Flexible Hybrid separation system for H_2 recovery from NG Grids

HyGrid

https://www.hygrid-h2.eu/

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking under grant agreement No 700355.This Joint Undertaking receives support from the European Union's Horizon 2020 research and innovation programme and Hydrogen Europe and N.ERGHY

Duration: 3 years. Starting date: 01-May-2016

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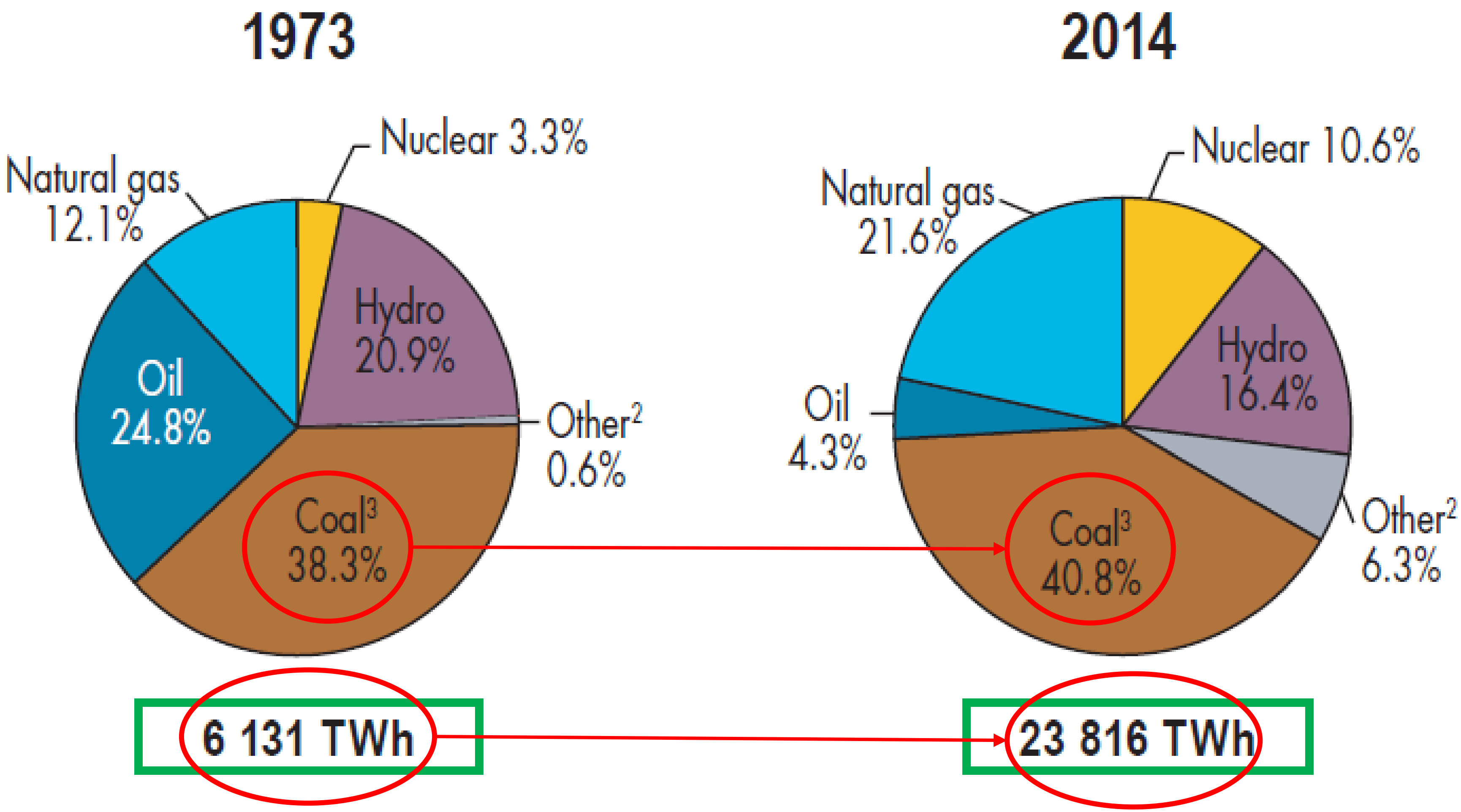
Introduction

Electricity consumption and CO_2 emissions

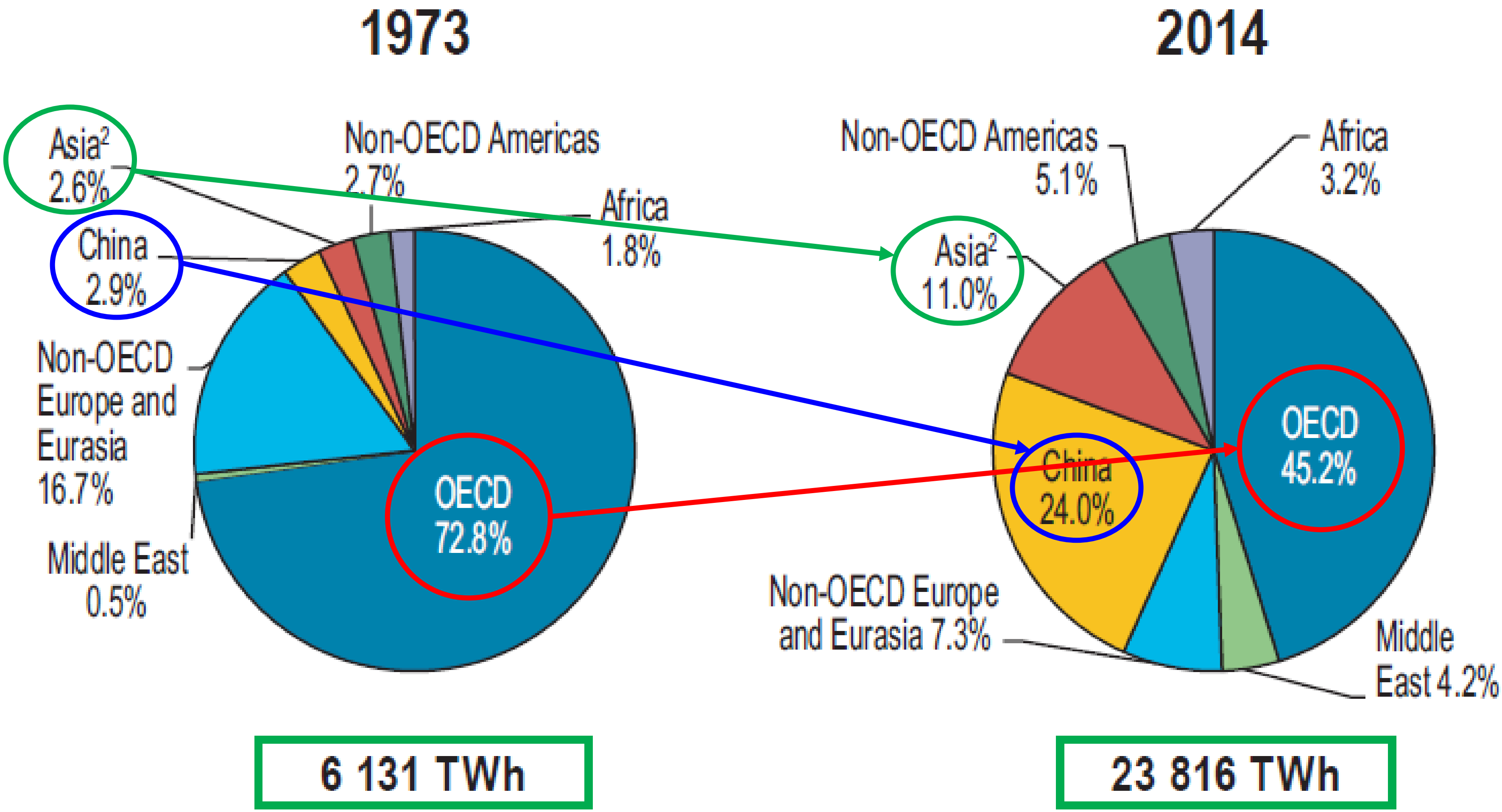
Fuel share of electricity generation in the world



* IEA Keyworld 2016

Electricity consumption and CO_2 emissions

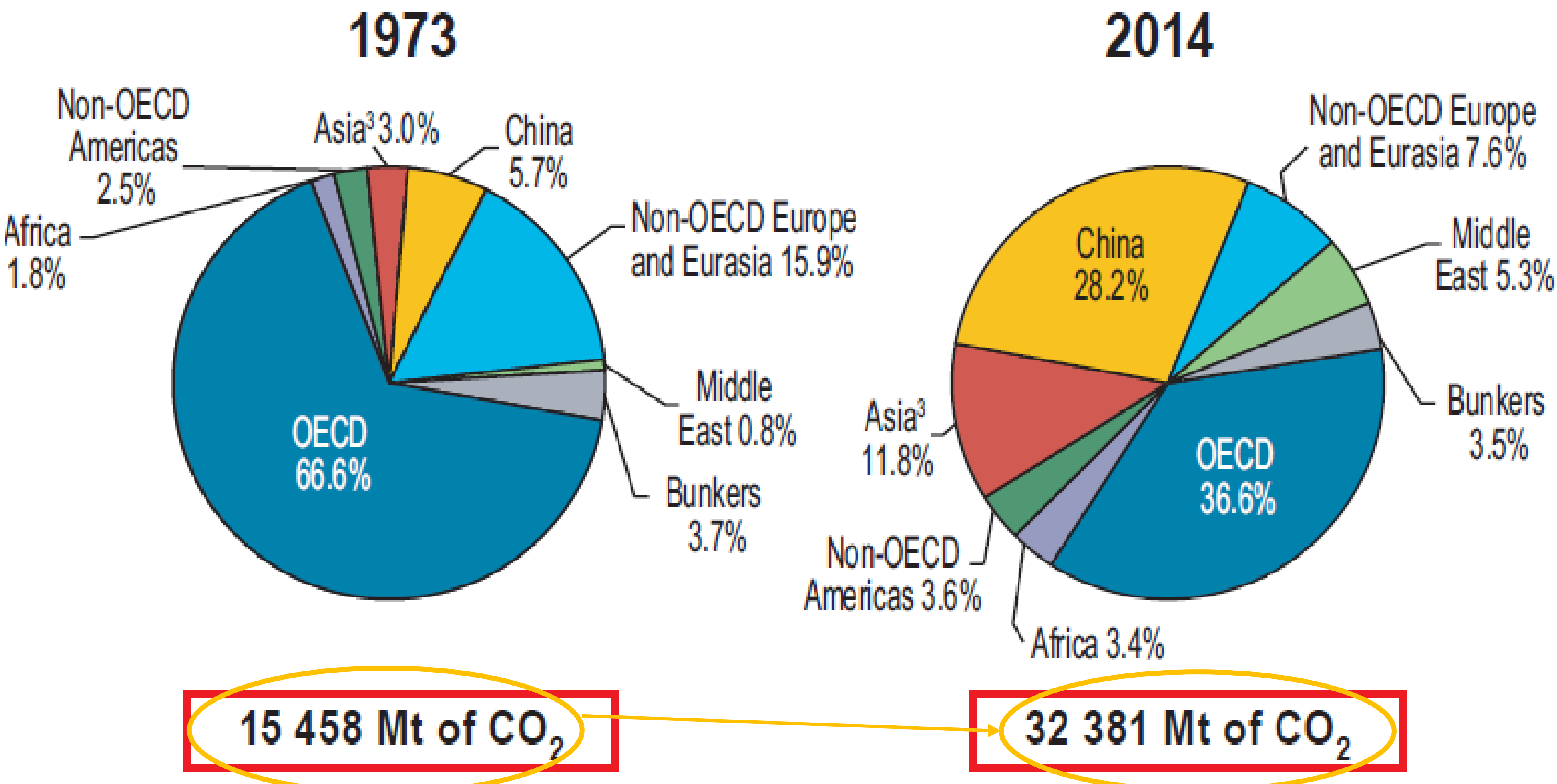
New actors in the CO_2 emission frame: China and India



* IEA Keyworld 2016

Electricity consumption and CO_2 emissions

Regional share of CO_2 emissions

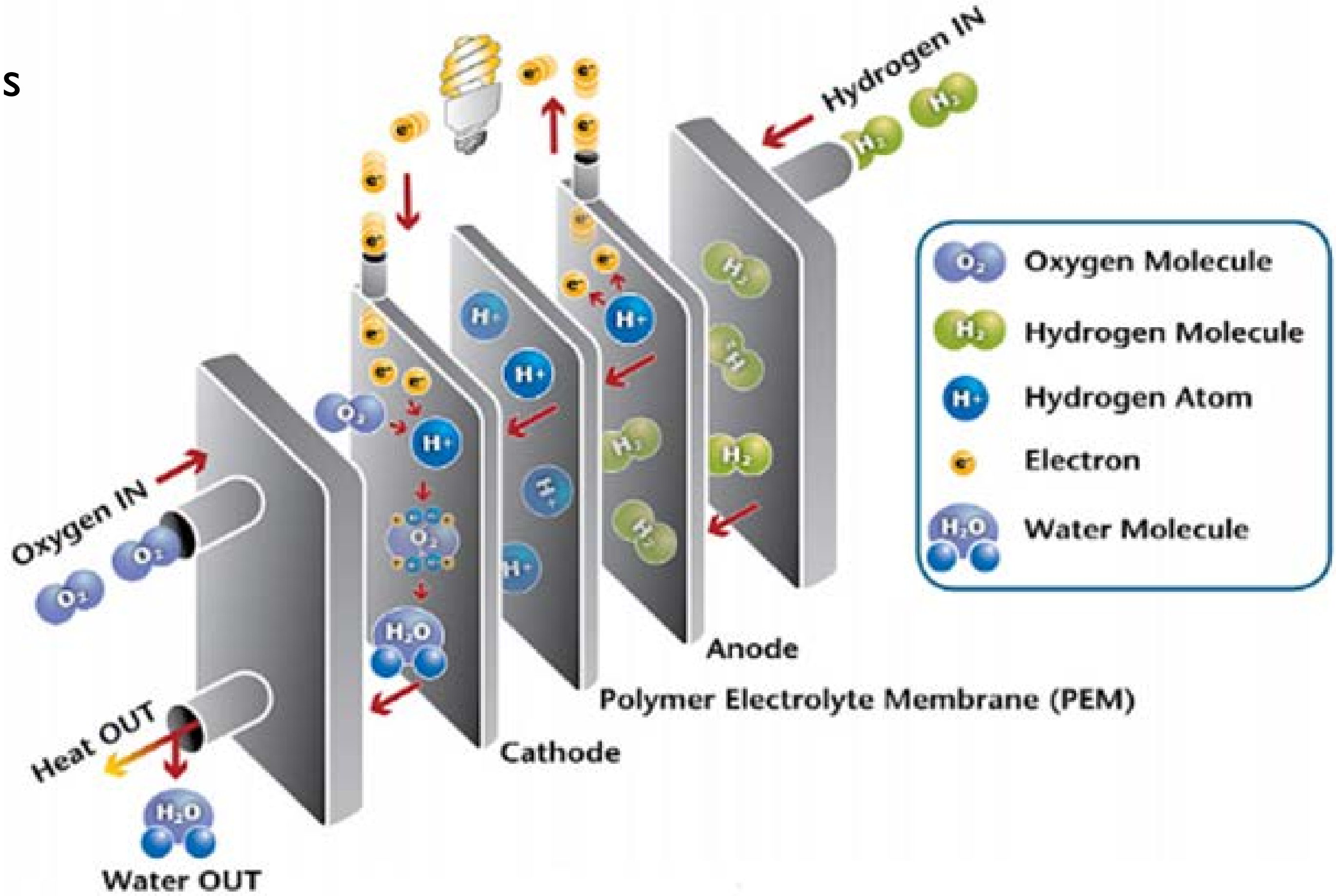


* IEA Keyworld 2016

Electricity consumption and CO_2 emissions

Advantages of the H_2 based economy:

- Direct transformation chemical energy in electricity
- Higher efficiency
- No CO_2 emissions
- Few moving parts



Introduction

- One of the main problems for the implementation of the hydrogen based economy is the transportation from production centers to the end user.

- One approach to solve this problem is to use the existing Natural Gas network for storing and distributing hydrogen.

The HyGrid technology will provide a route to:

- Increase the value of hydrogen blended into the natural gas grid, improving the economics of central hydrogen production from excess renewable energy couples with natural gas grid injection.
- Reduced cost, and therefore increased use of hydrogen from very dilute hydrogen streams in energy and transport applications.
- Further applications could be found in separating hydrogen from mixtures produced in chemical or biological processes, where it otherwise would be used to generate heat or even be vented.

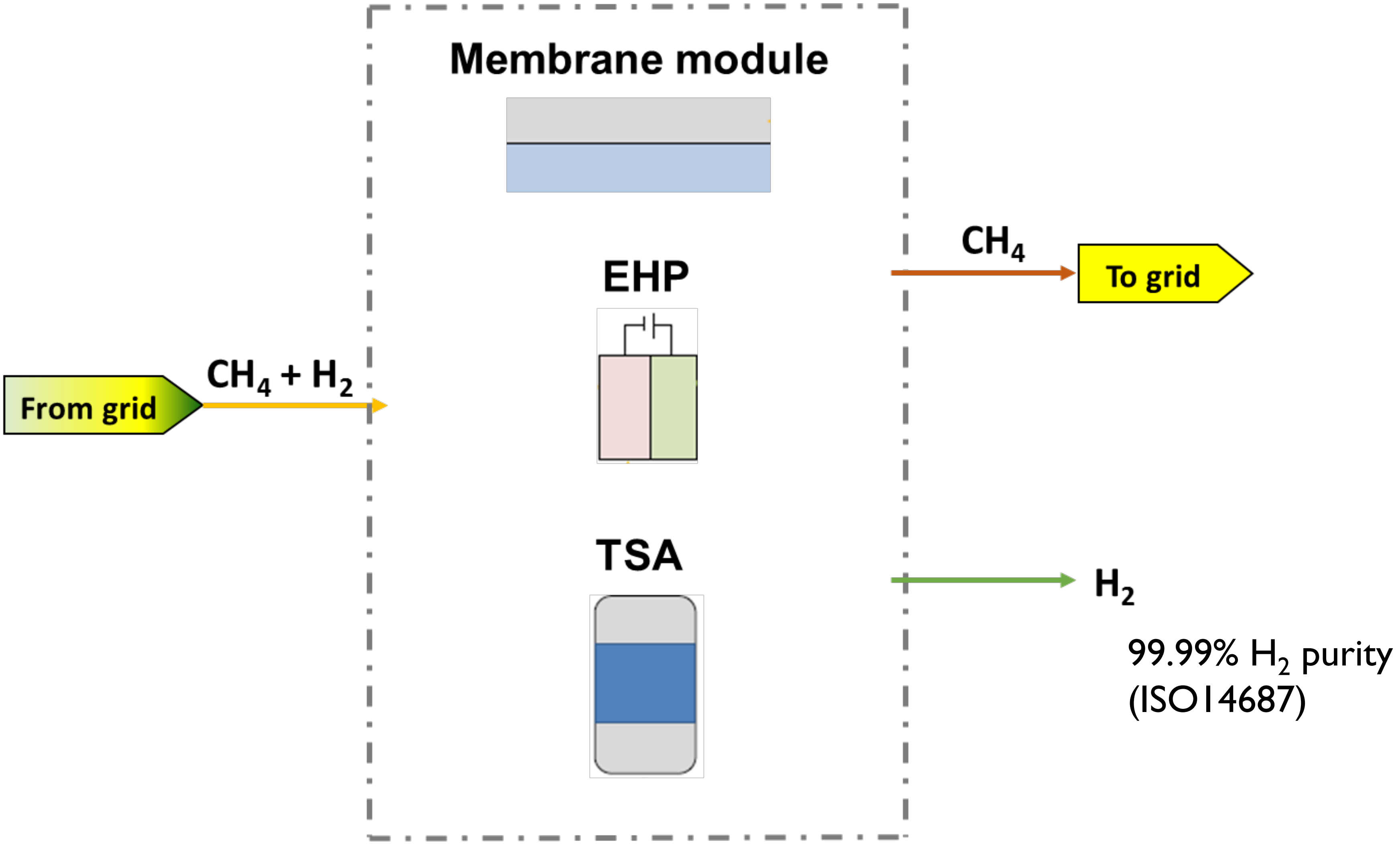
General concept

HyGrid **aims** at developing of an advanced **high performance**, cost effective separation technology for **direct separation of hydrogen from natural gas networks.**

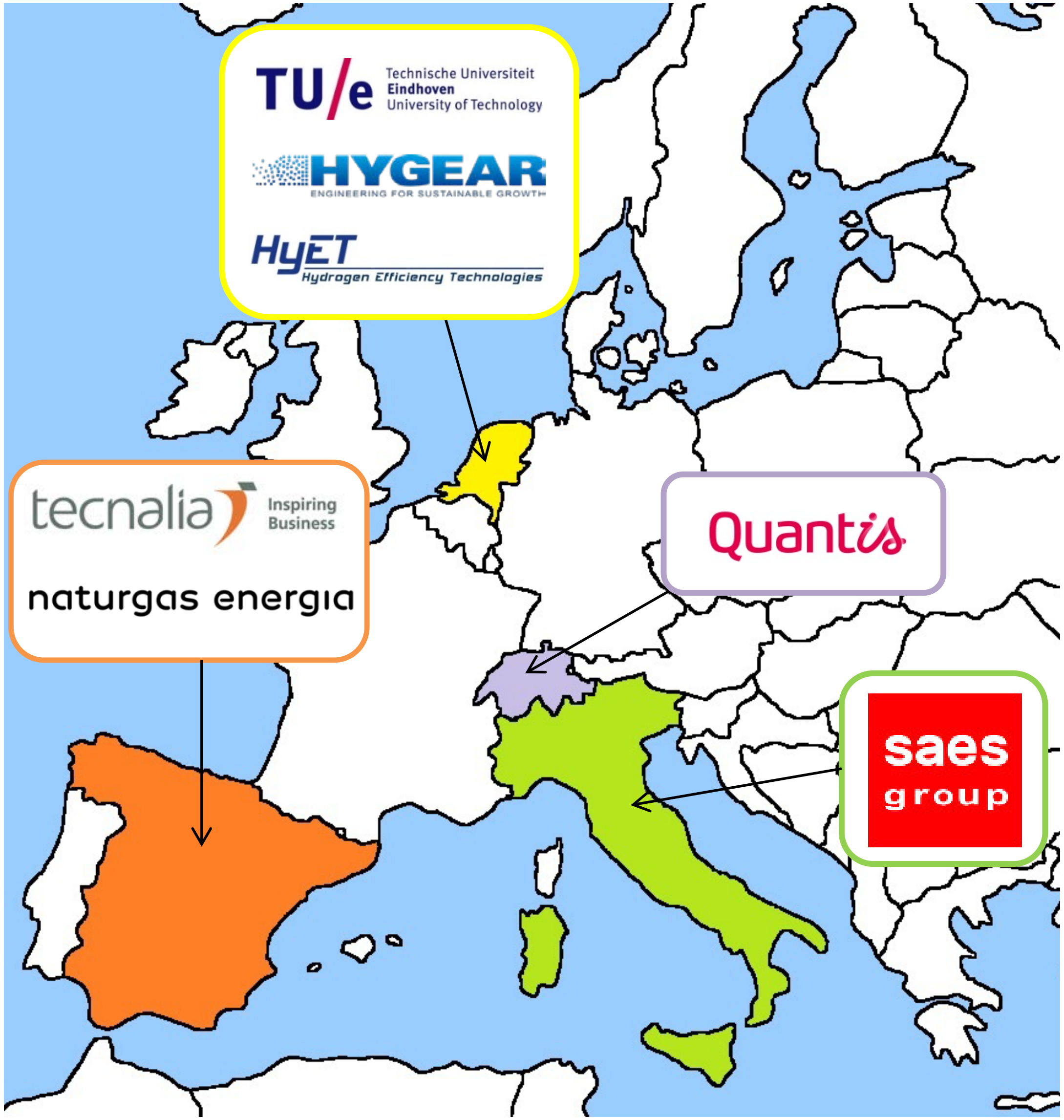
The system will be based on:

- Design, construction and testing of an **novel membrane based hybrid technology** for pure hydrogen production (ISO 14687) combining three technologies for hydrogen purification integrated in a way that enhances the strengths of each of them: **membrane separation technology** is employed for removing H2 from the "low H_2 content" (e.g. 2-10 %) followed by **electrochemical hydrogen separation** (EHP) optimal for the "very low H_2 content" (e.g. <2 %) and finally **temperature swing adsorption** (TSA) technology to purify from humidity produced in both systems upstream.
- The project targets a pure hydrogen separation system with **power** and **cost** of **< 5 kWh/kg$_{H2}$** and **< 1.5 €/kg$_{H2}$**. A pilot designed for **>25 kg/day** of hydrogen will be built and tested at industrially relevant conditions (TRL 5).

General concept



Partnership



Multidisciplinary and complementary team: 7 top level European organisations from 4 countries: 2 research institutes and 5 top industries (3 SME) in different sectors (from materials development to membrane modules and separation systems, etc.).

1 TU/e, Netherlands
2 TECNALIA, Spain
3 HYG, Netherlands
4 SAES, Italy
5 HYET, Netherlands
6 QUANTIS, Switzerland
7 Nortegas Energía, Spain

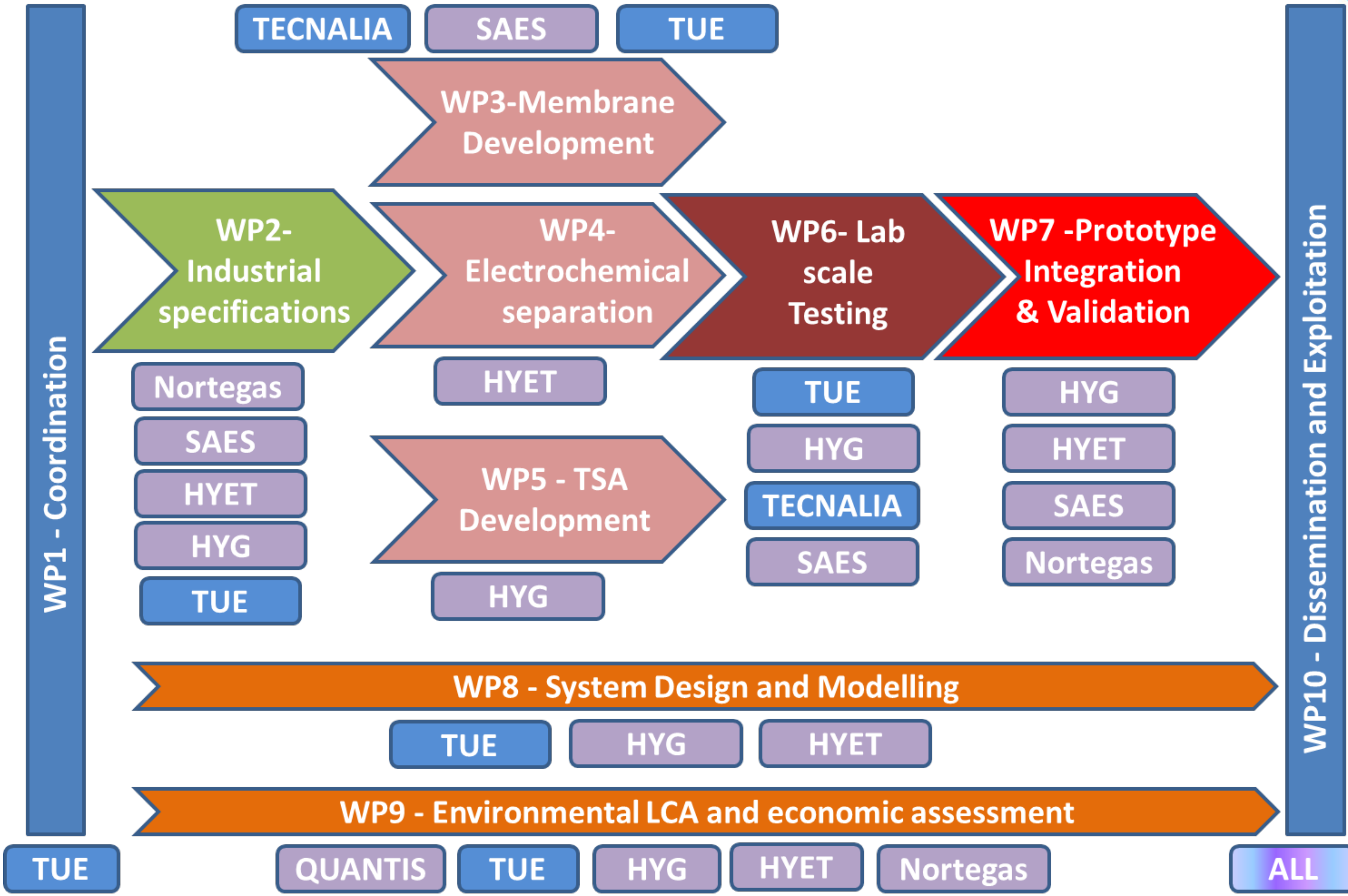
Consortium

1 TU/e, Netherlands
2 TECNALIA, Spain
3 HYG, Netherlands
4 SAES, Italy
5 HYET, Netherlands
6 QUANTIS, Switzerland
7 Nortegas Energía, Spain

Project objectives

- Development of a hydrogen separation system capable of targeting low (2-10%) and very low (<2%) H_2 blends in natural gas.
  - Membranes for H2 recovery from low hydrogen content streams (2-10%).
  - EHP for H_2 recovery from very low concentration streams (<2%) .
  - TSA for water removal from hydrogen/water streams.
- Technical validation of the novel modules at lab scale.
- Optimization of the hybrid system.
- Energy analysis of the new HyGrid technology on different scenarios:
  - recovery of H_2 from low concentration streams (2% -10%) up to 99.99% H_2 purity (ISO14687) in the whole range of pressures of the NG grid.
  - Different configurations/combinations of the three separation technologies
- The validation of the novel hybrid system at prototype scale (TLR 5)
- The environmental LCA of the complete chain.
- Dissemination and exploitation of the results.

Work Structure - Partnership Synergies



Membranes development

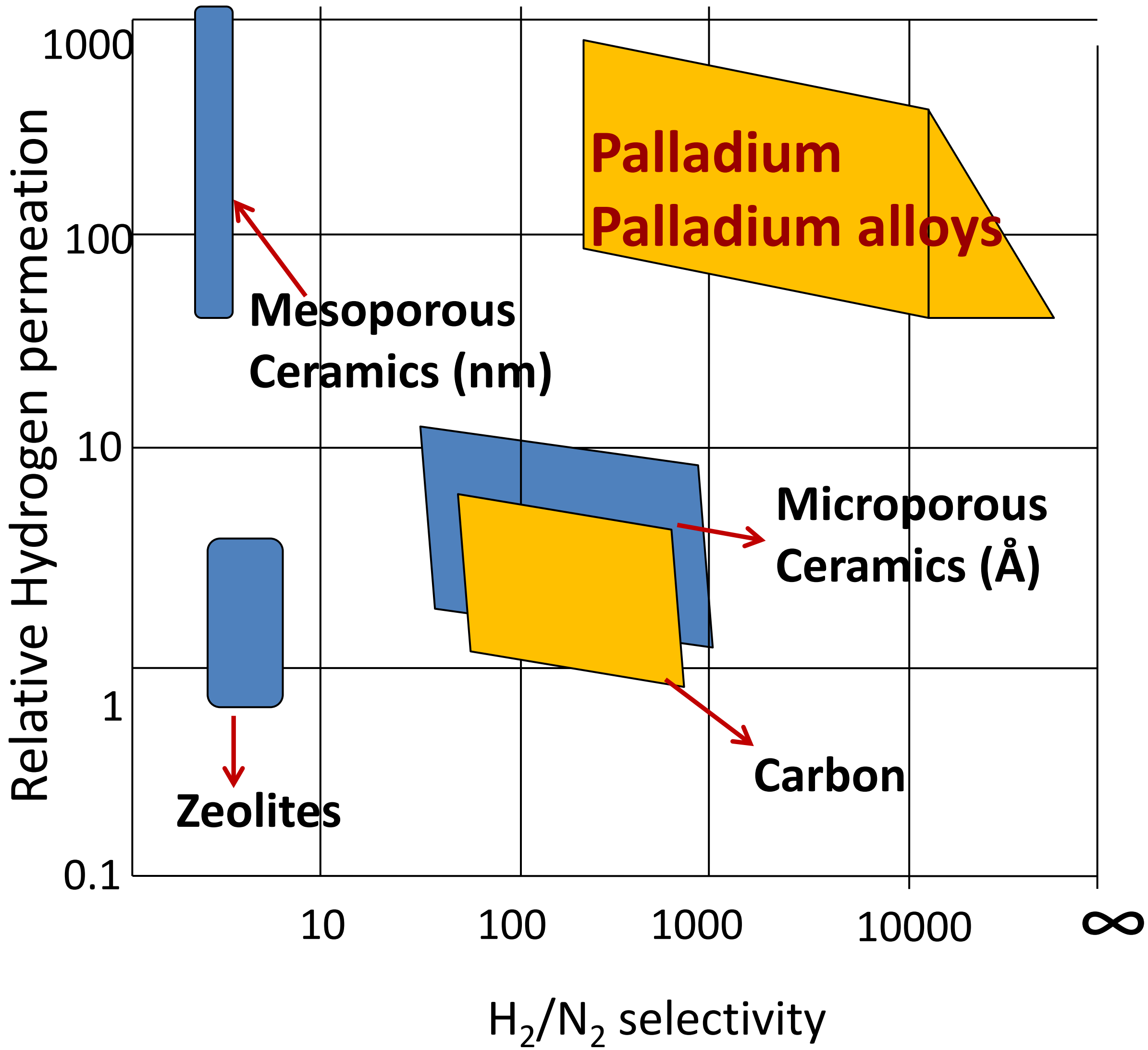
Objectives:

Development of cost effective tubular supported membranes for the recovery of hydrogen from low concentration streams (2% -10%) in the whole range of pressures of the Natural Gas Network. Two different types of membranes will be developed as well as the final membrane module:

- **Pd-based membranes** for the medium to the lowest Natural Gas Grid pressures with improved flux and selectivity.
- **Carbon Molecular Sieve membranes** for the high pressure range.
- Membrane **module for the prototype**.

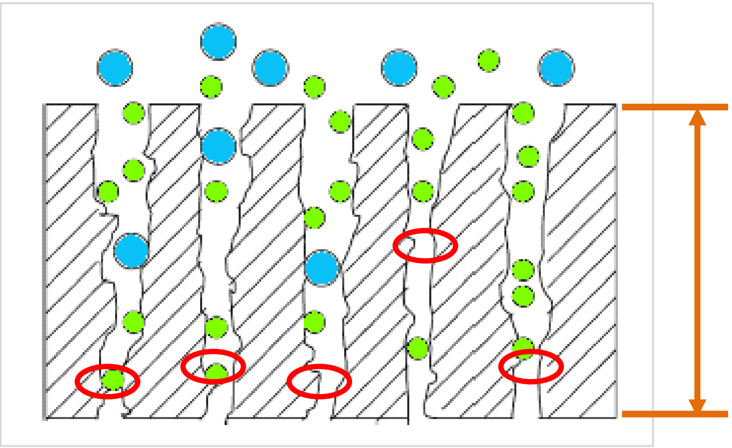
Inorganic, metallic & carbon membranes

Permation of H_2 against H_2/N_2 selectivity

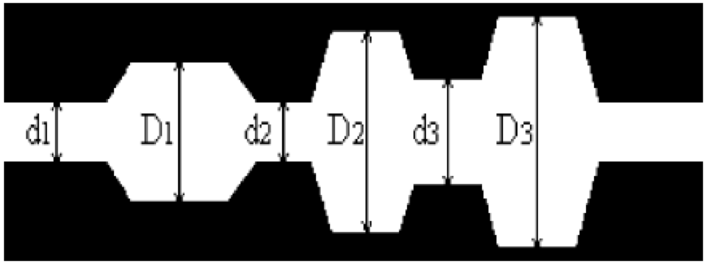


Carbon Molecular Sieve membranes

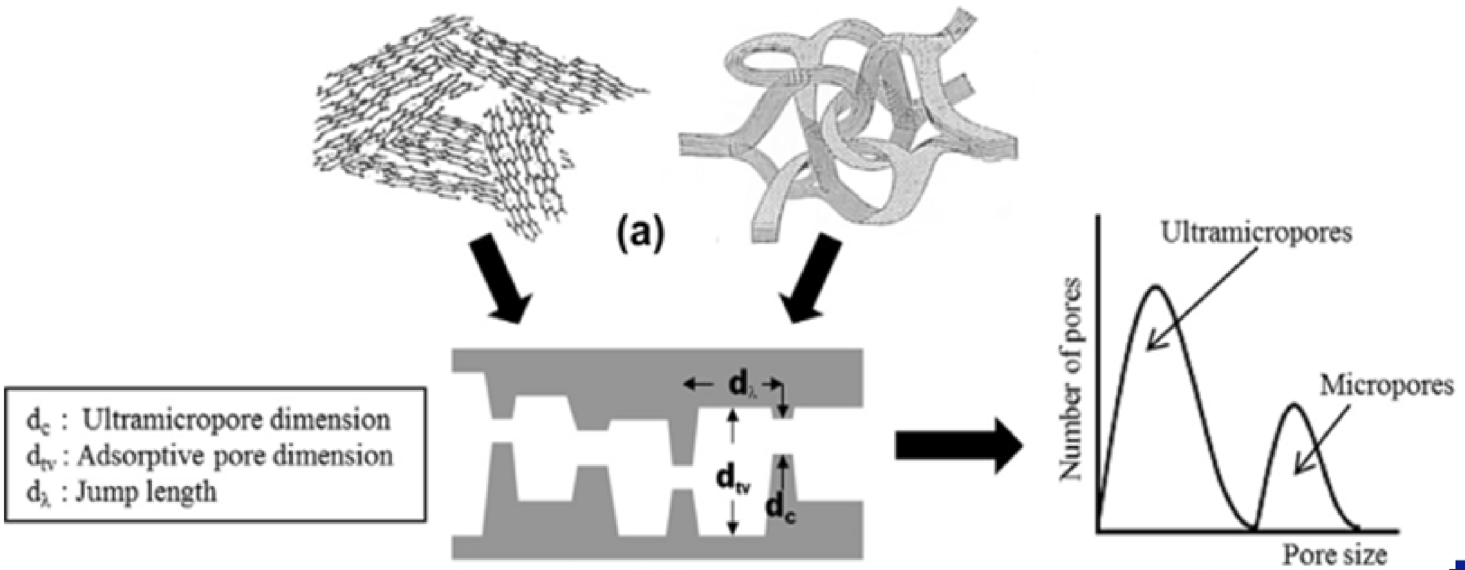
Transport mechanism



Membrane thickness

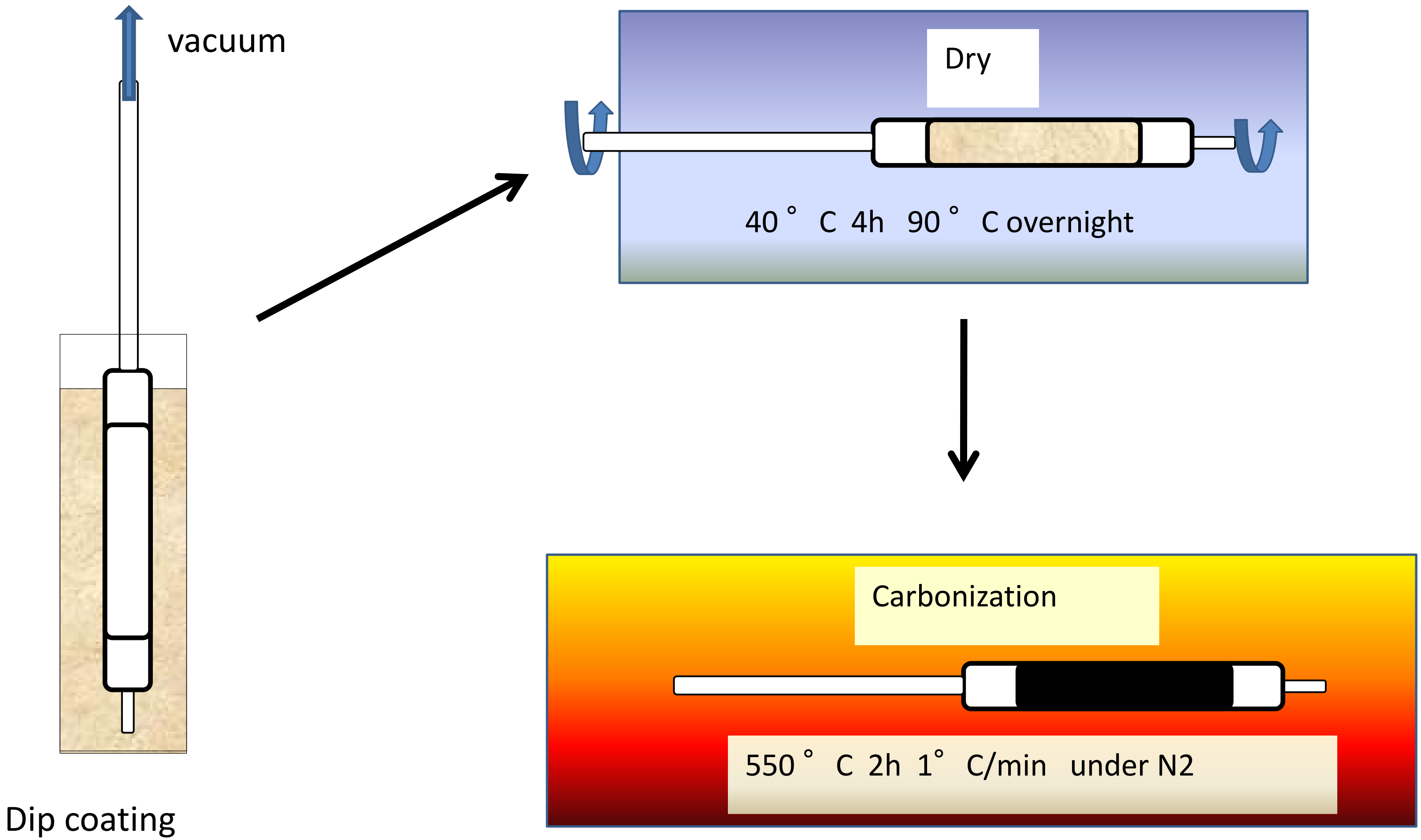


Nanopores + constrictions



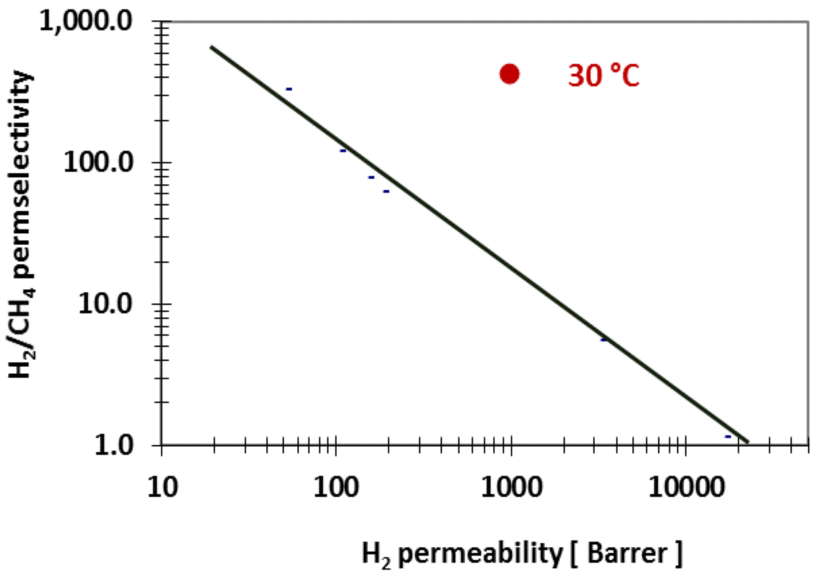
Carbon Molecular Sieve membranes

Preparation of composite Al2O3 – CMSM

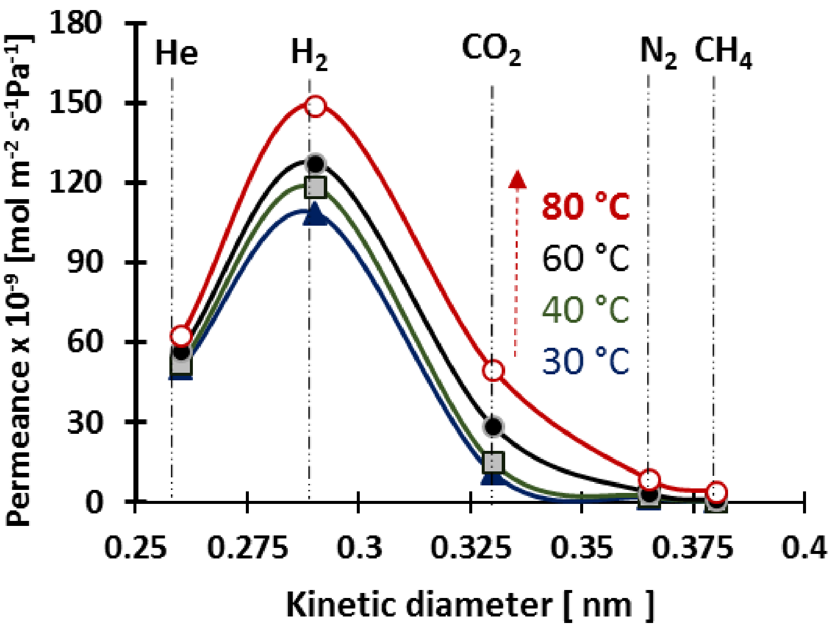


Carbon Molecular Sieve membranes

Robeson plot of the of composite Al-CMSM



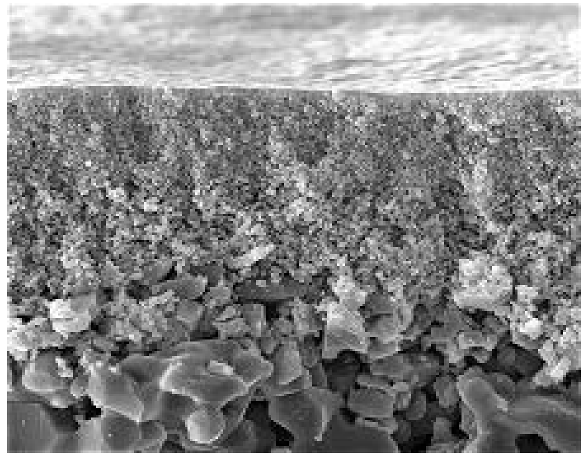
Gas permeation of composite Al-CMSM at various temperatures

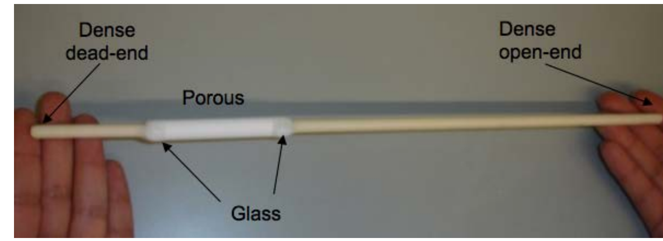


Ceramic supported Pd-based membrane

Porous Support:

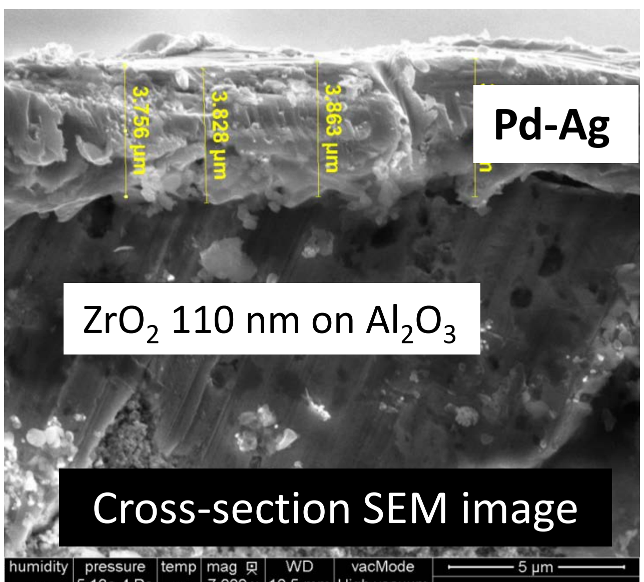
- Supplied by Rauschert
- 100nm pore size Al_2O_3





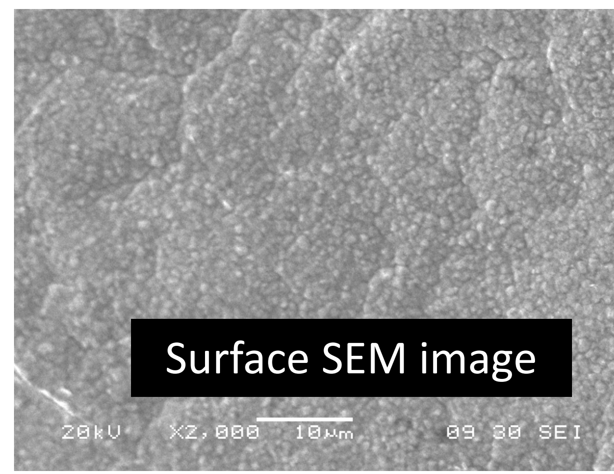
Join to dense ceramic tube at Tecnalia

Pd-Ag membrane layer deposition by Electroless Plating technique



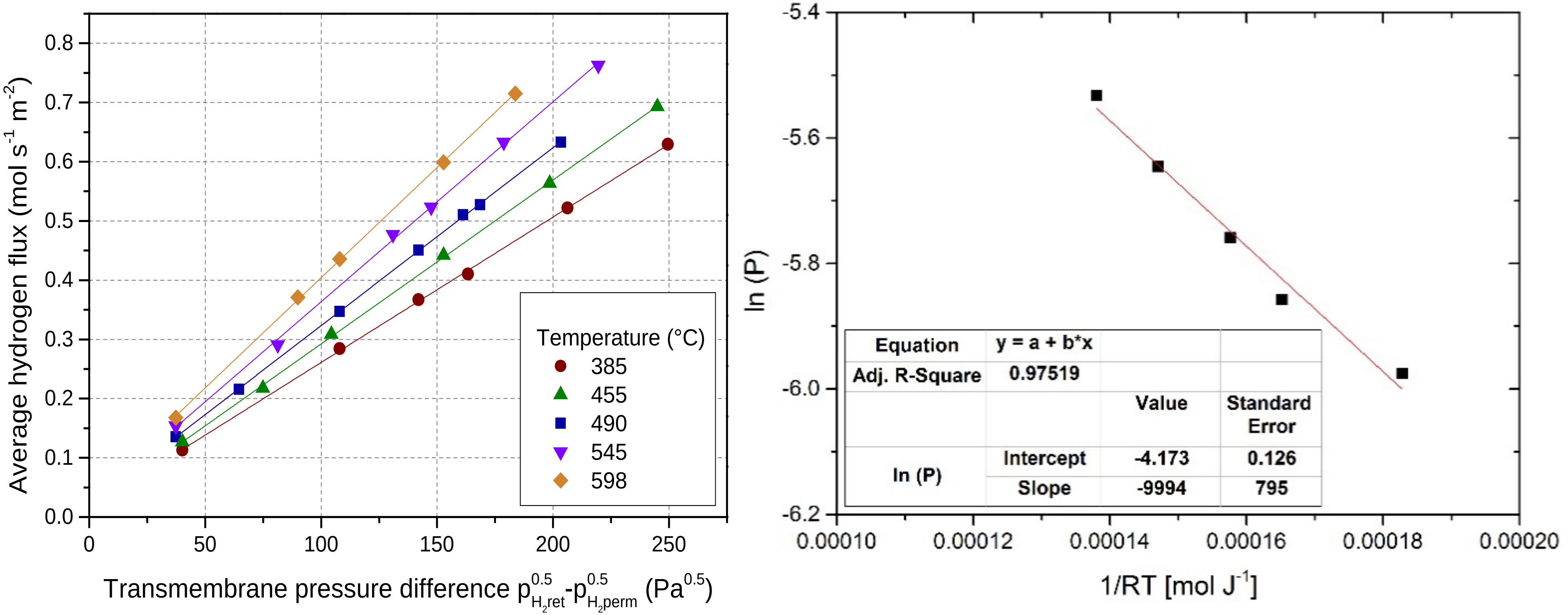
- ~4 µm thick Pd-Ag membrane
- Membrane length before sealing: 14-15 cm

tecnalia Inspiring Business



Ceramic supported Pd-based membrane

Single gas permeation test

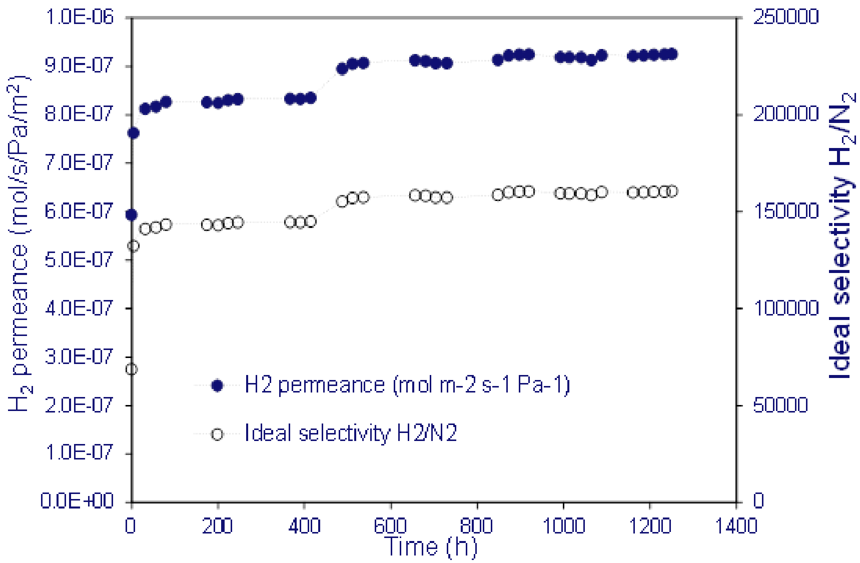


Ea: 10 kJ/mol; P^0: 6.93×10^{-8} mol m^{-1} s^{-1} $Pa^{-0.5}$

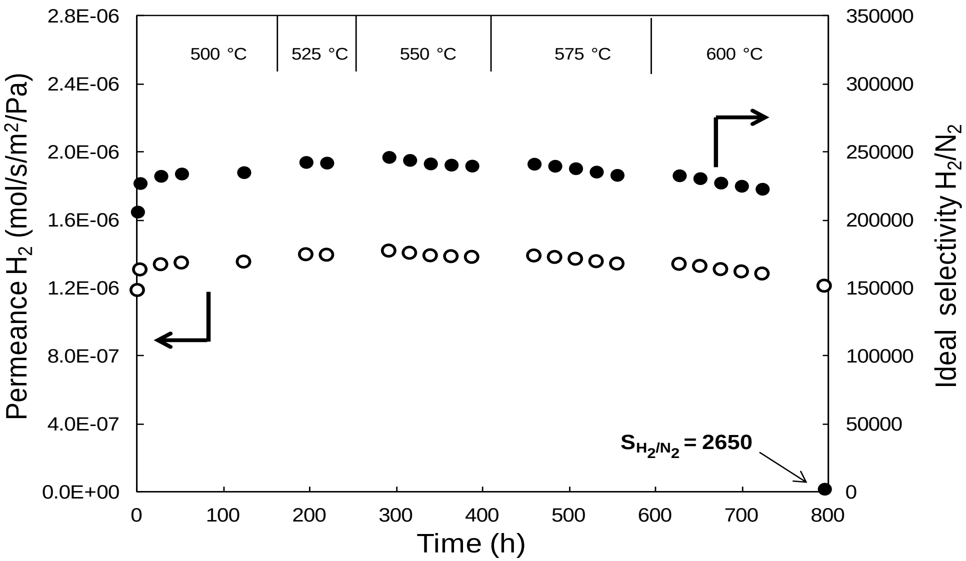
Fernandez et al., Preparation and characterization of thin-film Pd-Ag supported membranes for high-temperature applications. International Journal of Hydrogen Energy 40:13463-13478, 2015.

Metallic supported Pd-based membrane

Long-term stability test



Metallic supported membrane M14.
*Long-term stability test over time at **400 ºC***

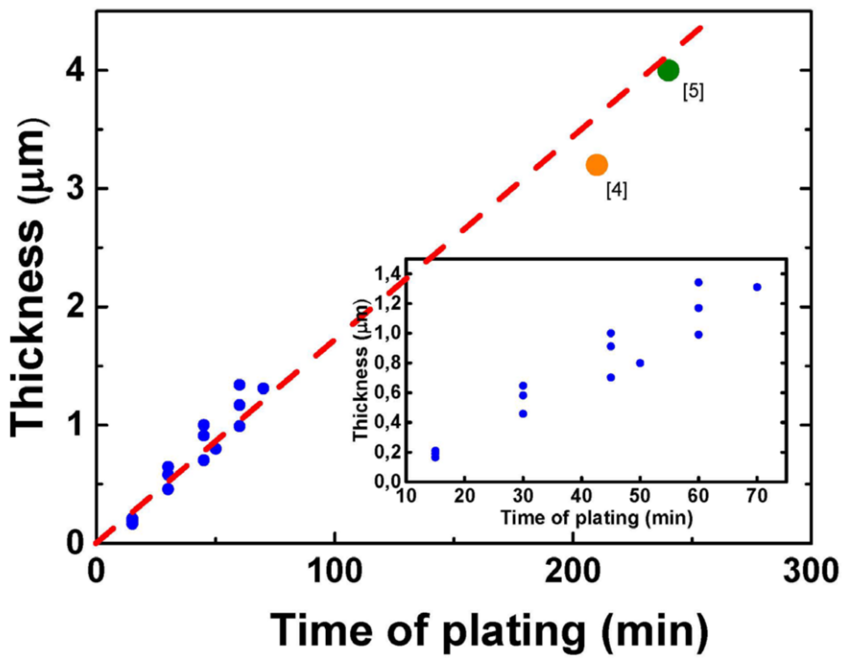


Membrane M17-E94.
Long-term stability test (**500-600 ºC**)

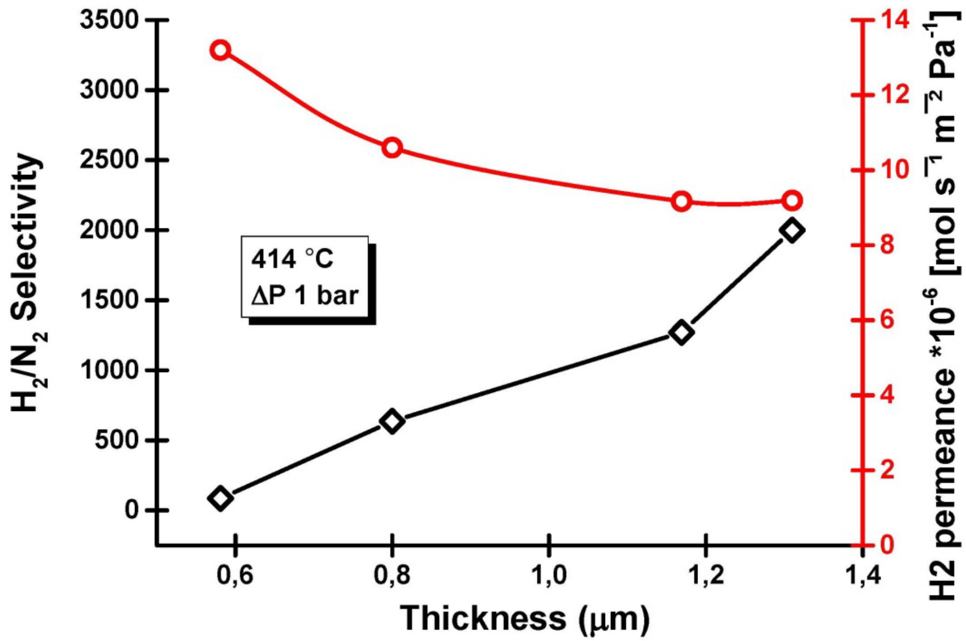
Medrano et al., Pd-based metallic supported membranes: high-temperature stability and fluidized bed reactor testing, International Journal of Hydrogen Energy, 2015. http://dx.doi.org/10.1016/j.ijhydene.2015.10.094

Ultra-thin (≈ 1 μm) supported Pd-Ag membranes by Electroless Plating

Thickness versus plating time



Selectivity and H_2 permeance versus thickness



- ● (orange) H_2 permeance (400°C)= 3.1x10^{-6} (mol m^{-2} s^{-1} Pa^{-1}); H_2/N_2= 8,000 – 10,000
- ● (green) H_2 permeance (400°C)= 4.2x10^{-6} (mol m^{-2} s^{-1} Pa^{-1}); H_2/N_2= 20,000

- The thickness is controlled by the plating time
- There is a trade off between permeance and selectivity

Background on Pd-based membranes

Separation properties of membranes previously developed at TECNALIA

Membrane	Thickness	Porous support	H_2 permeance x10^{-7} mol m^{-2} s^{-1} Pa^{-1} @ ΔP 1 atm	H_2/N_2 selectivity
Thin Pd-Ag	4-5 μm	Metallic	≈ 10 at 400 °C	>100.000
		Alumina*	≈ 30 at 400 °C	>20.000
Ultra-thin Pd-Ag	≈ 1 μm	Alumina	≈ 100 at 400 °C	> 2.000
CMSM	3-4 μm	Alumina	≈1 at 30°C	≈ 500

* Over DOE targets 2015

Permeation tests at gas compositions similar to the HyGrid (90% CH4 & 10% H2)

Membrane	Thickness	Porous support	H_2 permeance x10^{-7} mol m^{-2} s^{-1} Pa^{-1} @ ΔP 1 atm	H_2/N_2 selectivity
Thin Pd-Ag	4-5 μm	Alumina	≈ 3,3 at 400 °C	>20.000
Ultra-thin Pd-Ag	≈ 1 μm	Alumina	≈ 11.8 at 400 °C	> 2.000

Electrochemical hydrogen separation development

Objectives:

Development of an electrochemical hydrogen purifier (EHP) for the recovery of the hydrogen from very low concentration streams (≤ 2 %).

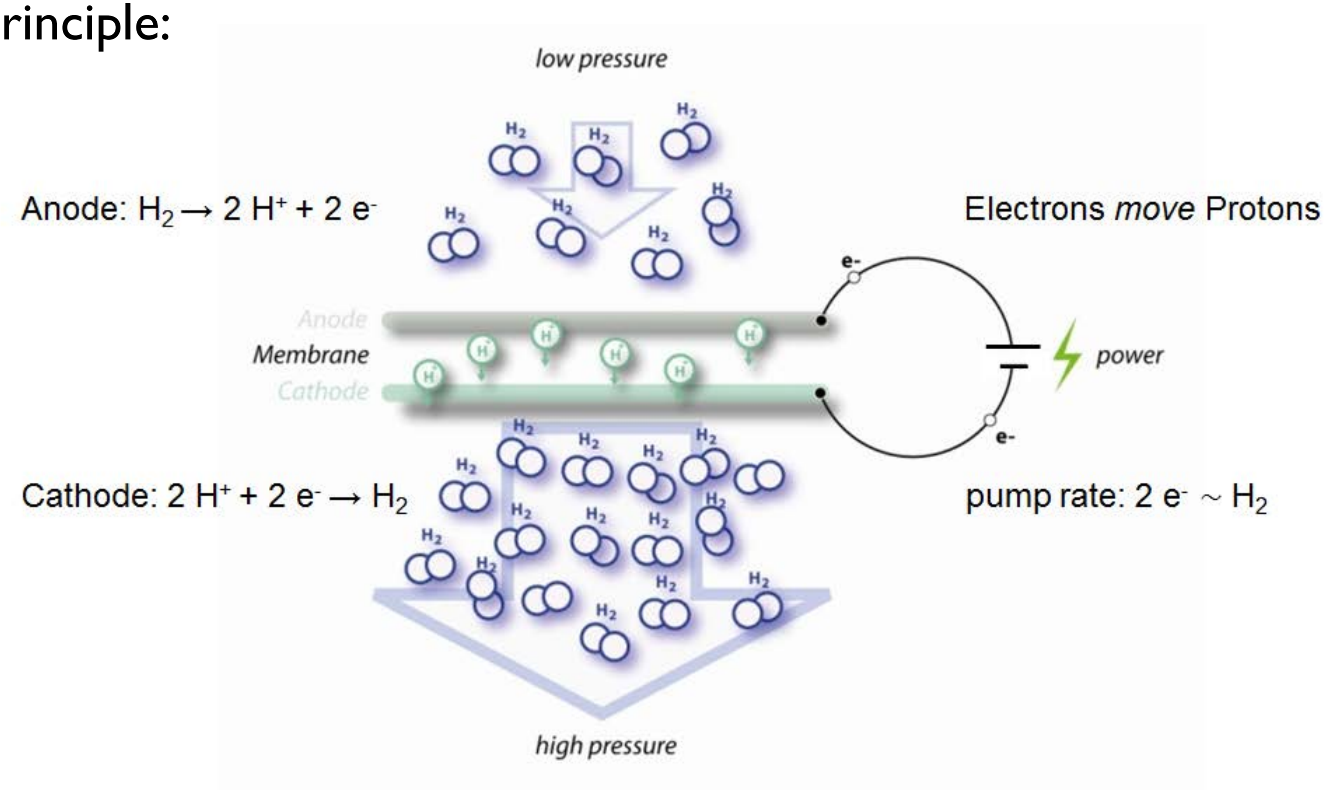
- Capable of recovering the majority of the remaining hydrogen from the retentate of the membrane separator.
- Optimum configuration of membrane-electrode-assembly for low concentration hydrogen extraction.
- Theoretical modelling assisted optimum design of stack and gas distribution plate geometry for low concentration electrochemical hydrogen extraction (<3%).
- Construction and testing of sub- and full size electrochemical compressor stacks for model validation and prototype preparation.

Electrochemical hydrogen separation development

Key performance indicators for EHP:

Key Performance Indicator	Unit	Actual	Target
Energy consumption of electrochemical hydrogen purification at ambient pressure	kWh / kg H_2	6	4
Hydrogen recovery rate of feed gas with 2% H_2	%	30	60

Working principle:



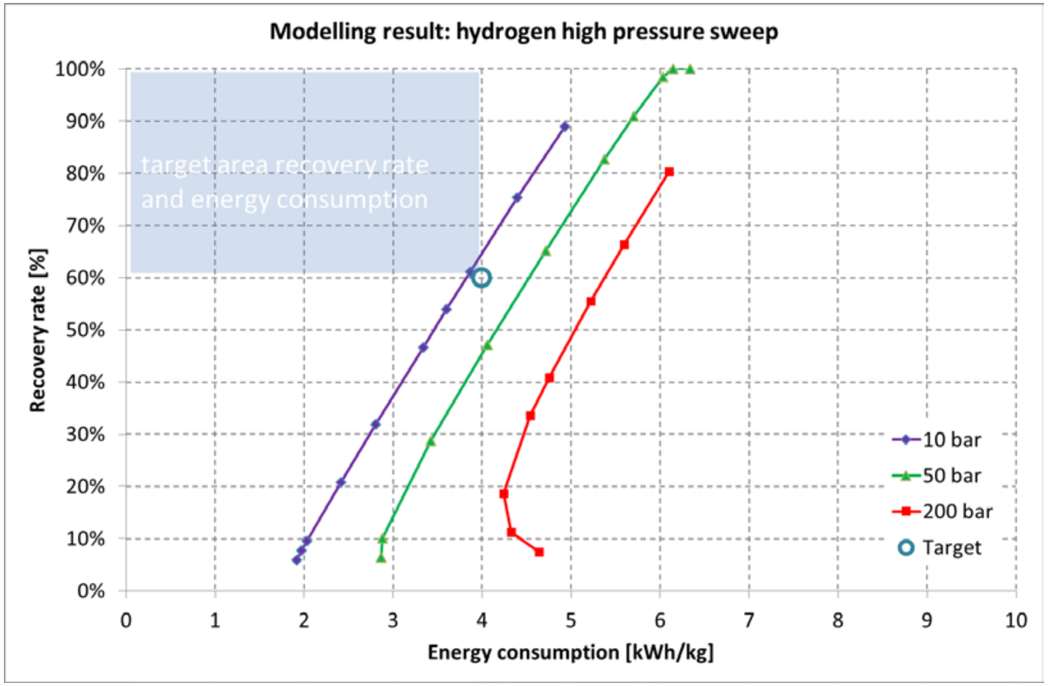
Electrochemical hydrogen separation development

Modelling EHP:

Model set up in Matlab for EHP system configurations to find setup of the system meeting the KPIs

Iterations:

- Operating temperature
- Number of cells
- Type of membrane
- Hydrogen concentration
- Pressure



- Conclusion: Meeting the KPIs for EHP is possible with the right number of cells, operating temperature, membrane and pressure for hydrogen concentration in the feed gas between 2 and 10%

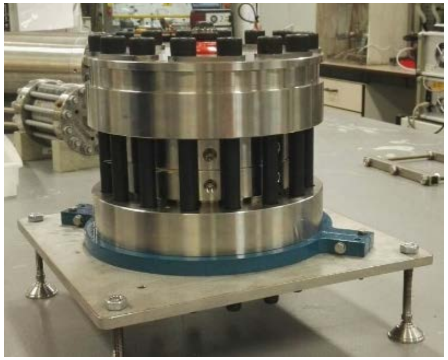
Electrochemical hydrogen separation development

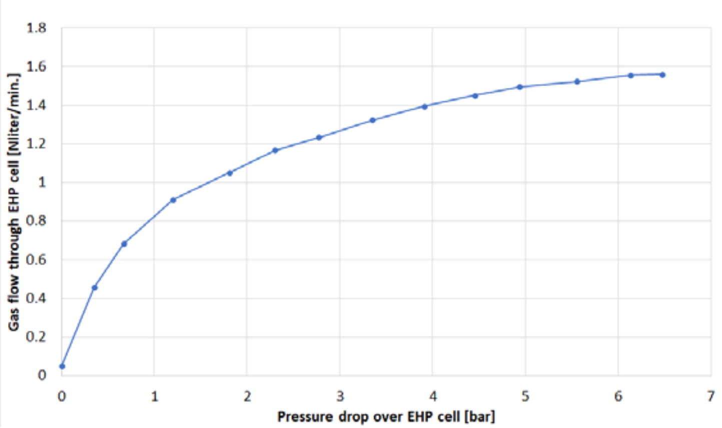
Sub scale testing EHP:

Platform HCS100 developed, capable of pure hydrogen pressure of 700 bar and pump rate (current density) of 1 A/cm^2

Conclusions purification testing:

- Two flow field design tested and analysed. One has been selected
- Humifidication of feed gas highly influences stable performance of EHP





Outlook:

- Review anode flow field design needed for HyGrid EHP cell: lowering pressure drop and expanding holdup time in EHP cell
- Continuing testing on stability for multi-cell stacks

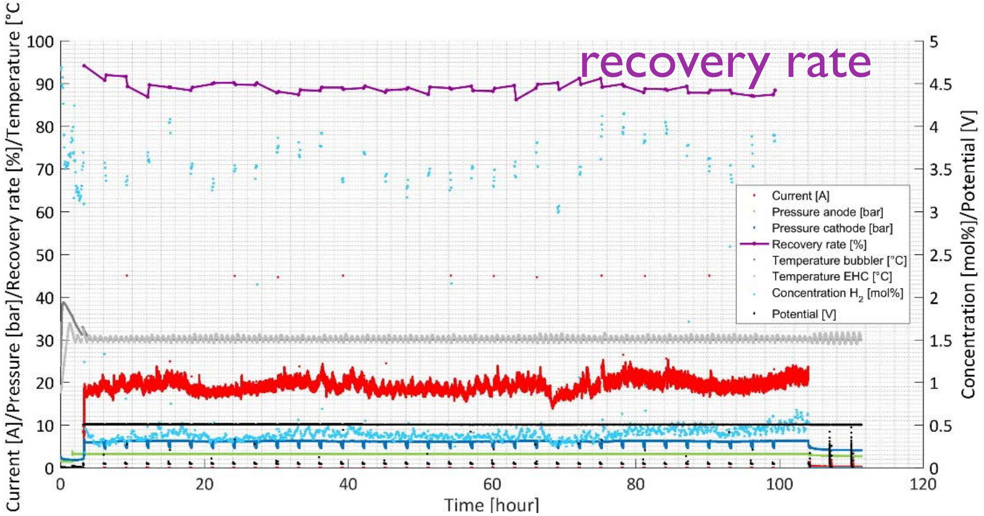
Electrochemical hydrogen separation development

System development around EHP:

Small scale system tested in Rozenburg (NL), started within project PurifHy. Established base-line EHP performance with sub-optimal EHP cell hardware.

- Conclusion: 90% recovery rate is feasible with high surface area and with high energy demand

The Rozenburg test location



Testing data Rozenburg

Temperature Swing Adsorption development

Objectives:

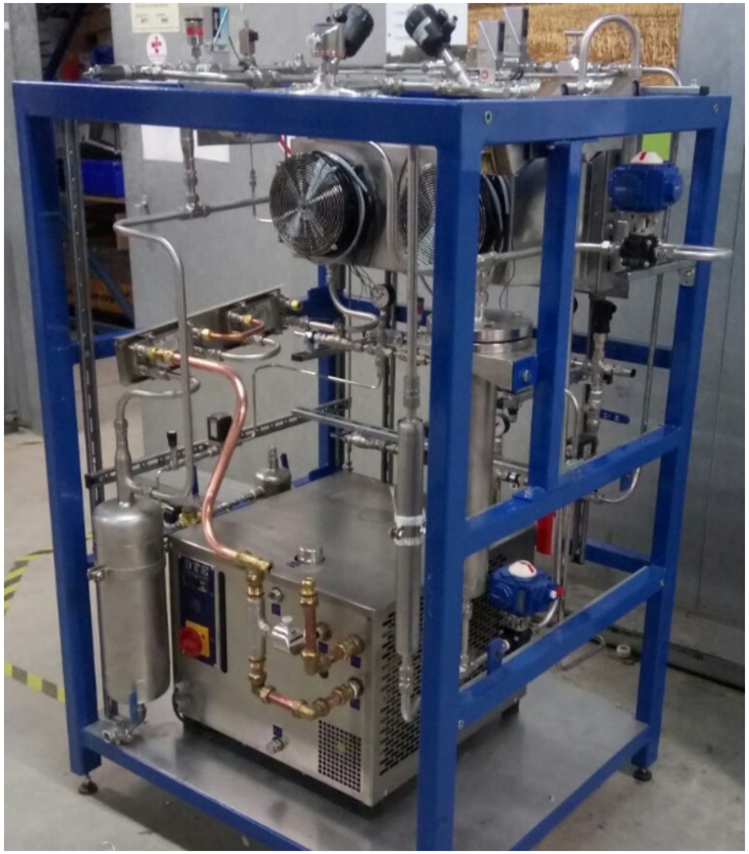
Design, construction and test of the TSA unit.

- Better comprehension of the behaviour and performance of the adsorption materials used in TSA.
- Understanding of the response of adsorbents to the dynamic temperature control.
- Implementation of the know-how gained through lab tests onto the up-scaled design.
- Design of prototype TSA unit for integration in pilot scale HyGrid system.
- Testing of pilot scale TSA unit.

Development of TSA strategy and sizing

Sorbent materials tested:

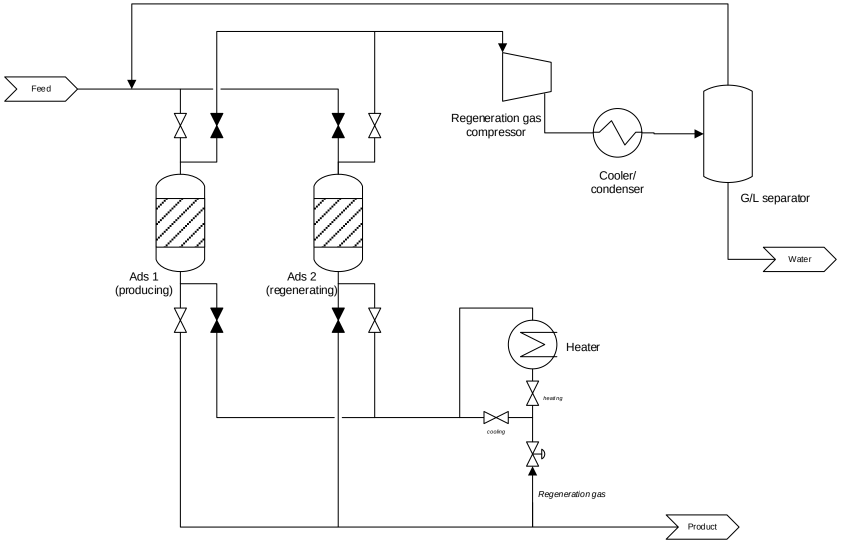
- Several materials tested in test rig regarding sorption capacity as function of process variables
- Sorbent material selected as function of product dew point
- Most optimal regeneration procedure defined for prototype TSA based on optimized operational costs
- Mathematical model validated and TSA sizing ready



Laboratory test rig

Prototype TSA

- Prototype TSA:
  - Process flow diagram defined
  - Operational safety assessed
  - Control strategy implemented
  - Prototype assembly ready
- Next steps: testing prototype integration with membrane and EHP module



PFD prototype TSA

Prototype TSA assembly

Lab scale testing

Objectives:

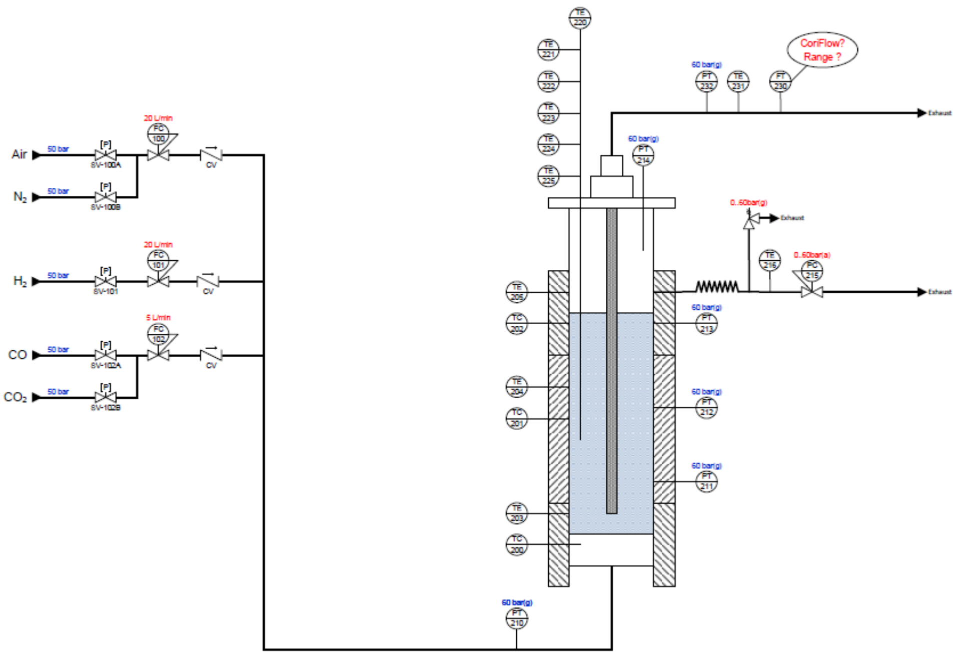
Design and test a small version of the prototype and test it at lab scale especially in conditions not feasible for the prototype.

- Investigate the recovery of the membrane system at different pressures and different concentrations of hydrogen.
- Sorbents for the TSA selected will be further studied in TGA experiments to evaluate the cyclic sorbent capacity and adsorption isotherms.
- Evaluation of different configurations to identify the optimum separation system along the natural gas network.

Design and building of the lab scale rig

A small test rig will be updated at TUE to be able to test smaller versions of the hybrid separation technology of HyGrid at different conditions.

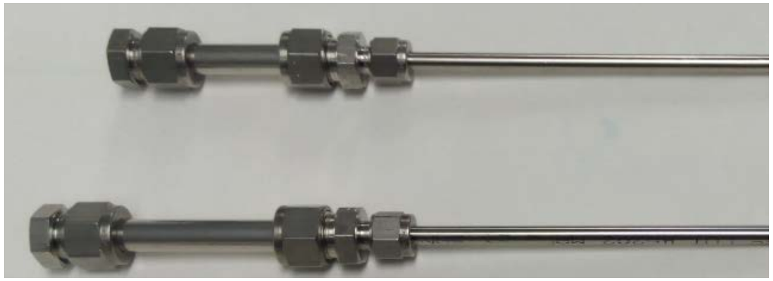
In particular the system will be designed to be able to work
- at up to 20 bar (now up to 50 bar)
- at low hydrogen contents recovery

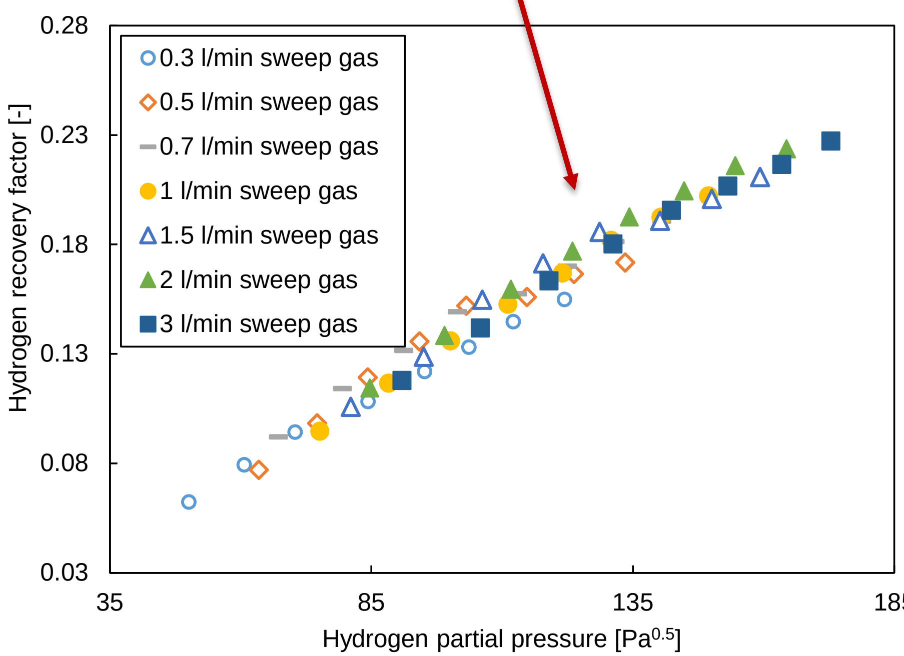


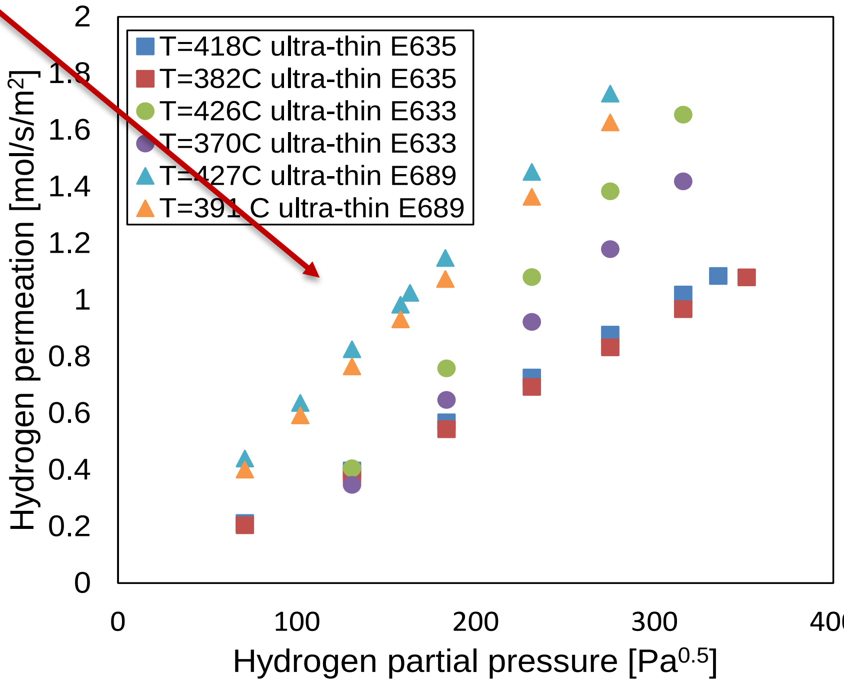
Testing of membranes and sorbents

Different Pd-Ag membranes has been tested changing the following operating conditions:

- Temperature and pressure
- Type and amount of sweep gas

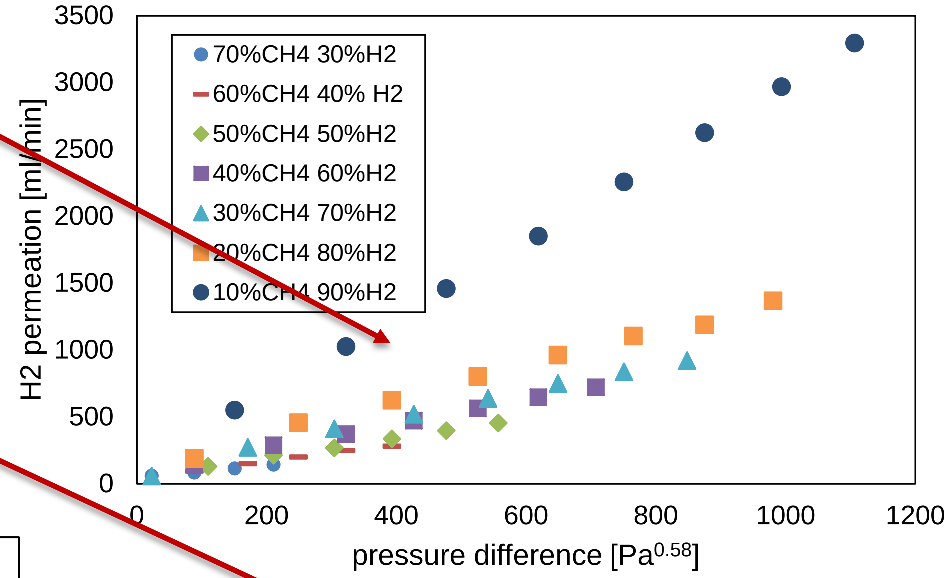


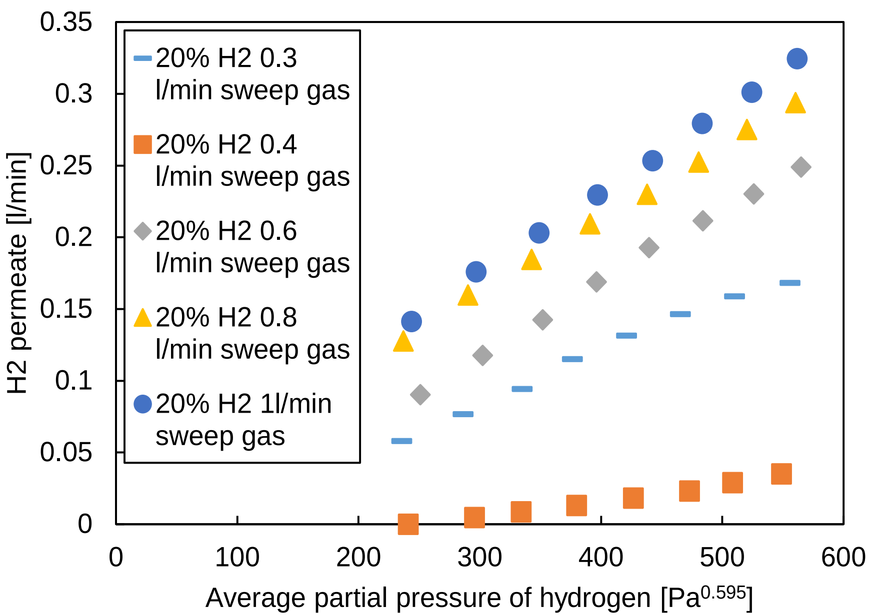


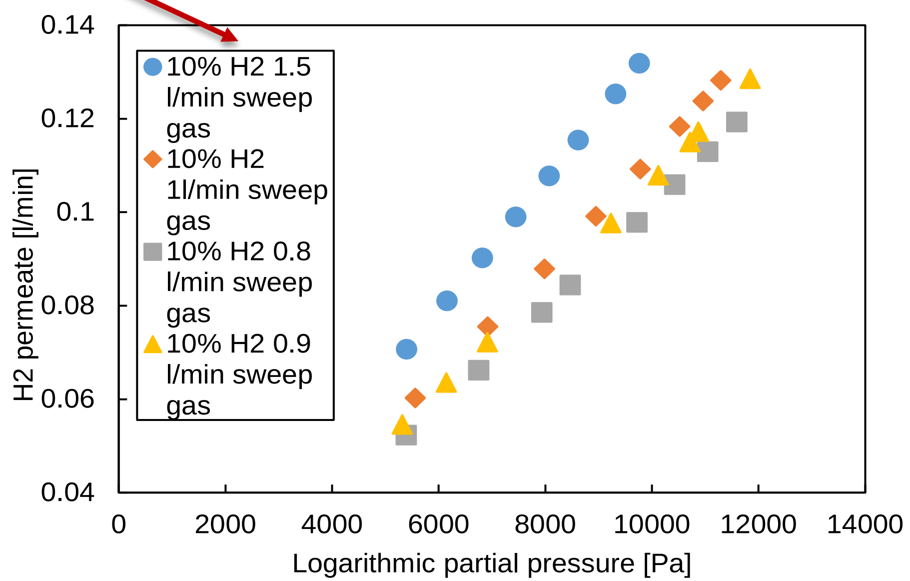


Testing of membranes and sorbents

- Changing H2 concentration
- Changing H2 concentration with sweep gas

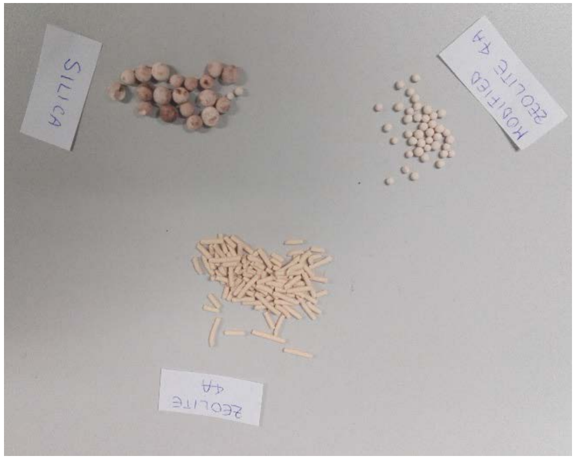


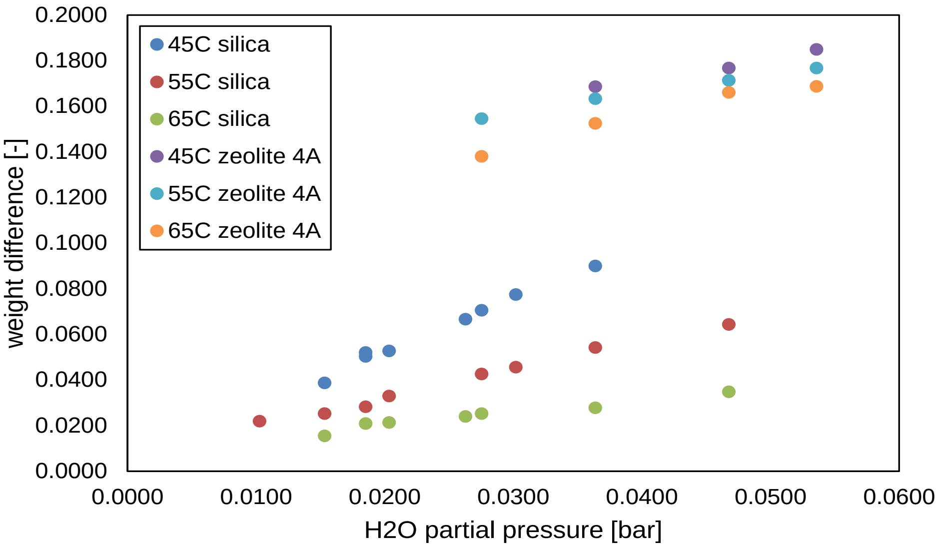


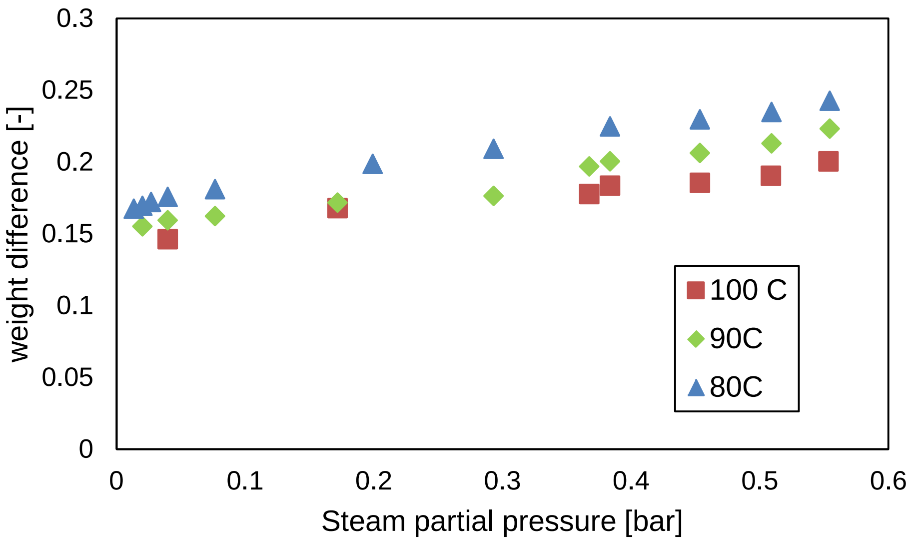


Testing of membranes and sorbents

Zeolite 4A, modified zeolite 4A, zeolite 13X and silica have been tested at different temperature and different steam content in order to study the adsorption capacity.







There is a significant difference between zeolite and silica in adsorption capacity.

Prototype integration and validation

Objectives:

- Design of the integrated hydrogen recovery pilot plant
- Construct and assemble the hydrogen recovery pilot plant including controls
- Testing and assessment of hydrogen recovery pilot plant

System modelling and simulation

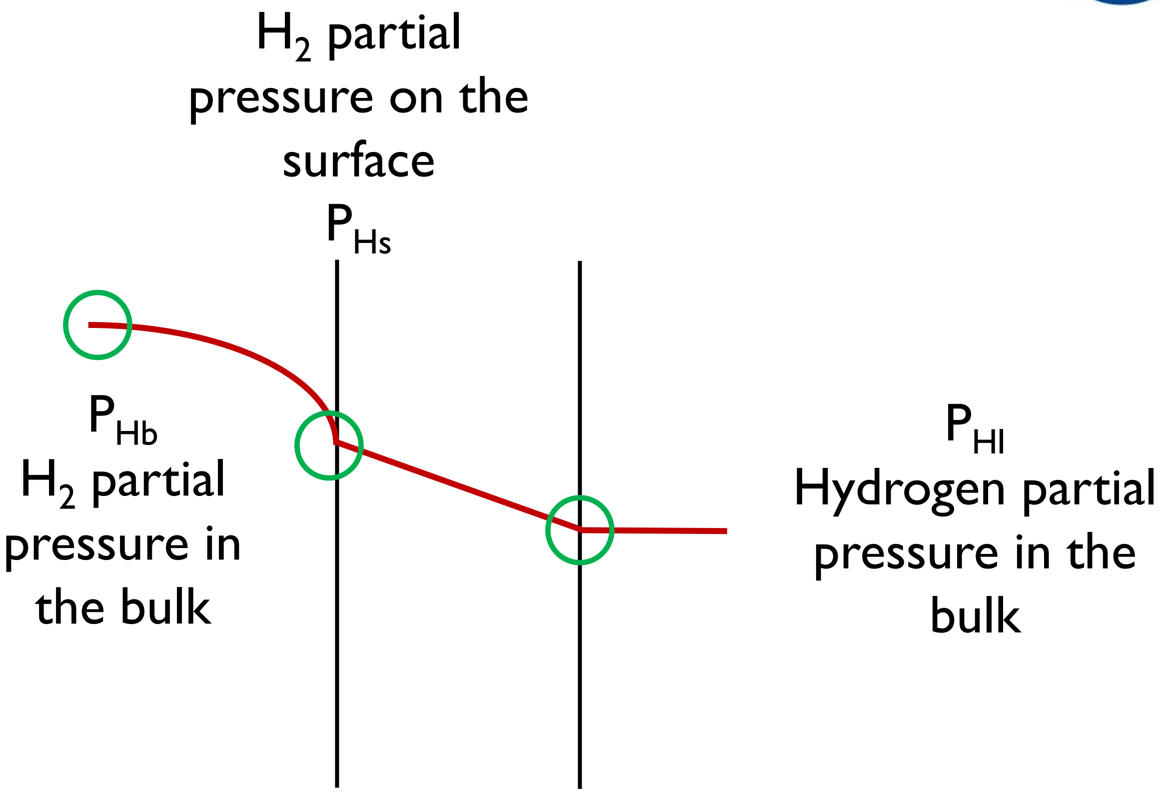
Objectives:

To assess the energy analysis, and economic performance (in terms of primary energy consumption and cost of pure H_2) of the HyGrid system for H_2 separation from NG grid.

- Membrane module model and simulation.
- Development of dynamic model for TSA.
- Modelling of electrochemical separation and compression.
- Simulation and economic optimization of integrated hydrogen recovery

Membrane modelling

The difference between experimental and modelled results should be find in the mass transfer limitation due to a hydrogen-depleted layer adjacent to the membrane surface.



There are 3 different possible mass transfers in the Pd membrane:

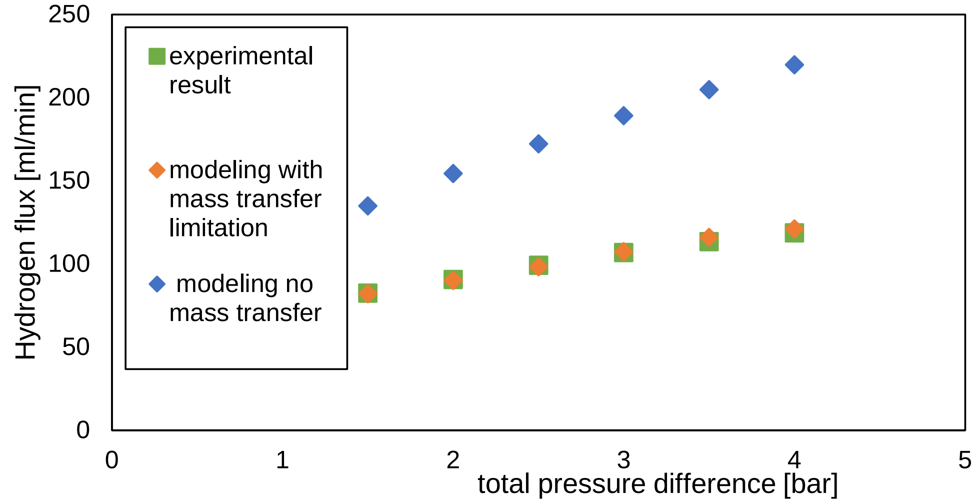
- Retentate side
- Porous support
- Permeate side

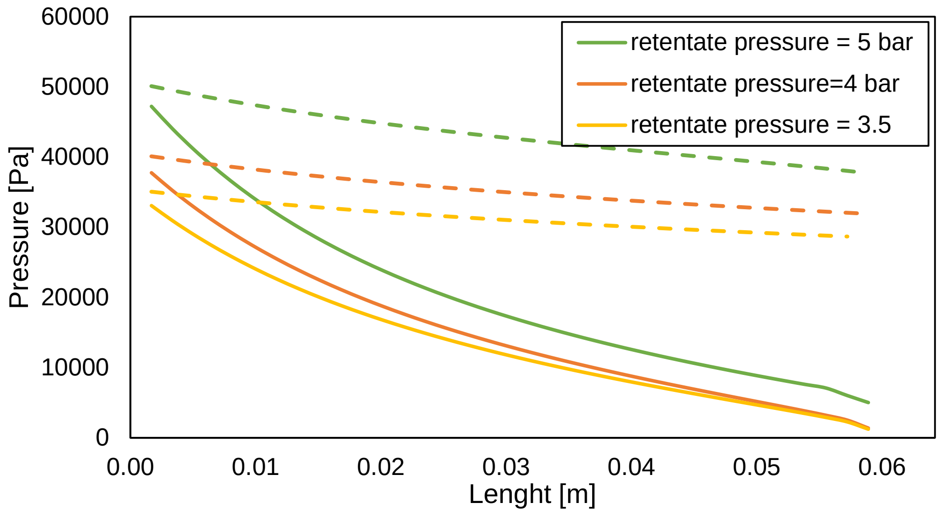
Membrane modelling

$$J_H = \frac{k_H * \left(\frac{P_{Hb} - PHs}{RT}\right)}{1 - (0.5 * (PHb - PHs)/PTs}$$

$$\frac{dF_{Hs}}{dz} = -2 * \pi * R * QH * (P_{Hb}^n - P_{Hl}^n)$$

$$J_H = \frac{k_H * \left(\frac{P_{Hb} - PHs}{RT}\right)}{1 - (0.5 * (PHb - PHs)/PTs} - QH * (P_{Hb}^n - P_{Hl}^n) = 0$$





- - - - Retentate partial pressure

——— Surface partial pressure

The pressure on the surface is remarkably different from the retentate partial pressure.

Simulation of the hybrid system

Two different configuration has been modelled to optmize the targets required

First case: two membrane modules

Total electric consumption	3.9	kWh/kgH_2	<	5	kWh/kgH_2	✓
Total hydrogen separated	27.26	kgH_2/day	>	25	kgH_2/day	✓
purity	99.98	%	>	99.97	%	✓
HRF	90	%	>	85	%	✓
Total membrane area	3.33	m^2				

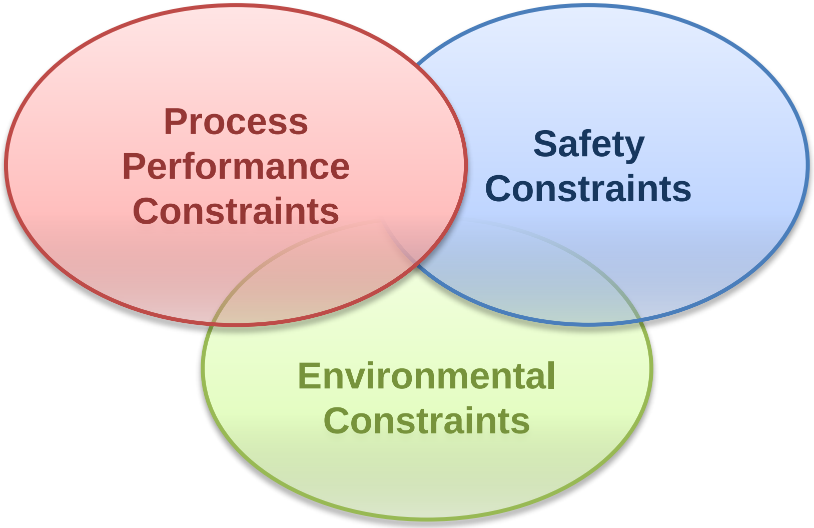
Second case: one membrane module

Total electric consumption	3.88	kWh/kgH_2	<	5	kWh/kgH_2	✓
Total hydrogen separated	26.055	kgH_2/day	>	25	kgH_2/day	✓
purity	99.977	%	>	99.97	%	✓
HRF	86.906	%	>	85	%	✓
Total membrane area	4.91	m^2				

Environmental LCA and economic assessment

The new H_2 separation technology will be analysed and compared to other available technologies using LCA and LCC in an iterative process to guide the design and development of the novel technologies and products towards sustainable solutions.

- An Environmental Life Cycle Assessment will be performed by applying and testing the most up-to-date life cycle impact assessment methods
- Life Cycle Costing will be performed and the latest advances in monetary valuation of impacts will be tested
- A business plan will be developed as part of the economic assessment



Goal and scope definition

Overall, the main questions analysed during the goal and scope development include:

- What is the aim of the study?
- What is the function of the analysed system?
- What systems exactly are going to be analysed?
- What reference system/ technology will we compare our system against?
- What are the system boundaries of the analysed product?
- What environmental indicators will be calculated?
- What is the data availability for the study?

Main outcomes of goal and scope definition

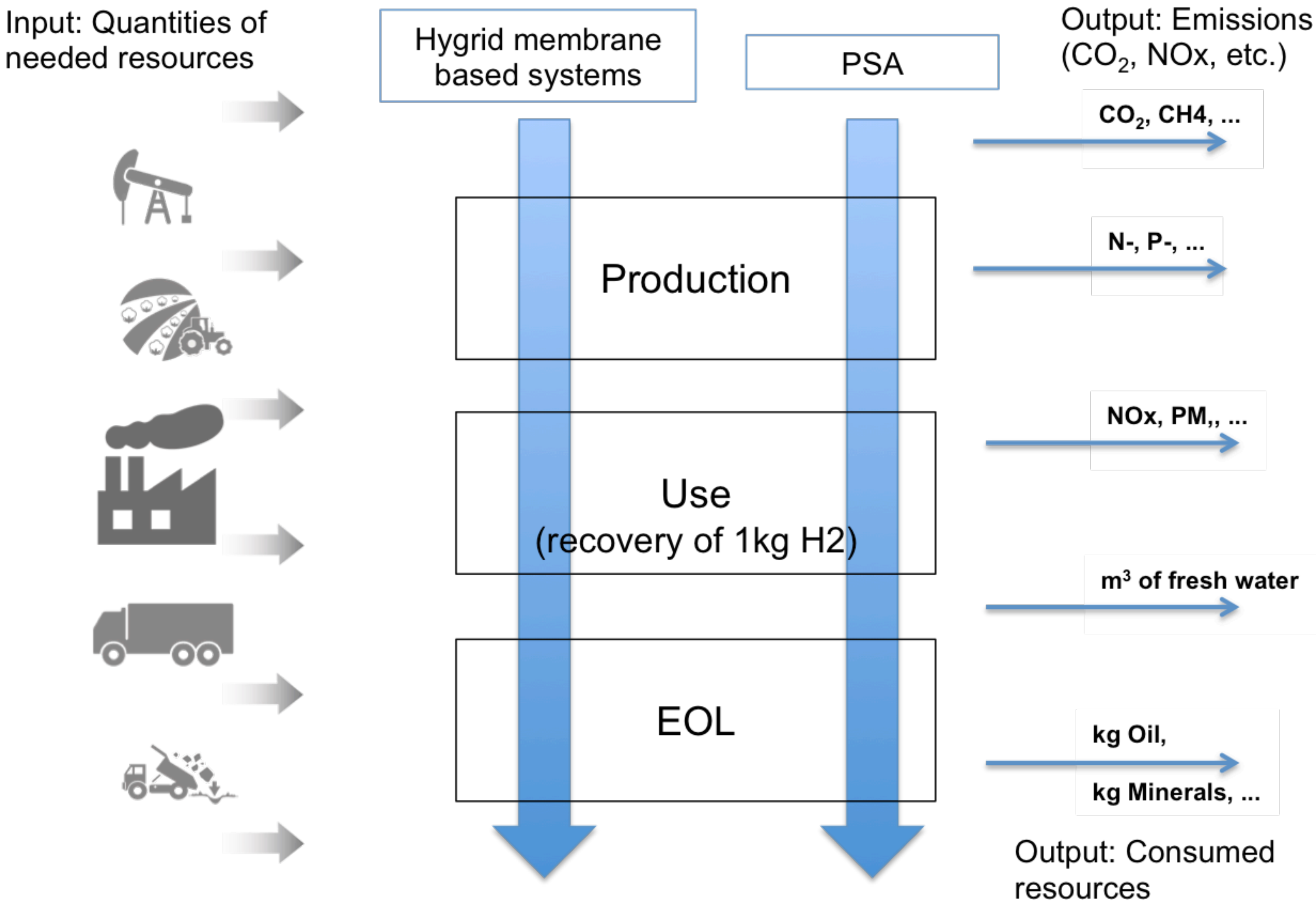
- Functional unit:

  "The recovery from an average European natural gas grid of 1 kg of hydrogen with a purity of at least 99.97%."

- Reference technology (to compare with the HyGrid system):

  pressure swing adsorption (PSA)

System boundaries



Flexible Hybrid separation system for H_2 recovery from NG Grids

HyGrid

https://www.hygrid-h2.eu/

Thank you for your attention

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