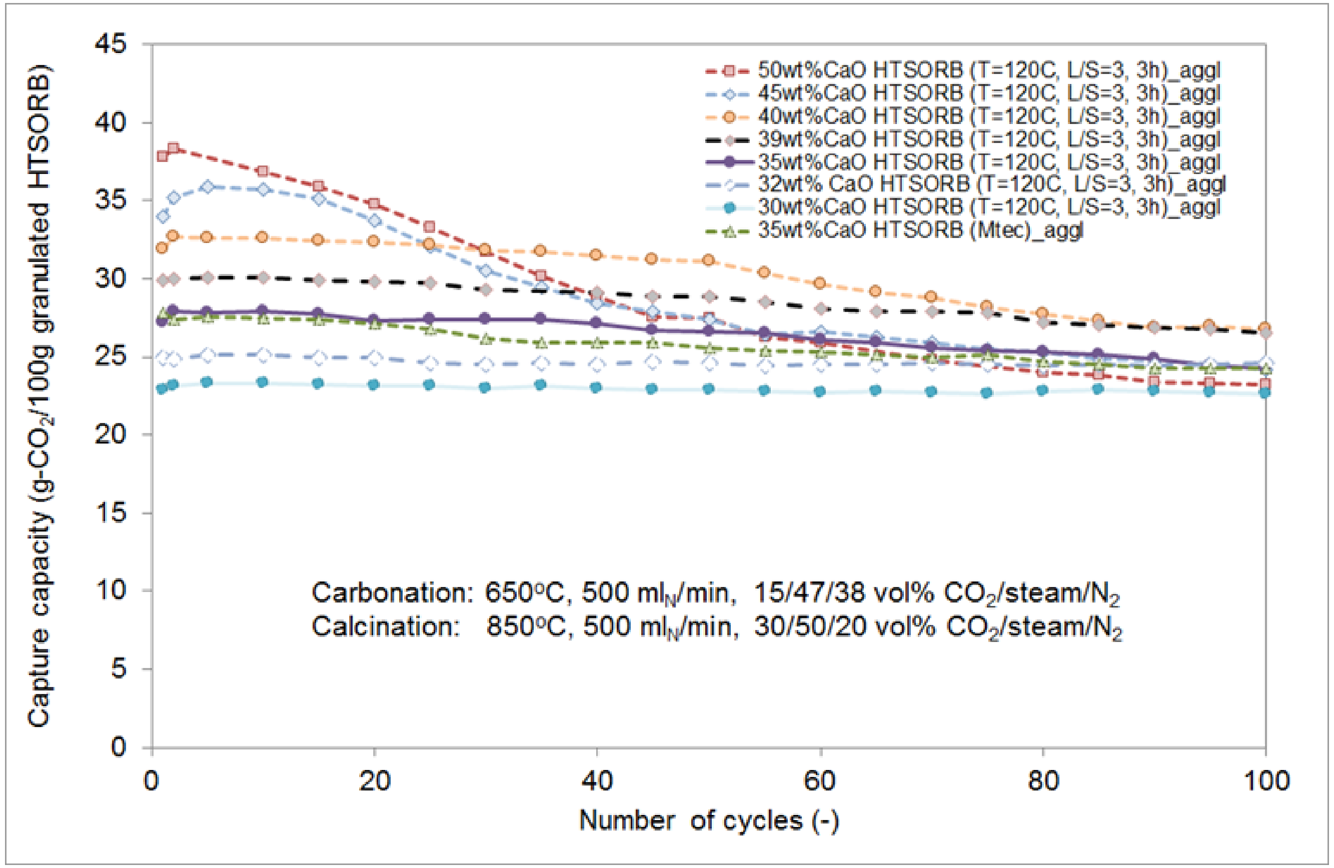
CaO, $Ca_{12}Al_{14}O_{33}$ after granulation and thermal treatment

HTSORB granule



HTSORB stability as function of CaO loading

- Optimum CaO loading of 30-32 wt% for high capacity stability and sintering limitation



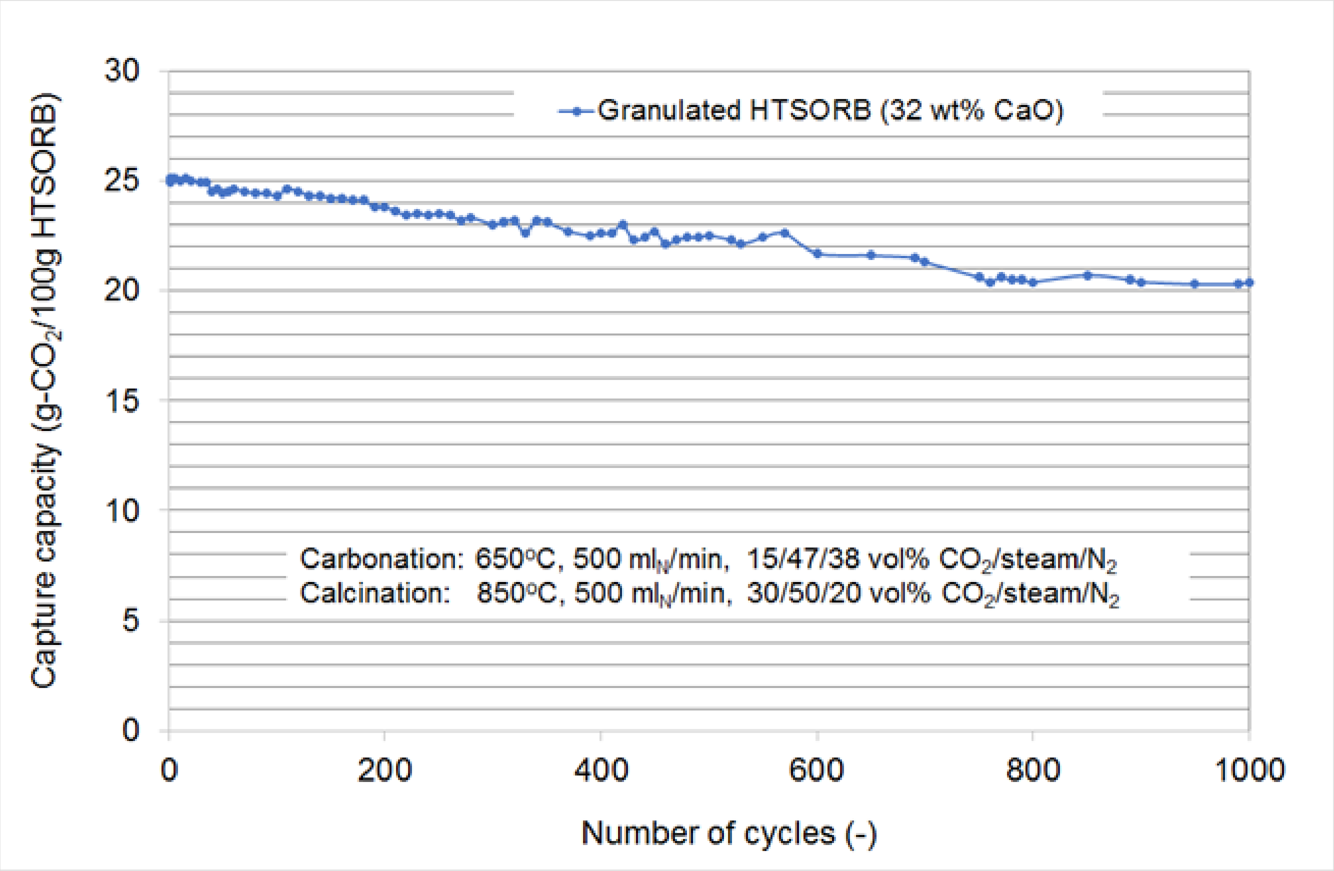
Upscaling of CaO-based solid sorbents

Development objectives for sorbent in MEMBER

- Optimize sorbent formulation for the SER process
  - Optimize the production method in view to minimize the production costs
  - Achieve chemical and mechanical multi-cycling stability
  - Upscale the production method to 50 kg/day
  - Test the material in relevant process conditions at TRL6

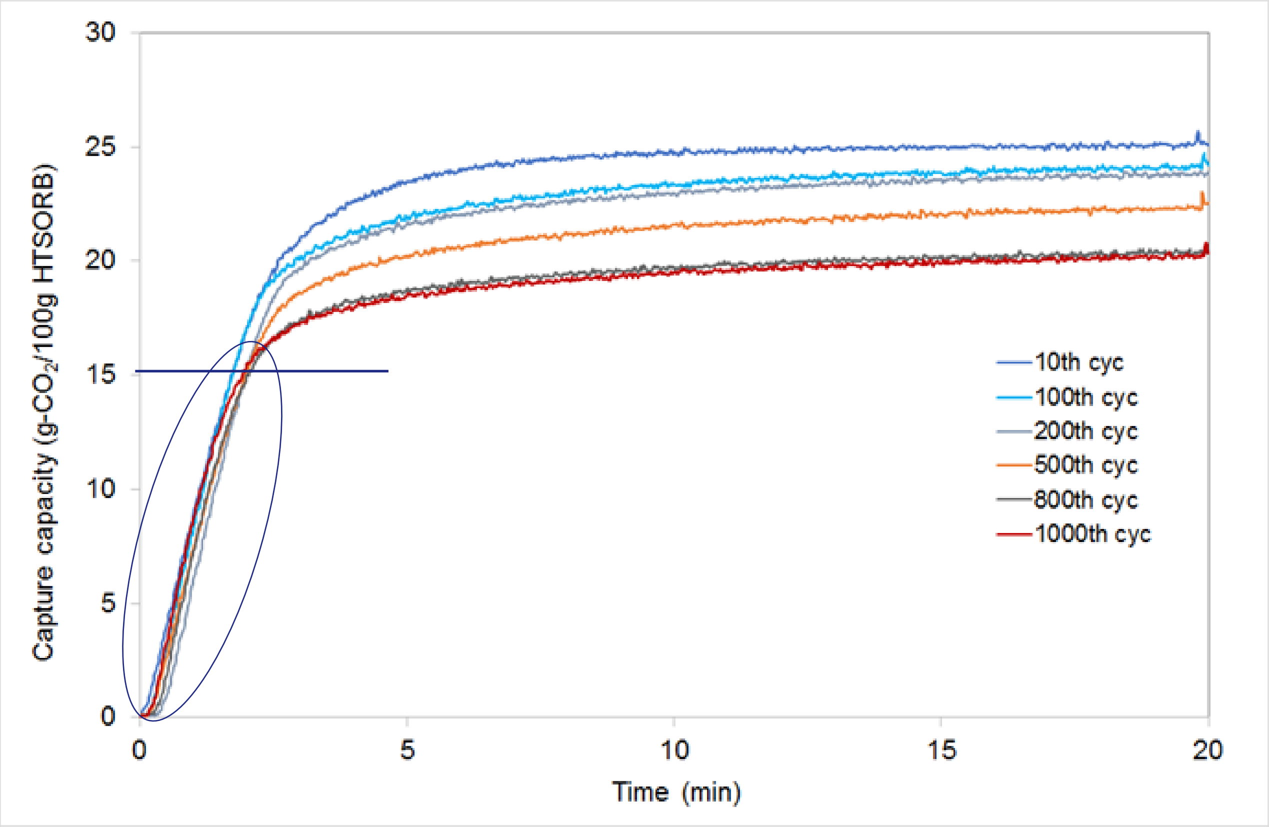
HTSORB (32 wt% CaO) long-term sorption capacity

- Stable capacity of 0.20 g-CO_2/g HTSORB after 1000 cycles

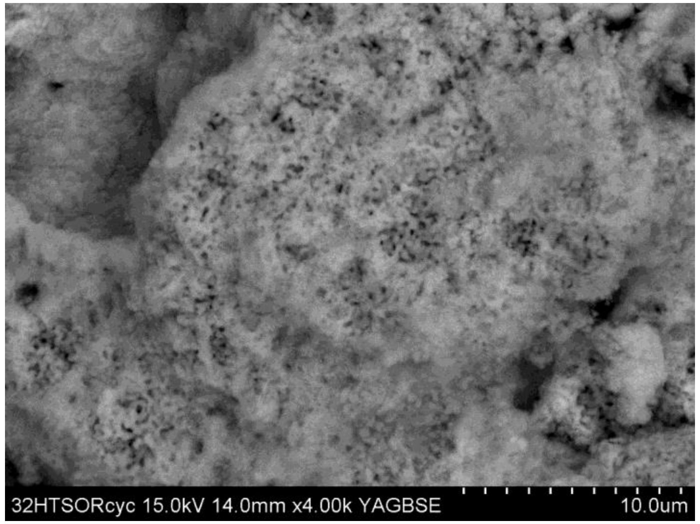


HTSORB (32 wt% CaO) long-term sorption capacity

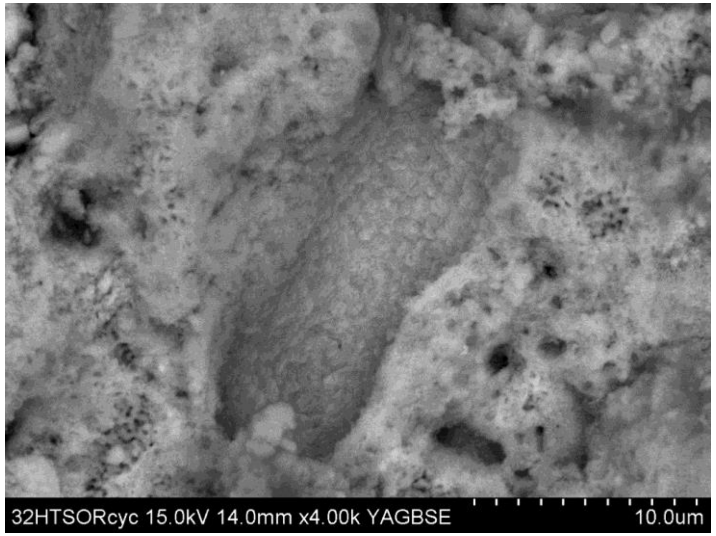
- Maximum operating capacity of 0.15 g-CO_2/g HTSORB for fast kinetics
- Stable reaction kinetics during multi-cycling

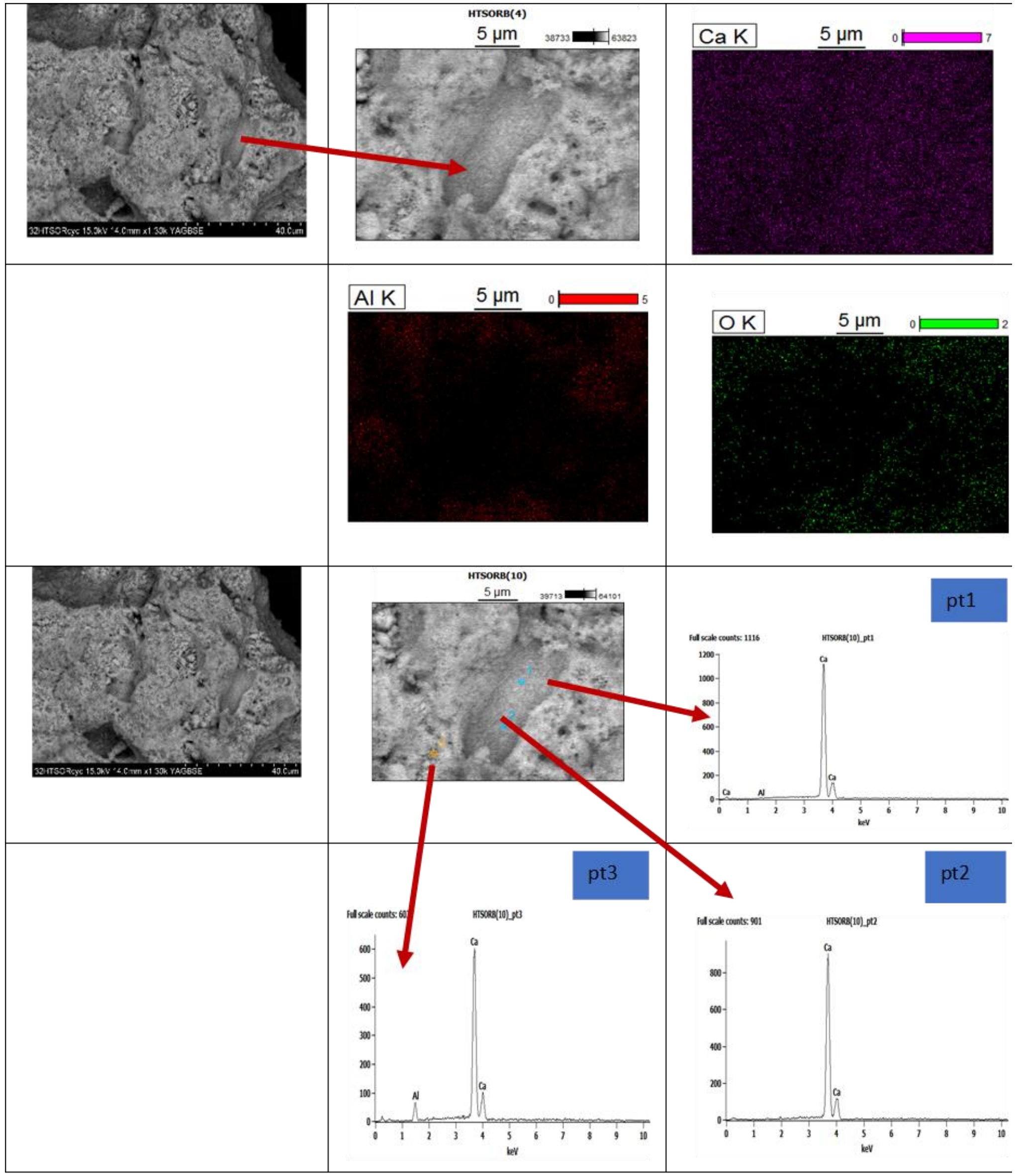


HTSORB characterization after long-term multi-cycling



- Partial gradual sintering of CaO





Up-scaling of production method at 50 kg/day scale

Hydrothermal synthesis

Centrifugation

Granulation

Thermal treatment

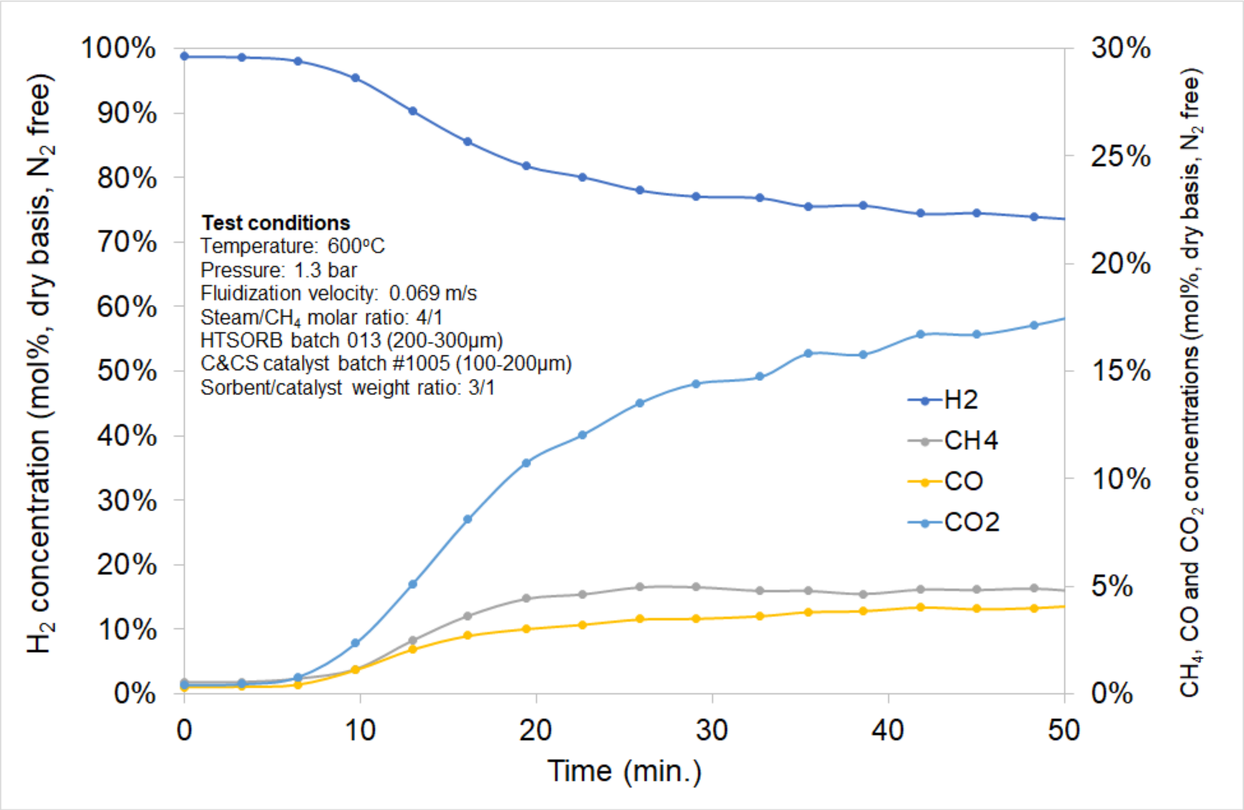
HTSORB

Marion Technologie
Nanomatériaux
Matériaux Nanostructurés
& Poudres Céramiques

MEMBER

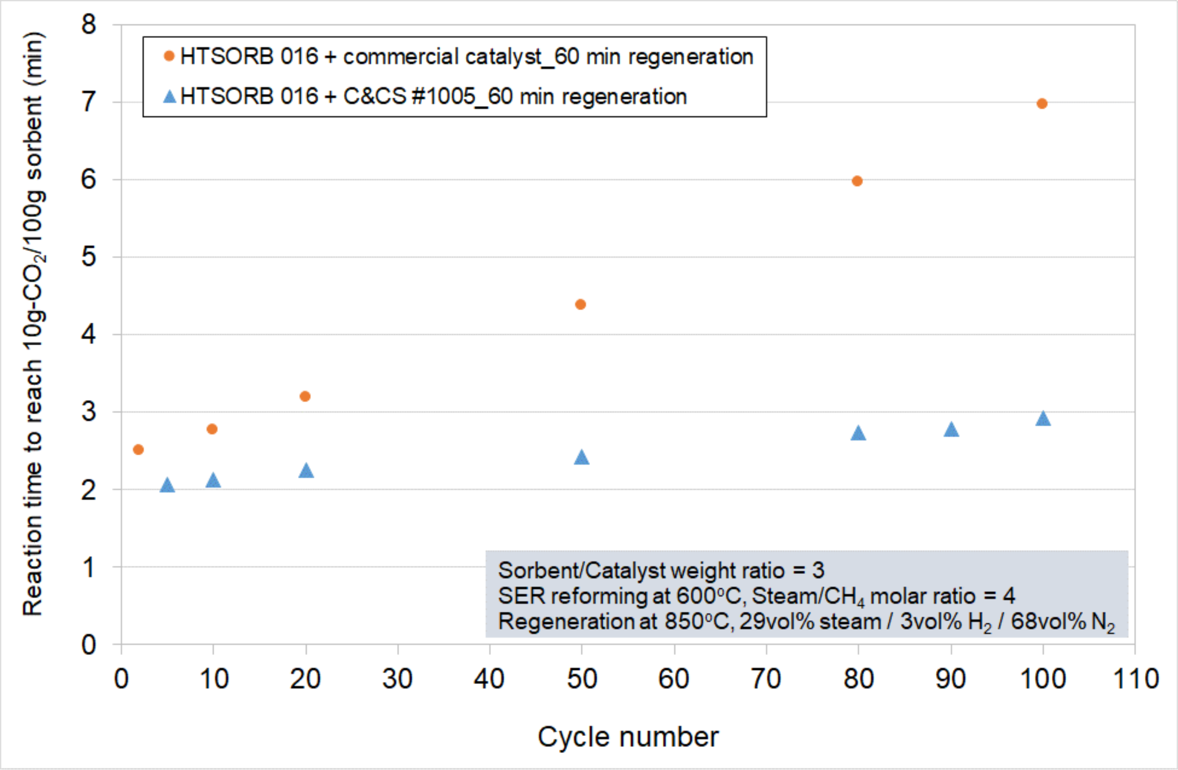
SER in lab-scale batch fluidized bed reactor

- HTSORB + novel fluidizable reforming catalyst (Ni-based)
- Satisfactory SER performance in FBR (about 98.5 vol% H_2) for 2 consecutive cycles



Mixed material stability during multi-cycling in TGA

- Gradual decrease of reaction rate with increasing number of cycles
- The novel catalyst performs better than the commercial one
- Indication of gradual activity loss of the reforming catalyst
  - High steam partial pressure at high temperature leading to sintering



Mechanical performance of the materials
Air Jet Index measurements

	AJI 1 hour	AJI 5 hours
HTSORB (calcined)	7.6%	16.4%
C&CS #1005 catalyst (reduced)	7.5%	15.6%
Commercial catalyst (reduced)	2.5%	6.1%

- Measured at 850°C in N_2
- Reference material needed for test in similar conditions (FCC catalyst for example)
- Test of sorbent + catalyst mixture should be carried out

Demonstration at TRL6

SER reactor prototype at the IFE-HyNor H_2 technology Center

- H_2 production capacity
  - 13 Nm^3/h
- Reformer
  - 600°C; 0.5 barg max.
  - Steam/CH_4 ratio: 4
  - Biomethane as fuel (97% CH_4)
- Regenerator
  - 850°C; 0.5 barg max.
  - Steam as sweep gas
- Solids
  - CO_2 sorbent: HTSORB (200-300 µm)
  - Novel reforming catalyst (100-200 µm)
  - Ratio sorbent/catalyst: 3 w/w
  - Solids inventory: ca. 80 kg
  - Solids circulation rate: 75 kg/h

IFE-HyNor Hydrogen Technology Center

IFE, ZEG Power, TU/e, KT Kinetics Technology, Marion Technologie, C&CS catalysts & chemical specialties, tecnalia Inspiring Business, MEMBER

SER prototype

IFE-HyNor Hydrogen Technology Center

www.member-co2.com

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

Julien Meyer
Senior Research Scientist

julien.meyer@ife.no

2.4. Pd based membranes development (Ekain Fernández – TECNALIA)

tecnalia Inspiring Business

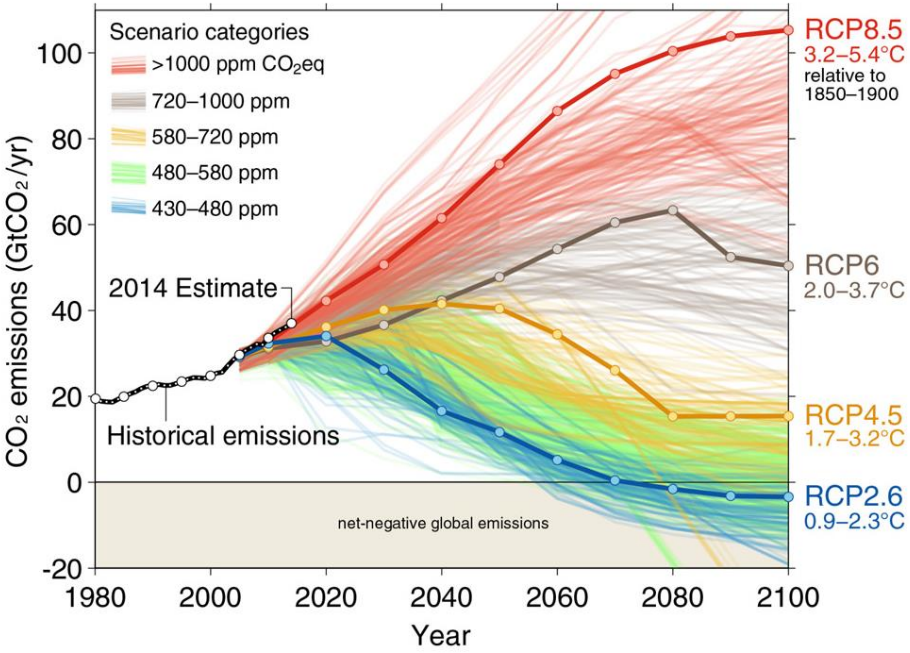
Palladium membranes for H_2 production / purification

Ekain Fernandez

ekain.fernandez@tecnalia.com

1st Workshop MEMBER project, 15th January 2020, Eindhoven (NL)

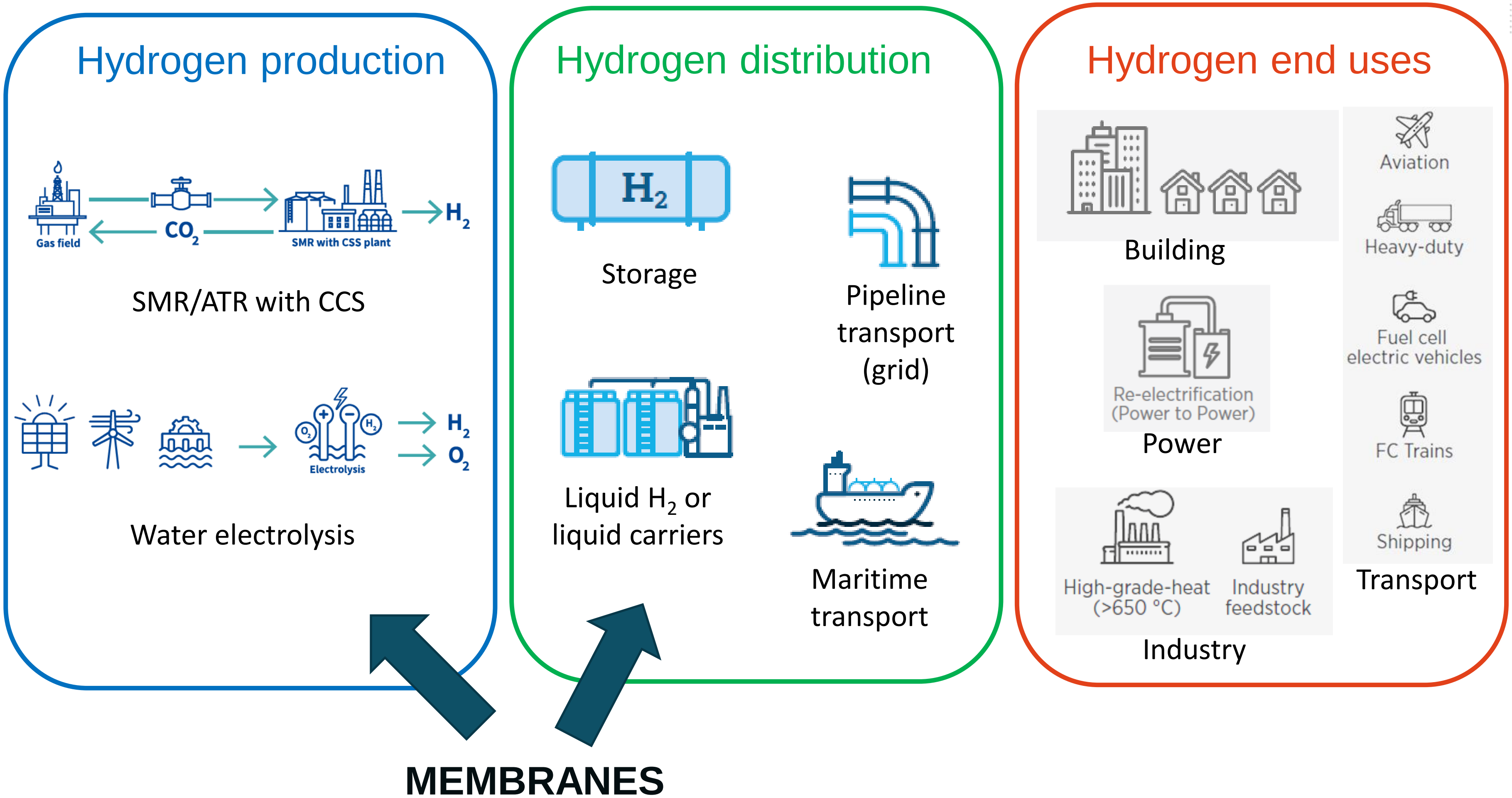
Climate goals. CO_2 emission scenarios until 2100



www.theconversation.com/global-carbon-report-emissions-will-hit-new-heights-in-2014-31834

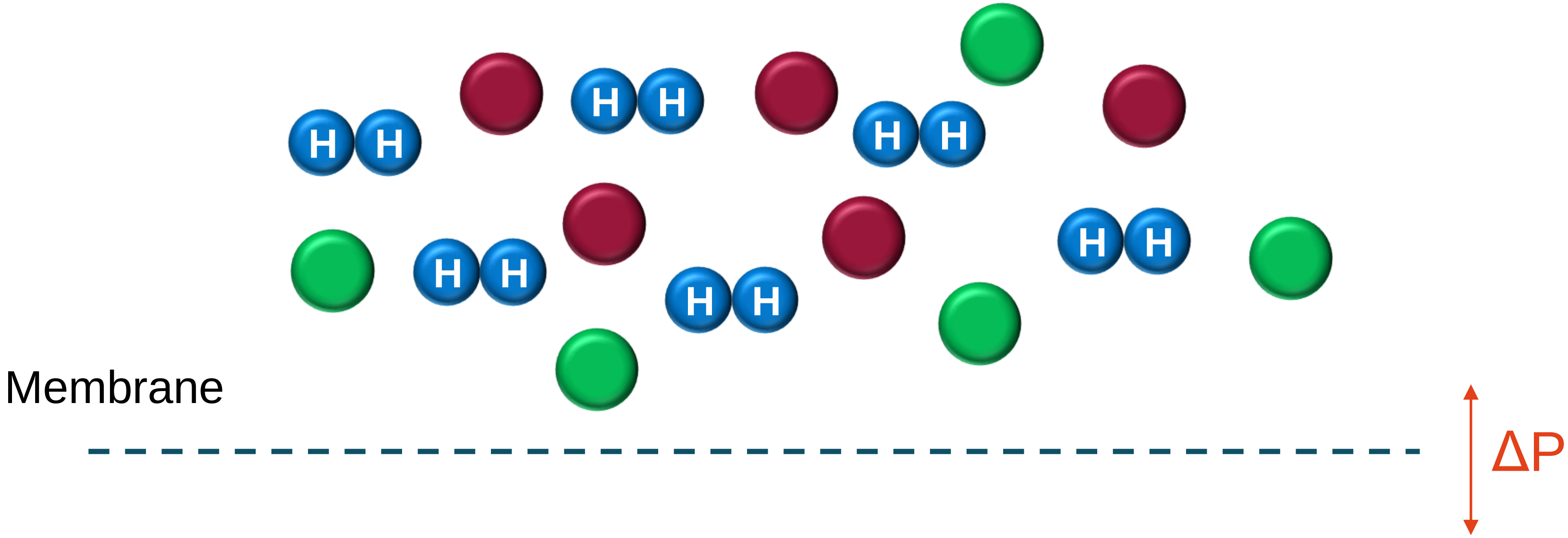
EU's target: reduction of >80% of CO_2 emission by 2050 compared to 2000.

Hydrogen economy



Hydrogen Roadmap Europe. FCH-JU. 2019; IRENA. Hydrogen from renewable power. 2018; Australian National Hydrogen Strategy 2019

Membrane



Palladium membranes

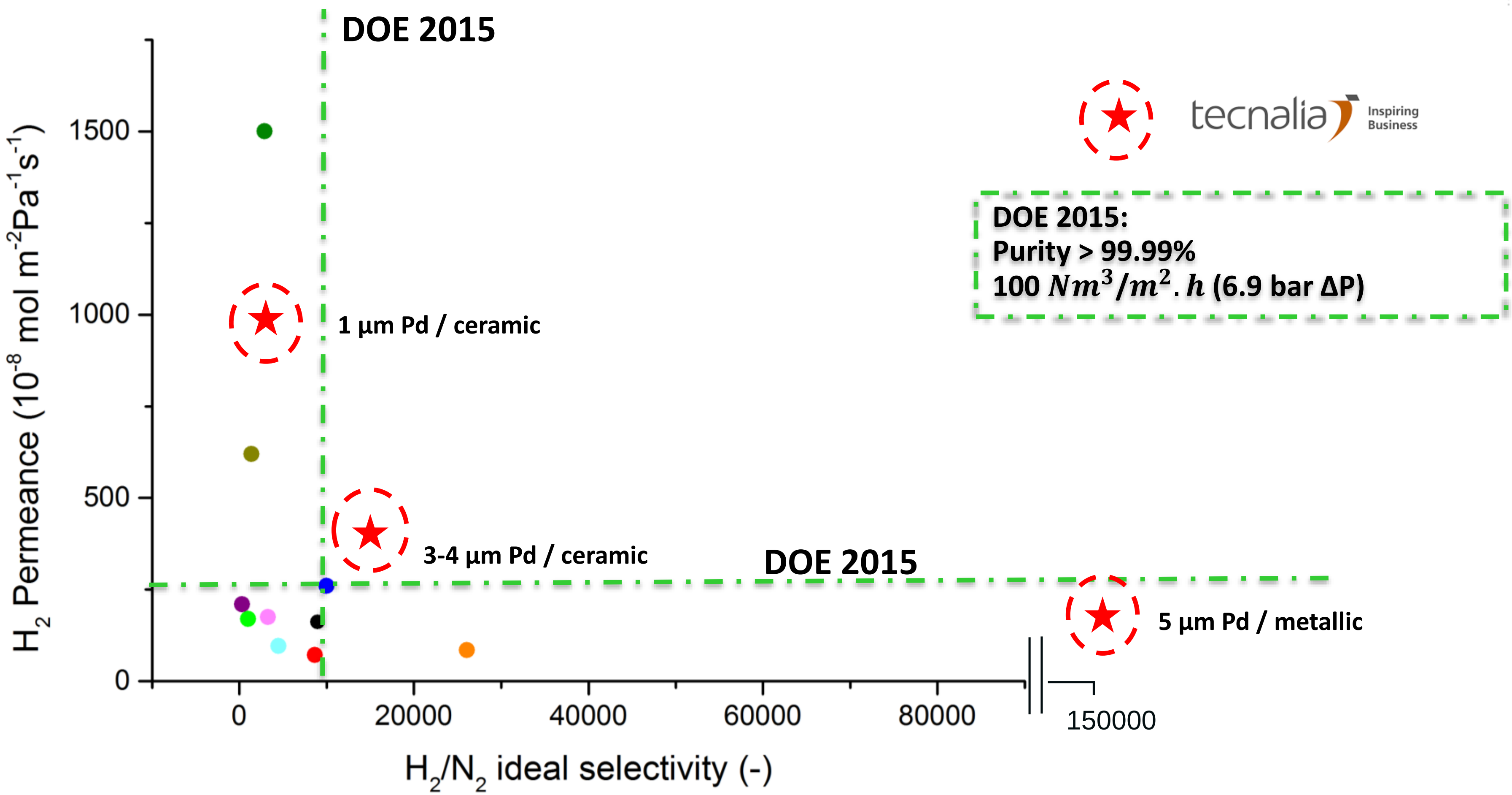
Thin Pd (< 5 µm) supported membranes for high H_2 permeation and selectivity

Ceramic supported thin Pd-based membranes
(with Swagelok-graphite connectors)

Metallic supported thin Pd-based membranes
(welded to dense metal tubes)

Palladium membranes

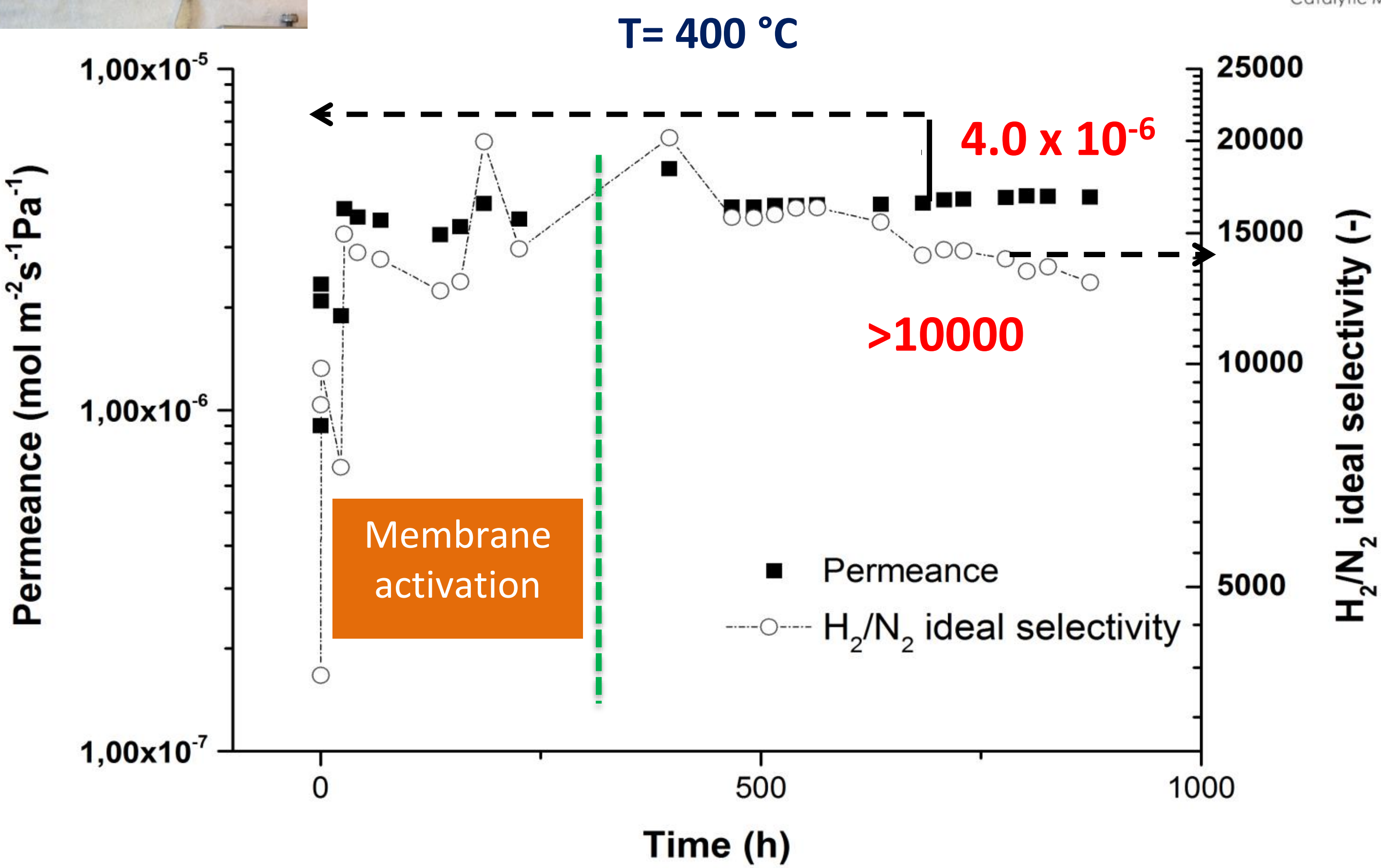
Comparison between other R&D and TECNALIA Pd membranes



F. Gallucci et al., Chem. Eng. Sci 92 (2013) 40–66

Palladium membranes

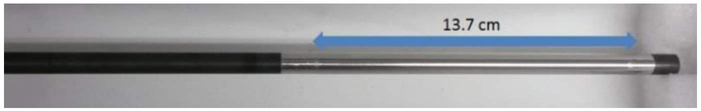
Thin (3-4 µm thick) Pd-Ag membranes (ceramic support)



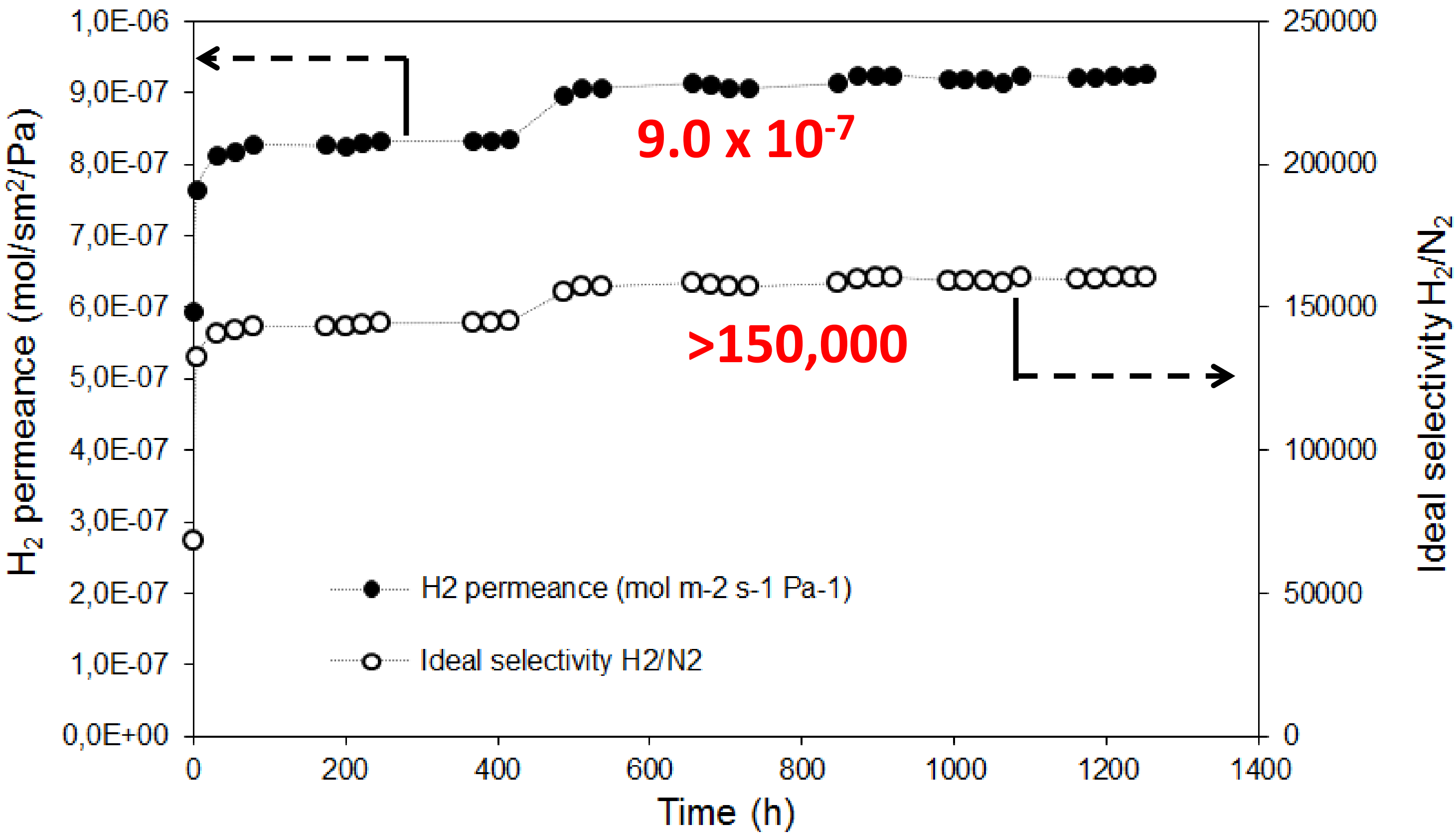
A. Helmi et al., Molecules 21 (2016) 376

Palladium membranes

Thin (5 µm thick) Pd-Ag membranes (metallic support)



T=400 °C

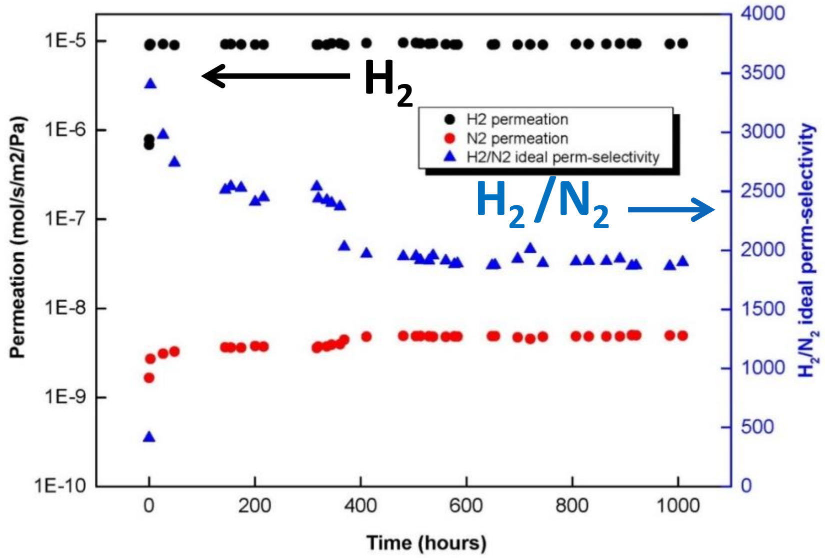


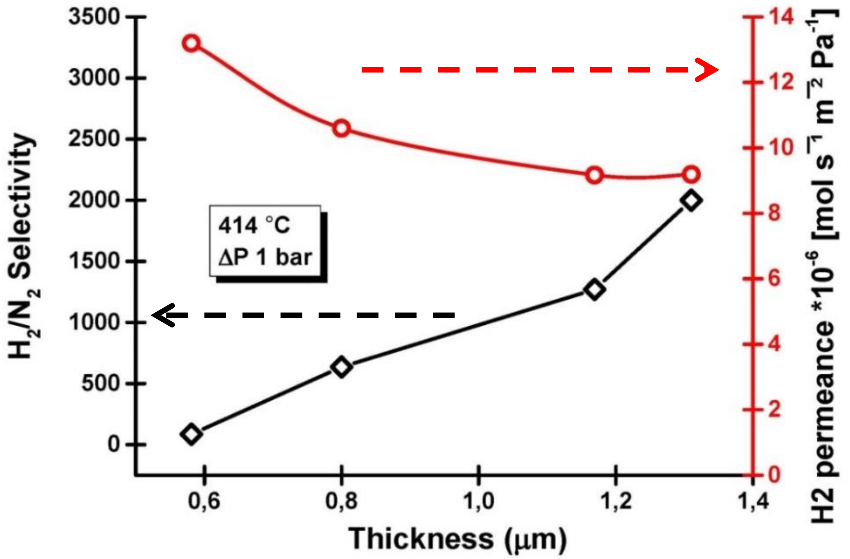
E. Fernandez et al., Chem. Eng. J. 305 (2016) 182-190

Palladium membranes

Ultra-thin (≤1 μm thick) Pd-Ag membranes (ceramic support)

1.3 μm thick Pd-Ag membrane (T=400 °C)



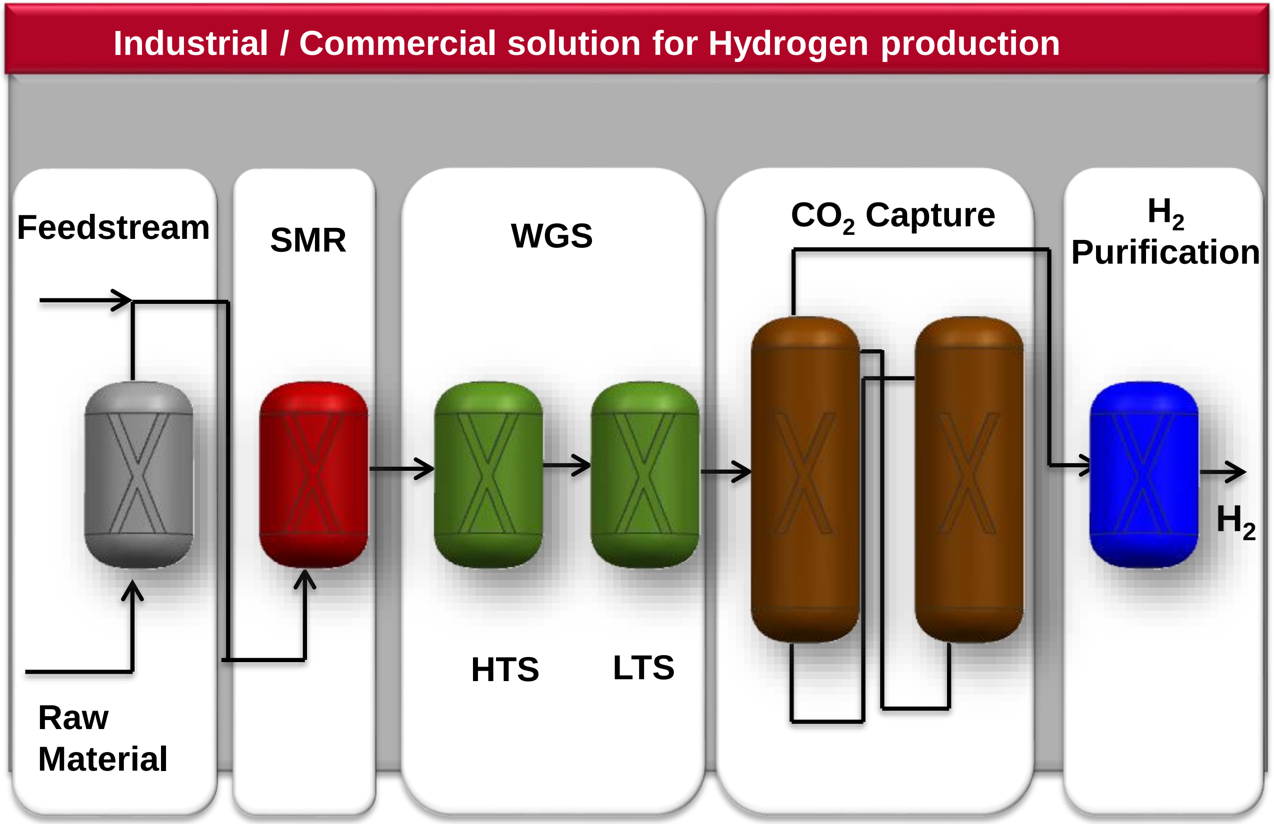


Tuning of H_2 permeance and selectivity with Pd-Ag layer thickness

J. Melendez et al., J. Membr. Sci 528 (2017) 12-23

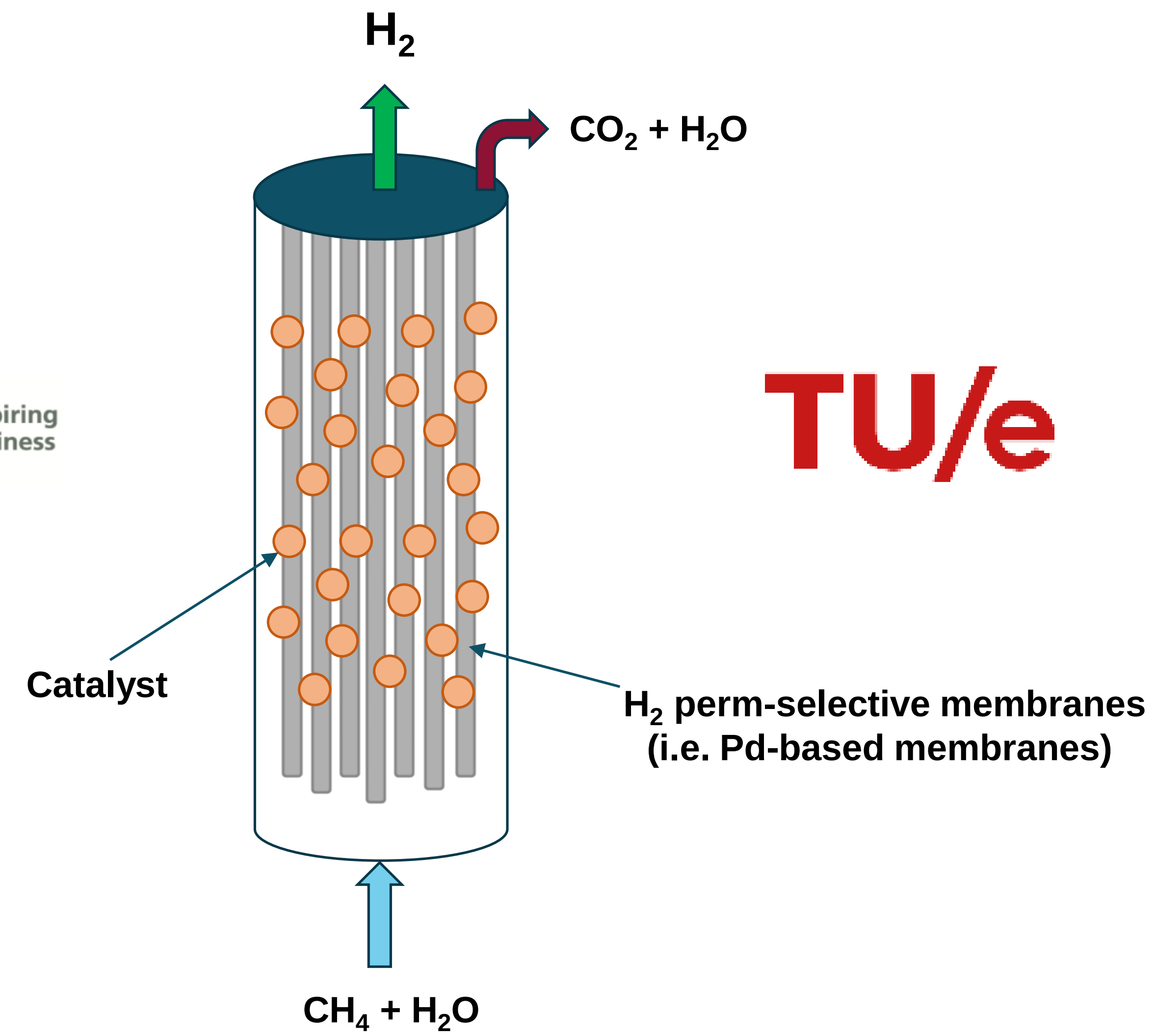
H_2 production

H_2 production



$$CH_4 + 2\,H_2O \rightleftharpoons CO_2 + 4\,H_2$$

Membrane reactor for H_2 production



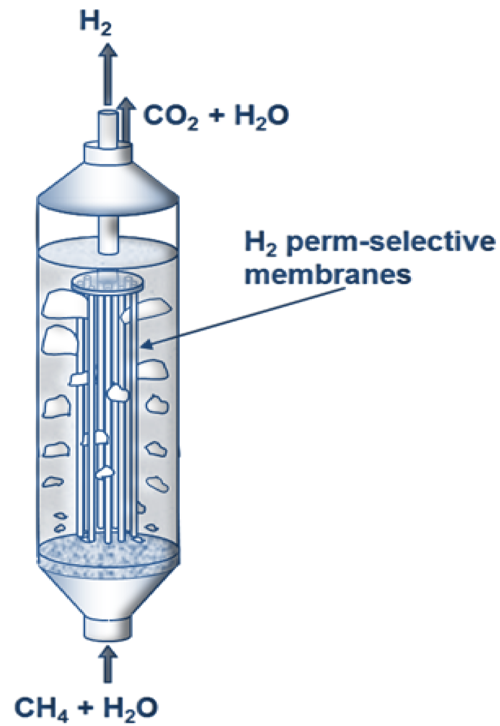
Membrane reactor for H_2 production

Feedstock

Membrane reactor

Reaction

Natural gas
Biogas
(Bio)ethanol



Reforming

Syngas

Water gas shift

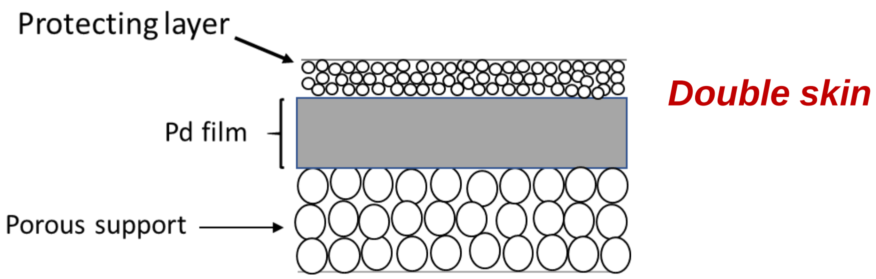
Propane
Ammonia

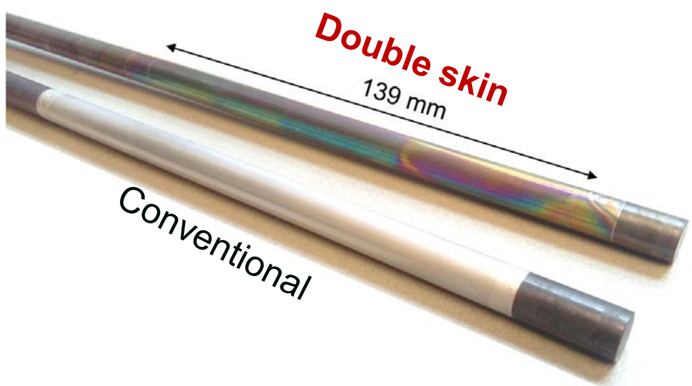
Dehydrogenation

2 new projects!

Double-skin Pd-based membranes

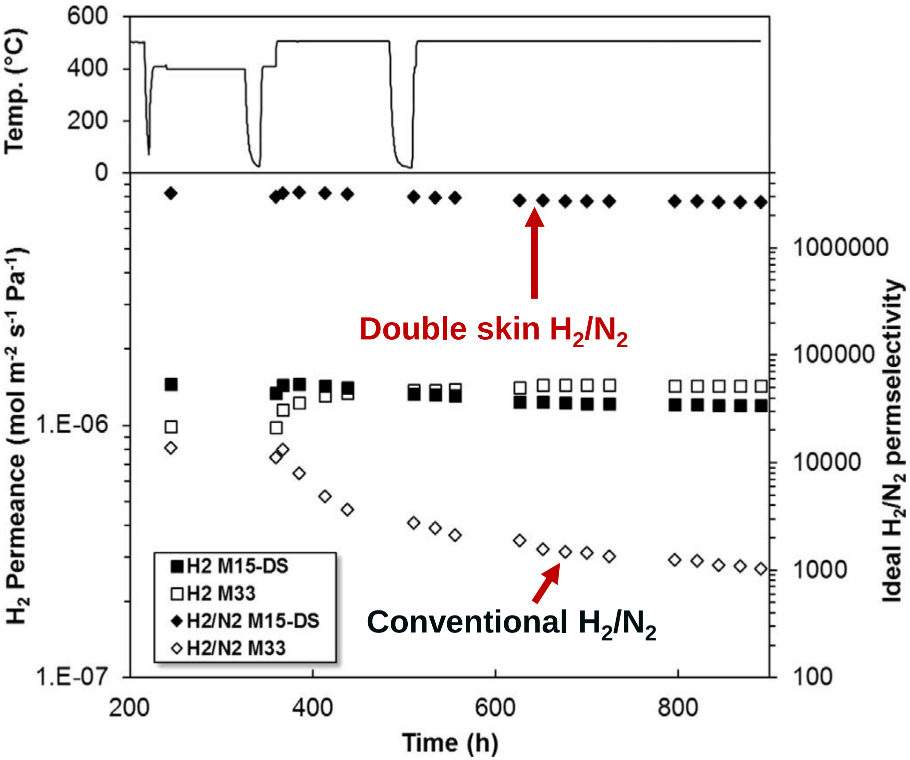
Attrition resistant membranes for fluidized bed Pd MR





H_2 permeation under fluidization

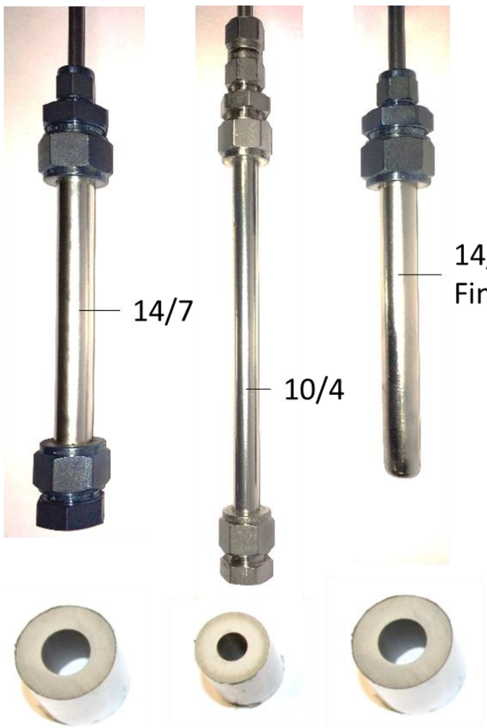
Rh on alumina (100-300 µm size)

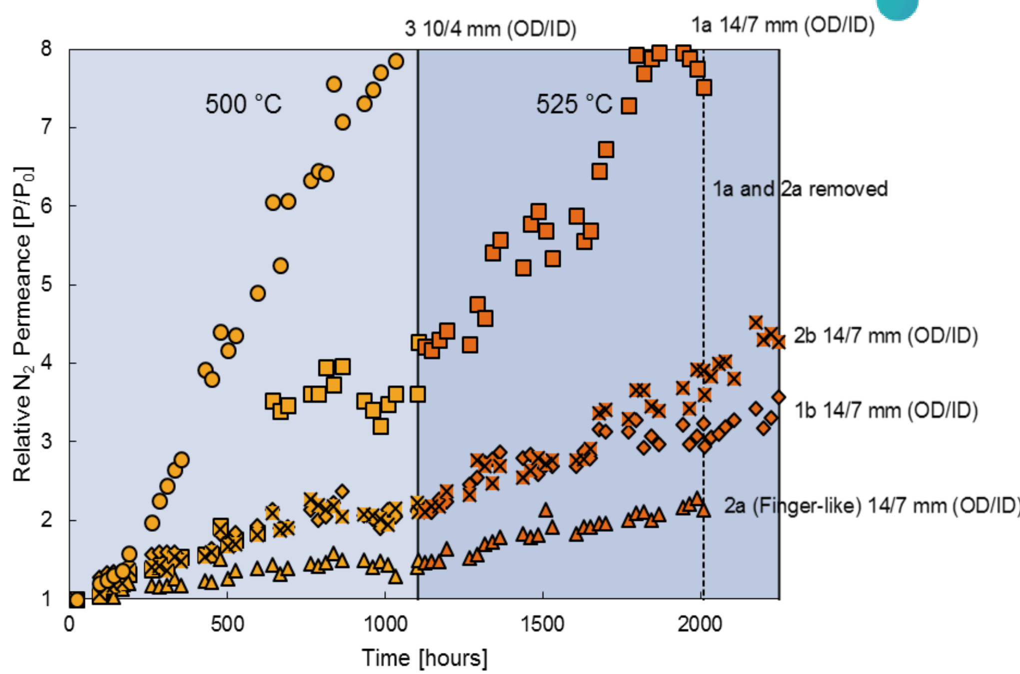


A. Arratibel et al., J. Membr. Sci. 563 (2018) 419

Pd-based membranes

Development of finger-like Pd membranes





- Thicker wall ceramic tubes (14/7 mm o.d.) present higher sealing torque and higher stability.
- New Finger-like ceramic support (50 cm long) avoids the use of one Swagelok and the leak rate with the finger-like is reduced after 2000 h by more than 30%

N. Nooijer et al., Processes, 2019, 7(2), 106

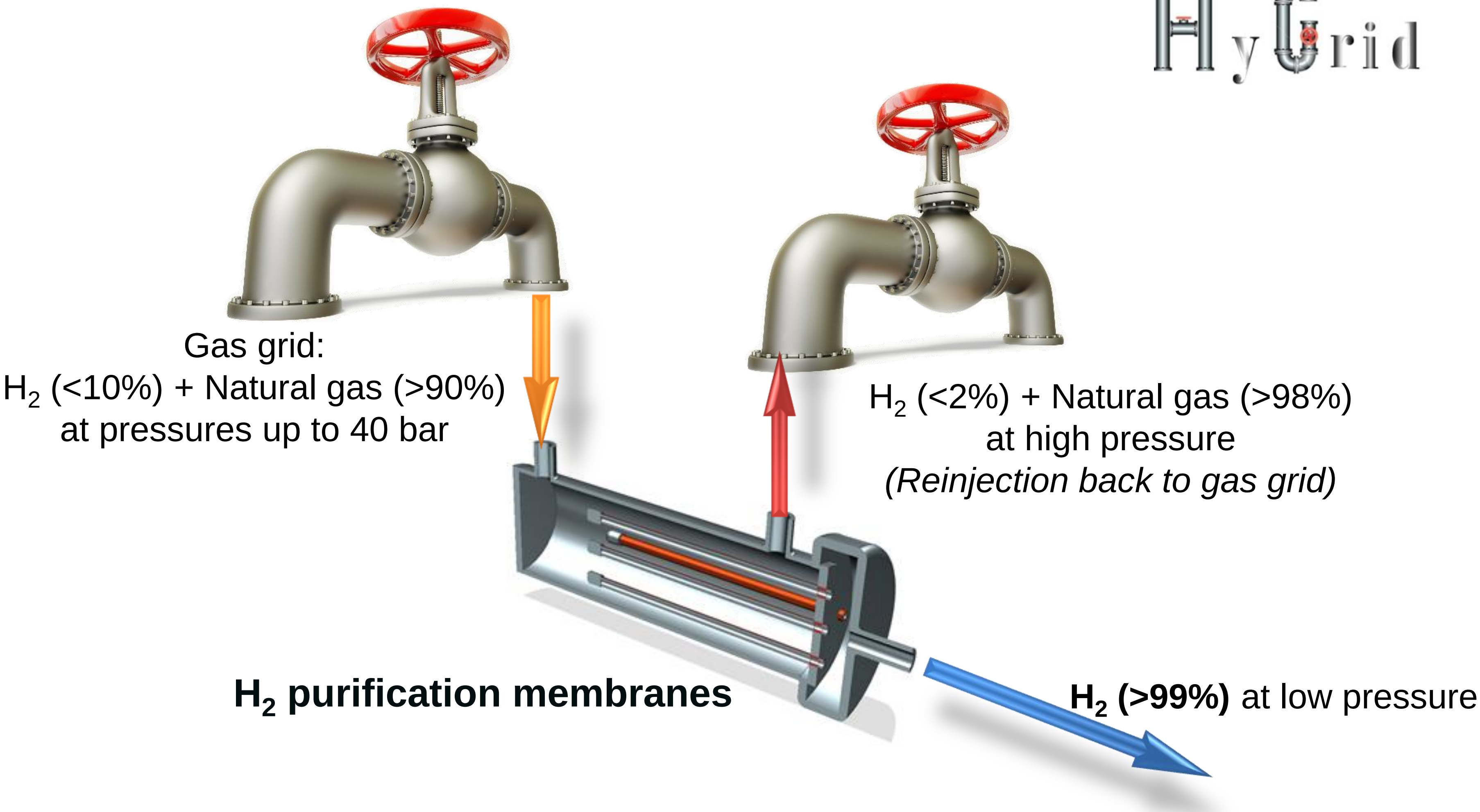
Pd-based membranes

Scale-up of Pd-based membrane manufacturing

125 membranes of ~40 cm long manufactured for the BIONICO membrane reactor prototype

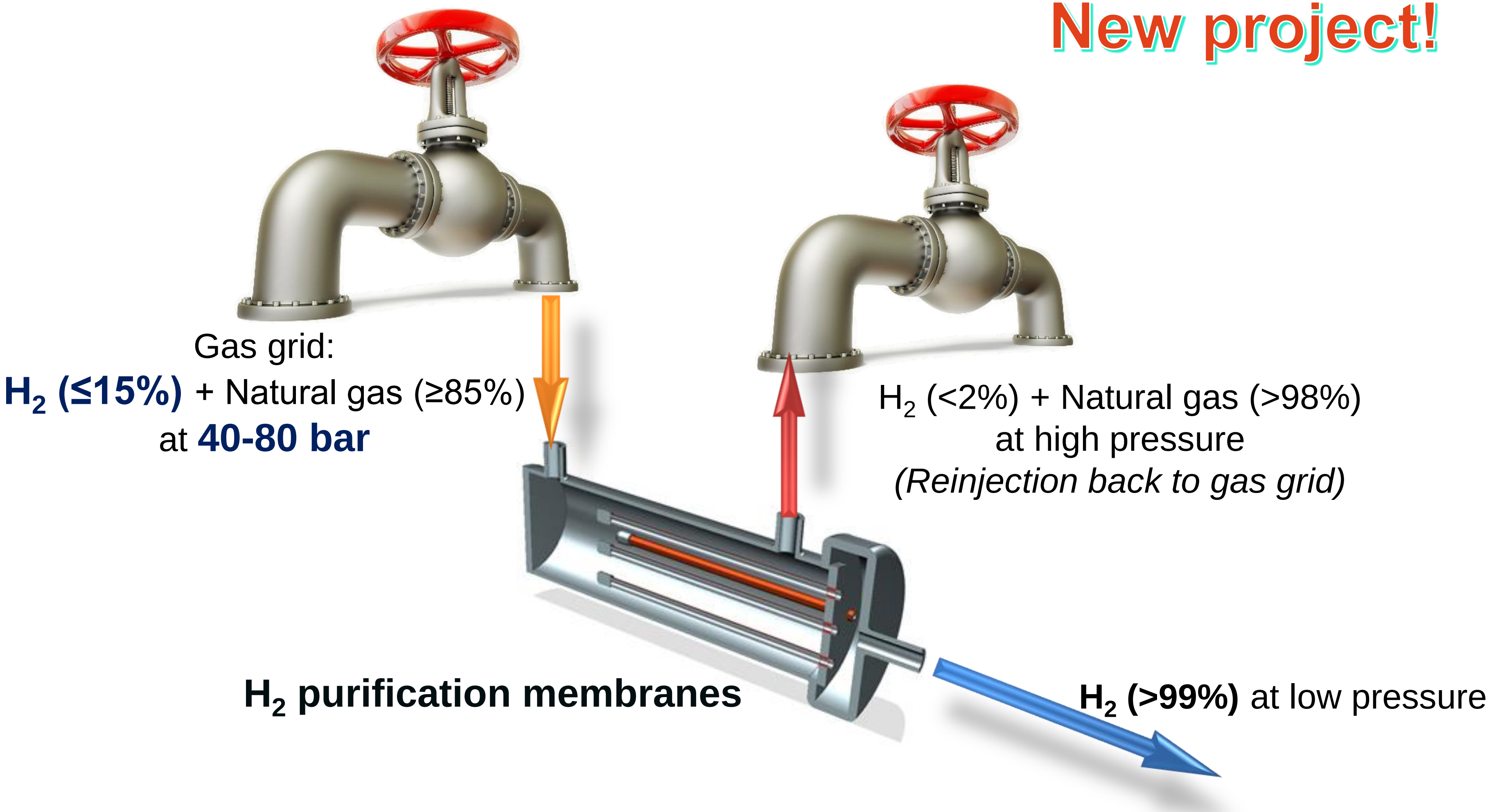
H_2 distribution

Membranes for H_2 purification (Distribution)



Membranes for H_2 purification (Distribution)

New project!



Conclusions

- Pd-Ag (≤ 5 µm) supported membranes with high H_2 permeation and selectivity have been developed.
- Membranes show long-term stability (>1,000 h) at temperatures up to 500 °C.
- Membrane manufacturing process has been scaled up (more than 100 membranes and up to 50 cm long)
- Pd membrane reactors improve the conversion with respect to traditional reactor.
- High purity H_2 can be produced from different feedstocks (i.e. natural gas, ethanol, biogas) using membrane reactors.
- Pd-based membranes can be used for H_2 purification from H_2-CH_4 admixtures

Future developments / Challenges

- Long-term stability test (next target: >8000 h)
- Recycling of membranes and supports
- Use membrane technology for other reactions / applications

THANK YOU FOR YOUR ATTENTION

Ekain Fernandez

ekain.fernandez@tecnalia.com

2.5. Membrane reactors – current status and perspectives (Fausto Gallucci – TUE)

Inorganic Membranes & Membrane Reactors

EINDHOVEN UNIVERSITY OF TECHNOLOGY

Membrane and Membrane Reactor for Sustainable Process Development

Fausto Gallucci, Prof. Inorganic Membranes and Membrane Reactors

Chemical Engineering and Chemistry, Sustainable Process Engineering

Outlook

- Who we are
- Why Membrane reactors
- Large-scale
- Small-scale
- Where we are

Our Labs


NORTH SEA
NETHERLANDS
Amsterdam
Schiphol
Eindhoven
GERMANY
BELGIUM

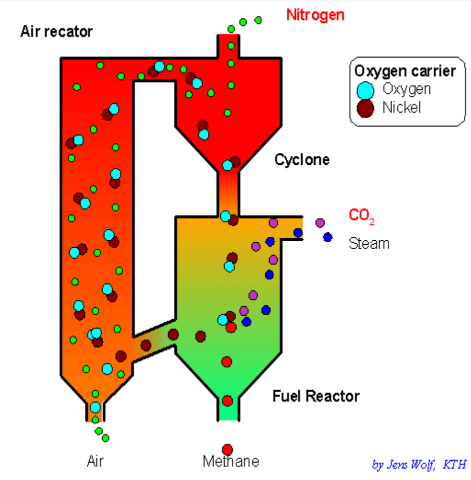

San Sebastian
Basque
La Rioja
Navarra
PORTUGAL
SPAIN

Research themes - SIR

Novel intensified reactor concepts via:

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

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



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

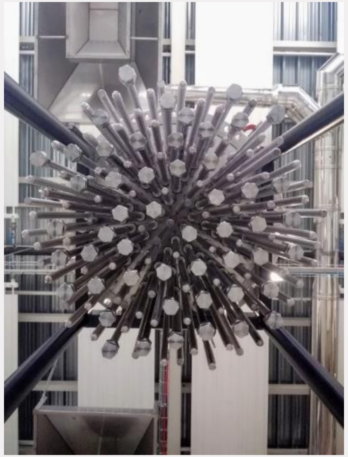
Research themes - SIR

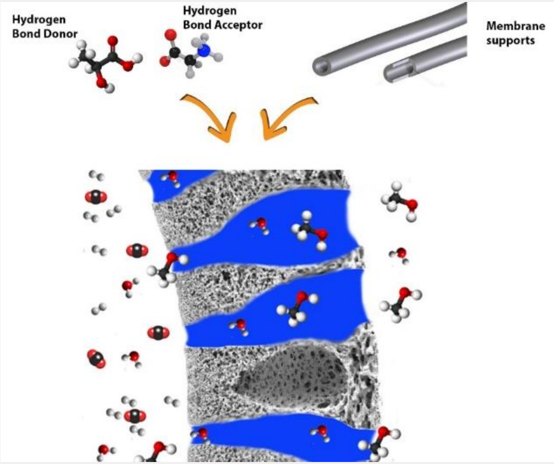
Integration reaction + separation

Packed bed and fluidized bed membrane reactors

(H_2, syngas, oxidative dehydrogenations, partial oxidations)

- Optimal design for maximum yields
- Liquid supported membranes





MEMBRANE TECHNOLOGY

MEMBRANE MATERIALS

- Polymer
- Mixed-matrix
- Carbon molecular sieve
- Palladium

Hollow fiber membranes

Tubular membranes

SCALABLE MEMBRANE CONFIGURATIONS

- CO_2 capture
- H_2 purification
- CH_4 purification
- Olefin / paraffin separation
- Water separation

APPLICATIONS

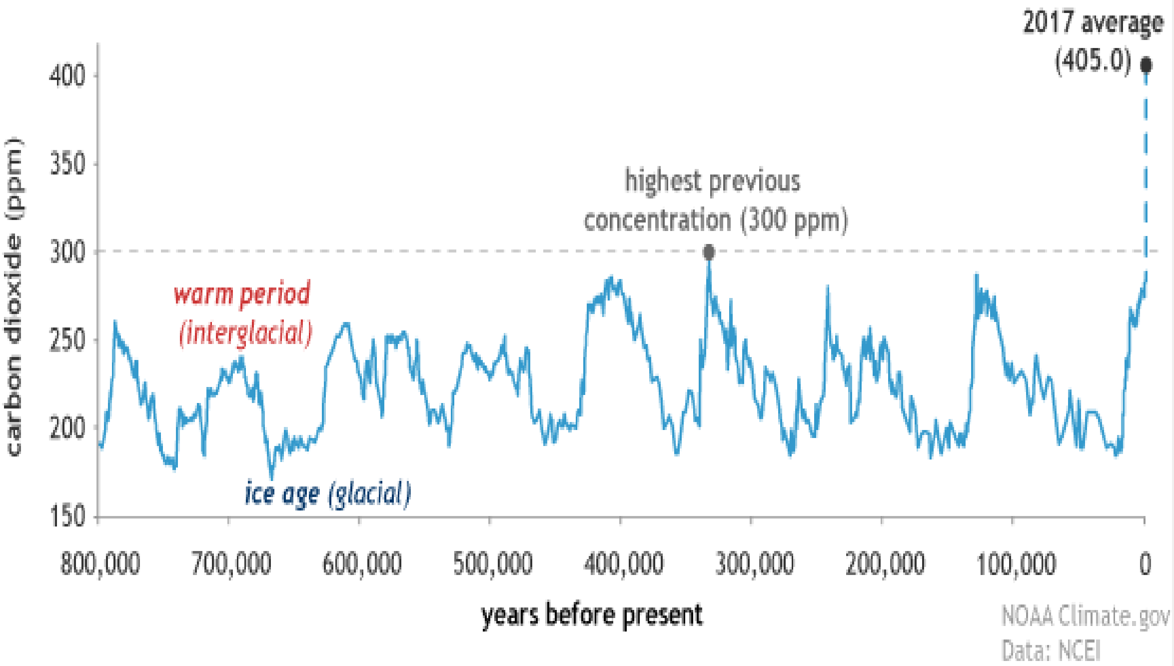
MEMBRANE TECHNOLOGY

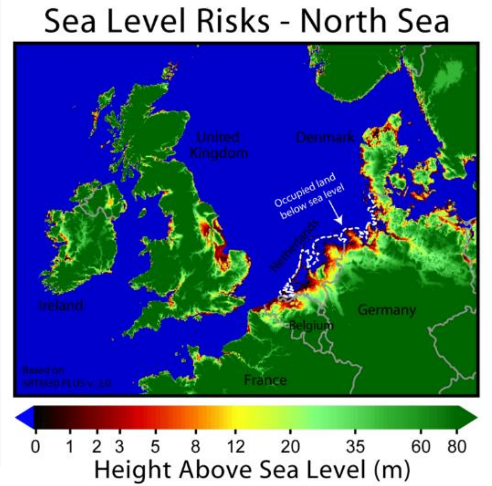
Polymeric / MMM

CMS

Pd-based

One of our challenges





TU/e

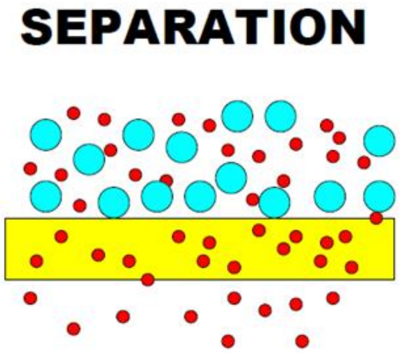
Solutions

1) Reduce the number of people;

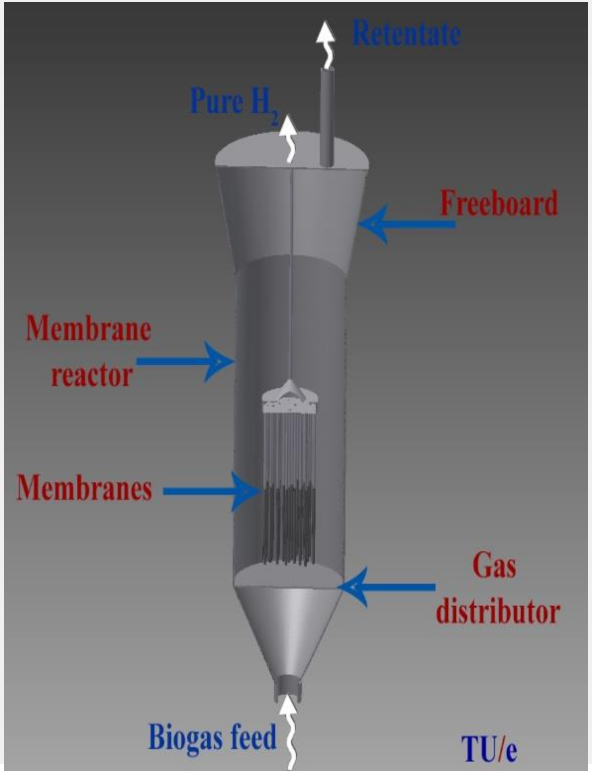
2) Reduce the fossil energy use (by use of renewables and improved efficiency)

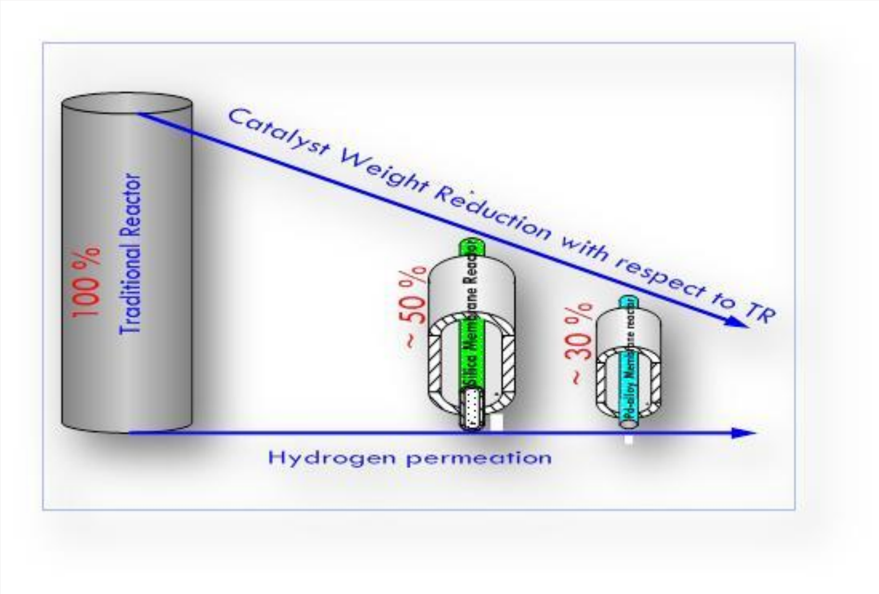
3) Capture the CO_2 (at the production point but also from the atmosphere)

Membrane functions



A membrane reactor

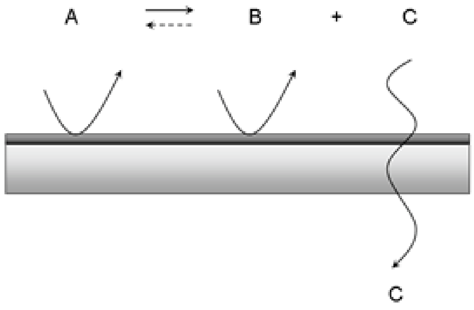


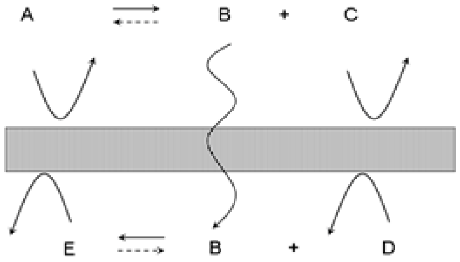


Brunetti A.; Caravella C.; Barbieri G.; Drioli E.; "Simulation study of water gas shift in a membrane reactor", *J. Membr. Sci.*, 2007, 306(1-2), 329-340

Why a membrane reactor?

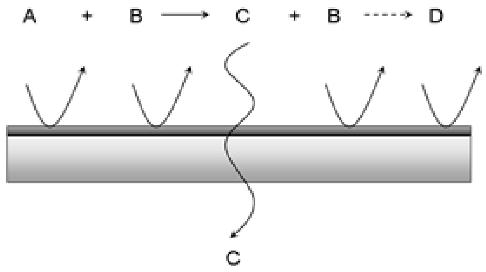
conversion enhancement by selective permeation of a reactant product of an equilibrium limited reaction

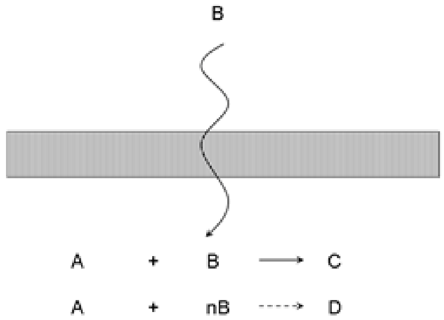




conversion enhancement by coupling of reactions

selectivity enhancement by selective permeation of an intermediate product



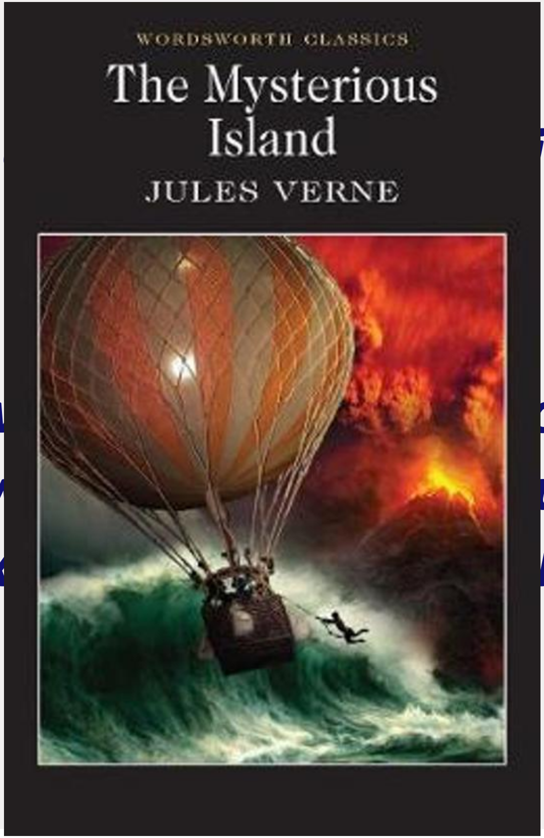


selectivity enhancement by dosing a reactant through the membrane

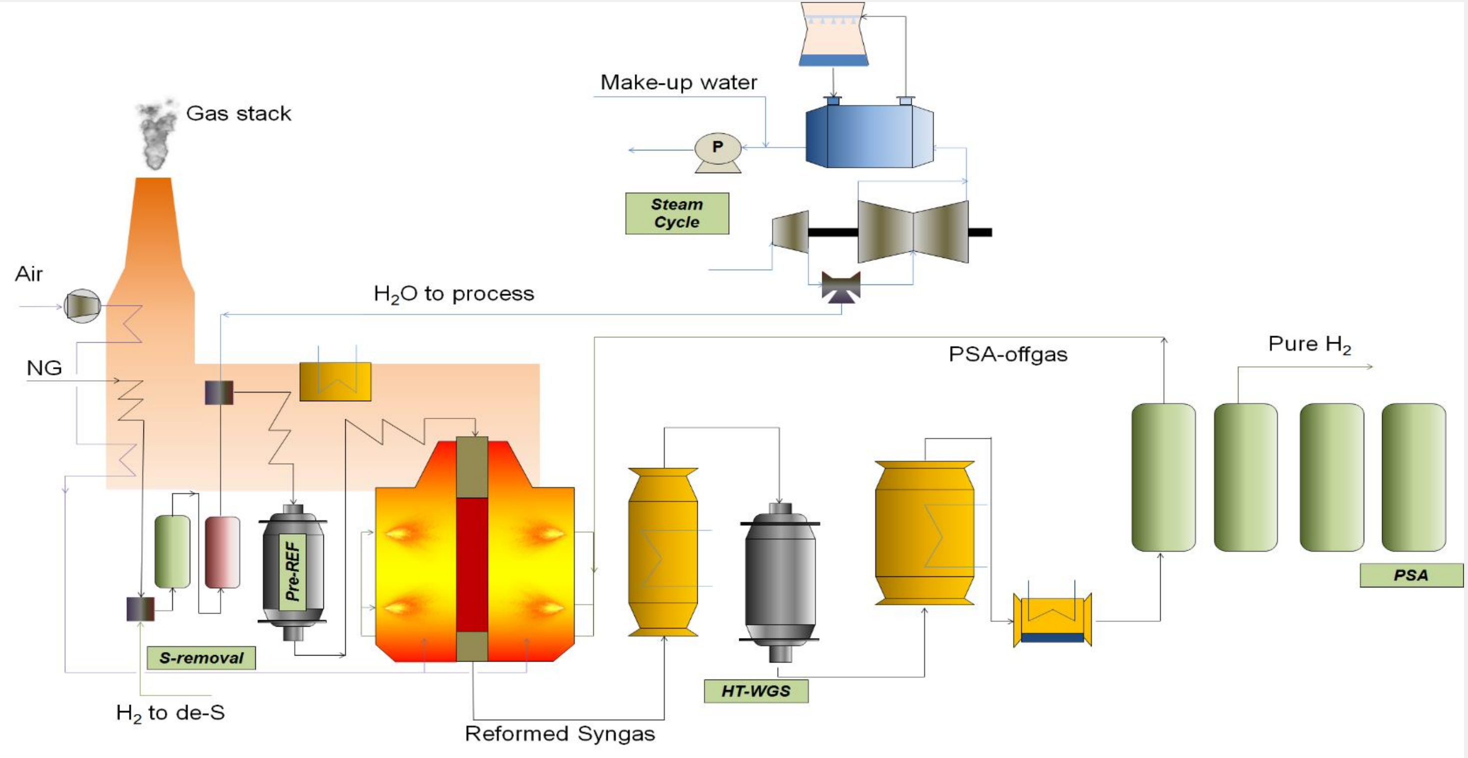
Examples

e two m ... ials

water w ... oyed
xygen v ... used
an inex ... heat

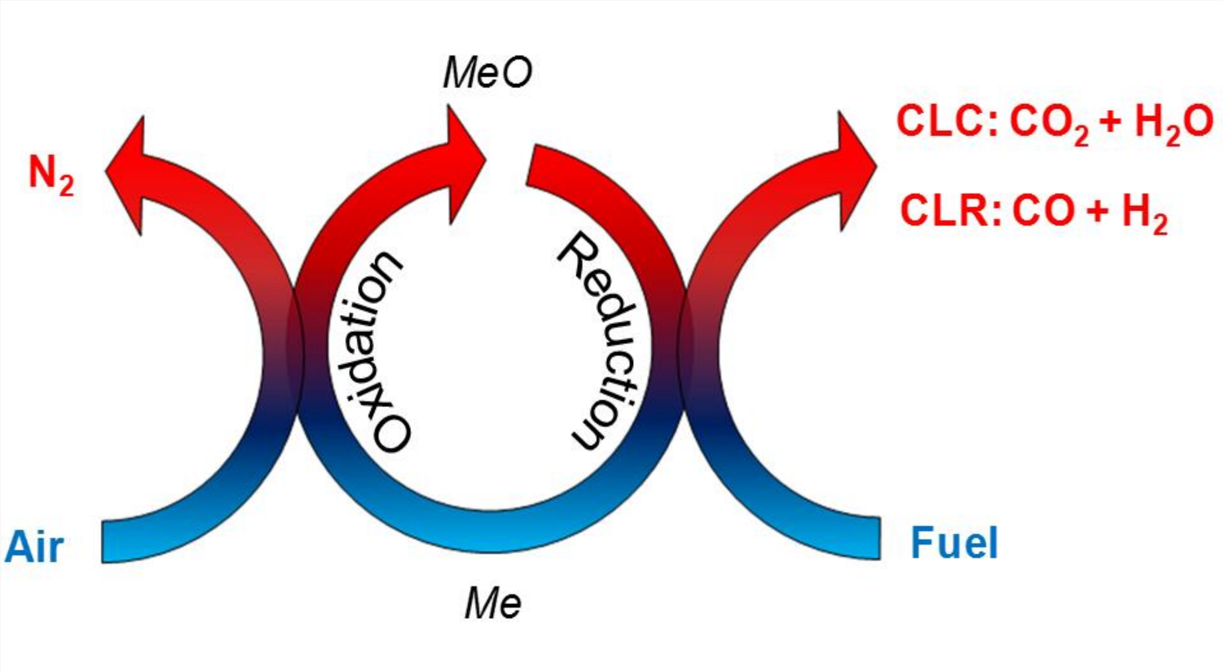


Hydrogen production



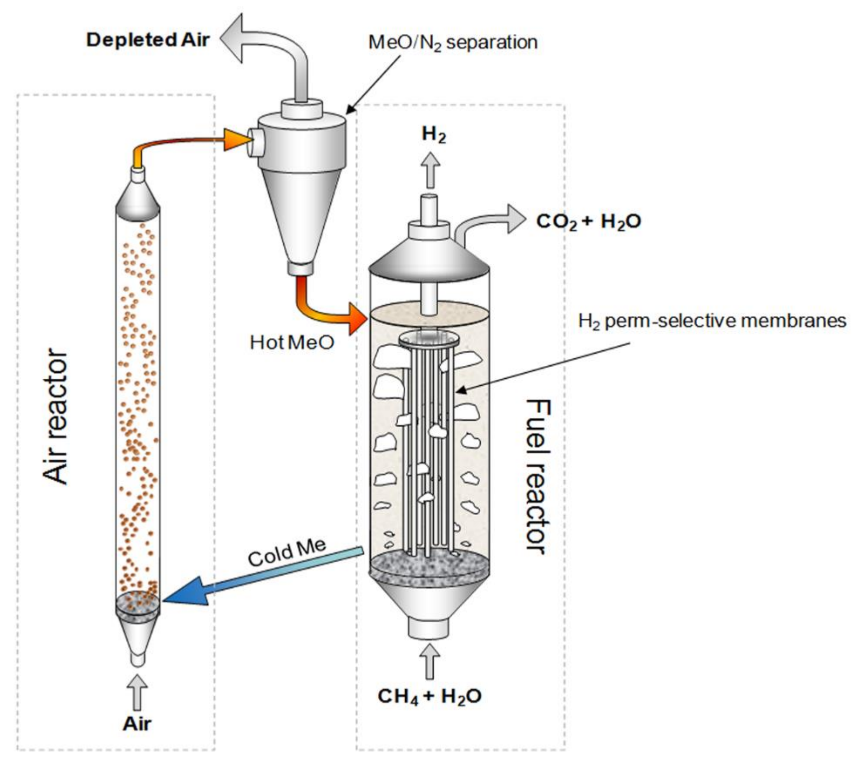
TU/e

Interesting technologies to improve reforming with CO_2 capture



TU/e

Integrate Membranes and CLC

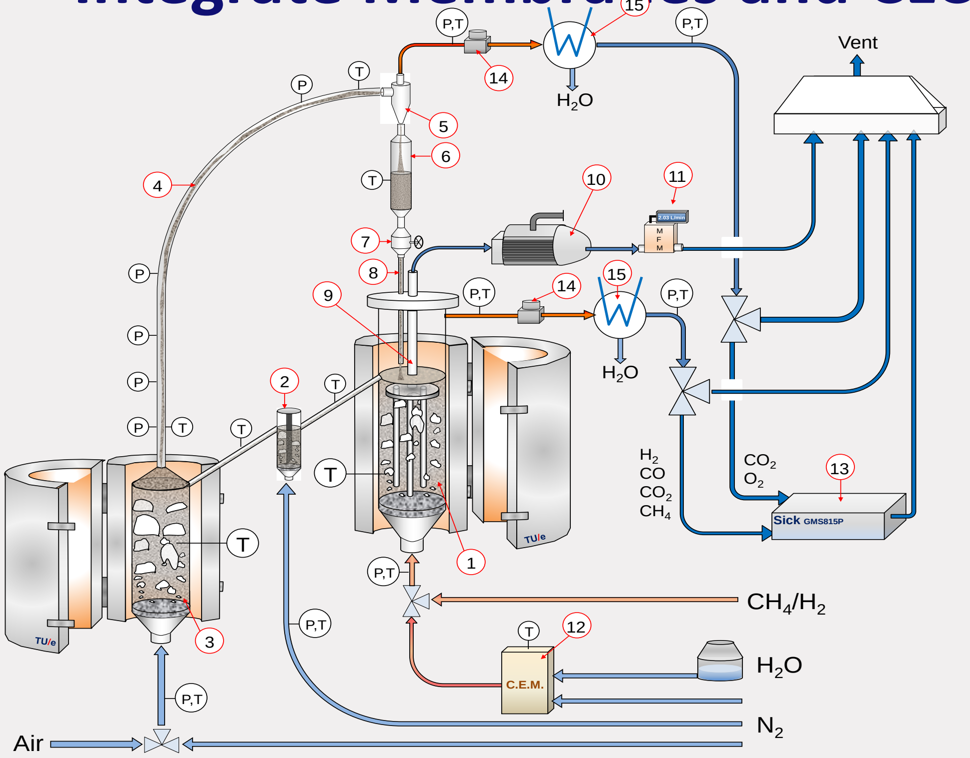


VIDI - 12365

2012 – TRL1

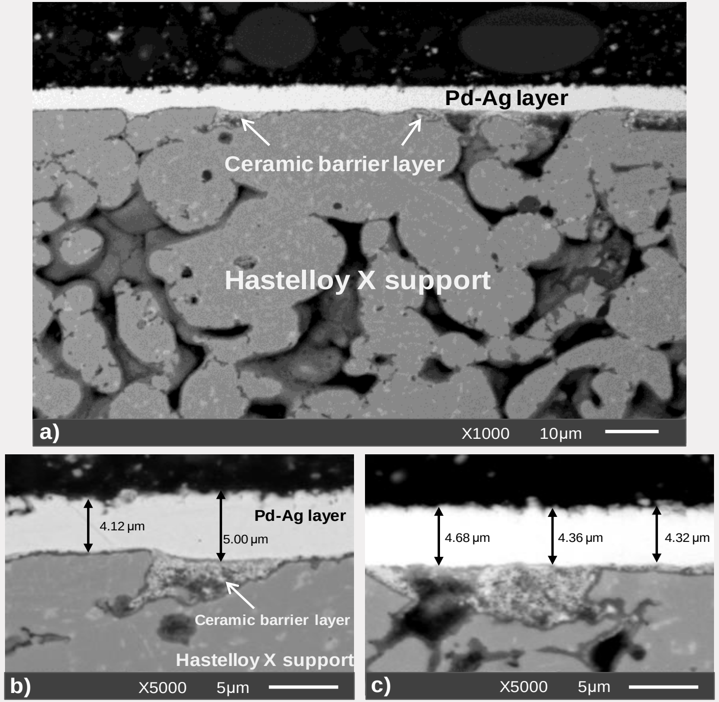
2017 – TRL4/5

Integrate Membranes and CLC

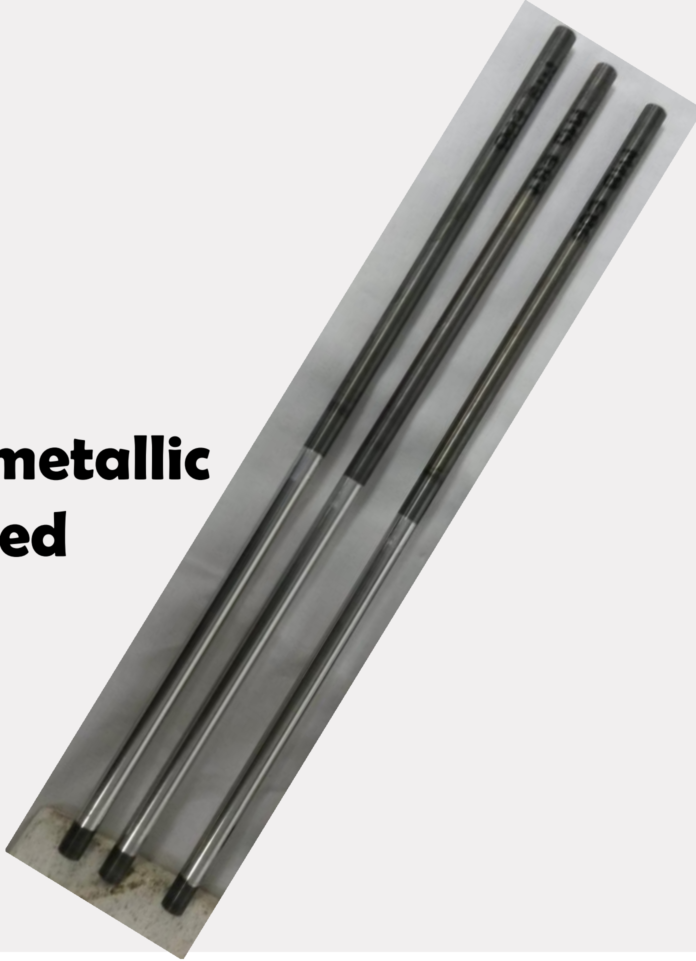


TU/e

Integrate Membranes and CLC

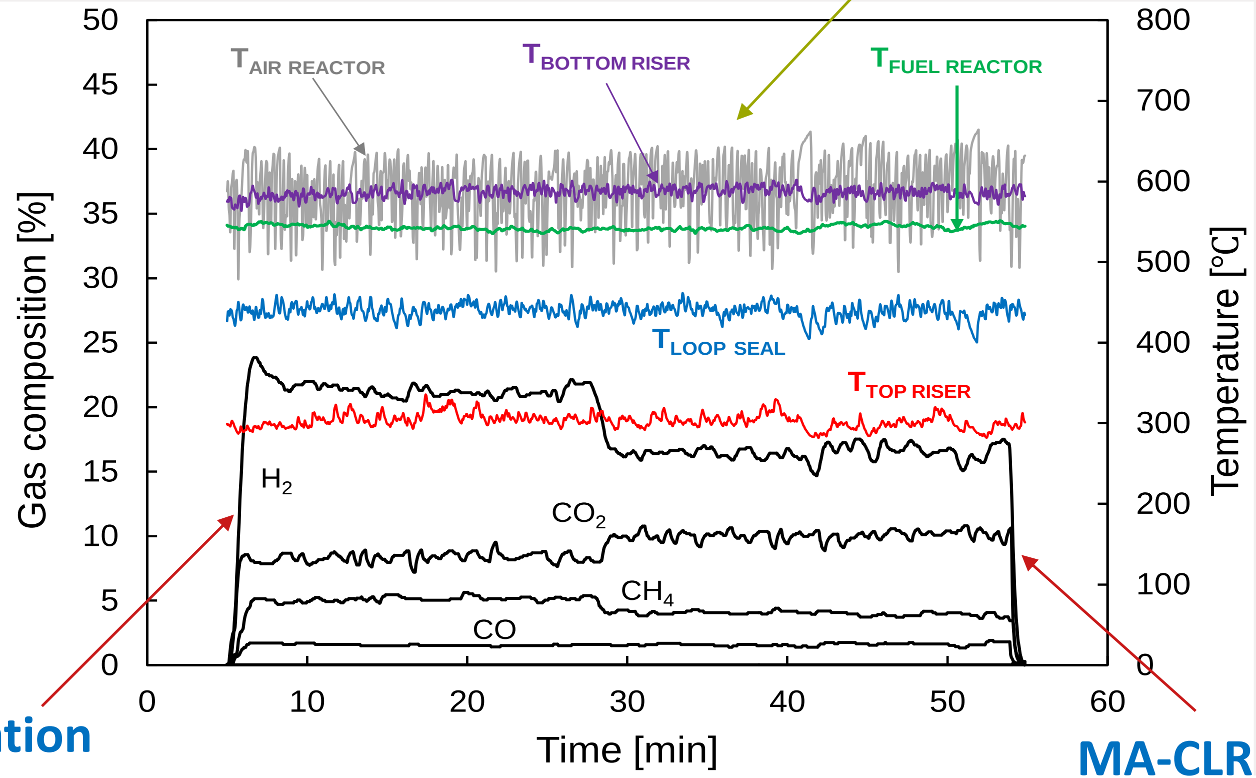


Pd-Ag metallic supported



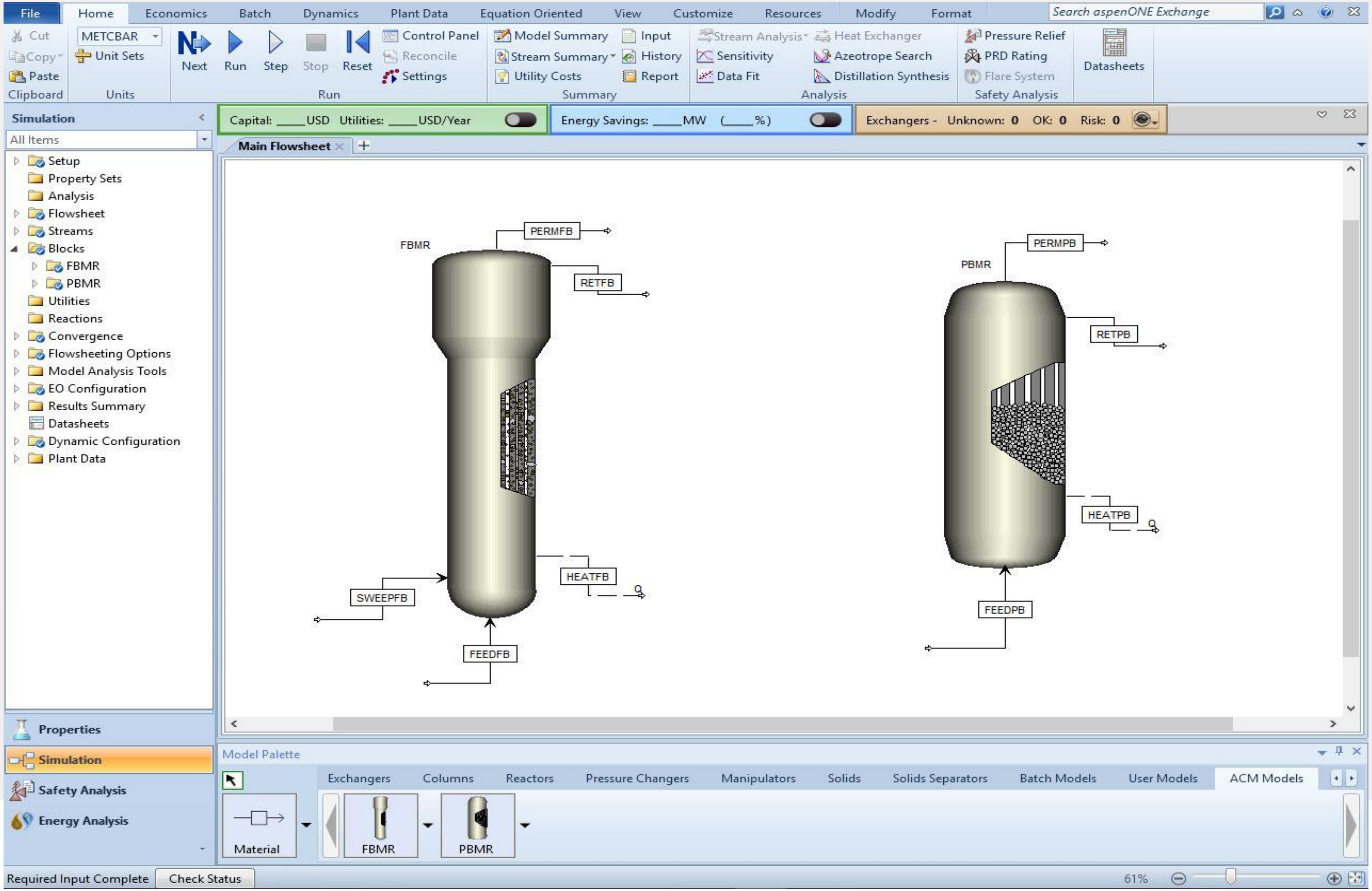
Integrate Membranes and CLC

Oscillations in temperature indicate solids movement



CLR configuration

MA-CLR configuration


File
Home
Economics
Batch
Dynamics
Plant Data
Equation Oriented
View
Customize
Resources
Modify
Format
Search aspenONE Exchange
Cut
Copy
Paste
Clipboard
METCBAR
Unit Sets
Units
Next
Run
Step
Stop
Reset
Control Panel
Reconcile
Settings
Run
Model Summary
Stream Summary
Utility Costs
Input
History
Report
Summary
Stream Analysis
Sensitivity
Data Fit
Heat Exchanger
Azeotrope Search
Distillation Synthesis
Analysis
Pressure Relief
PRD Rating
Flare System
Safety Analysis
Datasheets
Simulation
All Items
Setup
Property Sets
Analysis
Flowsheet
Streams
Blocks
FBMR
PBMR
Utilities
Reactions
Convergence
Flowsheeting Options
Model Analysis Tools
EO Configuration
Results Summary
Datasheets
Dynamic Configuration
Plant Data
Capital: ____USD Utilities: ____USD/Year
Energy Savings: ____MW (____%)
Exchangers - Unknown: 0 OK: 0 Risk: 0
Main Flowsheet
FBMR
PERMFB
RETFB
HEATFB
SWEEPFB
FEEDFB
PBMR
PERMPB
RETPB
HEATPB
FEEDPB
Properties
Simulation
Safety Analysis
Energy Analysis
Model Palette
Exchangers
Columns
Reactors
Pressure Changers
Manipulators
Solids
Solids Separators
Batch Models
User Models
ACM Models
Material
FBMR
PBMR
Required Input Complete
Check Status
61%

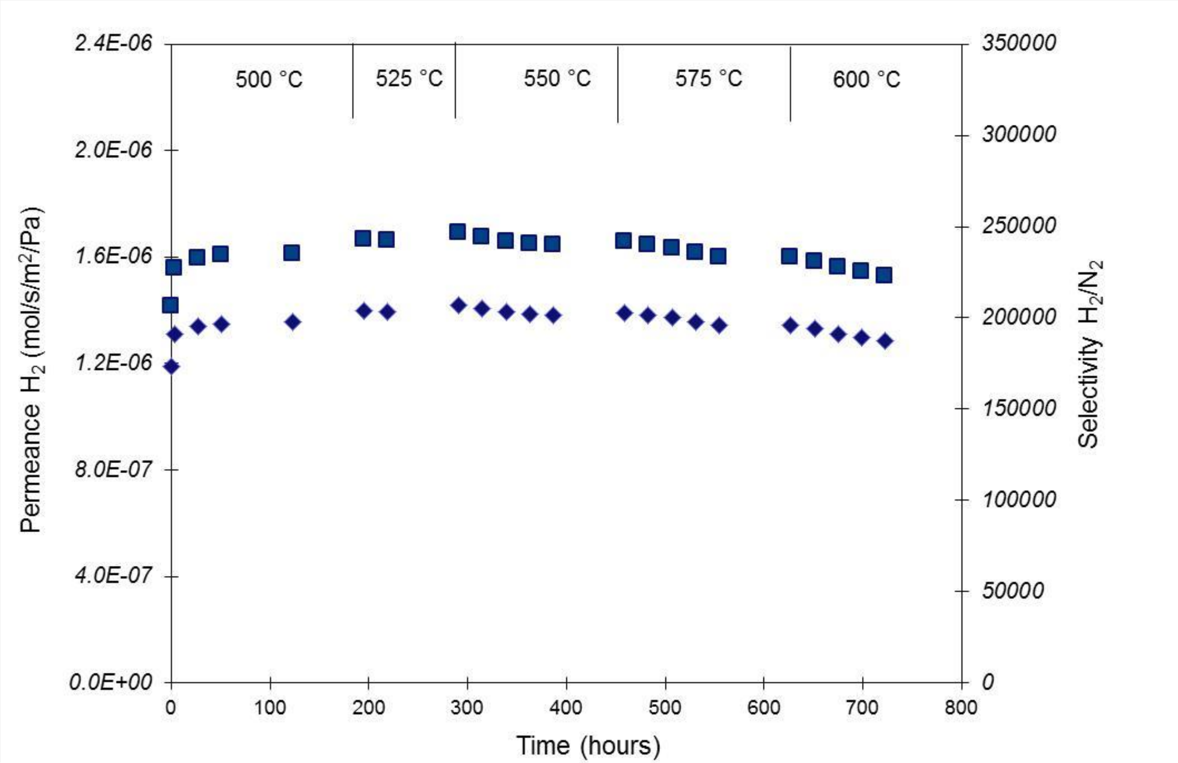
TU/e

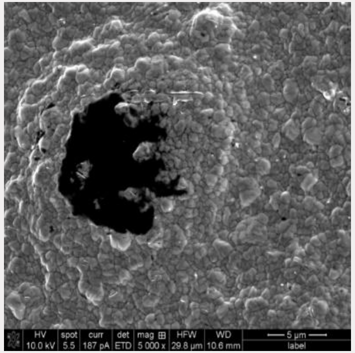
Is MA-CLR really interesting?

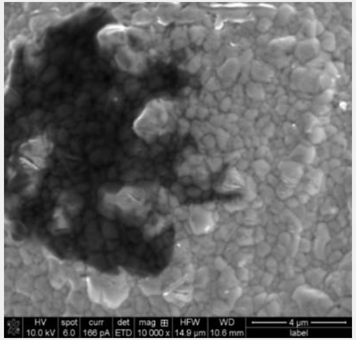
	Conventional NO CO_2 capture	Conventional WITH CO_2 capture	MA-CLR concept
Efficiency (%)	81	67	82
CO_2 avoided (%)	-	74	91
Cost of H_2 (€/m^3)	0.216	0.282	0.213

TU/e

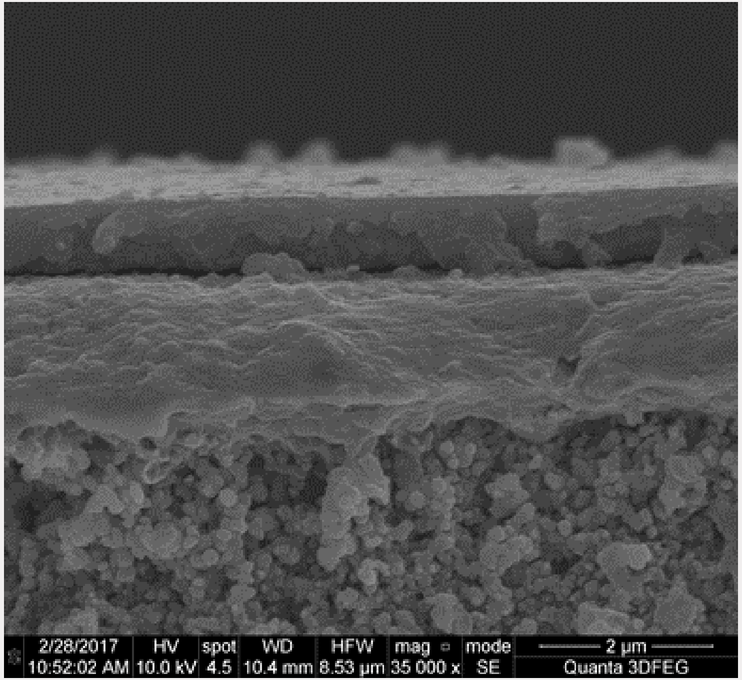
Challenges


500 °C
525 °C
550 °C
575 °C
600 °C
Permeance H_2 (mol/s/m^2/Pa)
Selectivity H_2/N_2
2.4E-06
2.0E-06
1.6E-06
1.2E-06
8.0E-07
4.0E-07
0.0E+00
350000
300000
250000
200000
150000
100000
50000
0
0
100
200
300
400
500
600
700
800
Time (hours)





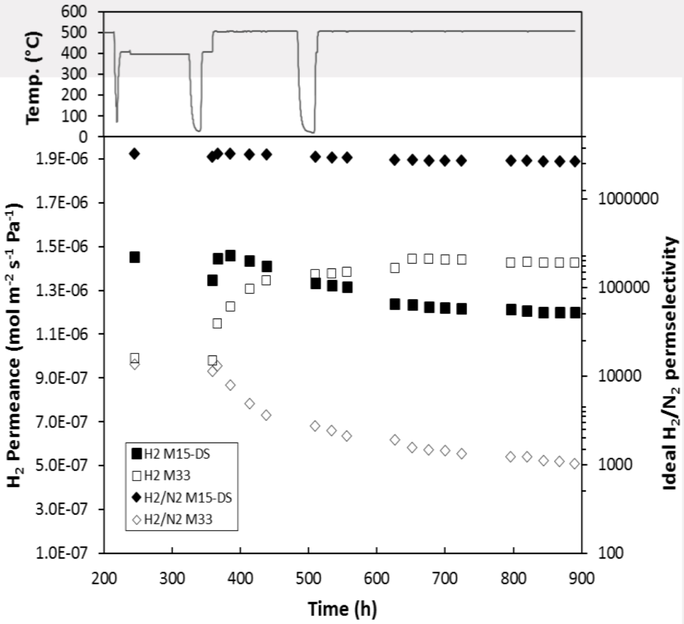
Challenges = Research questions



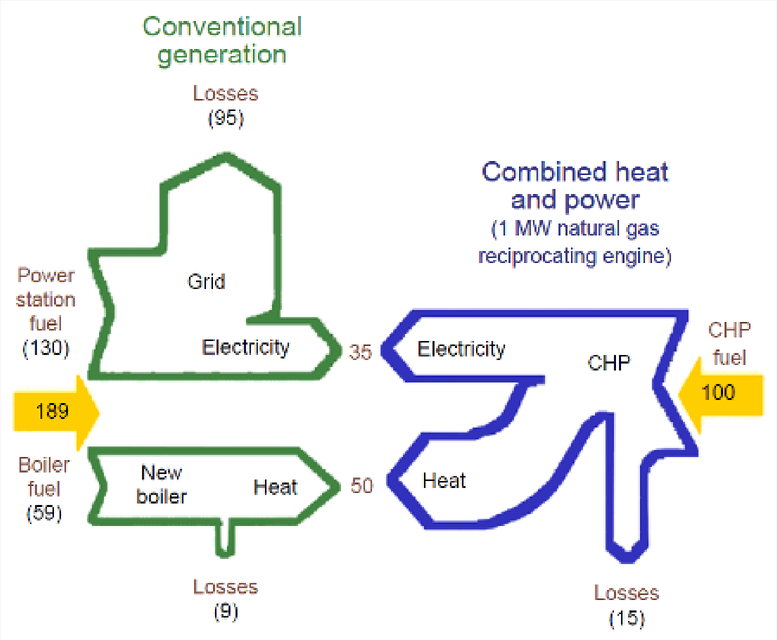
Protective layer

Selective layer

Asymmetric support



The next steps – extension to micro-CHP



The objective:

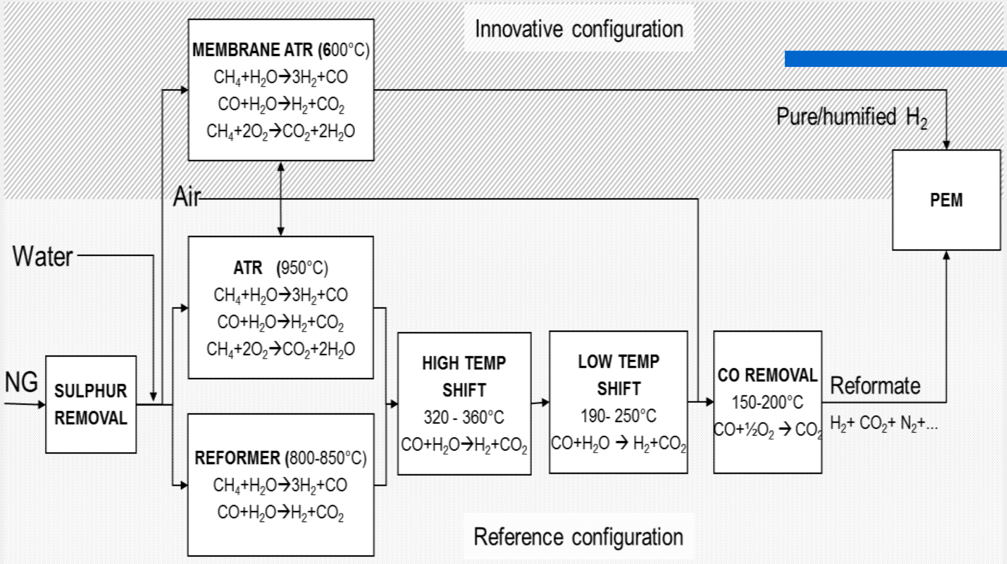
Advanced m-CHP systems

Advanced Multi-Fuel Reformer for Fuel CELL CHP Systems (ReforCELL - 278997)

A Flexible natural gas membrane Reformer for m-CHP applications (FERRET - 621181)

Advanced m-CHP fuel CELL system based on a novel bio-ethanol Fluidized bed membrane reformer (FluidCELL - 621196)

Applications



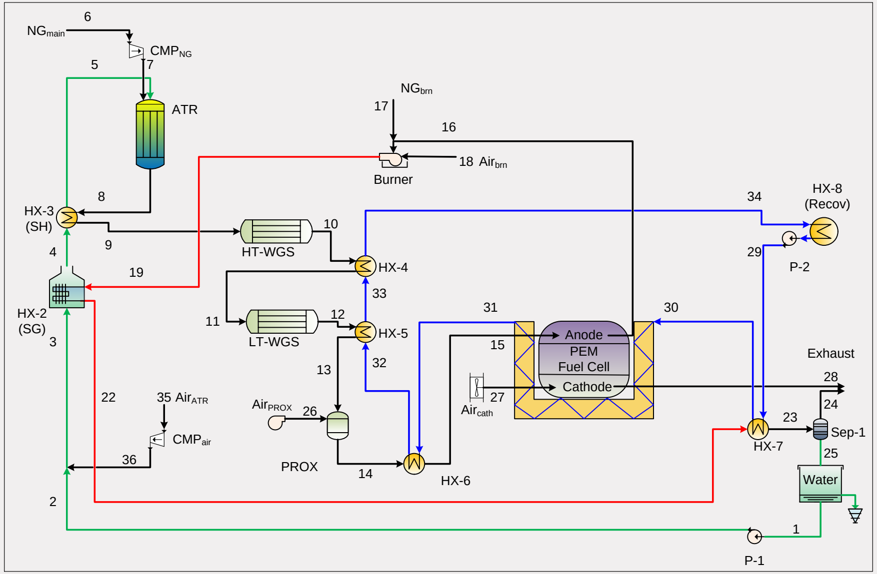
NG

Flexibility vs. NG composition

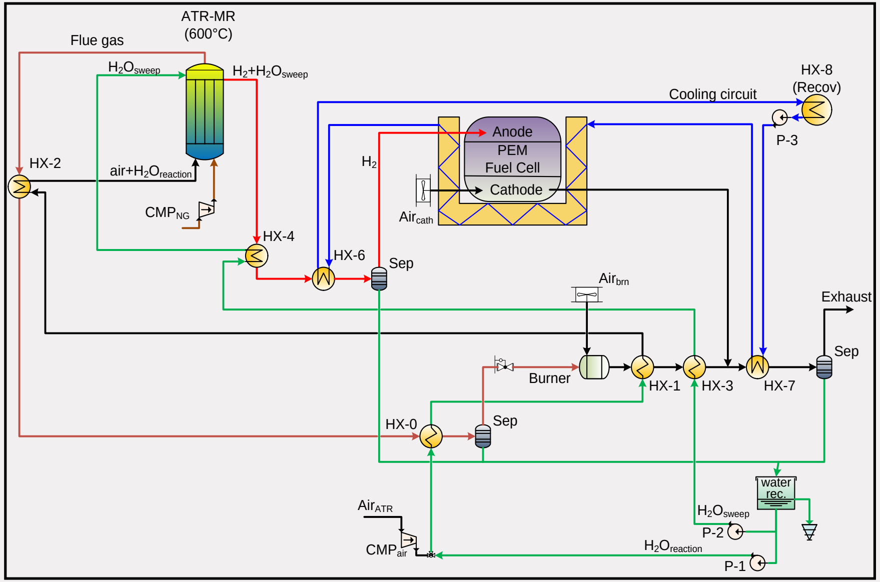
Ethanol

The Concept

PEM m-CHP unit



Conventional reforming for fuel processing



New concept with CMR for fuel processing

Conventional NG processing technology

CH_4 → **Steam Methane Reformer** (800-850°C) ← H_2O

$CH_4+H_2O \Leftrightarrow CO+3H_2 \quad (\Delta H>0)$

HT Water Gas Shift Reactor (300-400°C)

LT Water Gas Shift Reactor (200-250°C)

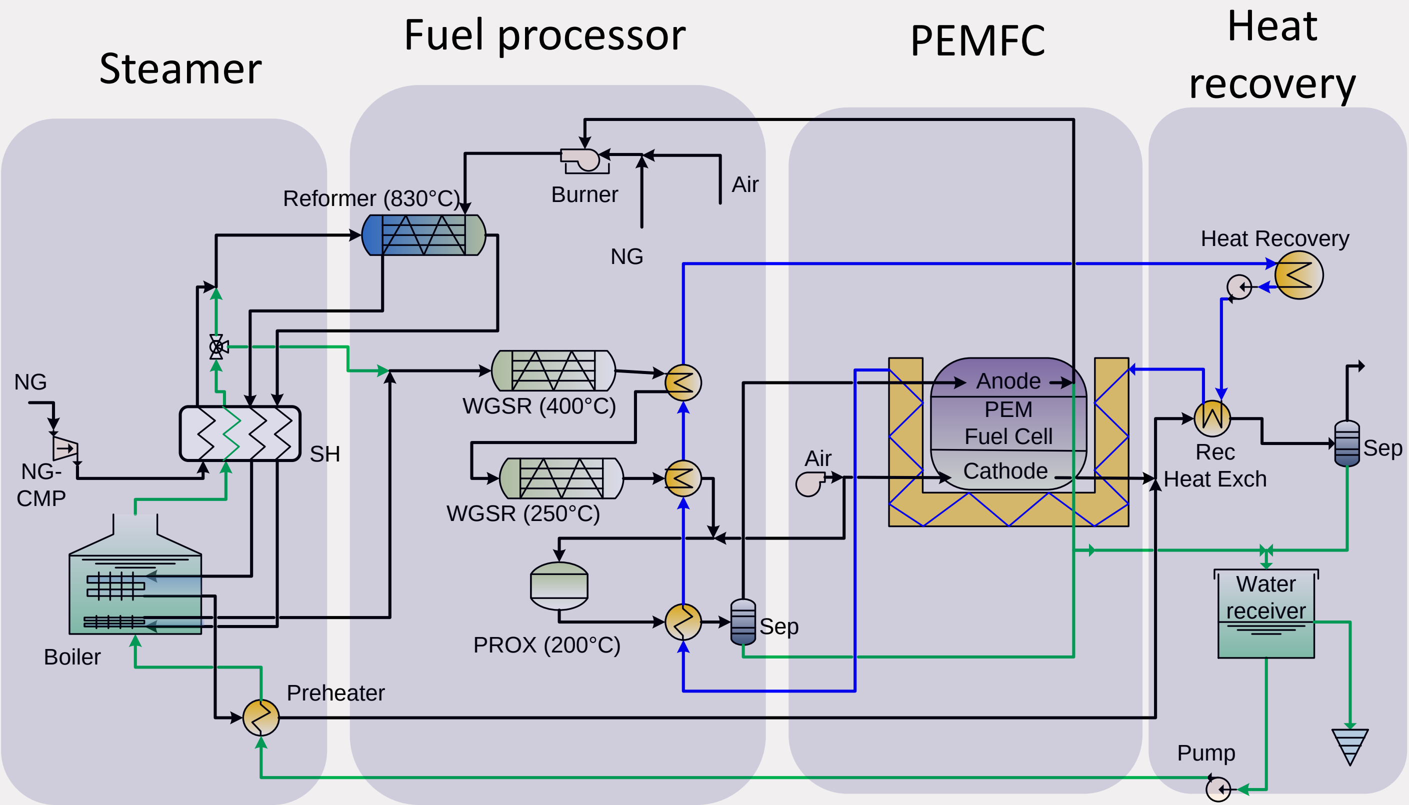
$CO+H_2O \Leftrightarrow CO_2+H_2 \quad (\Delta H<0)$

Preferential Oxidation (150-200°C) → **PEMFC**

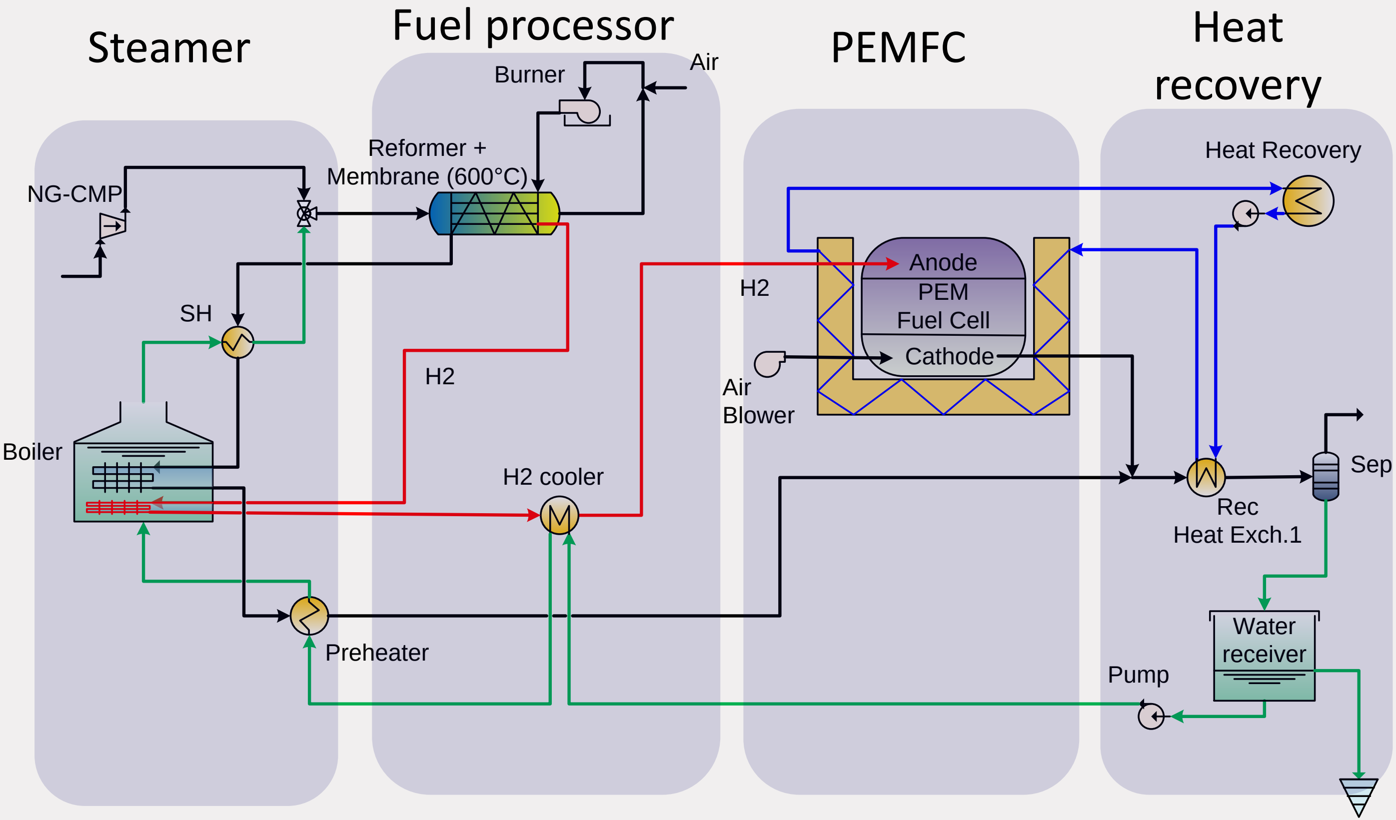
$CO+O_2 \rightarrow CO_2 \quad (\Delta H<0)$

- Diluted hydrogen to PEMFC
- Retentate stream to flow through anode
- 3 or 4 reacting stages

PEMFC mCHP system layout



Membrane reformer for NG processing



System performance

Simulation of system with Membrane Reactors:

η_{el} = up to 34%

$Fuel_U$=75%

Max reacting temp=830°C

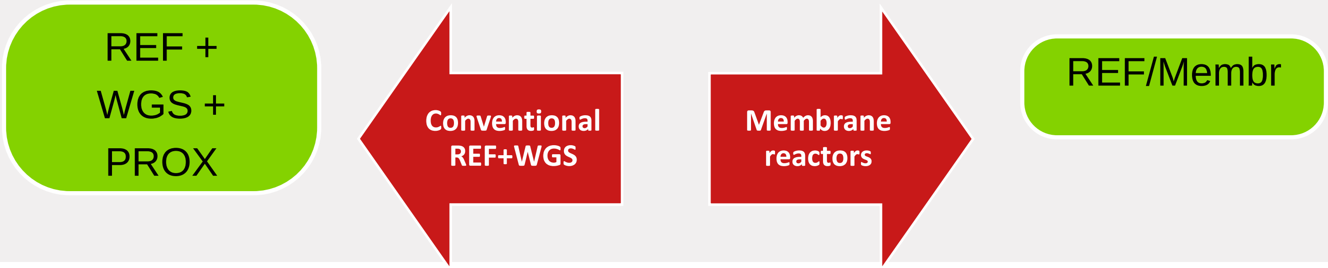
3-4 step processing

η_{el} = up to 43%

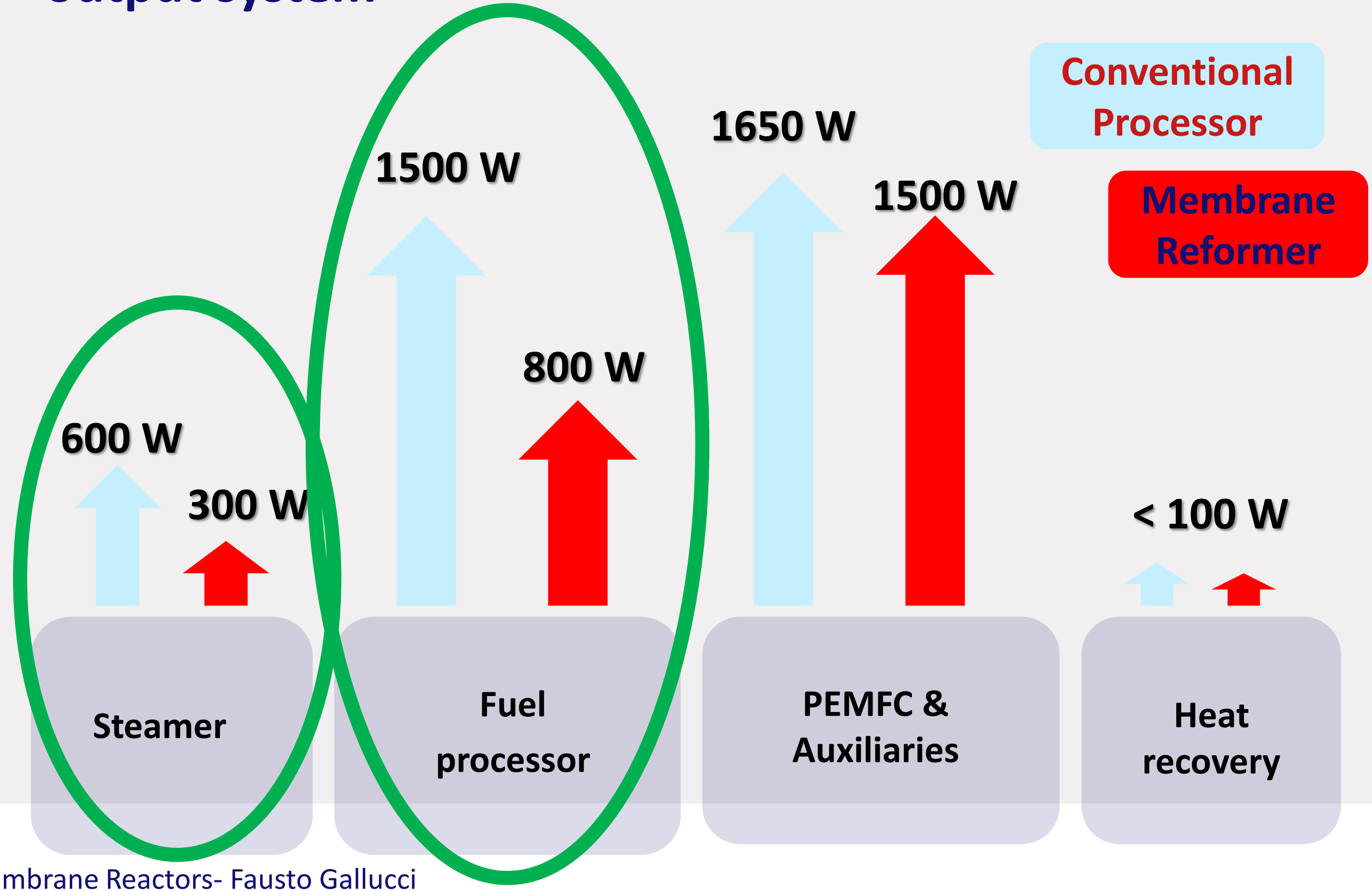
$Fuel_U$=100%

Max reacting temp=600°C

1 step processing for REF/membr



Exergy loss analysis on 2kW electric output system

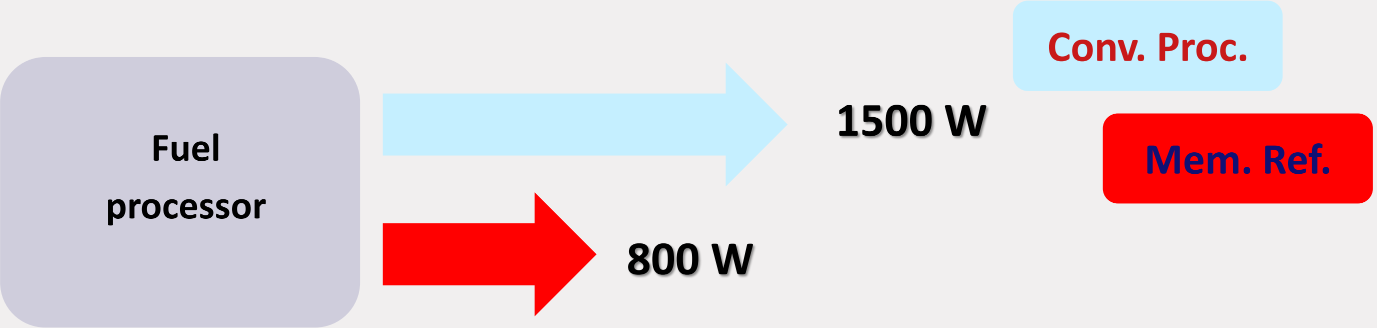


Exergy loss analysis on 2kW electric output system

Higher Exergy loss with conventional processing scheme:

- ≈ 2/3 more water to evaporate
  - Steam reinsertion to WGSR’s
- Higher ΔT
  - Conventional reformer at 830°C.
  - Membrane reformer at 600°C

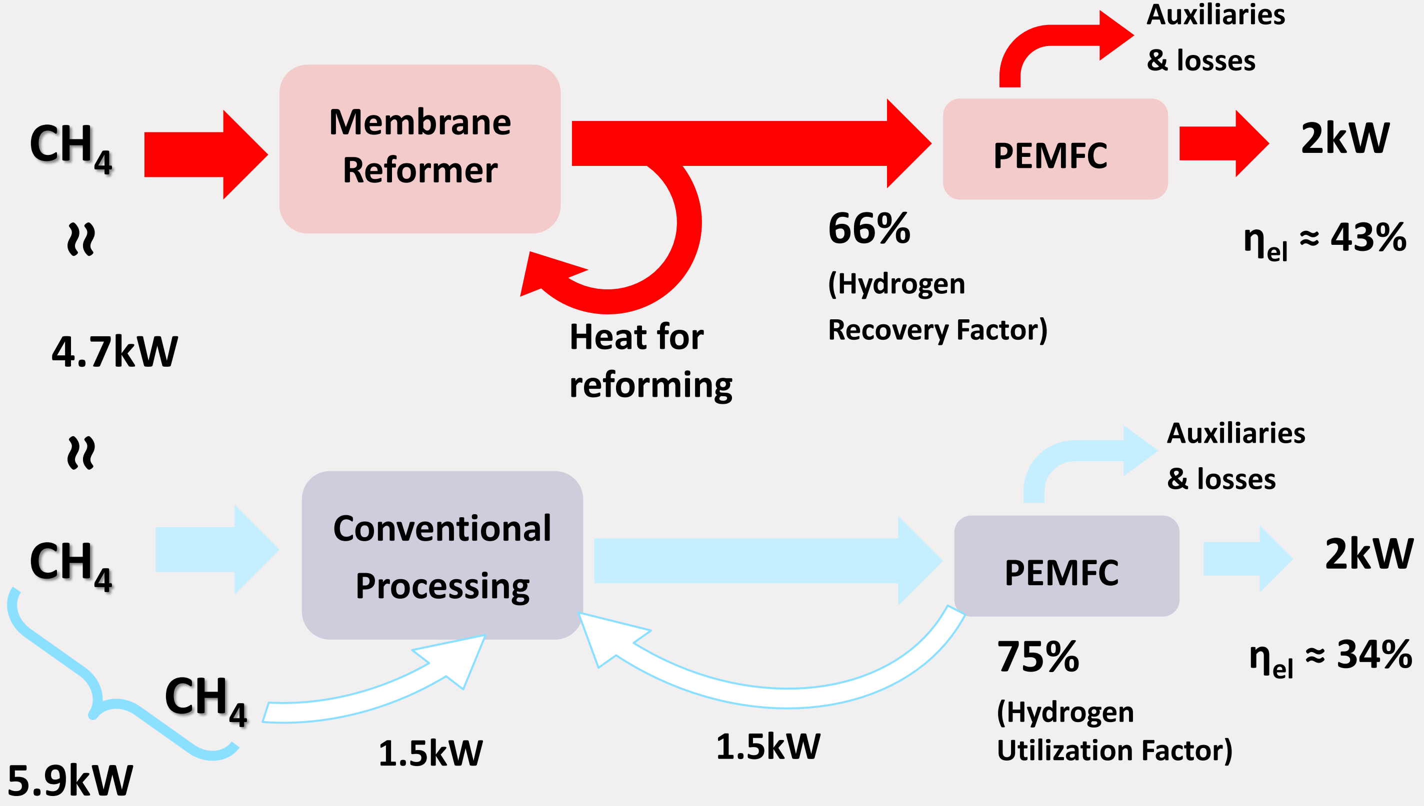
Exergy loss analysis on 2kW electric output system



Higher Exergy loss with conventional processing scheme:

- 4 reacting stages instead of 1
- Complete CH_4 conversion at reforming stage
- Higher ΔT
  - Conventional reformer at 830°C.
  - Membrane reformer at 600°C

Energy balance on 2kW electric output system



STEPS TAKEN TILL NOW

2010
SINGLE MEMBRANE TUBE
10CM LONG

2012
MULTI TUBE MEMBRANE
15CM LONG

2014
MULTI TUBE MEMBRANE
15CM LONG
Fluid bed
<10 ppm CO

2016
MEMBRANE
25CM LONG
Fluid bed
ethanol

2018
MEMBRANE
50CM LONG
Fluid bed
>65% recovery
Biogas reforming
>99.8% purity

Design and construction
$2 m^3/h$ prototype

2019
Design and construction
$20 m^3/h$ prototype

11 EU projects
Several Spanish and Dutch projects

STEPS TAKEN TILL NOW

2010

2012

2014

2016

2018

EINDHOVEN UNIVERSITY OF TECHNOLOGY

2.6. Process design for CO2 capture (Vittoria Cosentino – KT & Leonardo Roses – HYGEAR))

Processes for CO_2 Carbon Capture

1st Workshop MEMBER Project
TU/e, 15-01-2020

Emma Palo
Lorena Mosca
Vittoria Cosentino
Robert Makkus
Leonardo Roses

Contact: v.cosentino@kt-met.it, leonardo.roses@hygear.com

Outline

- Introduction on CO_2 emissions
- Processes for CO_2 Capture
  - State of the art
- MEMBER Objectives
  - Novel membrane based technologies
  - Techno-economic targets
- MEMBER solutions
  - Pre-combustion CO_2 Capture (Prototype A)
  - Post-combustion CO_2 Capture (Prototype B)
  - Hydrogen production with integrated CO_2 capture (Prototype C)
- Conclusions and Future Perspectives

Introduction on CO_2 emissions

- CO_2 emissions from fossil materials contribute for ~ 60% to global warming [2]

- CO_2 is the undesired by-product of Hydrocarbon Conversion Processes and the product of Combustion in Power Production, Building Heating, Transportation, etc.

PROCESS	CO_2 emissions 10^6 metric ton / year[1]	% on the Total
Power production	10,539	78.8 ~80%
Cement production	932	7.0
Refineries	798	6.0
Iron and steel industry	646	4.8
Petrochemical industry	379	2.8
Oil and gas processing	50	0.4
Other sources	33	0.2

~20%

[1] IPCC reports 2018
[2] https://ec.europa.eu/clima/change/causes_it

Processes for CO_2 Capture

State of the art (1/3)

- CO_2 capture aims to limit CO_2 release and consequent accumulation in the atmosphere through its removal upstream

- A few technologies can separate CO_2 from gaseous streams up to an efficiency defined as Carbon Capture Rate (CCR), with different performance advantages and disadvantages[3]

ABSORPTION (chemical/physical)

ADVANTAGES
- High CCR >90%
- Regenerable sorbents
- Most Mature Technology

DISADVANTAGES
- High energy penalty
- Efficiency depends on CO vol.%
- Environmental impact by solvent

ADSORPTION

ADVANTAGES
- CCR >85%
- Reversible process

DISADVANTAGES
- HT sorbents under dev.
- Energy for HT CO_2 desorption

MEMBRANES SEPARATION

ADVANTAGES
- CCR >80%
- Simple process, few devices

DISADVANTAGES
- High pressure or CO_2 vol %
- Operational problems (fouling)

CRYOGENIC DISTILLATION

ADVANTAGES
- Mature technology

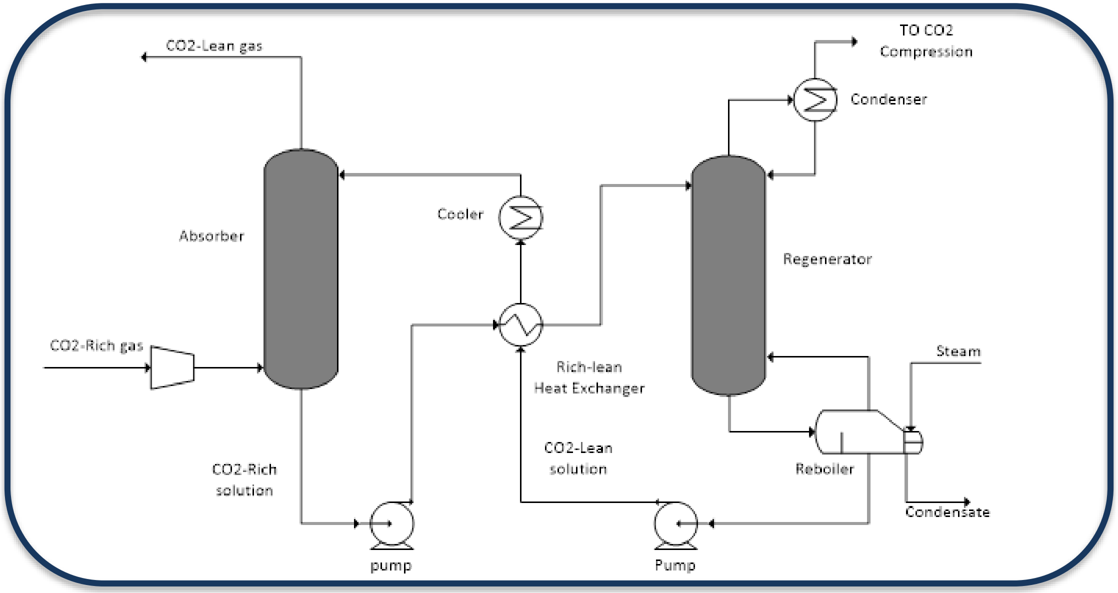
DISADVANTAGES
- Only for high CO_2 %vol (>90%)
- Very high energy intensity

[3] D.Y.C Leung & others, An overview of current status of carbon dioxide capture and storage tecnologies, Ren and Sust. En.Reviews Aug.2014

Processes for CO_2 Capture

State of the art (2/3)

- The absorption/regeneration process (both chemical and physical) is by far the most widespread technology for CO_2 separation from gaseous streams.
- It is applied in many industrial units such as ammonia production and gas processing and in some existing CCS applications (mainly aimed at EOR).
- This technology has been considered as a benchmark for the MEMBER project [4].



Typical flowsheet of a basic chemical absorption process for CO_2 capture

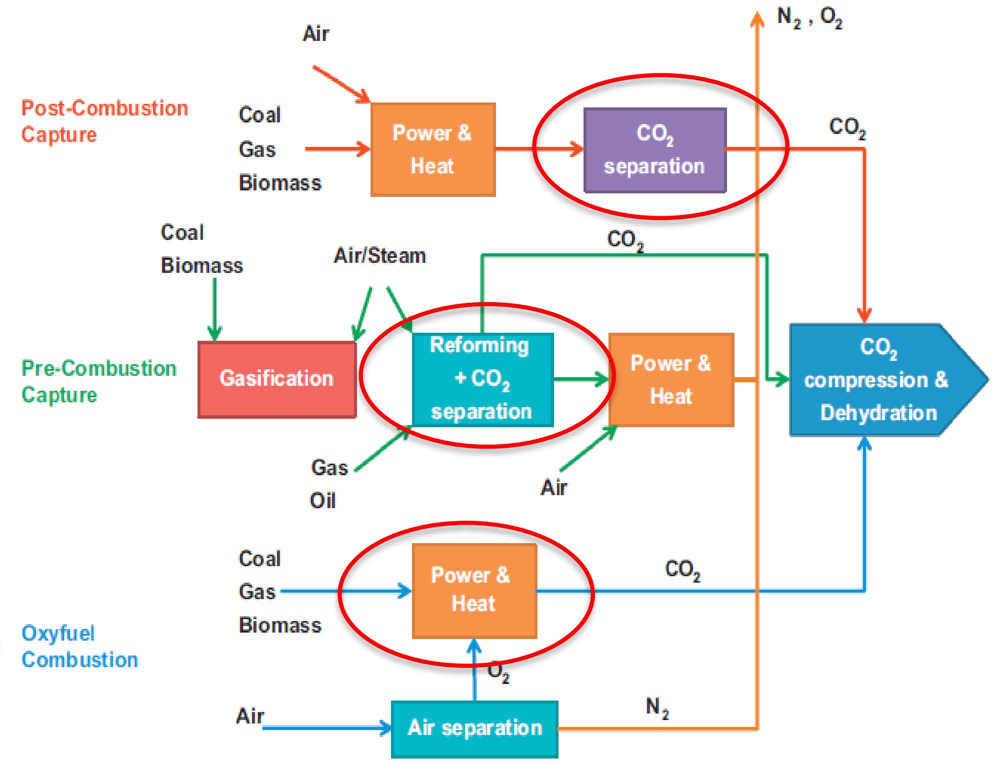
[4] D2.2 Industrial Requirements MEMBER-WP02-D22-DLR-KT-19-07-2018-v13

Processes for CO_2 Capture

State of the art (3/3)

- In combustion processes CO_2 can be captured via three different routes[5]:

  - Post-Combustion
  - Pre-Combustion
  - Oxyfuel-Combustion

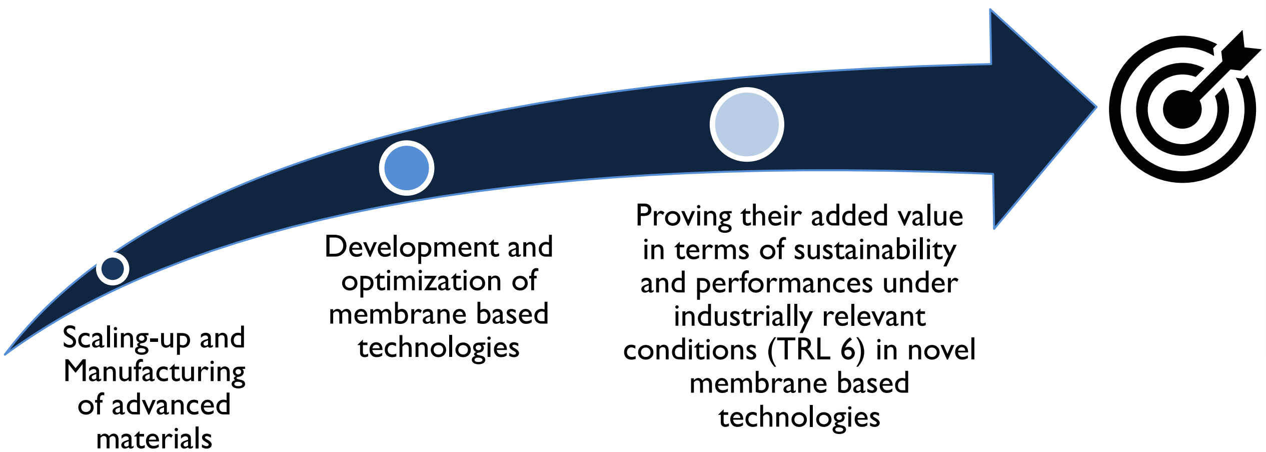


[5] F.Gallucci, E.Fernandez, P.Corengia, M. van Sint Annaland, Chem.Eng.Sc. 92 (2013)

MEMBER Objectives

Novel membrane based technologies (1/3)

- The main objective of the MEMBER project is the scale-up and manufacturing of advanced materials and technologies, aimed to reduce the cost of CO_2 capture.



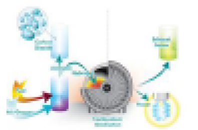
Outperforming current technologies for pre- and post-combustion CO_2 capture in power plants as well as H_2 generation with integrated CO_2 capture and meet the targets of the European SET plan.

- Each solution is going to be demonstrated through the operation and test of a prototype.
- Scale-up issues are addressed during the project and a Business Plan is prepared for the industrial application of each technology.

MEMBER Objectives

Novel membrane based technologies (2/3)

- Case studies and strategies:


Pre-Combustion

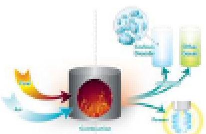
Pre-Combustion CO_2 capture in Power production

A combination of Mixed Matrix Membranes (MMM) for H_2/CO_2 separation

PROT A

MOFs


Polymers


Post-Combustion

Post-Combustion CO_2 capture in Power production

A combination of Mixed Matrix Membranes (MMM) for CO_2/N_2 separation

PROT B


Mixed Matrix Hollow Fibers

Hydrogen production integrated with CO_2 capture

A combination of metallic membranes, catalyst and sorbents into an advanced Membrane Assisted Sorption Enhanced Reforming (MA-SER) process

PROT C

Sorbents


Metallic membranes


Catalyst

Total cost of CO_2 capture

MEMBER Objectives

Novel membrane based technologies (3/3)

Targets

Prototype A

Pre-combustion capture in power plants using MMMs at the 2 MWth biomass gasifier of CENER (Spain) aimed for BIOCCS demonstration.

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

KT Kinetics Technology

MEMBER Objectives

Techno-economic targets (1/2)

- Reference and Target Performance and Cost for the MEMBER processes[4]

	Reference Technology	Reference CCR [%]	Reference Cost of CO_2 [€/ton]	MEMBER Targets for CCR [%]	MEMBER Targets for Cost of CO_2 [€/ton]
Pre-comb. Power (IGCC)	Absorption by SELEXOL	90.9	33.0	90	< 30
Post-comb. Power (Coal)	MEA absorption	88.1	54.3	90	< 40
Hydrogen via SMR (NG) +CO_2 pre-comb. capture	MDEA absorption	56	47.1	90	< 30
Hydrogen via SMR (NG) +CO_2 post-comb.capture	MDEA absorption	90	69.8	90	< 30

[4] D2.2 Industrial Requirements MEMBER-WP02-D22-DLR-KT-19-07-2018-v13

MEMBER Objectives

Techno-economic targets (2/2)

- Minimum CO_2 purity requirements per application[4].
- The target CO_2 purity of MEMBER technologies is 95%.

Application	Min. purity (%v/v)
Enhanced oil recovery (EOR)	90[6]
Food	99.9[7]
Beverages	99.9[8]
Refrigerants	99.9[9]
Industrial	99.5[10]
Storage	95[11]

[6] European Best Practice Guidelines EBTF-D4.9 CAESAR EU/FP7 (2011)
[7] Carbon Dioxide liquid foograde E290, Linde Gas Benelux
[8] ISBT carbon Dioxide Guidelines. Int. Soc. of Beverage Technologist (1999)
[9] AHRI Standard Specifications for Refrigerants (206)
[10] J.Pringle, Why the grade of CO2 is important, 2015
[11] Eickhoff, Brown, Neele, Energy Procedia 114 (2017) 6698

MEMBER solutions

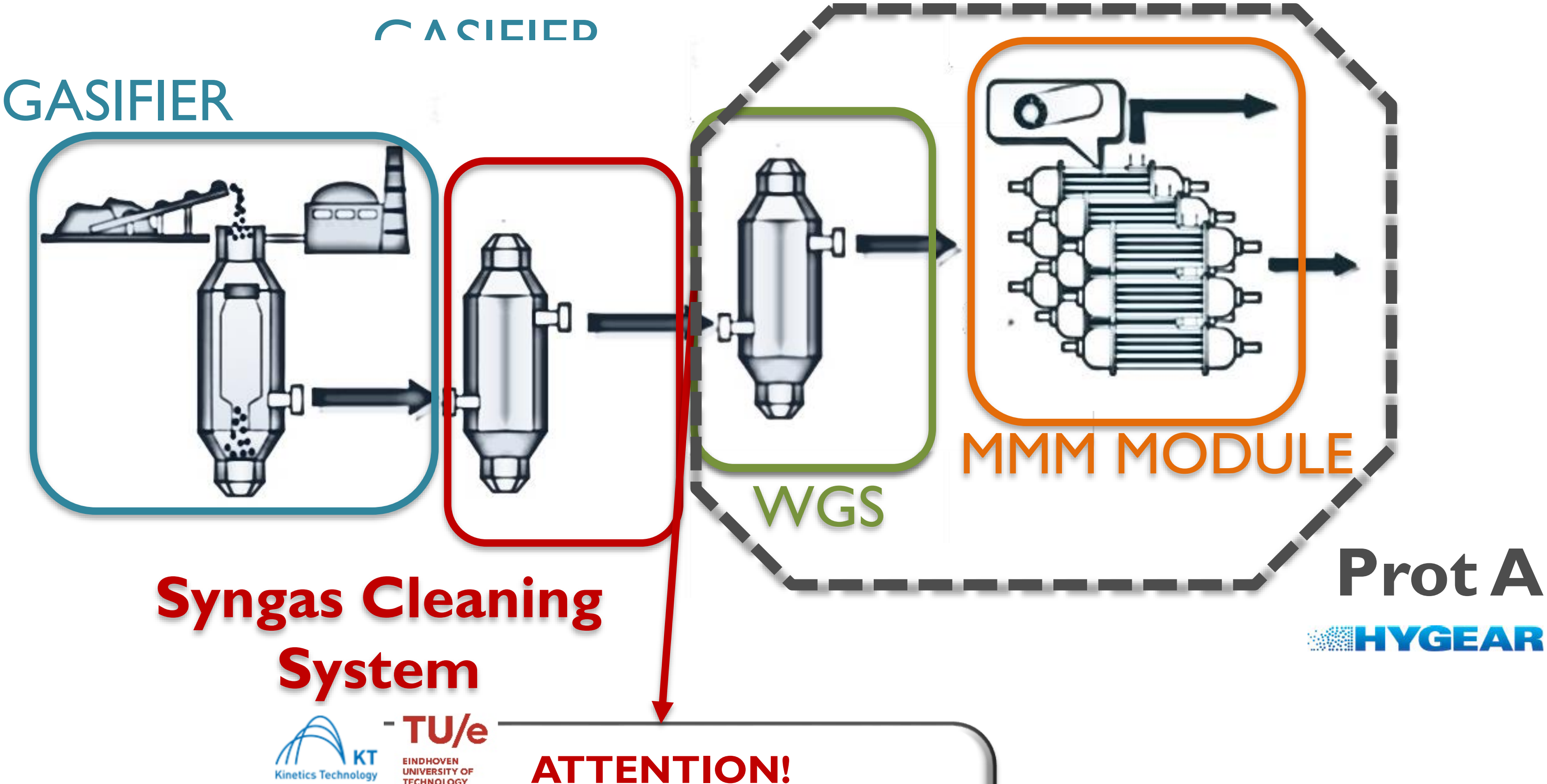
Prototype A (1/6)

➤ Demo Site: CENER - Centro National de Energías Renowables - Spain

- Semi-industrial pilot scale test facility able to develop 2nd generation biofuel production processes based on raw materials and the application of biorefinery concepts.
- The gasification unit is a pilot plant with a nominal power of 2 MWth capable of generating a fuel gas suitable for the following cleaning and synthesis processes of 2nd generation biofuels.
- This unit is designed to work with a wide range of biomass and a wide range of bed materials and additives.
- The gasification unit is based on the technology of atmospheric bubbling fluidized bed (ABFB) working at temperatures between 650-1000 °C and with two operating modes: using air as gasifying agent or using steam/oxygen as gasifying agent.

MEMBER solutions

Prototype A (2/6)



ATTENTION!

Process gas from Gasifier is not cleaned in this case. It must be purified before being fed to Prototype A

MEMBER solutions

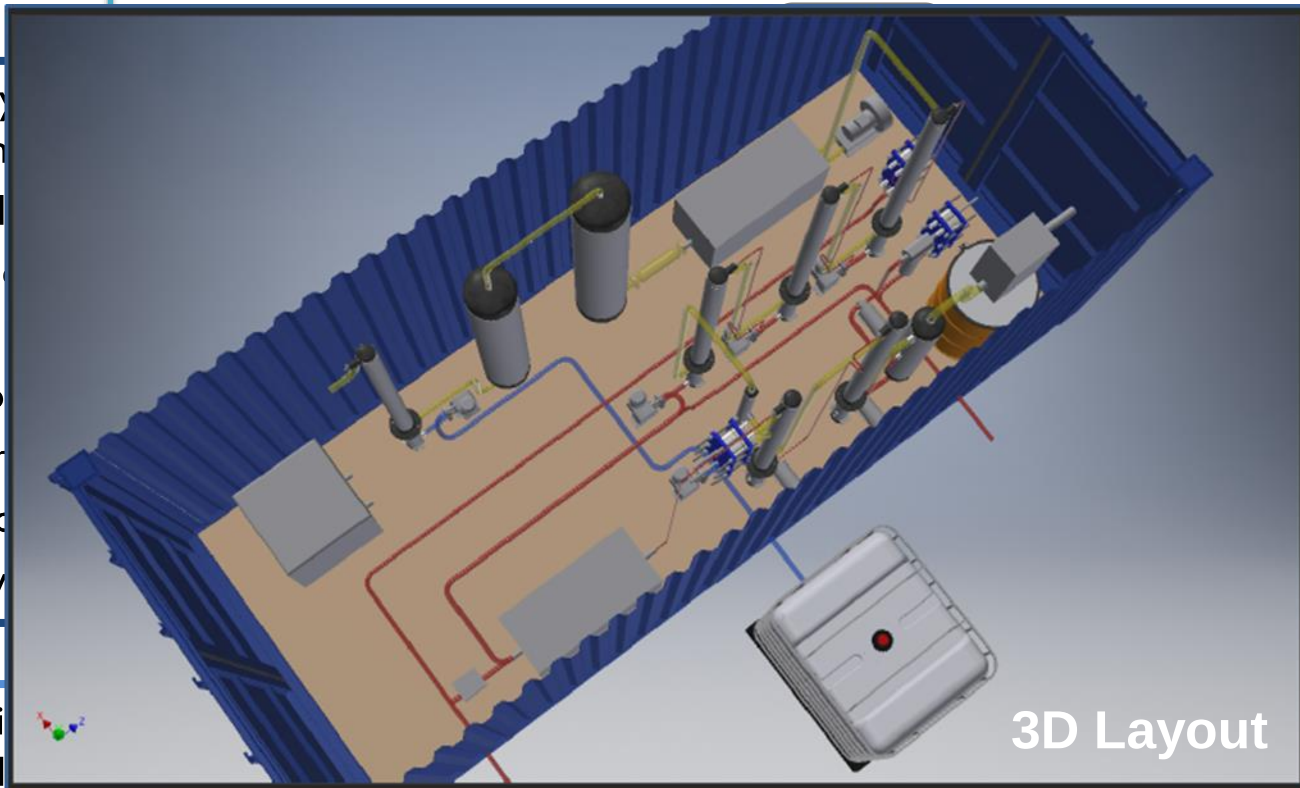
Prototype A (3/6) - Syngas Cleaning System

- Feed & Specification
- Optimized sequence of removal

Typical sy
of bion

- Alkal
- Parti
- Tar
- Chlo
- Sulph
- Nitro
- Heav

Speci
by d



onia

Heavy metals

Final configuration is a compromise between site requirement and downstream unit specification

MEMBER solutions
Prototype A (4/6)

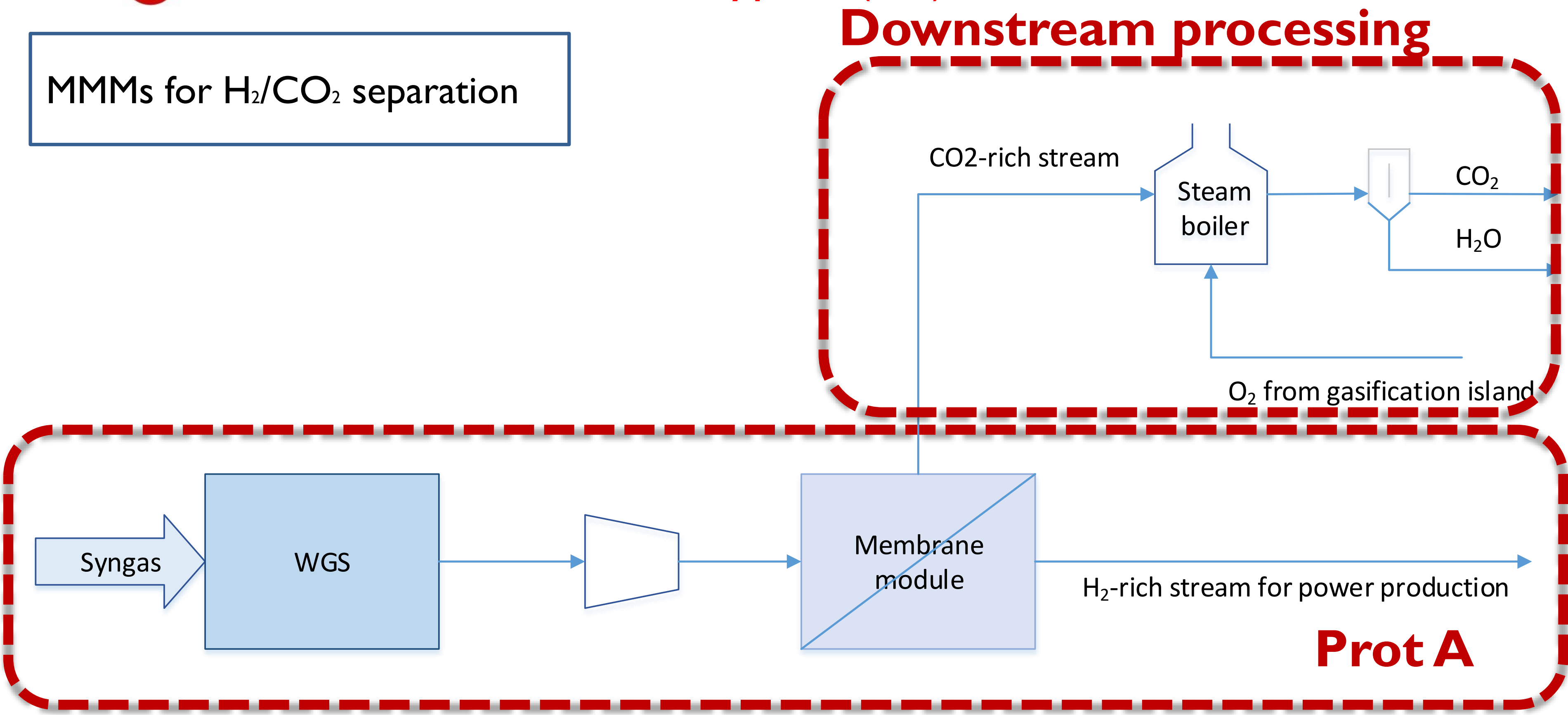
- Materials and Process targets
  - MMM Material production & Scale-up
  - Prototype Design
    - SCS
    - PROT A
  - LCA & LCC

Target MMM	Value	Unit
H_2/CO_2 separation	100	GPU
H_2/CO_2 selectivity	18	-
Membrane area	10	m^2
Design temperature	200	°C
Design pressure	10	bar
Cost	<150	€/m^2
Target Process	**Value**	**Unit**
CCR	90	%
CO_2 purity	95	%

MEMBER solutions

Prototype A (5/6)

MMMs for H_2/CO_2 separation



- Syngas from CENER biomass gasification unit / SCS
- 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

1st Workshop MEMBER Project
TU/e, 15-01-2020

MEMBER solutions

Prototype A (6/6)

- Simulation results

Permeance (GPU)	Selectivity (-)	Rec_tot	CO2 purity	H2 separation
100 (nominal target)	18 (nominal target)	>90 %	>95 %	73 %
50	18	>90 %	>95 %	44 %
25	18	>90 %	>95 %	23 %
100	14	<90 %	>95	73 %

- A lower permeance lowers the hydrogen yield
- A lower selectivity reduces the CO_2 recovery

- More complex layouts (multiple modules, recircualtion) will yield higher hydrogen yields

MEMBER solutions

Prototype B (1/4)

- Demo Site: AGROGER CHP plant - property of Galp Energia - Portugal

- Galp Energia is a vertically integrated multi-energy operator operating in the oil and natural gas business and as a producer and seller of electricity for industrial and home consumption.
- AGROGER cogeneration plant consists of 2 sets of Natural Gas fuelled electrical power-generators providing up to 8.8 MW of Power

MEMBER solutions
Prototype B (2/4)

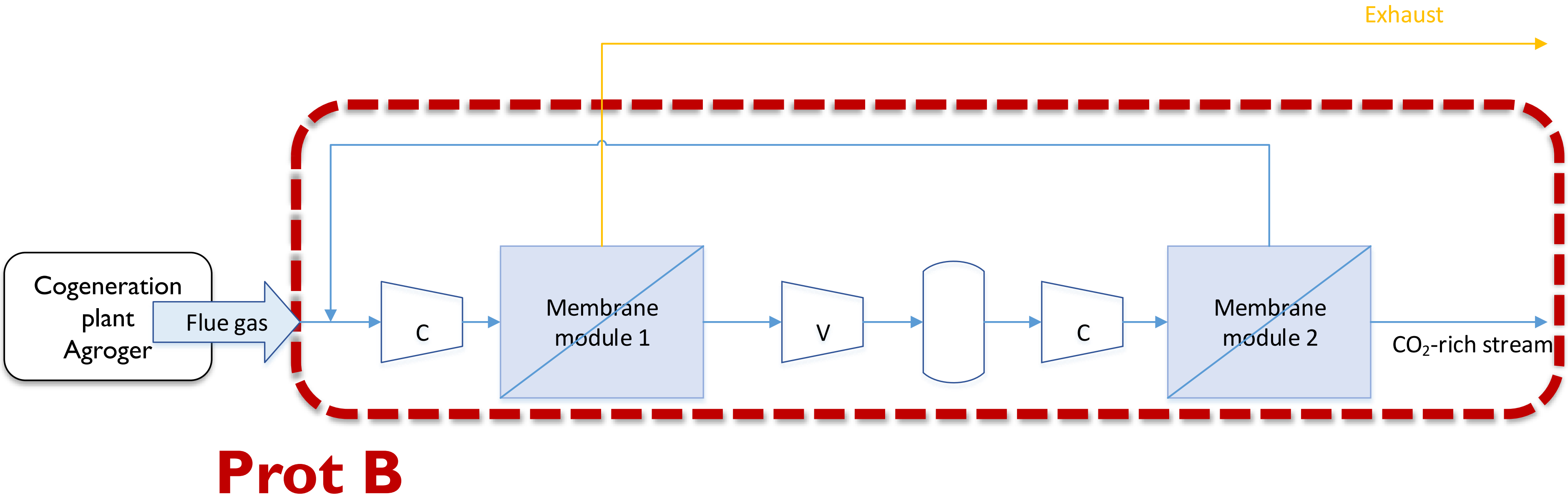
- Materials and Process targets
  - MMM Material production & Scale-up
  - Prototype Design
  - LCA & LCC

Target MMM	Value	Unit
CO_2/N_2 separation	300	GPU
CO_2/N_2 selectivity	70	-
Membrane area	10	m^2
Design pressure	7	bar
Cost	<100	€/m^2
Target process	**Value**	**Unit**
CCR	90	%
CO_2 purity	95	%

MEMBER solutions

Prototype B (3/4)

MMMs for CO_2/N_2 separation



- CO_2 is separated from the N_2-rich flue gases from a combustion process
- Size module 2 is much smaller than module 1

MEMBER solutions
Prototype B (4/4)

- Simulation results

Permeance (GPU)	Selectivity (-)	Rec_tot	CO2 purity
300 (nominal target)	70 (nominal target)	>90 %	>90 %
200	70	86 %	>90 %
100	70	67 %	>90 %
300	40	>90 %	90 %

- CO_2 recovery is reduced when permeance decreases
- Purity not compromised
- Increase in operating pressure counteracts the reduced recovery

- A reduction in selectivity results in a reducing purity

MEMBER solutions

Prototype C (1/2)

➢ Demo Site: IFE-HyNor Hydrogen Technology Centre - Norway

Institutt for energiteknikk

- Non-profit international research foundation for energy and nuclear technology.
- Advanced infrastructure fully dedicated to the test and demonstration of future clean hydrogen technologies.

Combination of metallic membranes, catalyst and sorbents

Target process	Value	Unit
CCR	≥90	%
CO_2 purity	≥95	%
H_2 production	10	Nm^3/h
H_2 purity	≥99.9	%

➢ Process scheme is under evaluation for Patent Application

MEMBER solutions

Prototype C (2/2)

- Materials and targets

- Materials production & Scale-up

- Prototype Design

Target Membrane	Value	Unit
Life time	>4000	h
Design temperature	500	°C
Membrane area	1	m^2
Target Sorbent	**Value**	**Unit**
Sorption Capacity	Min 0.3	g_{CO2}/g_{sorb}
Cycling stability	Min. 1000	cycles
Attrition jet index	Max. 10	%
Target Catalyst	**Value**	**Unit**
Cycling stability	Min. 1000	cycles
Attrition jet index	Max. 10	%

- LCA & LCC

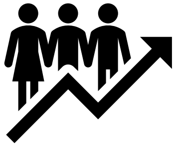
Conclusions and Future Perspectives

- The main purpose of the MEMBER project is the development of technologies that exceed the state of the art in pre/post-combustion for both power and hydrogen production.

- Advanced materials like MMMs for CO_2 separation, metallic Pd-membranes, catalyst and sorbents are being developed to this aim.

- The prototypes will be demonstrated in an industrially relevant environment, allowing validation of the performance and stability of the technological solutions and materials.

- A techno-economic assessment of the novel processes at an industrial scale is in progress to address the future commercialization of MEMBER technologies.



Processes for CO_2 Carbon Capture

1st Workshop MEMBER Project
TU/e, 15-01-2020

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)

2.7. An overview on BIONICO project (Marco Binotti – POLIMI)

Workshop on membrane processes for CO_2 capture

BIONICO
BIOGAS MEMBRANE REFORMER FOR DECENTRALIZED H_2 PRODUCTION

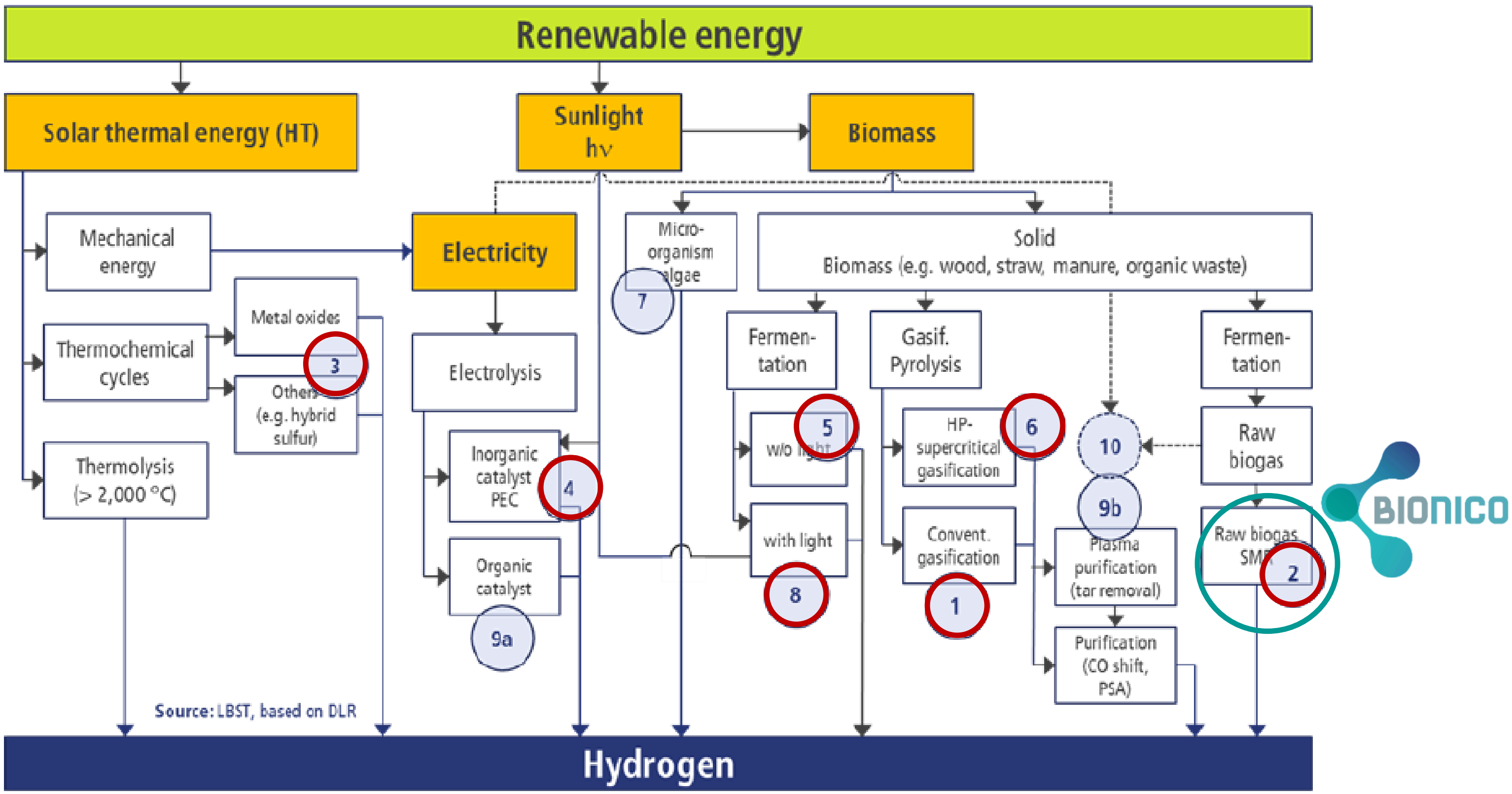
TUE 15-01-2020 - Worshop on membrane processes for CO_2 capture -

Marco Binotti

MOTIVATION

Nowdays about **95% of the H_2** produced worldwide comes from **fossil fuels**.

To be sustainable H_2 should be produced by RES. Which are the best routes?



**Fuel Cells and Hydrogen Joint Undertaking. Study on Hydrogen from renewable resources in the EU, 2015*

Summary

BIONICO

Biogas membrane reformer for decentralized H_2 production

BIONICO will develop, build and demonstrate at a real biogas plant **(TRL6)** a catalytic membrane reactor integrating production and separation of **100 kg/day of H_2**. Direct conversion of biogas to pure hydrogen is achieved in a **single step**, with **increased overall efficiency** (>70%), strong decrease of volumes and auxiliary heat management units and reduction of operating temperature.

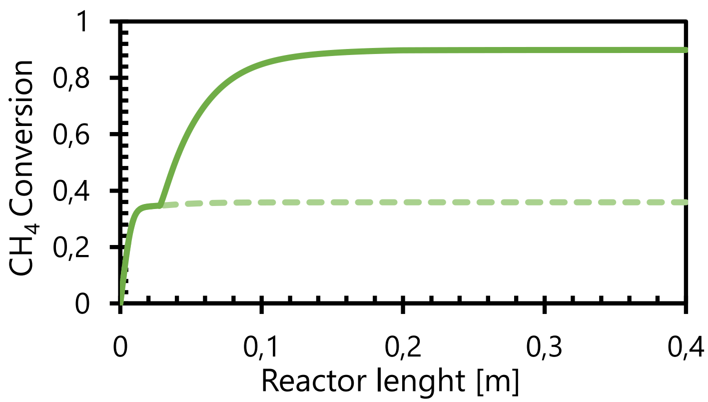
BIONICO CONCEPT

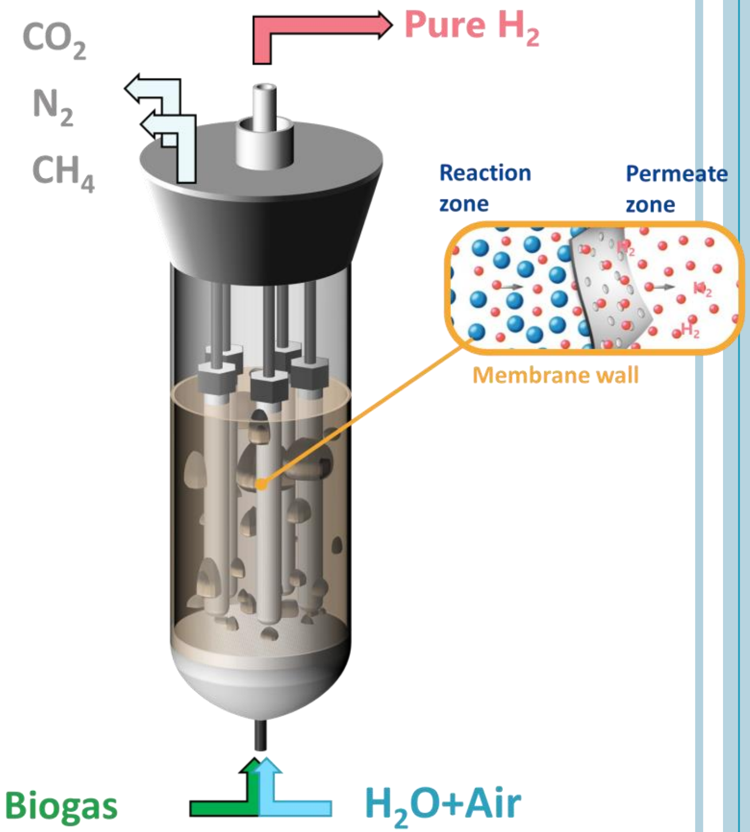
- **Fuel conversion** and **H_2 separation** take place in a single reactor thanks to a **membrane** perm-selectivity for H_2
- The chemical equilibrium is shifted towards products (as H_2 is removed with the membranes) **enhancing CH_4 conversion at lower T**

BG Oxidation: $CH_4 + 2O_2 \Rightarrow CO_2 + 2H_2O$

BG Reforming: $CH_4 + H_2O \Leftrightarrow CO + 3H_2$

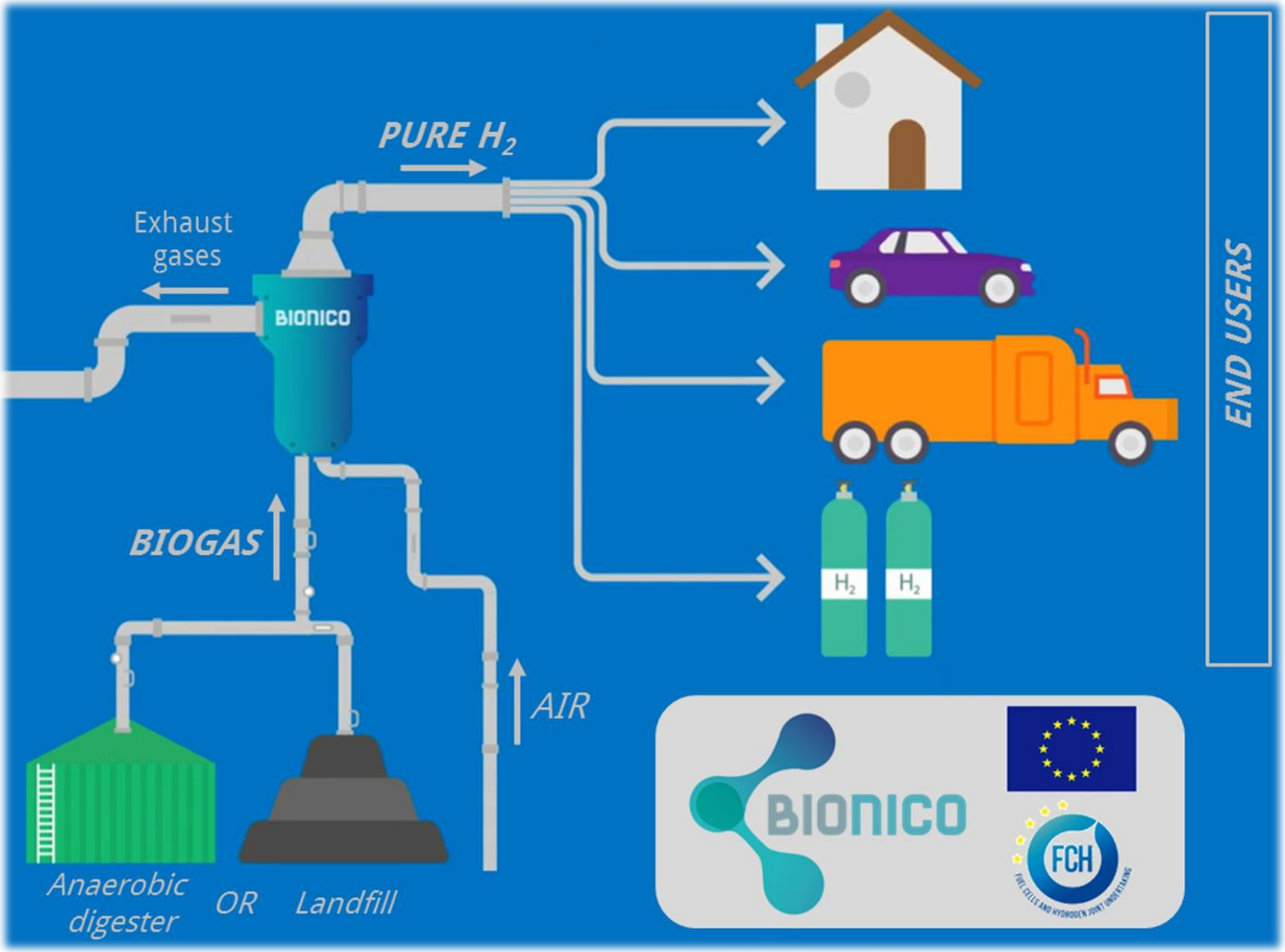
WGS: $CO + H_2O \Leftrightarrow CO_2 + H_2$



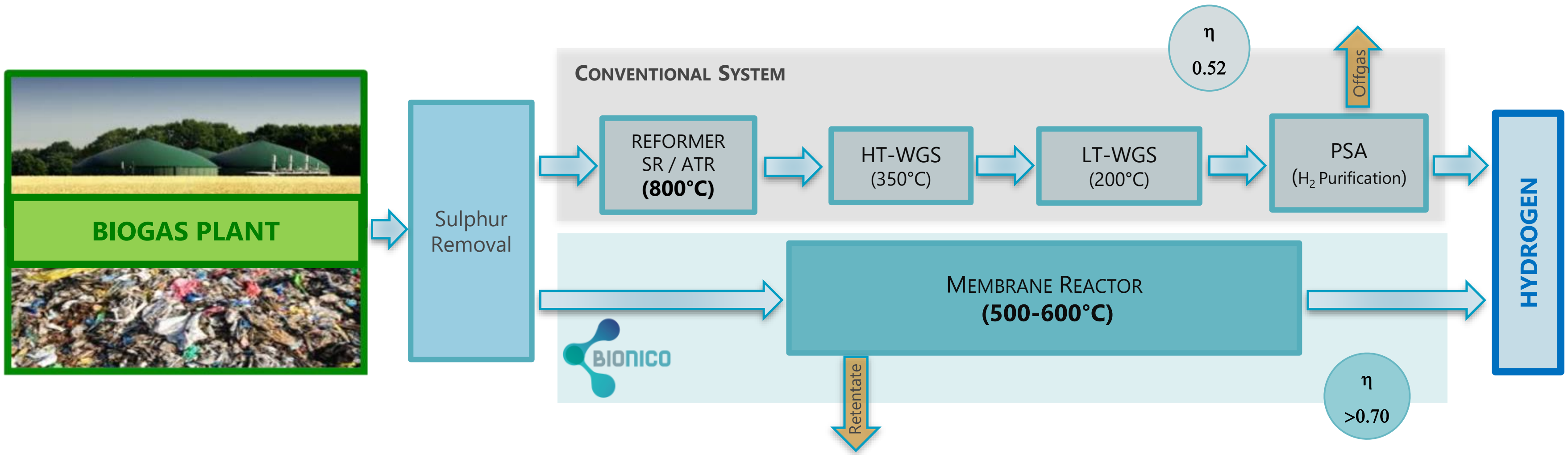


- Catalyst **fluidization allows to: i) overcome problems with T control, ii)** to operate with smaller particles **maintaining very low Δp** and **iii) to limit concentration polarization issue**

BIONICO CONCEPT

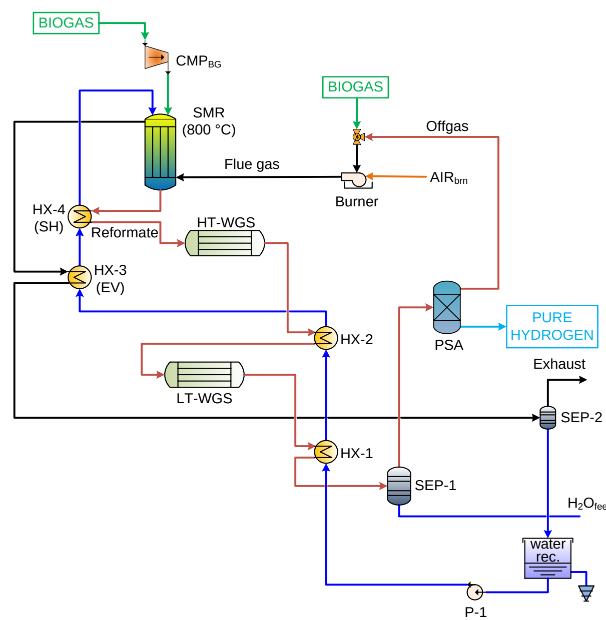


WHY BIONICO?



Two reference cases (based on SR and ATR) identified and simulated to benchmark BIONICO

Conventional System - Results			
	units	SR	ATR
Biogas feed	Nm^3/h	39.5	63.5
Total Biogas Input	kW	229	368
System efficiency	$\%_{LHV}$	51.7	27.8
H2 delivery pressure	bar	20	20
H2 production cost	€/kg	4.21	6.37



The target of BIONICO is a system efficiency > $70\%_{LHV}$, about 25% higher than SR ($52\%_{LHV}$). Higher efficiency and equipment savings will end up in lower H_2 costs.

PROJECT OVERVIEW

Call year: 2014

Call topic: FCH-02.2-2014 Decentralized hydrogen production from clean CO2-containing biogas

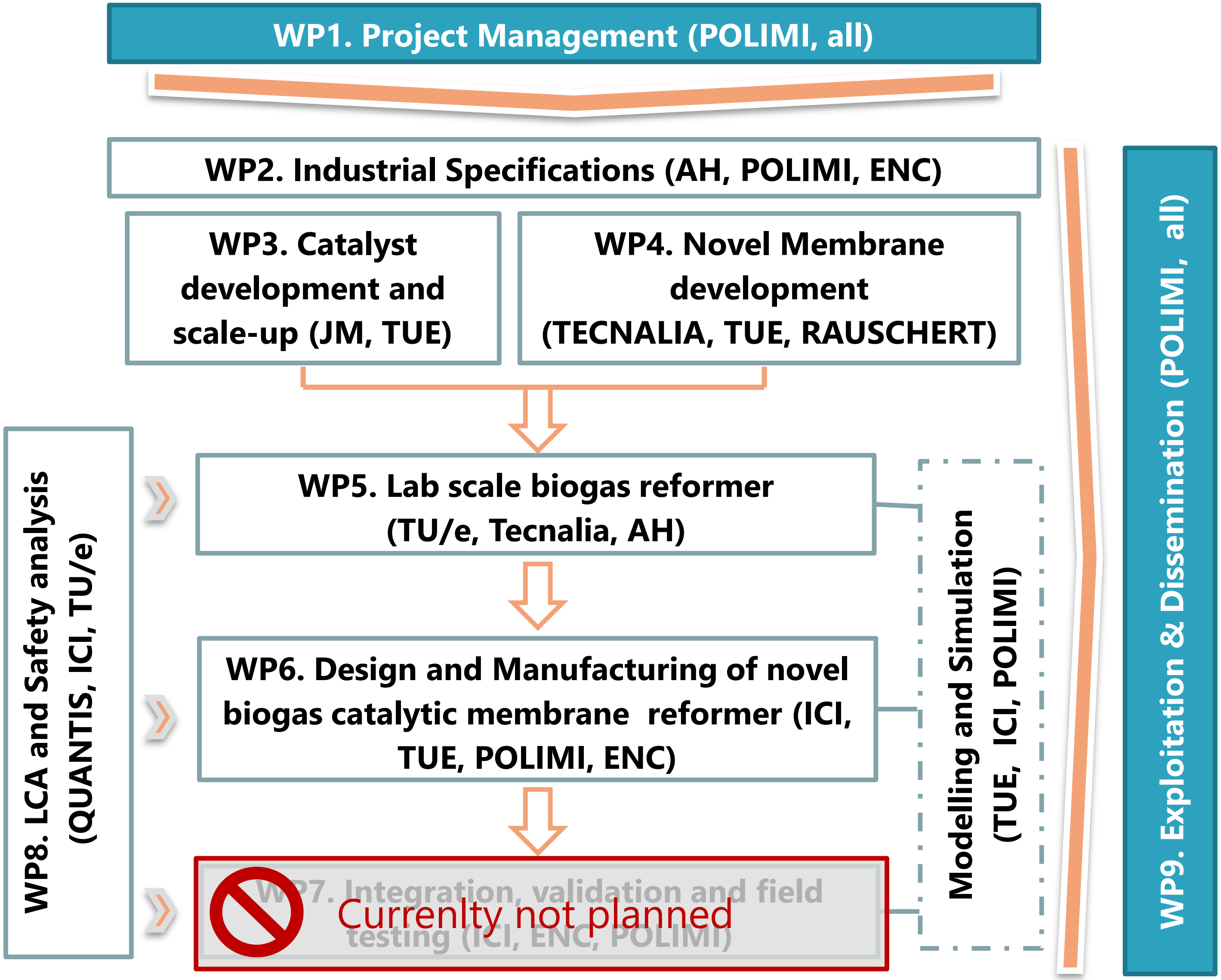
Project dates: 01/09/2015 – 31/12/2019 (?)

Total project budget: 3,396,640 €

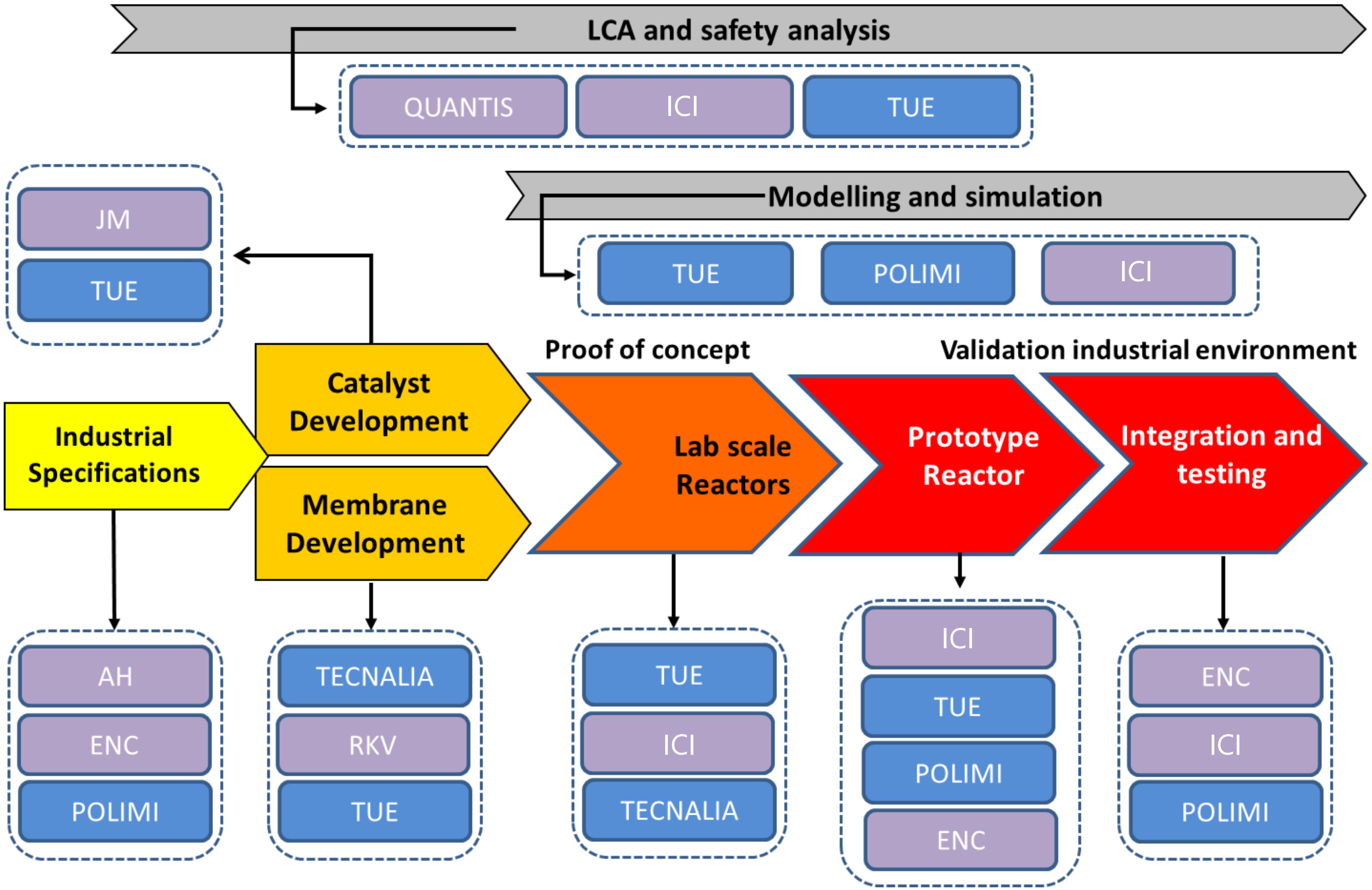
Partners:

- 8 partners from 7 countries
  - 2 university
  - 1 reserach center
  - 3 Industries
  - 2 SME

WORK STRUCTURE



PARTNERSHIP SYNERGIES



Novel Catalyst

Goal

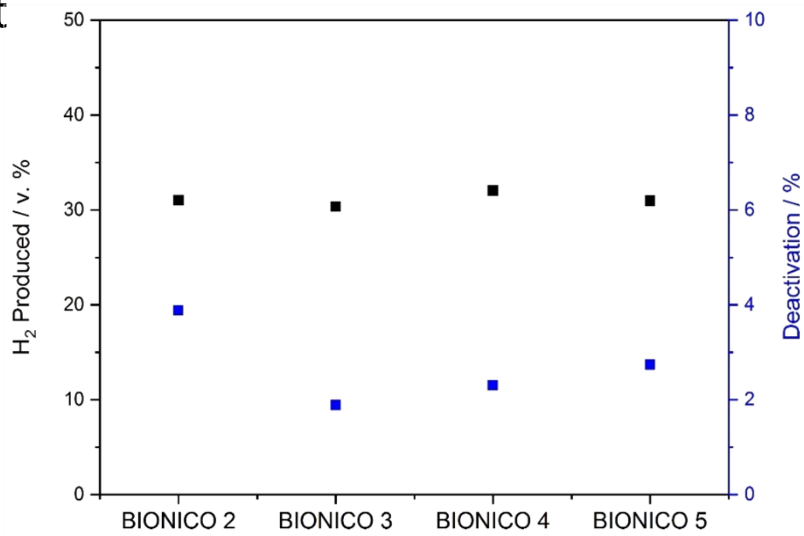
Development of highly active reforming catalysts to produce hydrogen from diverse biogas mixture coupled with steam and air in a fluidised bed regime.

Project Activities

- PGM doped alumina catalysts have been tested under biogas reforming conditions for dry, steam or autothermal reforming
- Coke formation resistance improvement

Achievements

- 1st generation catalyst and 2nd generation catalyst able to work under fluidisation regime and at low T
- **Final Catalyst formula produced and shipped to ICI (32 kg)**



NOVEL MEMBRANE & SUPPORT

GOAL

Development of Pd based tubular supported membranes, for application in biogas reforming catalytic membrane reactors

PROJECT ACTIVITIES

- Preparation of porous ceramic tubes of larger diameters (14/7mm) and materials for their use as supports for thin Pd-based membranes
- Manufacturing of thin film (<5 μm thick) Pd-Ag and Pd-Ag-Au membranes on the ceramic supports.
- Development of **new finger-like porous asymmetric ceramic supports** in which one of the ends of the tube is a closed porous part.

Finger-like asymmetric porous ceramic supports

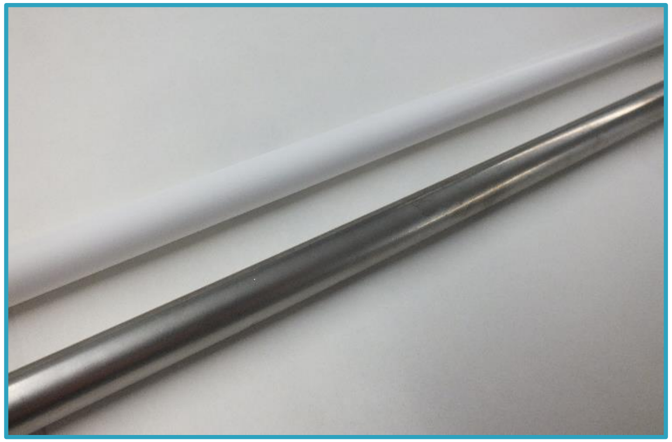
Novel Membrane & Support

Goal

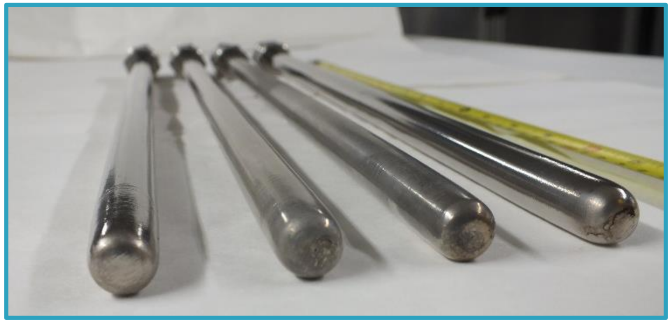
Development of Pd based tubular supported membranes, for application in biogas reforming catalytic membrane reactors

Achievements

- **1st generation** membrane & support
- Installation of a new plating system for preparation of >40 cm long membranes.
- **2nd generation** membrane & support.
  - ***Thin Pd-Ag layers have been deposited onto the 50 cm long finger-like supports***
- Definition of criteria for support quality



2nd generation thin film Pd-alloy supported membranes (>40 cm long)



Novel Membrane & Support

Goal

Development of Pd based tubular supported membranes, for application in biogas reforming catalytic membrane reactors

Achievements

- **Improvement of manufacturing** procedure for membrane prototype production
- **125 tubular membranes** produced for BIONICO prototype

Perm-selectivity >10,000

N_2 leakage level <10^{-10} mol m^{-2} s^{-1} Pa^{-1}

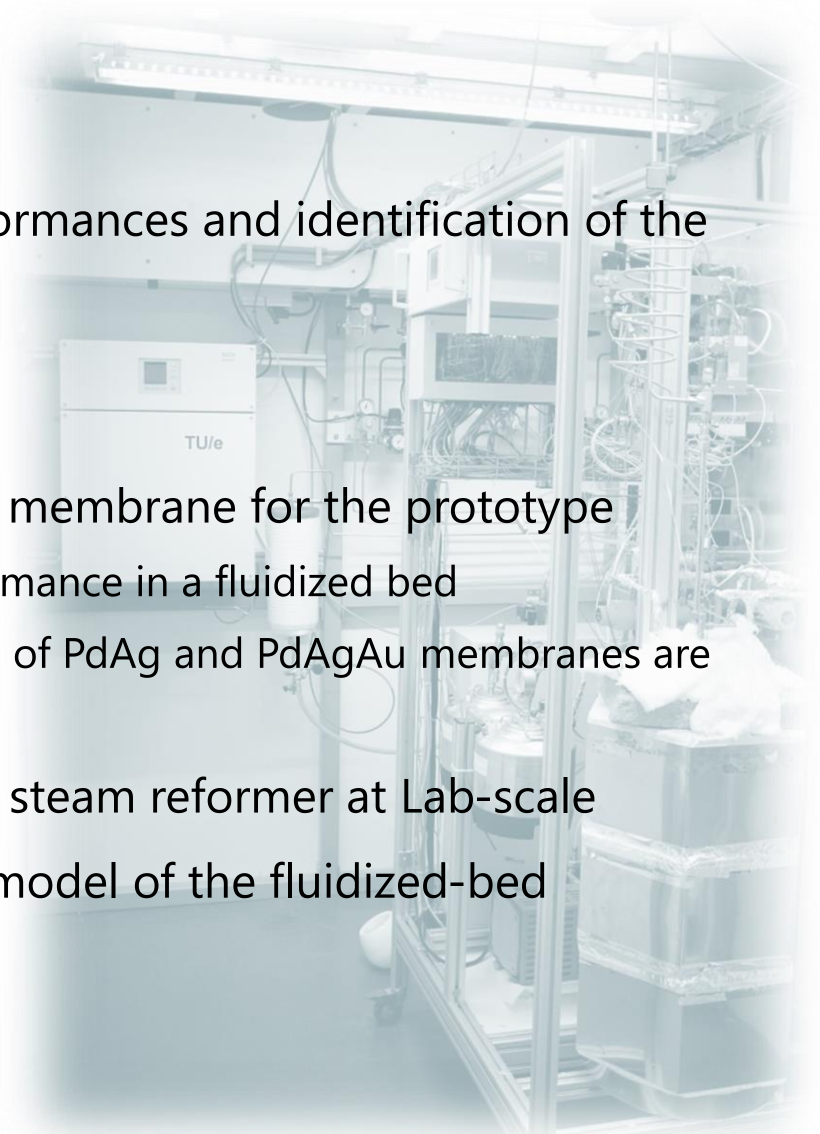
NOVEL MEMBRANE & SUPPORT: LESSON LEARNED

- Membrane production:
  - **Finger-like** end need to be **improved** to avoid using Swagelok end connector.
  - In order to ensure large-scale membrane production:
    - Suitable **quality check procedure for supports** should be implemented
    - **An optimized & reproducible membrane preparation procedure** required
  - The tracking and naming of supports & membranes is important during the membrane preparation phase.

- Membrane integration:
  - **The alignment** of the "**membrane + Swagelok connector + dense tube" is crucial** to avoid breakages during handling, integration and operation steps.
  - **Sealing** of ceramic supported thin Pd-based membrane need to be **improved**
  - **Detailed protocol for the integration** of the membranes in the prototype is necessary

- Membrane use:
  - **Membrane start-up, testing and shut-down protocol** need to be clearly defined
  - Avoid the contact of impurities that can damage membranes (i.e. H2S content in biogas)

LAB SCALE REACTOR



GOAL

Definition of the lab scale reactors performances and identification of the best design for prototype pilot.

PROJECT ACTIVITIES

- Selection and characterization of the membrane for the prototype
  - Study of long-term membrane performance in a fluidized bed
  - The effect of H_2S on the performance of PdAg and PdAgAu membranes are studied
- Design and demonstration of biogas steam reformer at Lab-scale
- Development of phenomenological model of the fluidized-bed membrane reactor

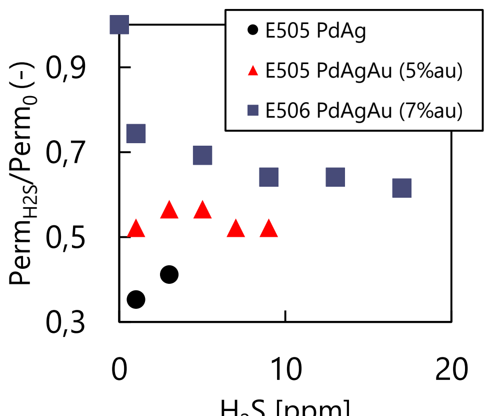
Lab Scale Reactor

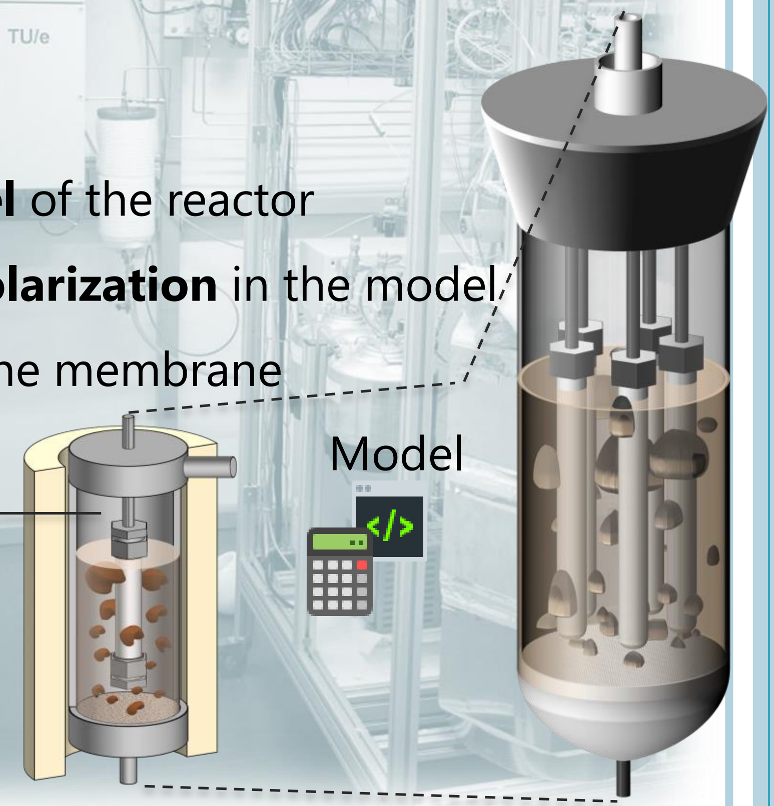
Goal

Definition of the lab scale reactors performances and identification of the best design for prototype pilot.

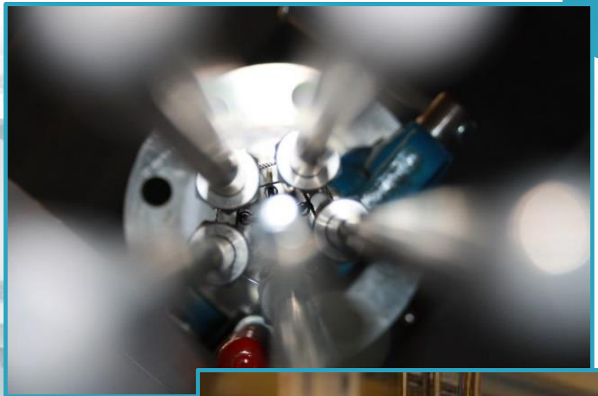
Achievements

- Integration of catalyst and membrane
- One dimensional **phenomenological model** of the reactor
- Successful **description** of **concentration polarization** in the model
- **Effect of Au** addition on H_2S resistance of the membrane





Lab Scale Reactor

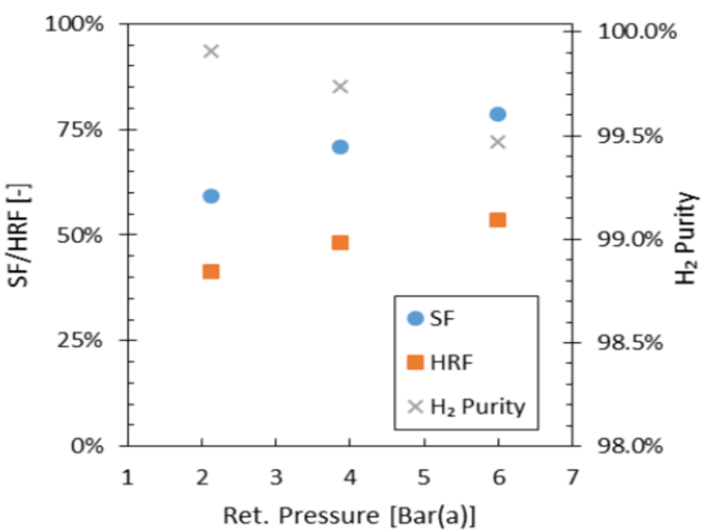


Goal

Definition of the lab scale reactors performances and identification of the best design for prototype

Achievements

- Successful testing of the **Lab scale** system with **5 membranes** and catalyst



$$X_{CH_4} = \frac{\left(F_{CH_4,in} - F_{CH_4,out}\right)}{F_{CH_4,in}}$$

$$\mathrm{SF} = \frac{F_{H_2,Perm.}}{\left(F_{H_2,Perm.} + F_{H_2,ret.}\right)}$$

$$\mathrm{HRF} = SF\,\frac{\left(F_{H_2,Perm.} + F_{H_2,Ret.}\right)}{\left(4 \cdot F_{CH_4,in} - 2 \cdot F_{O_2,in}\right)}$$

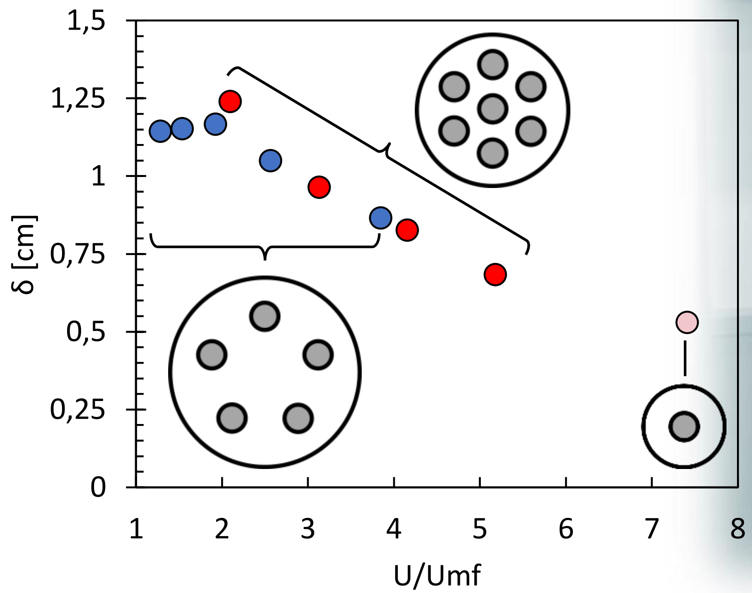
Lab Scale Reactor

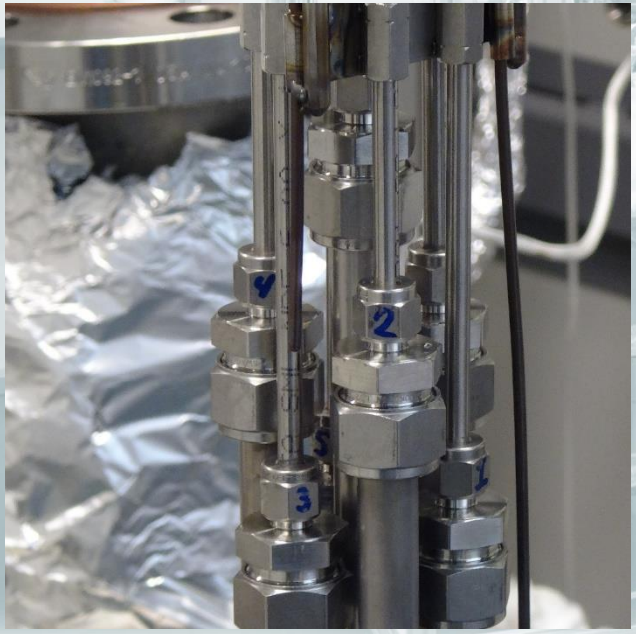
Goal

Definition of the lab scale reactors performances and identification of the best design for prototype

Achievements

- Successful testing of the **Lab scale** system with **5 membranes** and catalyst





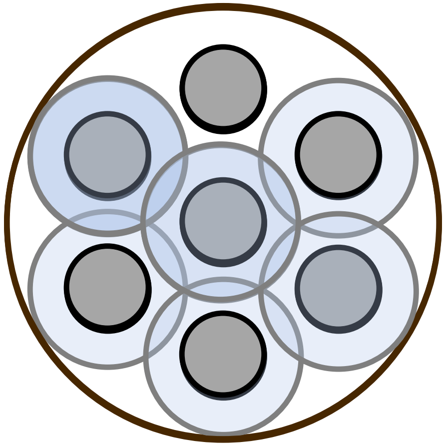
Lab Scale Reactor

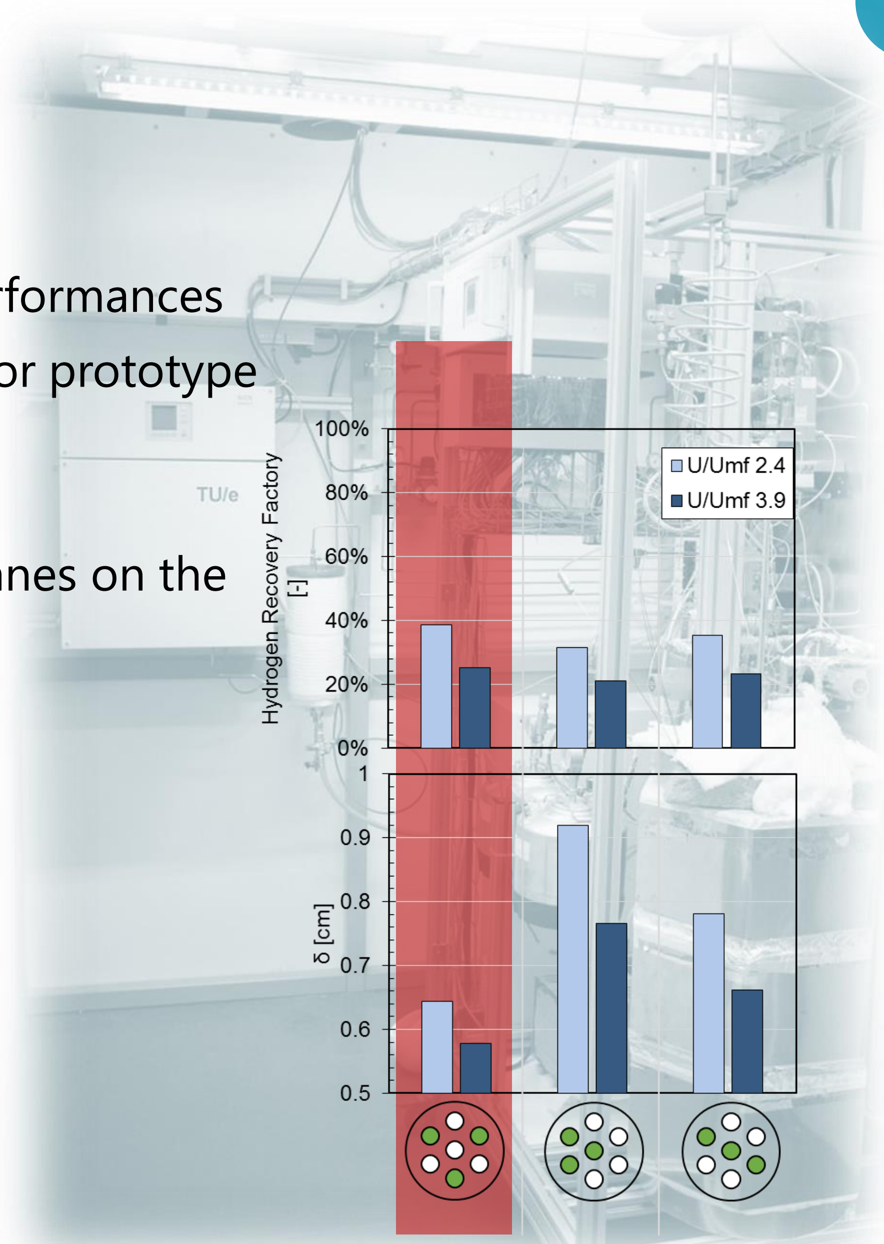
Goal

Definition of the lab scale reactors performances and identification of the best design for prototype

Achievements

- Effect of distance between membranes on the concentration polarization





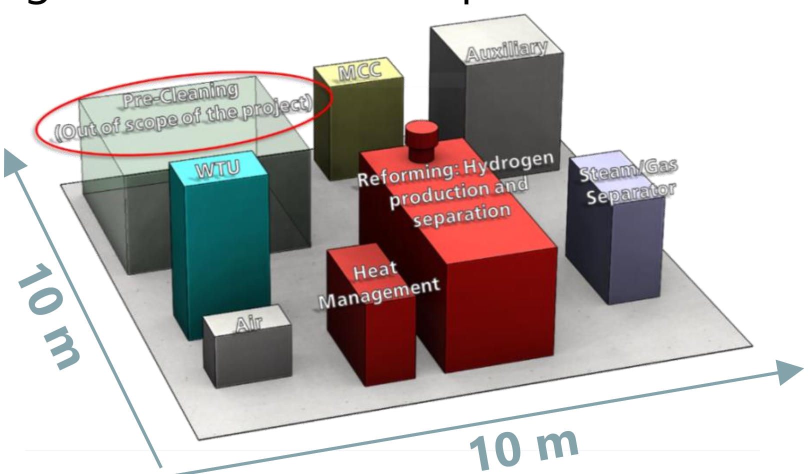
Prototype Reactor

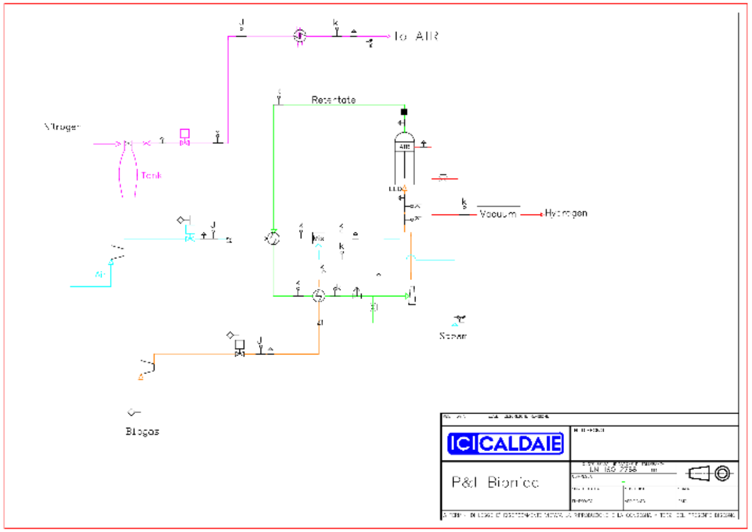
Goal

Final design and construction of MR prototype for the production of approximately 100 kg/day of pure hydrogen

Project Activities

- Design of the prototype catalytic membrane reactor at large scale including control system design
- Design of the balance of plant





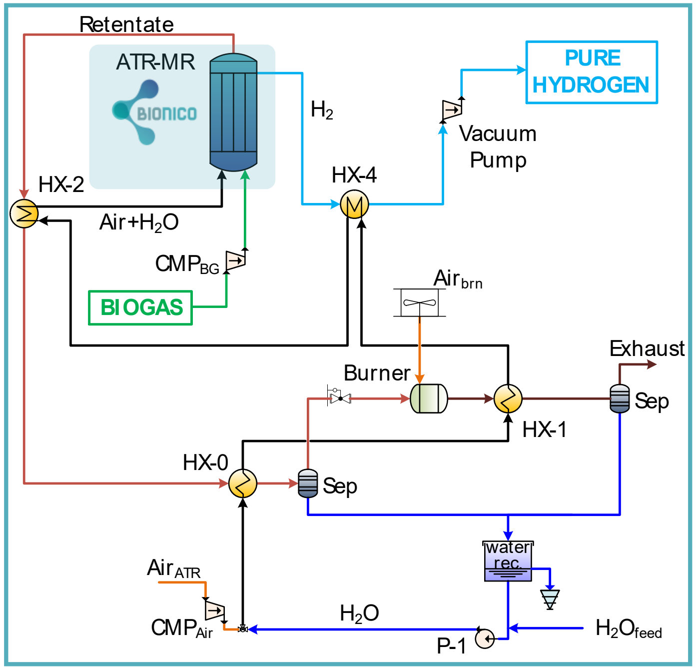
Prototype Reactor

Goal

Final design and construction of MR prototype for the production of approximately 100 kg/day of pure hydrogen

Achievements

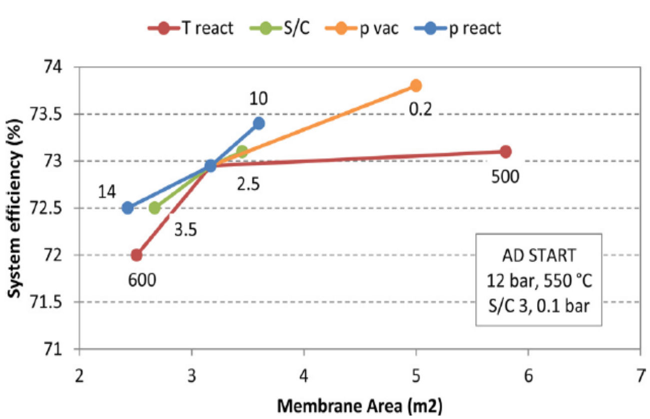
- A techno-economic optimization of BIONICO system was assessed
- Different operating conditions (T, p, S/C), biogas compositions and permeate side configuration were investigated
- Membrane reformer designed and manufactured by ICI



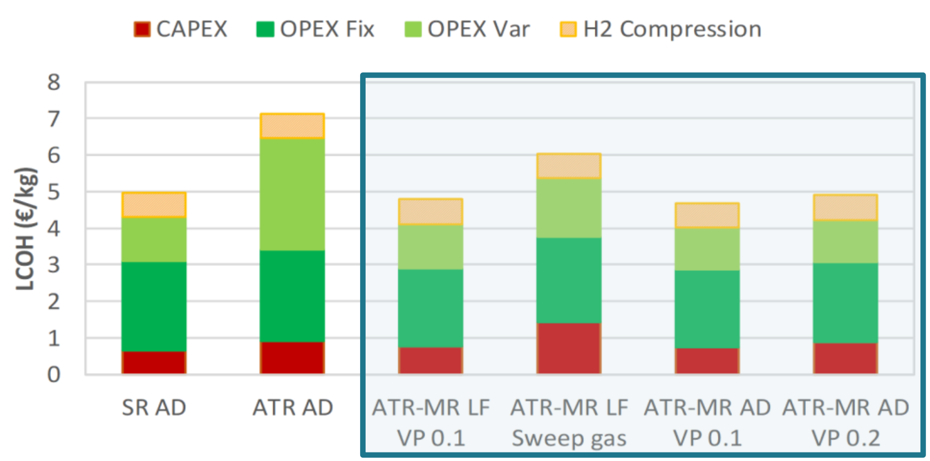
BIONICO PERFORMANCE

Parameter	units	BIONICO LF			BIONICO AD	
Temperature	°C	550	550	550	550	550
P feed	bar	12	10	20	12	12
P permeate	par	0.1	0.1	1.1/sw	0.1	0.2
BG Feed	Nm³/h	35.2	35.3	50.8	26.8	27.1
BG Input	kW	154.6	155.0	223.3	154.8	156.7
H_2 production	kg/day	100	100	100	100	100
System efficiency	%	71.5	71.9	55.4	73.0	73.8
System efficiency (H_2 @ 20 bar)	%	65.1	65.2	51.2	66.1	66.7
System efficiency (H_2 @ 700 bar)	%	56.2	56.4	45.6	57.0	57.5

Sensitivity to design parameters



Evaluation of the LCOH



Prototype Reactor

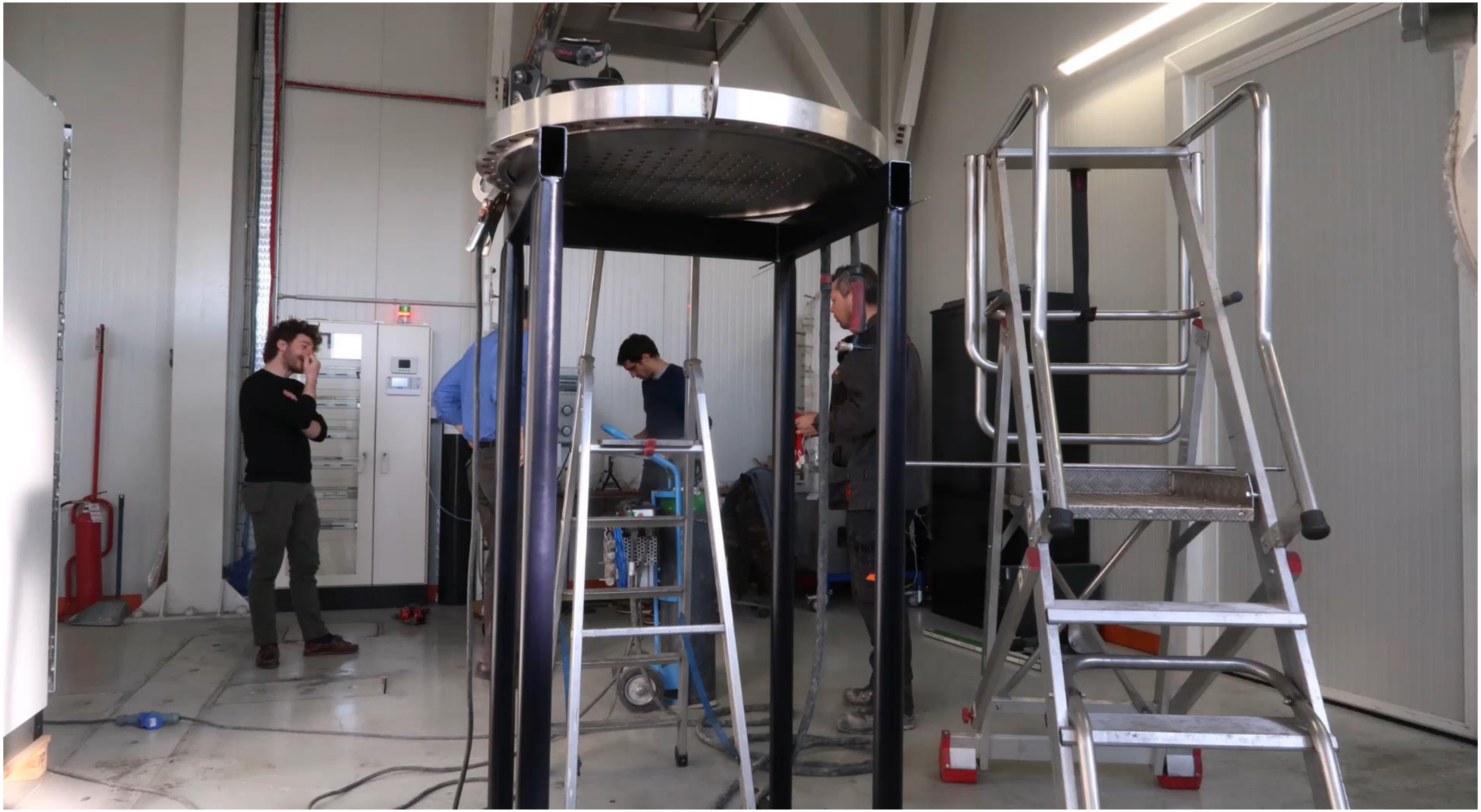
Goal

Final design and construction of MR prototype for the production of approximately 100 kg/day of pure hydrogen

Achievements

- Design, construction and installation of the CMR and BOP

Prototype Reactor



Prototype Reactor

Goal

Final design and construction of MR prototype for the production of approximately 100 kg/day of pure hydrogen

Achievements

- **Preliminary testing activity performed at ICI in December 2019**

Prototype Reactor

Goal

Final design and construction of MR prototype for the production of approximately 100 kg/day of pure hydrogen

Achievements

- **Preliminary testing activity performed at ICI in December 2019**

Pressure

P retentate = 6 bar

P permeate = 20 mbar

Reactants

CH_4	5.81 Nm^3/h
N_2	28.82 Nm^3/h
CO_2	1.45 Nm^3/h
Air	12.68 Nm^3/h
H_2O	20 kg/h

Products:

Retentate (volume %)

- CO = 1.9 vol%
- CO_2 = 12.6 vol%
- CH_4 = 2.3 vol%
- H_2 = 7.3 vol%

Permeate (volume %)

- CO_2 = 0.1 vol%
- CO = 0.01 vol% - 125 mg/m^3
- **H_2 = 99.3 vol%**

INTEGRATION&TESTING AT BIOGAS PRODUCTION SITE

GOAL

Final evaluation of the innovative process to directly produce pure hydrogen in a real biogas production site (ENC Landfill plant)

ACHIEVEMENTS

- Due to a failure occurred to the BIONICO system, no testing activity is foreseen in the identified real landfill plant.

  → The occurred failure is not related to the standard system operation

  → ICI is investigating the reason of the failure

  → discussion on how to further test the reactor in ICI is ongoing

LIFE CYCLE ASSESSMENT & SAFETY ISSUES

GOAL

Development strategy towards sustainable solutions and provide guidance on how to operate the reactor prototype under safe conditions.

PROJECT ACTIVITIES

- Refined goal & scope of LCA analysis, in particularly, with further clarifications with regard to: (i) reference systems (baseline), i.e., SMR and ATR, (ii) level of details of inventory modeling and (iii) system boundaries
- Improved data collection for key data points, especially related to functional unit, biogas input, conversion efficiency, energy and water use as well as direct GHG emissions during conversion processes
- Final LCA analysis between BIONICO CMR and reference technologies
- In progress of developing applicable safety protocol

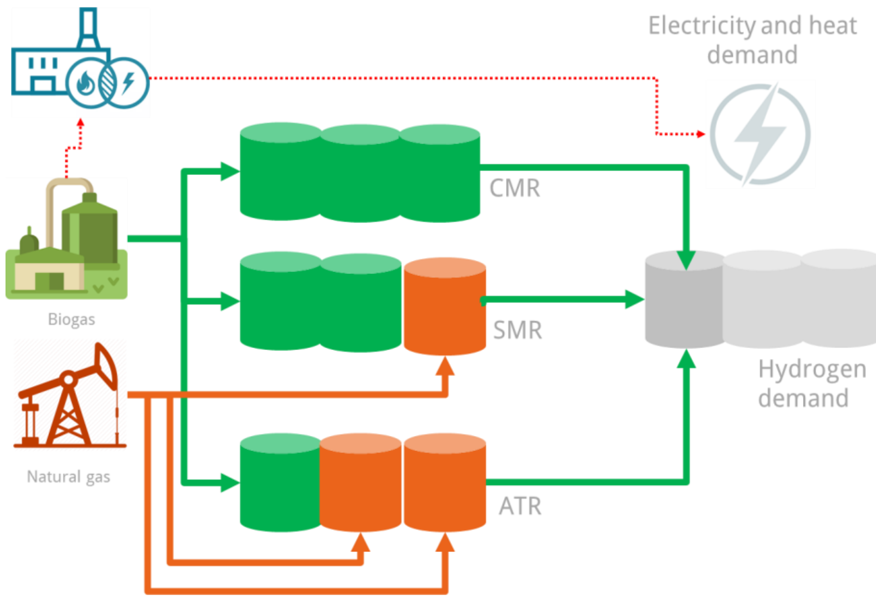
Life Cycle Assessment & Safety Issues

Goal

Development strategy towards sustainable solutions and provide guidance on how to operate the reactor prototype under safe conditions.

Project Activities

- Understanding biogas utilization effects on LCA



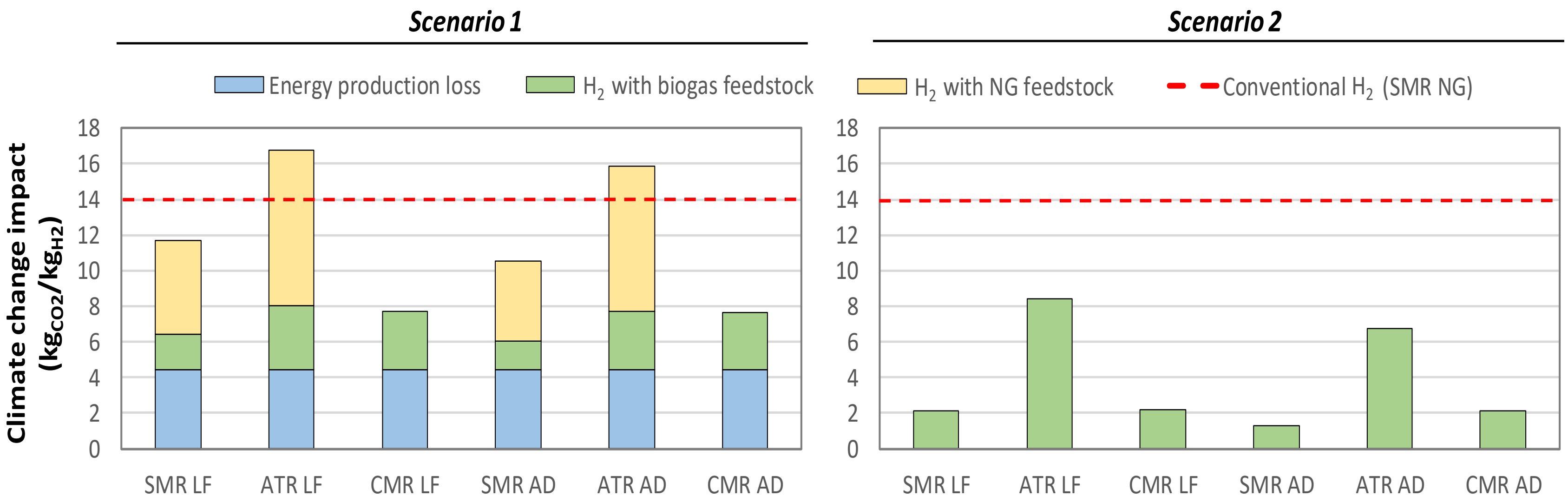
Life Cycle Assessment & Safety Issues

Goal

Development strategy towards sustainable solutions

Achievements

- Refined LCA modeling and results: BIONICO CMR only performs significantly better for most environmental indicators than reference systems when biogas utilization is limited (Scenario 1, Left)



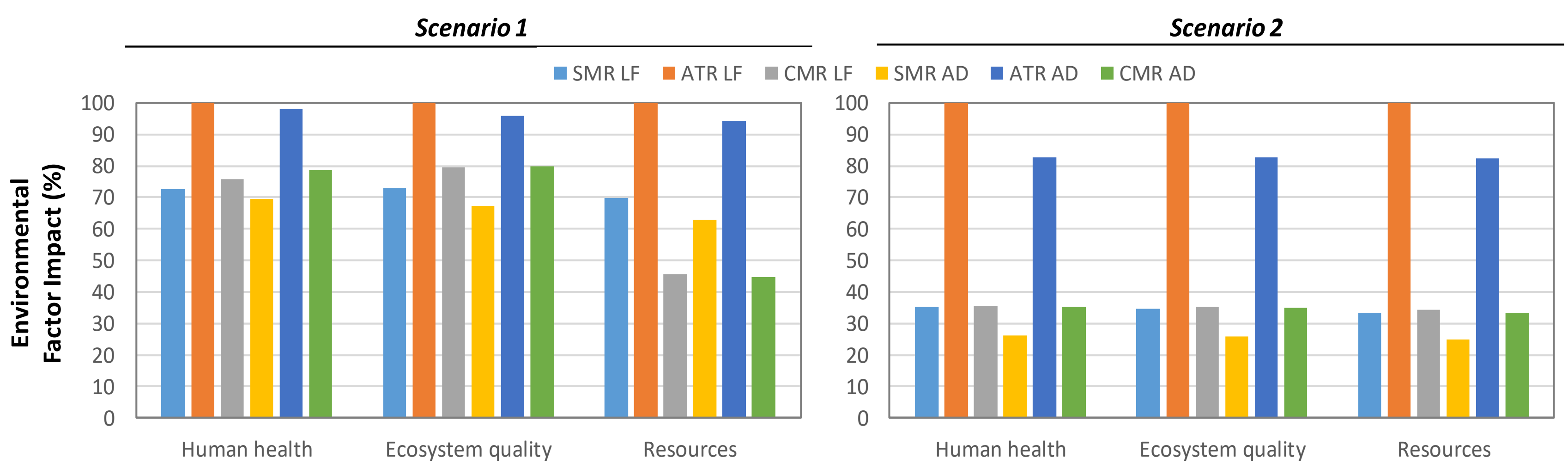
Life Cycle Assessment & Safety Issues

Goal

Development strategy towards sustainable solutions

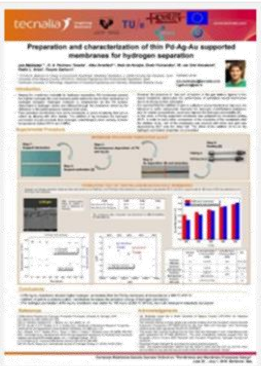
Achievements

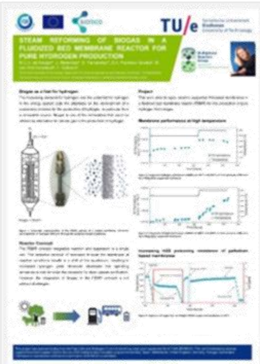
- Refined LCA modeling and results: BIONICO CMR only performs significantly better for most environmental indicators than reference systems when biogas utilization is limited (Scenario 1, Left)



Dissemination Activity

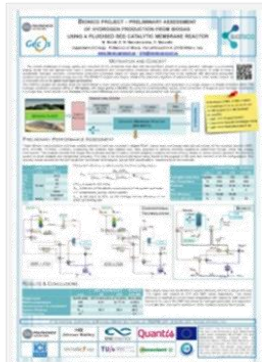
- Project website (+3700 single users) updated till now : www.bionicoproject.eu
- 8 Newsletter prepared and distributed during the project to lifetime to about 100 recipients
- 9 papers published during the project lifetime
- 16 presentations and 8 posters presented at international conferences

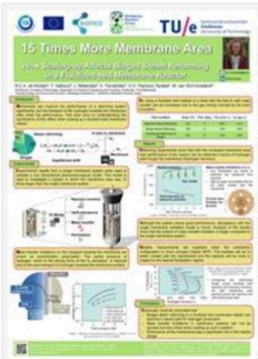

EMS summer school 2016


Dutch Mem. Society 2016


EBA 2016


MR4PI workshop 2017


REGATEC 2017



ICIM 2018

Dissemination Activity

- Project website (+3700 single users) updated till now : www.bionicoproject.eu
- 8 Newsletter prepared and distributed during the project to lifetime to about 100 recipients
- 9 papers published during the project lifetime
- 16 presentations and 8 posters presented at international conferences
- 2 dissemination videos (+3400 views) + timelapse
- Linkedin group on Membrane Reactor Technology
- Project on ResearchGate

Dissemination Activity

- Press-release and magazine articles
- 1 international workshop on Membrane Reactor for Process Intensification (MR4PI) with 4 other projects (~90 participants)
- 1 workshop in ICI Caldaie for Italian stakeholders (~15 participants)

References

- Long-term stability of thin film Pd-based supported membranes, *Journal of Membrane Science, Open Access*
- Life Cycle Assessment and Economic Analysis of an Innovative Biogas Membrane Reformer for Hydrogen Production, *Processes, Open Access*
- Potentiality of a biogas membrane reformer for decentralized hydrogen production, *Chem. Eng. and Processing: Process Intensification, Open Access*
- On concentration polarisation in a fluidized bed membrane reactor for biogas steam reforming: Modelling and experimental validation, *Chemical Engineering Journal, Open Access*
- Palladium based membranes and membrane reactors for hydrogen production and purification: An overview of research activities at Tecnalia and TU/e, *Int. Journal of Hydrogen Energy*
- Green hydrogen production from raw biogas: a techno-economic investigation of conventional processes using pressure swing adsorption unit, *Processes, Open Access*
- Achievements of EU projects on membrane reactor for hydrogen production, *Journal of Cleaner Production, open access*
- Effect of Au addition on hydrogen permeation and the resistance to H2S on Pd-Ag alloy membranes, *Journal of Membrane Science*
- Techno-economic assessment in a fluidized bed membrane reactor for small-scale h2 production: Effect of membrane support thickness, *Membranes,*

THIS PROJECT HAS RECEIVED FUNDING FROM THE FUEL CELLS AND HYDROGEN 2 JOINT UNDERTAKING UNDER GRANT AGREEMENT NO 671459. THIS JOINT UNDERTAKING RECEIVES SUPPORT FROM THE EUROPEAN UNION'S HORIZON 2020 RESEARCH AND INNOVATION PROGRAMME HYDROGEN EUROPE AND HYDROGEN EUROPE RESEARCH.

Thank you for your attention!

Site: www.bionicoproject.eu

Email: info@bionicoproject.eu

LinkedIn: https://www.linkedin.com/groups/8513530

ResearchGate: https://www.researchgate.net/project/BIONICO

2.8. Environmental aspects of membrane-based CO2-capture (Mireille Faist – QUANTIS)

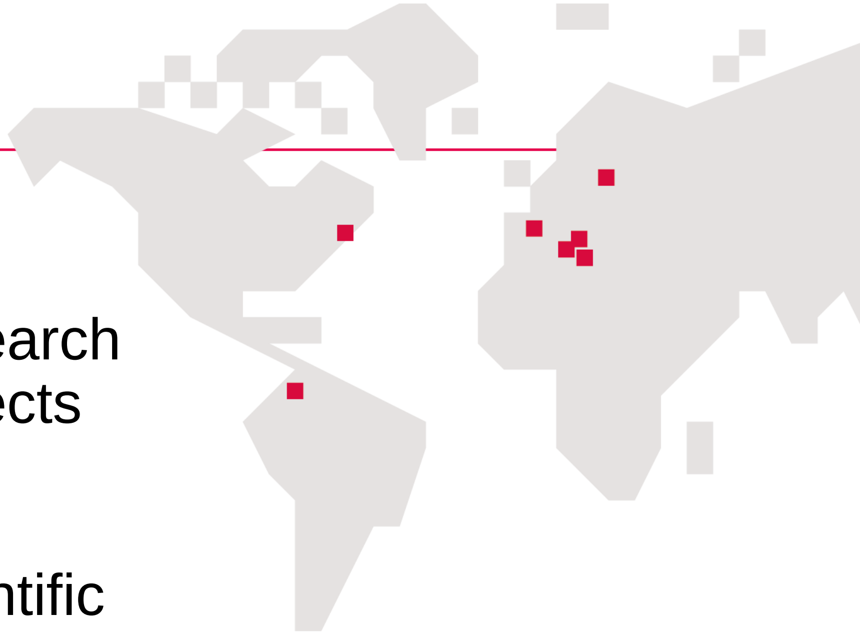
Environmental aspects of membrane-based CO_2-capture

1st Workshop MEMBER Project
TU/e, 15-01-2020

Mireille Faist
Samuel Willi

Contact:mireille.faist@quantis-intl.com, samuel.willi@quantis-intl.com

Our team



University Spin-off

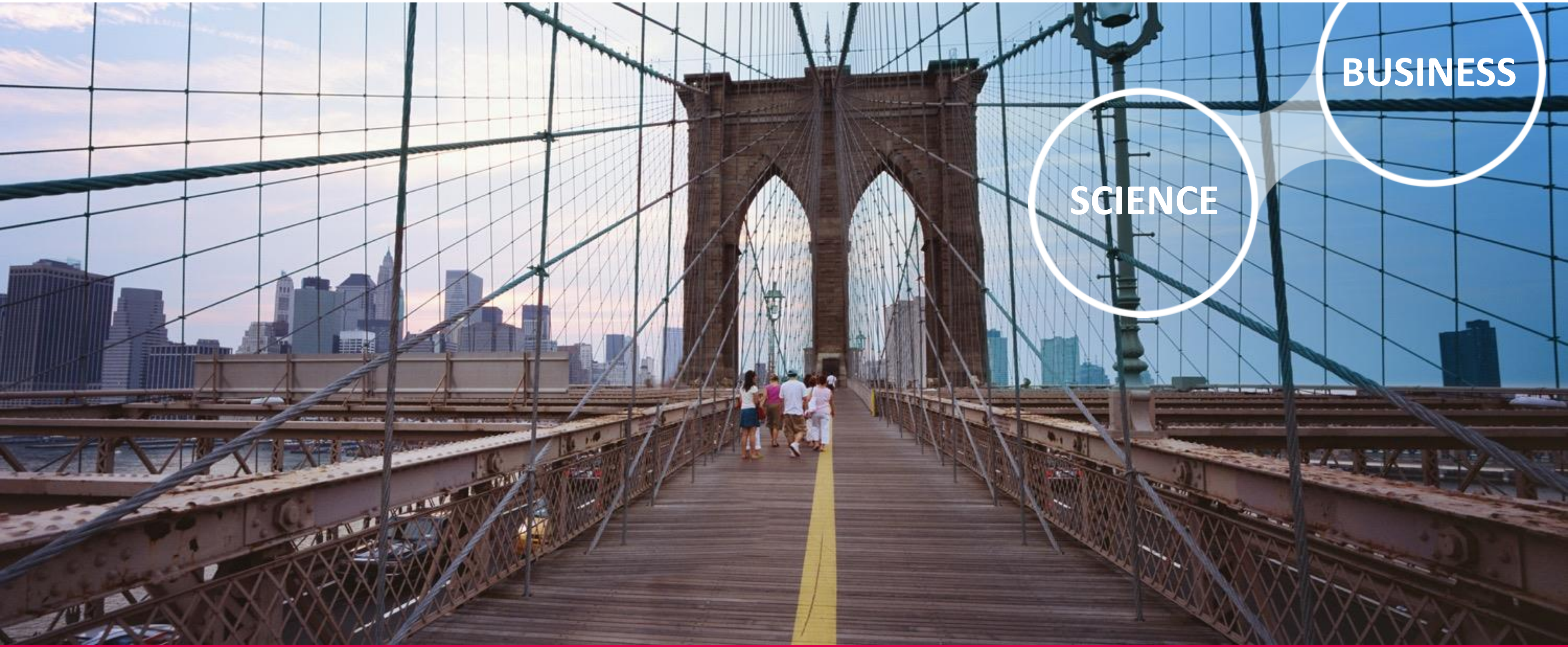
Research Projects

ISO standards

Scientific Thought Leaders

A global team of diverse and dynamic experts, backed by a strong **scientific background**

Our work



Building the bridge between the **science of sustainability** to its **application in business**

Our research projects

eurobioref
DEMCAMER Catalytic Membrane Reactors
DEMEAU
e-SAVE
OPTIFEL food for elderly
aScenT advanced solid cycles with efficient novel technologies
NanoValid
ECOPROT
RE4CELL
Fluid CELL
LC-IMPACT
RENESENG
TOX-TRAIN Getting USEtox™ out of the lab

13 FP7 projects

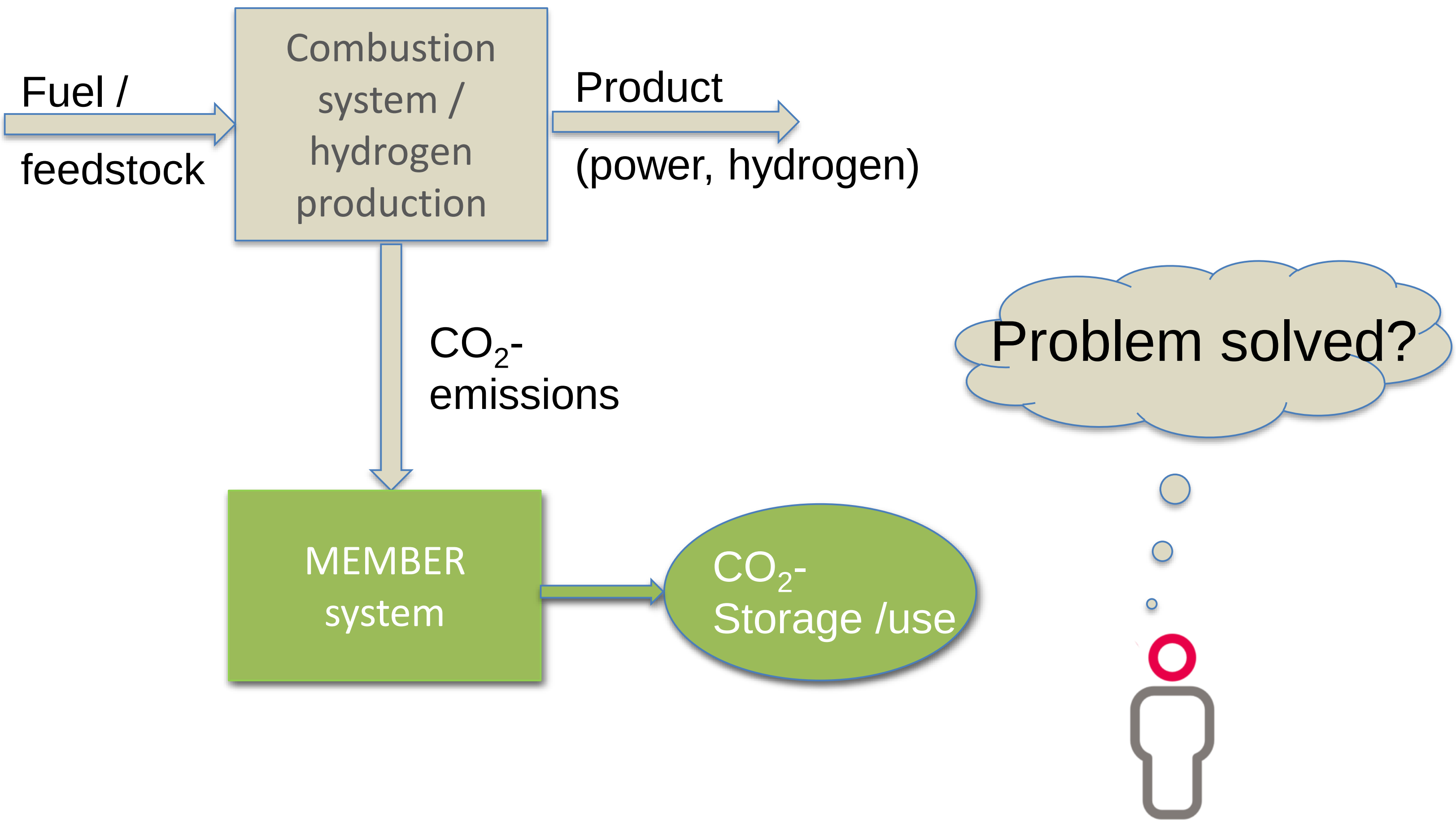
17 H2020 projects
(some yet about to start)

biodiesel 2020
ZELCOR
STAR ProBio
RESYNTEX
HyGrid
FLEDGED
Leilac
MEMERE O_2
EPOS SYMBIOSIS IN INDUSTRY
BIONICO

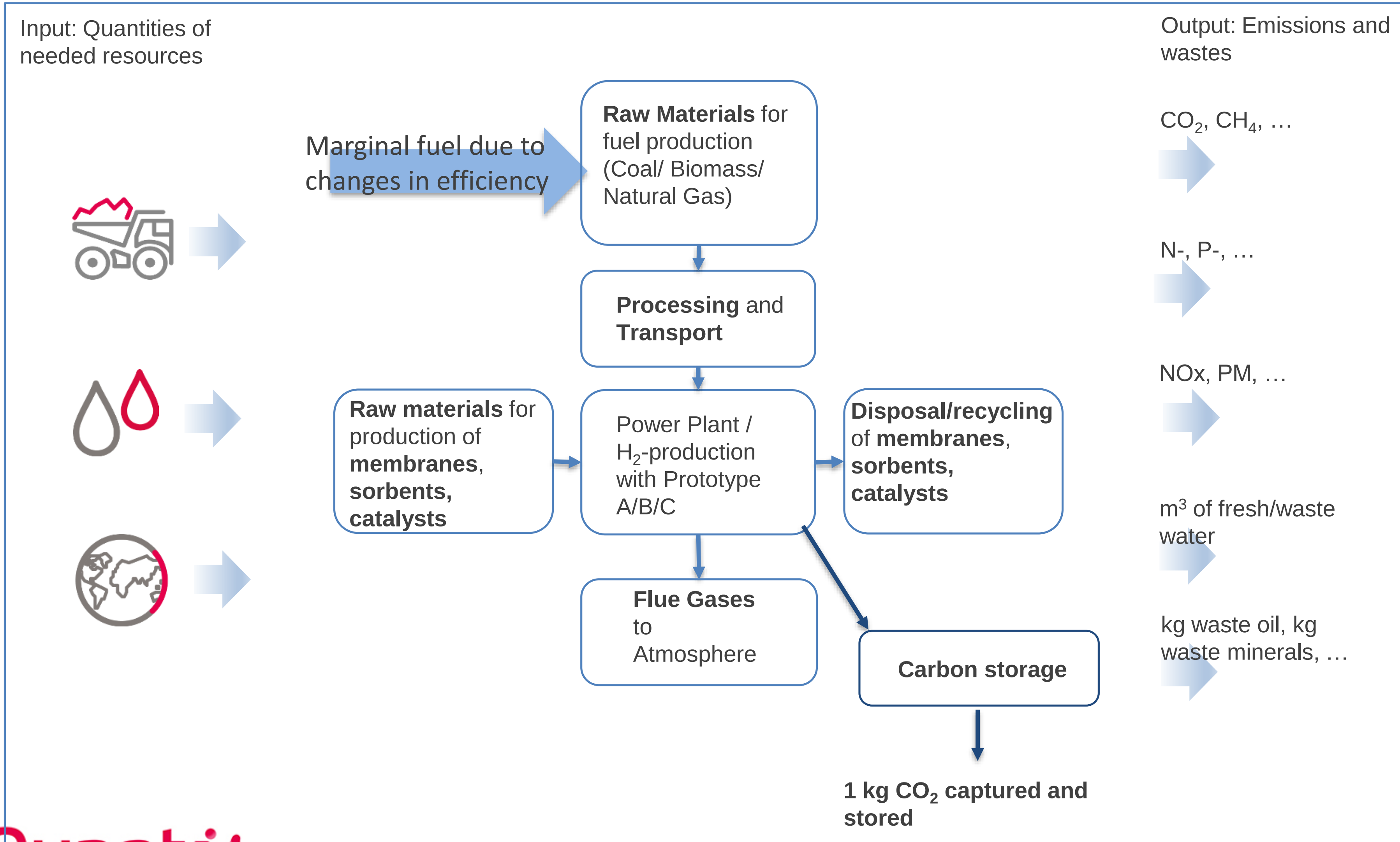
Outline

- Why assess environmental impacts?
- How do we assess them?
- Conclusions

Why assess environmental impacts?



Why assess environmental impacts?



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

Goals of the environmental assessment

- **inform and monitor** key performance indicators along the project
- **guide** the development of the MEMBER materials and technology towards more sustainable solutions
- **benchmark** the MEMBER materials and technology against alternative conventional and state-of-the-art technologies for pre- and post-combustion CO2 capture
- **help** future suppliers and customers make more informed decisions.

Environmental assessment: method

- Life Cycle Assessment (LCA) according to ILCD Handbook as well as the ISO series of norms 14040-44 and the recent ISO norm 14046 on water footprinting

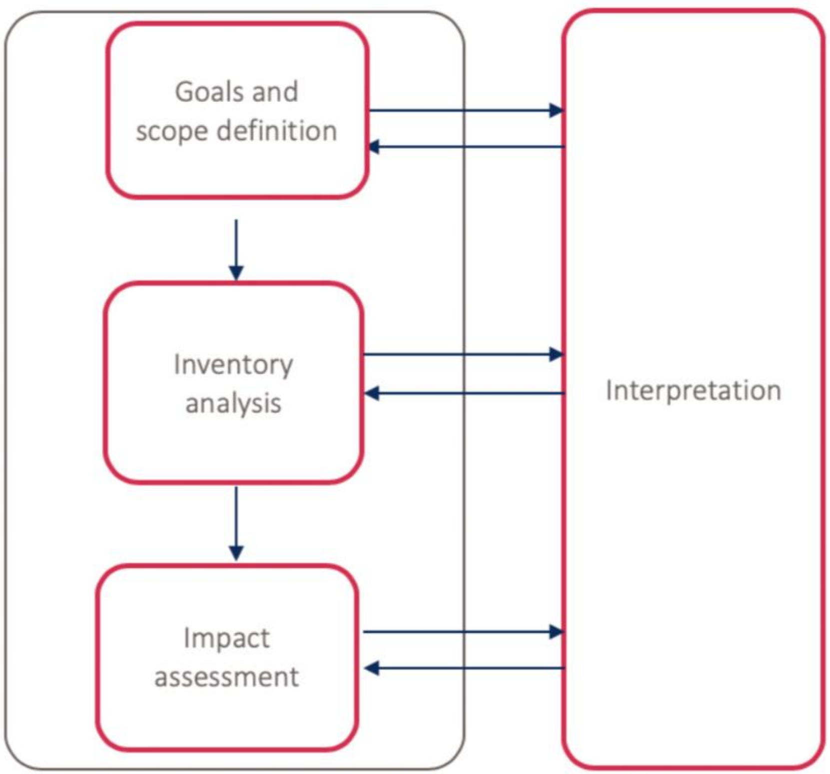
- Goal is to assess **all** environmental impacts of the novel technology «**from cradle to grave**»

- Using specific data from the partners and up-to-date database (ecoinvent)

1. Environmental assessment method

- A standardized method: Life Cycle Assessment according to ISO 14'040

LCA framework, as described by ISO 14040: 2006



1. Environmental assessment method

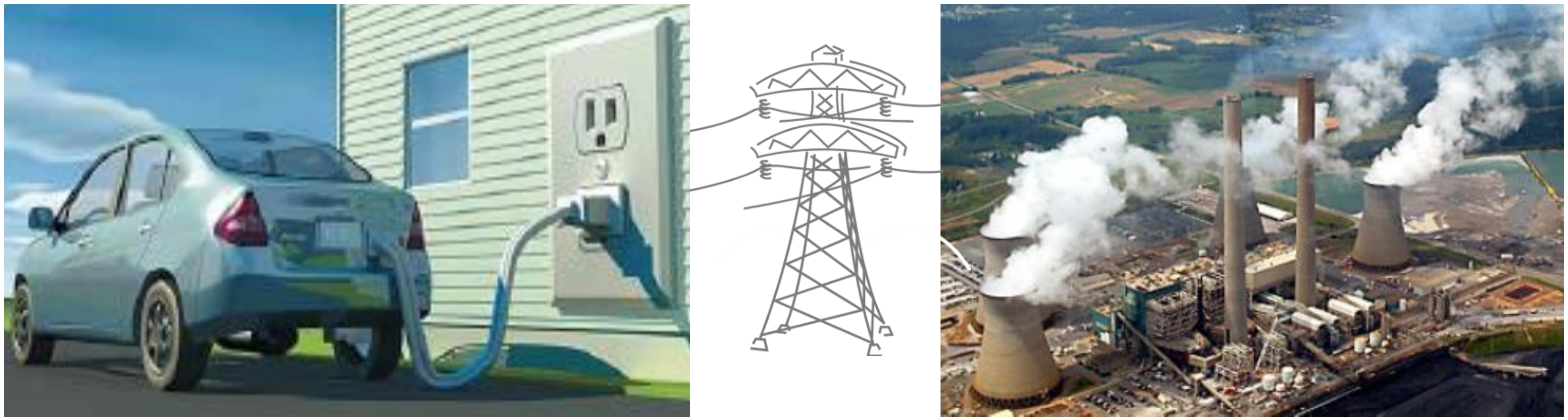
- A quantitative approach: assess all environmental impacts of technology «from cradle to grave»

1. Environmental assessment method

- Using up-to-date database: ecoinvent

- LCA can be used for:
  - Identify environmental issues along the value chain (hotspots)
  - Identify improvement possibilities and production optimization
  - Compare alternatives
  - Set goals and measure progress
  - Benchmark performance
  - Manage risk
  - Communicate
  - And more

Example



Zero emissions ?

Emissions elsewhere !

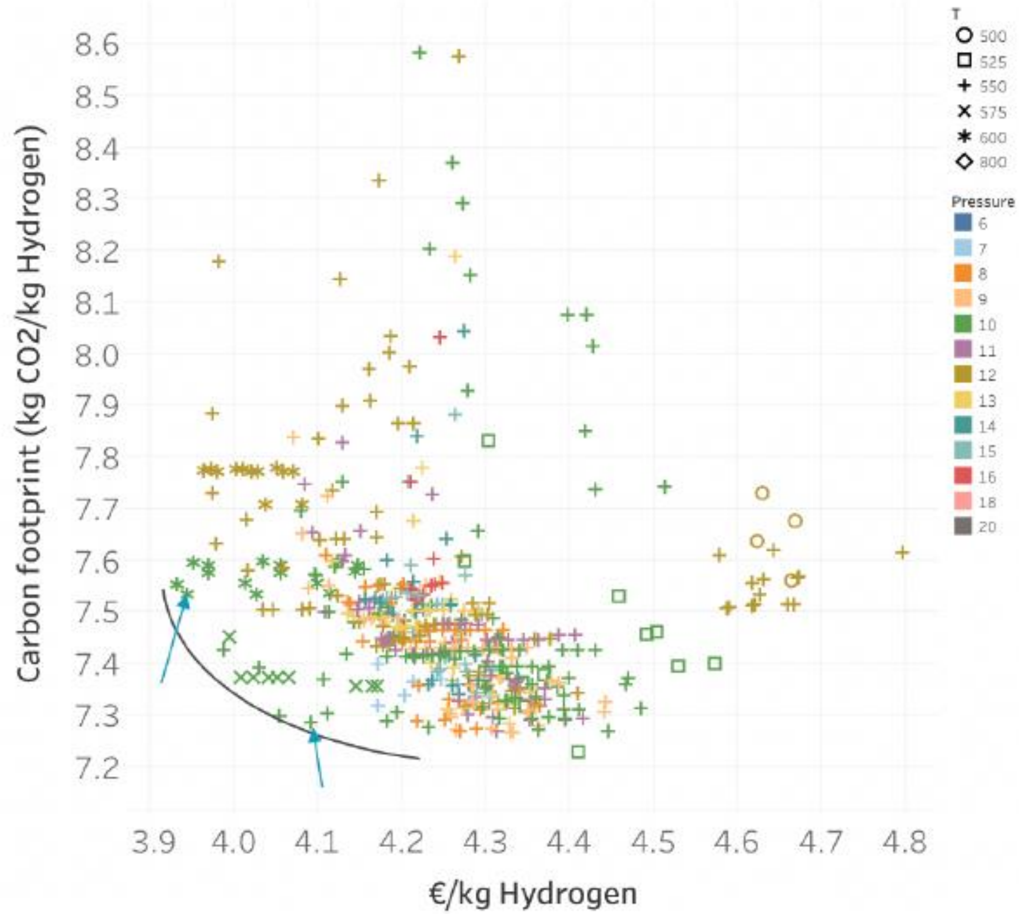
Avoiding the transfer of environmental issues

- From one life cycle stage to another
- From one region to another
- From one compartment to another
- From one generation to the next
- Among issues

Added value for innovative projects

- It is easier and economically more viable to address the environmental performance at the **early stages** of commercial development than at the later stages.
- The results can be used to **steer the project** towards the realization of more environmentally friendly and affordable systems, while highlighting environmental hotspots along the value chain.
- The results will also provide **knowledge and support** to the different stakeholders and decision makers like the industries, European commission services, research institutions and government agencies.

Example of results (BIONICO project)



Based on the **Pareto frontier analysis**, we can identify the most favorable for either economic cost or carbon footprint.
The **optimal solution** only exists along the Pareto curve (influenced by temperature, reactor design and pressure). The rest are inferior operating conditions or designs.

Example of results (ZELCOR project)

- ZELCOR project: ZEro waste Ligno-Cellulosic biO-Refineries
- LCA results helped the researchers **identify the problem** related to solvent and energy consumption in the **early stage design** of their experiments.
- As the result of the LCA analysis, they're exploring **different experiment design for biorefinery production**

Key LCA steps

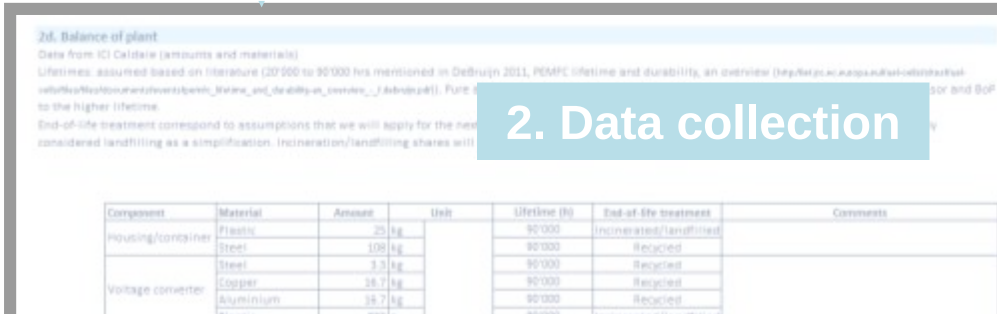
Reference system

Novel technology

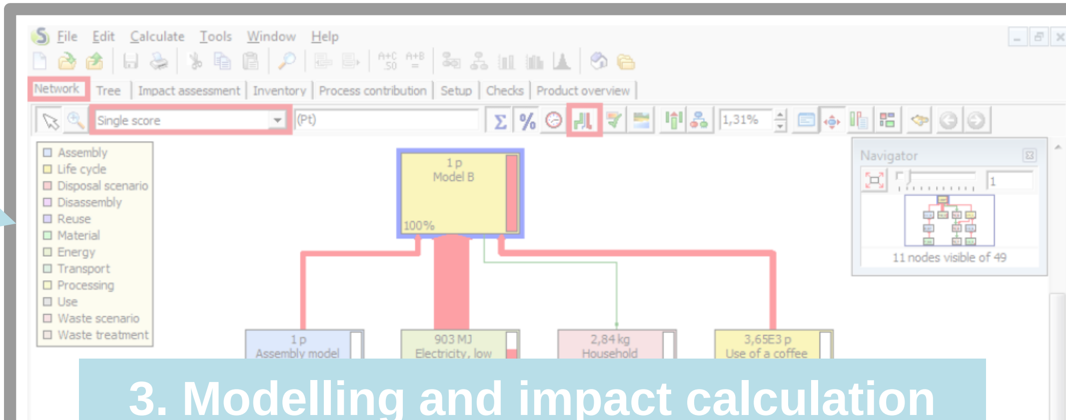
1. Goal and scope

Iterative process!

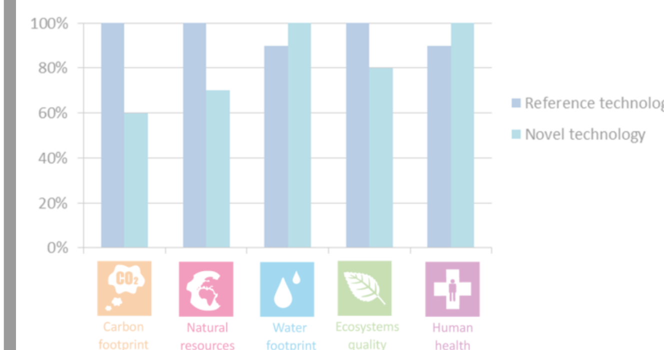
2. Data collection



3. Modelling and impact calculation



4. Result interpretation



Quantis

Main drivers of the environmental impacts

- Energy consumption of MEMBER system / efficiency loss of power plant
- Production of membranes and other key materials (sorbents, catalysts, MOFs, polymers, mixed matrix hollow fibers)
- Disposal of membranes and other key materials

‼ CO_2-emissions from energy consumption and from production of the MEMBER system can reduce the netto amount CO_2 stored.

Quantis

Benefits of environmental assessment

- Evaluation of the **overall CO_2-savings including storage phase** → overall **efficiency** of CO_2-capture

- Evaluation of **other environmental impacts** thanks to comprehensive indicator set → identification of **trade-offs**

- **Possible optimisation** of the MEMBER system at an **early stage** according to the environmental assessment

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

https://member-co2.com/

Thank you for your attention!

Contact: mireille.faist@quantis-intl.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)