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

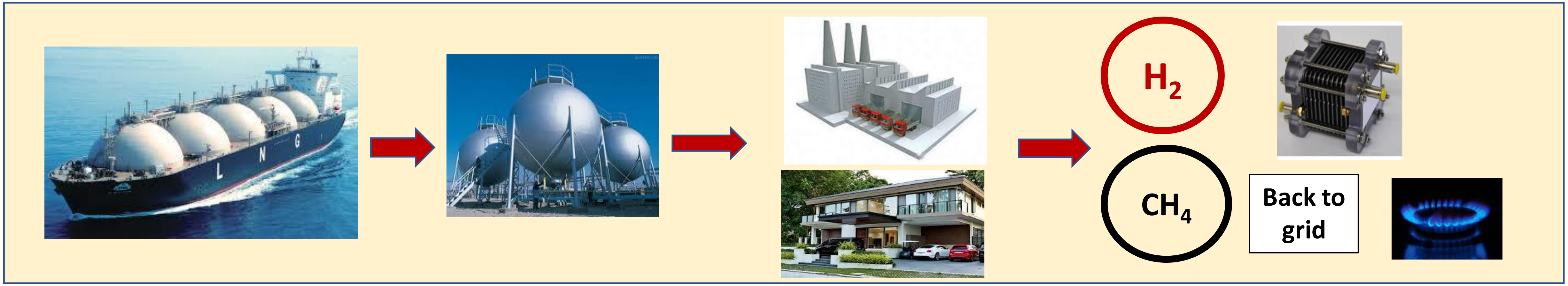
Duration: 3 years. Starting date: 01-May-2016

Contacts: F.Gallucci@tue.nl

The pre: are n

Use the natural gas network to store and distribute H_2

Blend hydrogen (10 %) with NG



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

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

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).

The present publication reflects only the author's views and the FCH JU and the Union are not liable for any use that may be made of the information contained therein.

HyGrid

Hybrid system

Membranes

Carbon

H_2
2- 10 %

Palladium

tecnalia Inspiring Business

Electrochemical Hydrogen Purification(EHP)

H_2
< 2%

HyET Hydrogen Efficiency Technologies

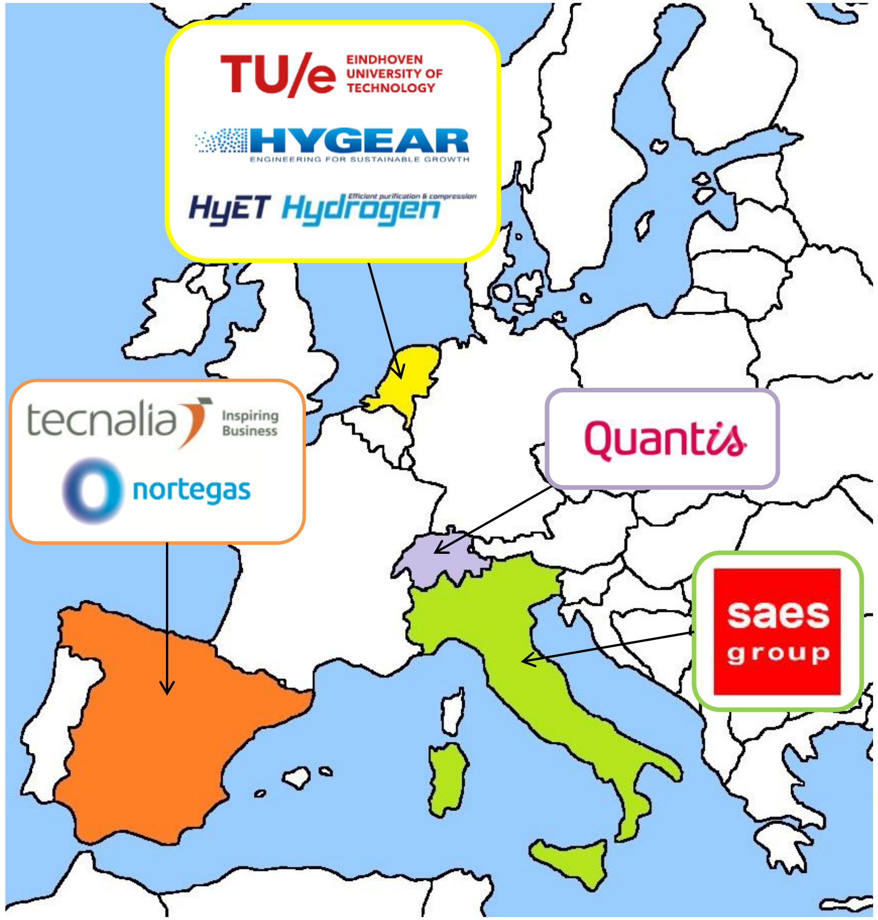
Temperature Swing Adsoption (TSA)

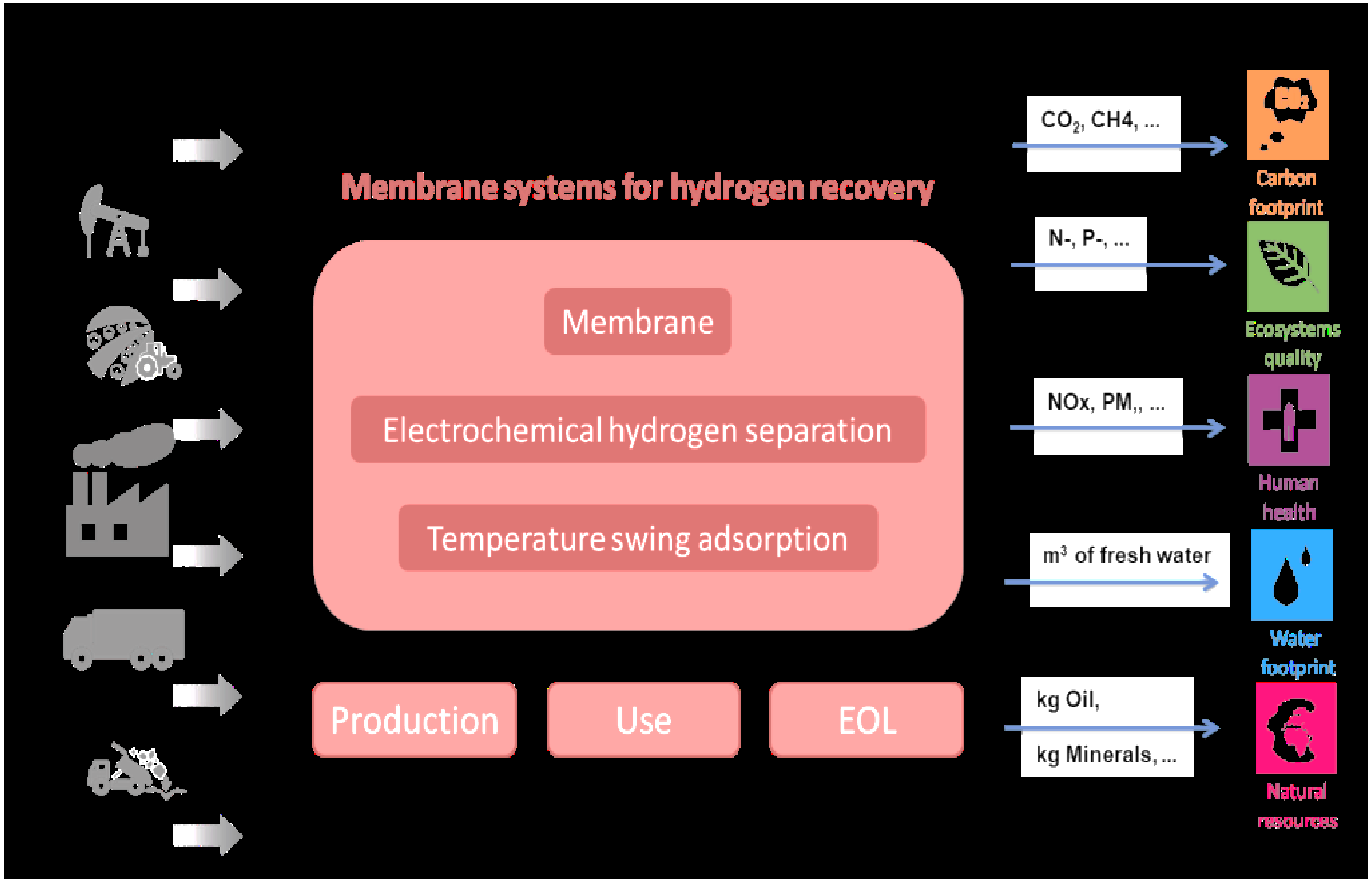
HYGEAR

Remove humidity

- ✓ Tecnical validation of the novel separation technologies at lab scale
- ✓ Hybrid system with different configurations/combinations of the technologyes
- ✓ Optimization of the hybrid system and validation at prototype scale (TLR5)
- ✓ Energy and Life Cycle Analysis

Quantis Life cycle analysis





Membrane development

Objective

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

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

HyGrid

Composite Al-Carbon Molecular Sieves Membranes (CMSM)

tecnalia Inspiring Business

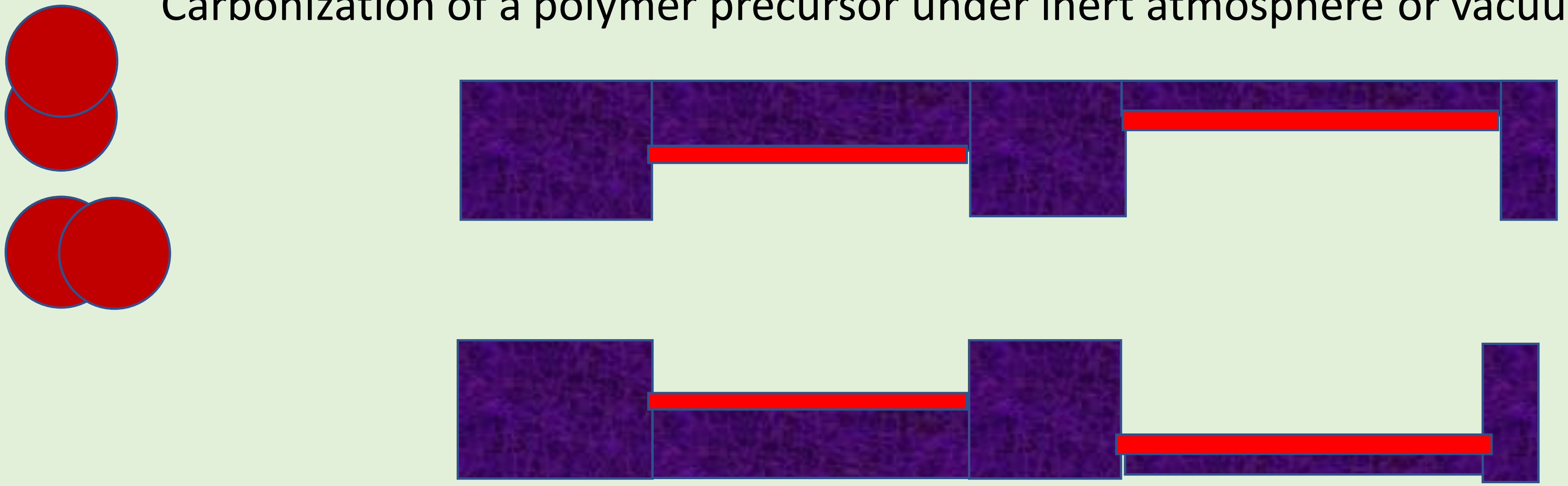
TU/e EINDHOVEN UNIVERSITY OF TECHNOLOGY

FCH

The present publication reflects only the author's views and the FCH JU and the Union are not liable for any use that may be made of the information contained therein.

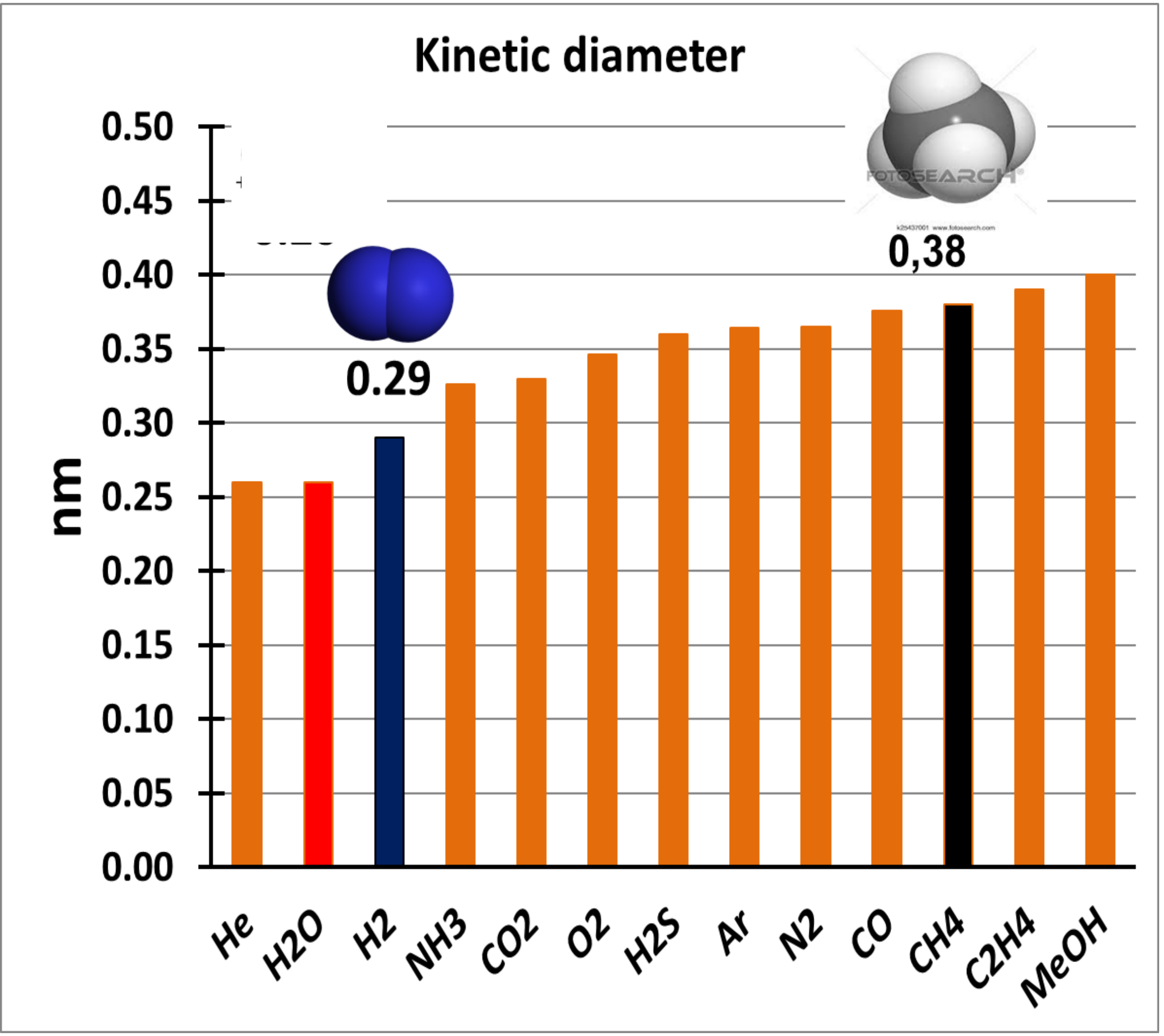
Carbon Molecular sieves membranes

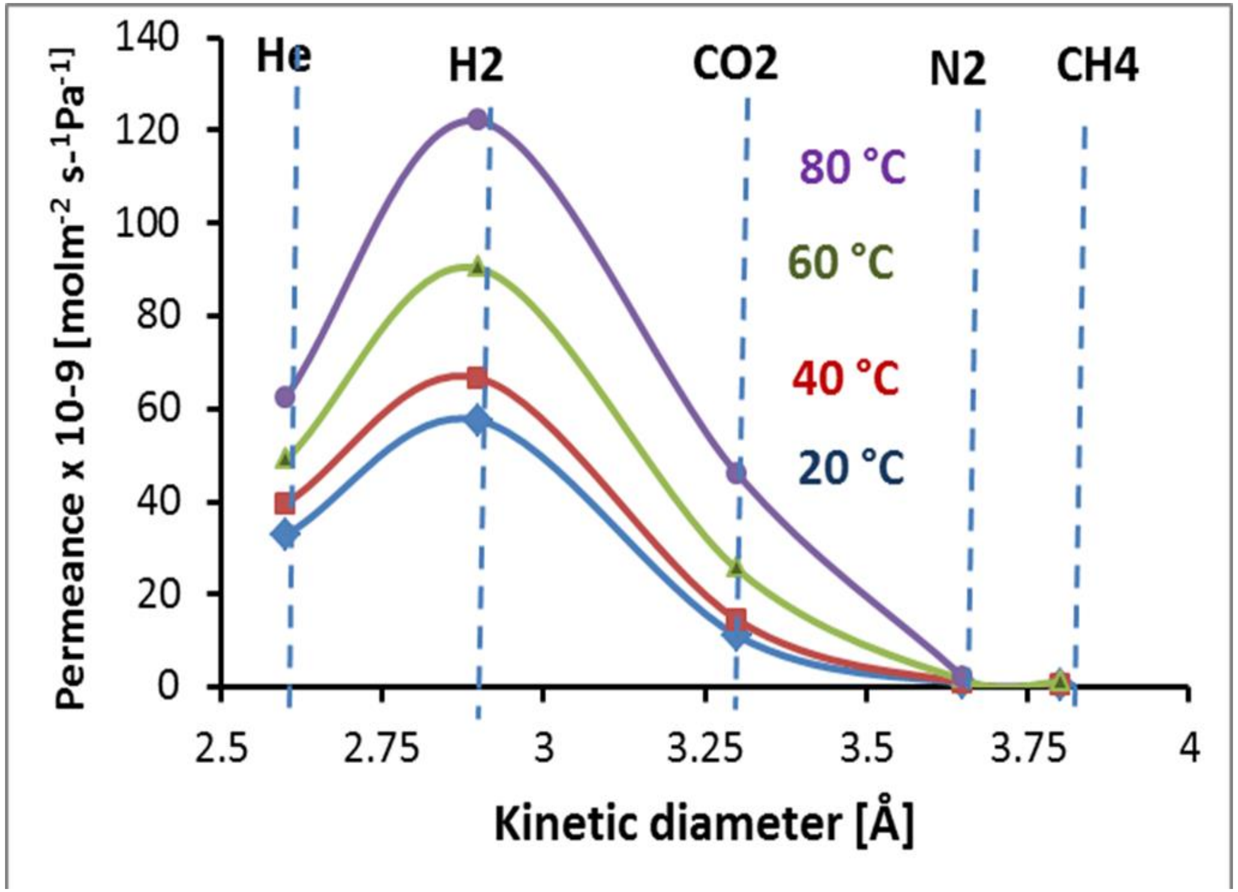
Carbonization of a polymer precursor under inert atmosphere or vacuum



micropores (adsorption diffusion) **0.7 – 2 nm**

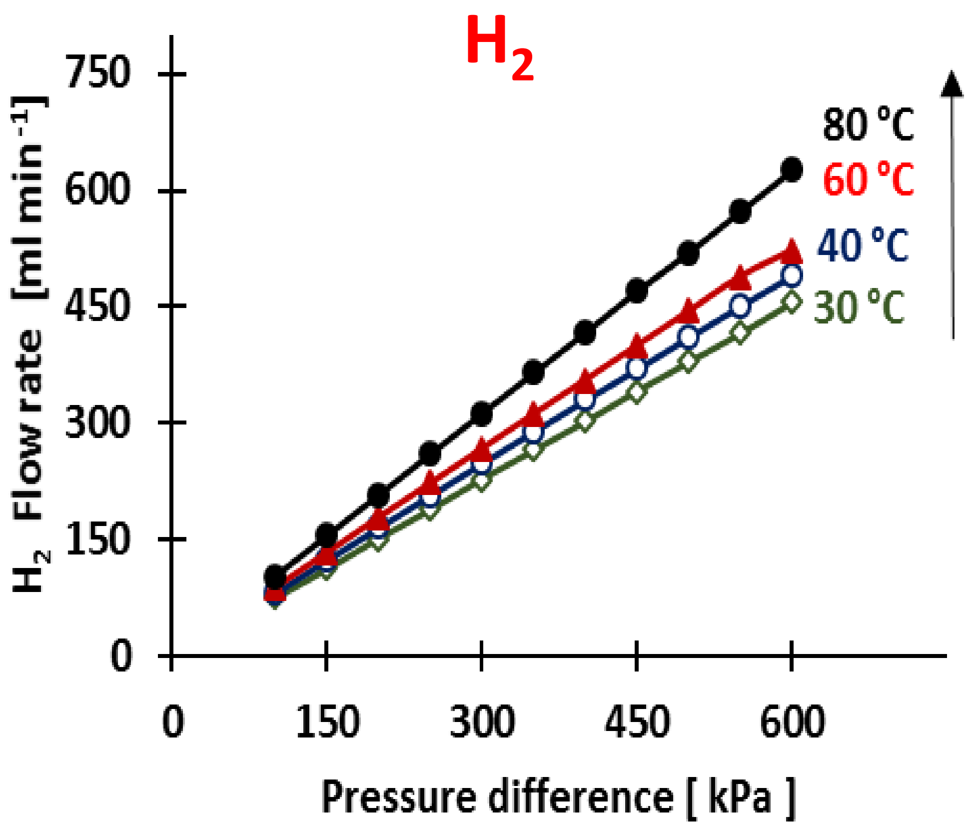
ultramicropores (molecular sieving) **0.25 0.7 nm**

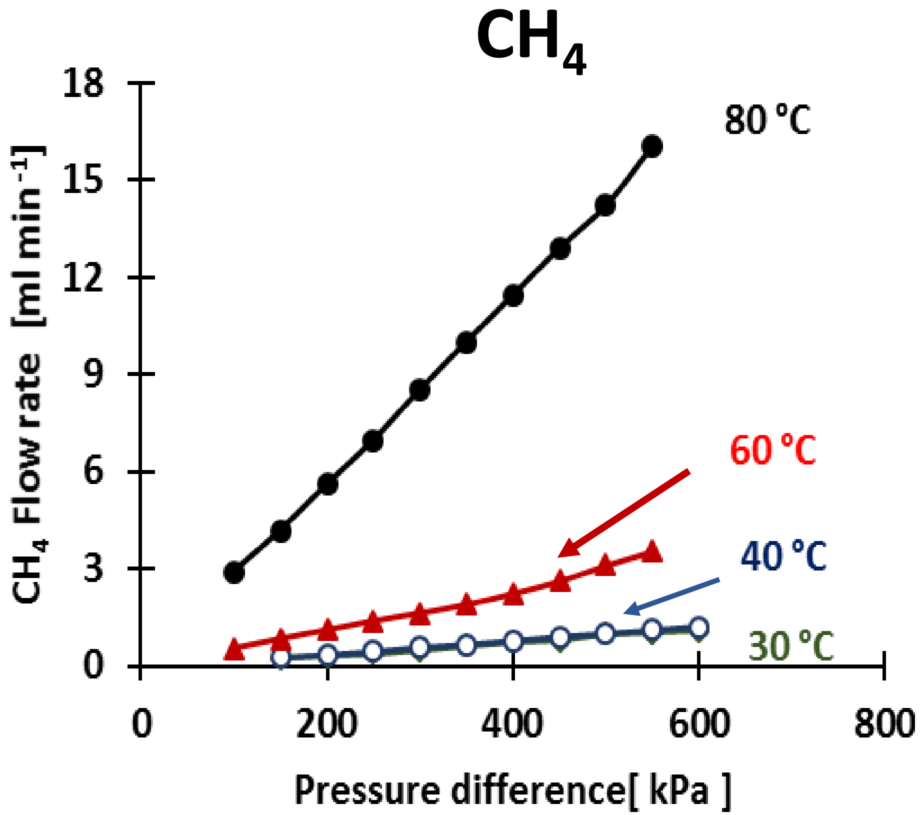

Kinetic diameter
0,38
0.29
nm
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
He
H2O
H2
NH3
CO2
O2
H2S
Ar
N2
CO
CH4
C2H4
MeOH


Permeance x 10-9 [molm-2 s-1Pa-1]
He
H2
CO2
N2
CH4
80 °C
60 °C
40 °C
20 °C
140
120
100
80
60
40
20
0
2.5
2.75
3
3.25
3.5
3.75
4
Kinetic diameter [Å]

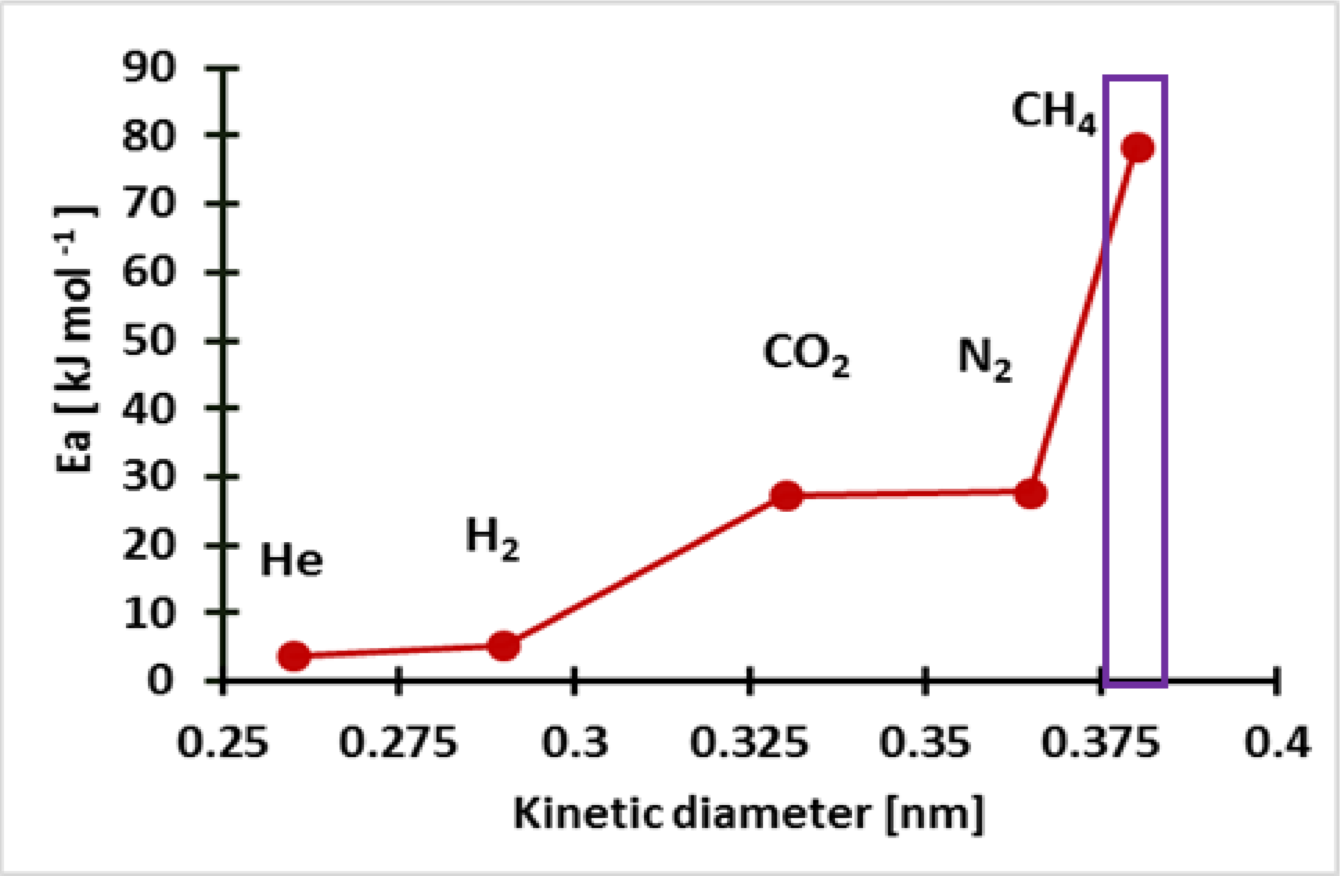
H_2 and CH_4 single gas permeation

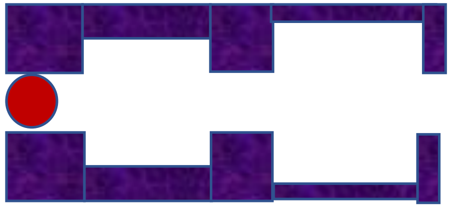
Activated at 100 °C





Activated 100 °C





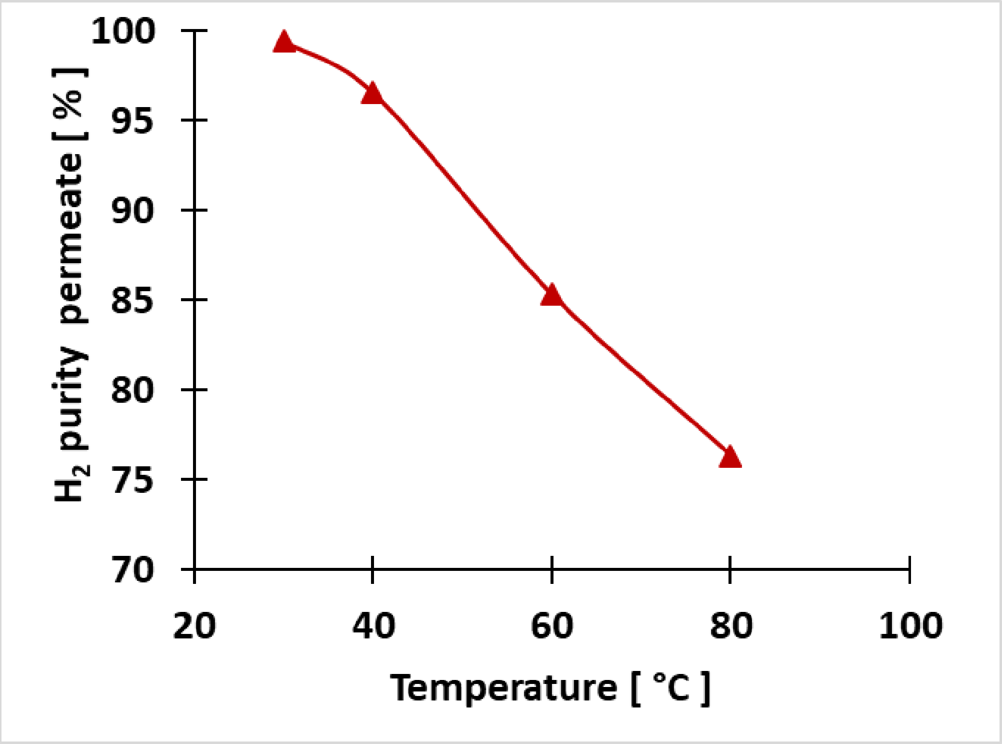
HyGrid

H_2/CH_4 gas mixture permeation at various temperatures

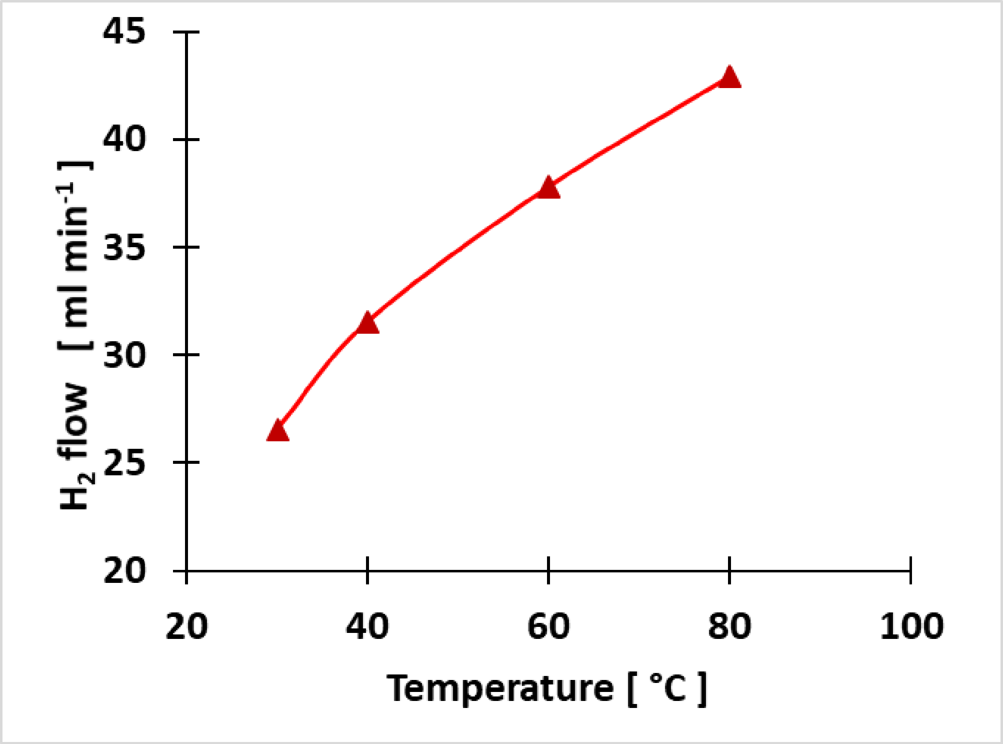
P inlet 7.5 bar,
P Permeated 0.01 bar

H_2 / CH_4 10 / 90 (10% H_2)

H_2 Purity



H_2 Flow



HyGrid

Supported thin PdAg membranes

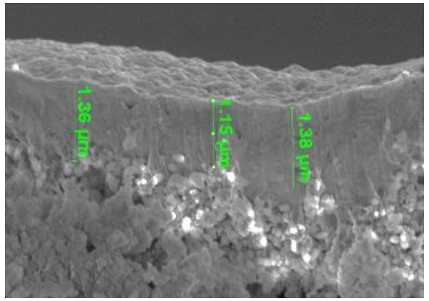
tecnalia Inspiring Business

TU/e EINDHOVEN UNIVERSITY OF TECHNOLOGY

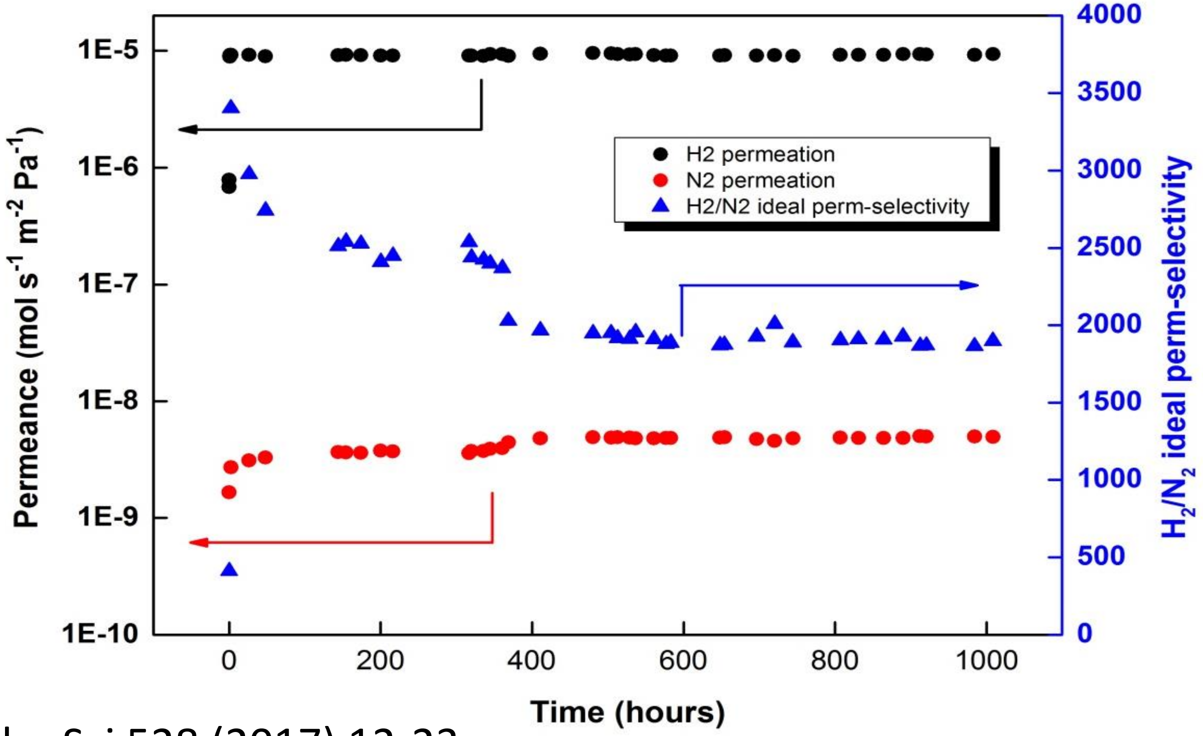
The present publication reflects only the author's views and the FCH JU and the Union are not liable for any use that may be made of the information contained therein.

Ultra-thin PdAg membranes

Tubular alumina Support 10/7



1.3 µm PdAg **at 400 °C** 1 bar

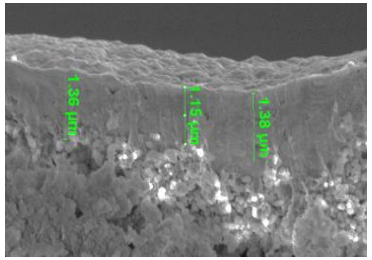


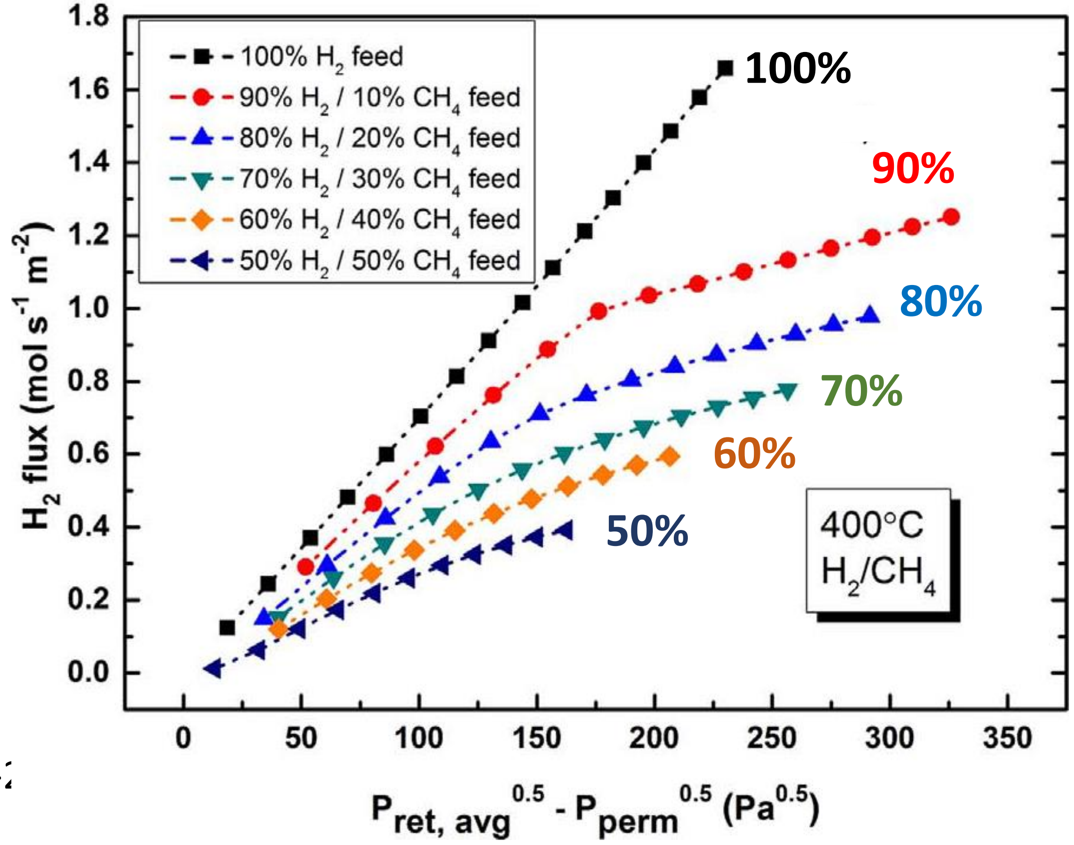
J. Melendez… J. Membr. Sci 528 (2017) 12-23

Effect of the concentration of H_2

1.3 µm PdAg at 400 °C

H_2/CH_4 and H_2 partial pressure





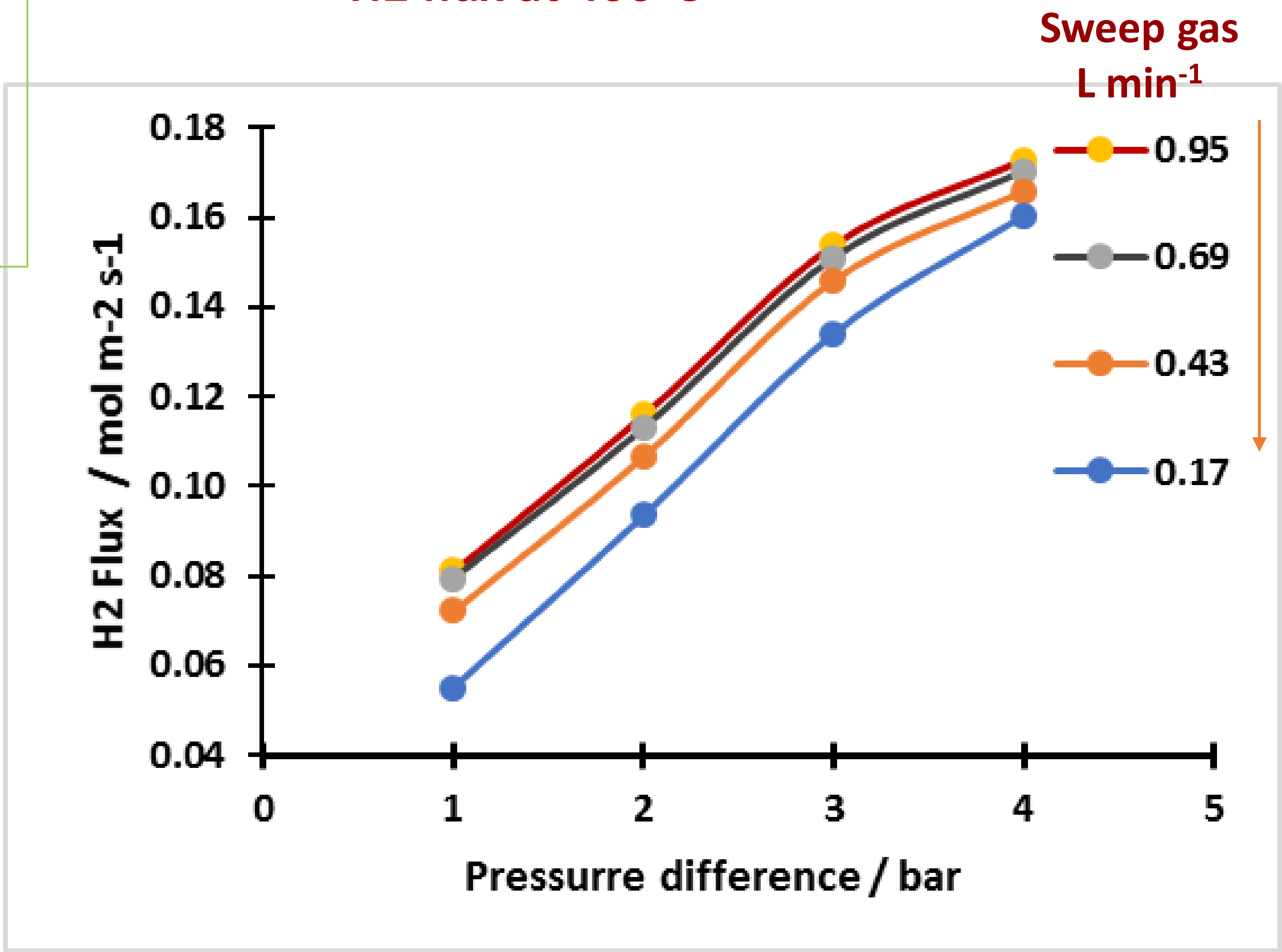
J. Melendez… J. Membr. Sci 528 (2017) 12-2

The present publication reflects only the author's views and the FCH JU and the Union are not liable for any use that may be made of the information contained therein.

Effect of the sweep gas flow in the H2 flux at 400°C

Inlet gas: 50% H_2- 50% CH_4
Total flow rate:2 l/min
N_2 Sweep gas permeate side

14/7 Finger type



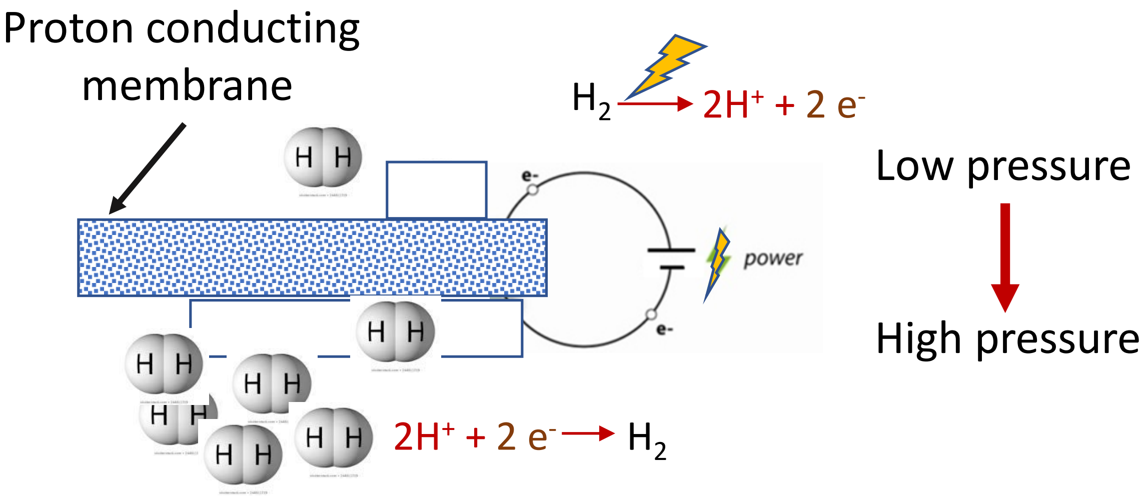
M Nordio et. Al International Journal of Hydrogen Energy 44 (2019) 4228

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.

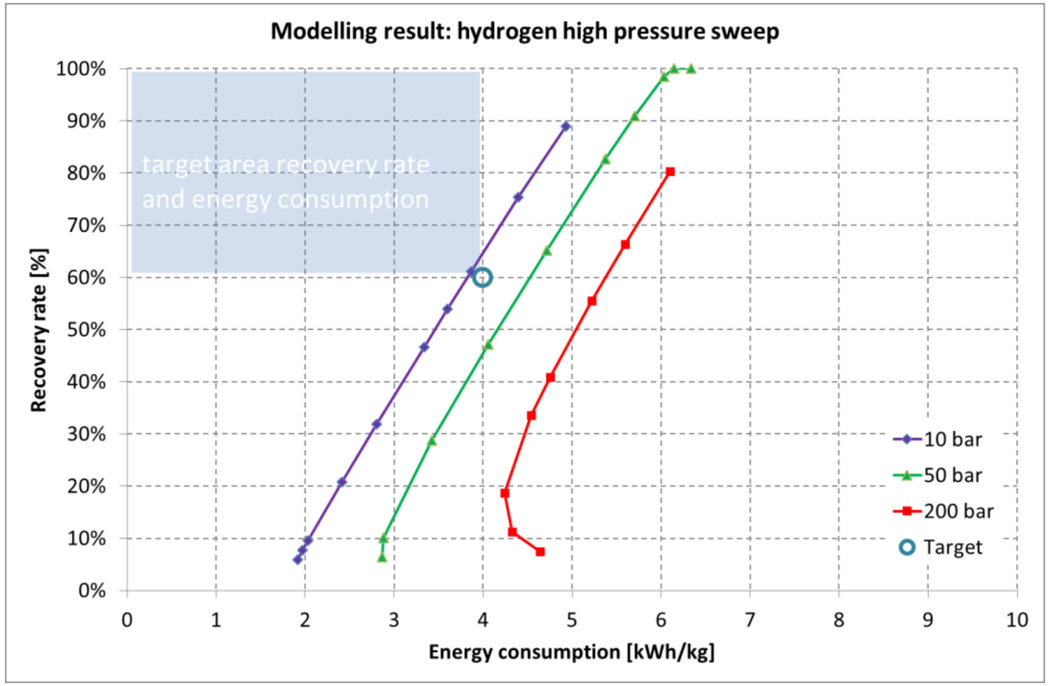

Proton conducting membrane
$H_2 \rightarrow 2H^+ + 2\,e^-$
Low pressure
High pressure
power
e-
e-
H H
$2H^+ + 2\,e^- \rightarrow H_2$


HyET

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%

HyGrid

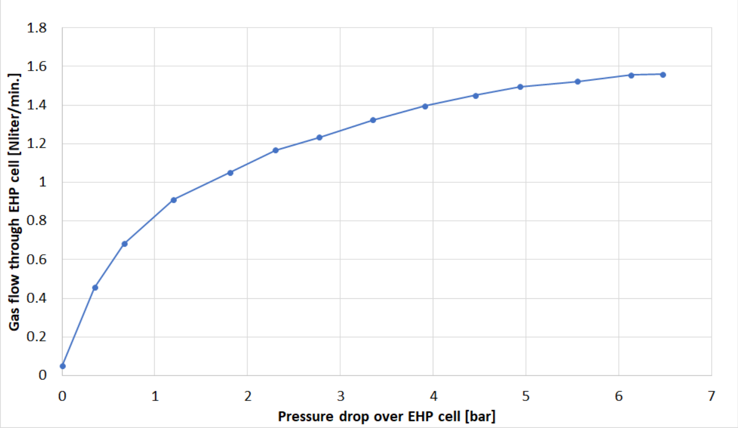
Electrochemical hydrogen separation development

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

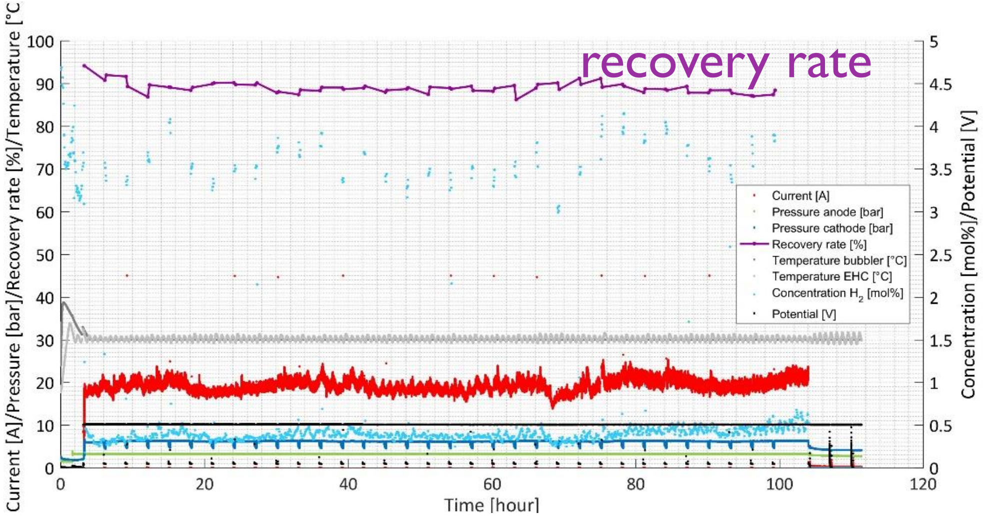
Electrochemical hydrogen separation development

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

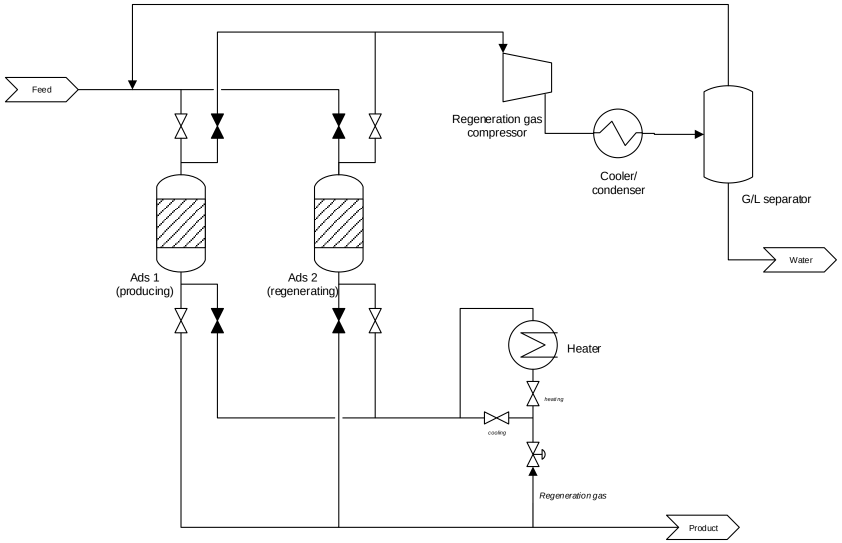
Sorbent materials tested:

- 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

The present publication reflects only the author's views and the FCH JU and the Union are not liable for any use that may be made of the information contained therein.

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.

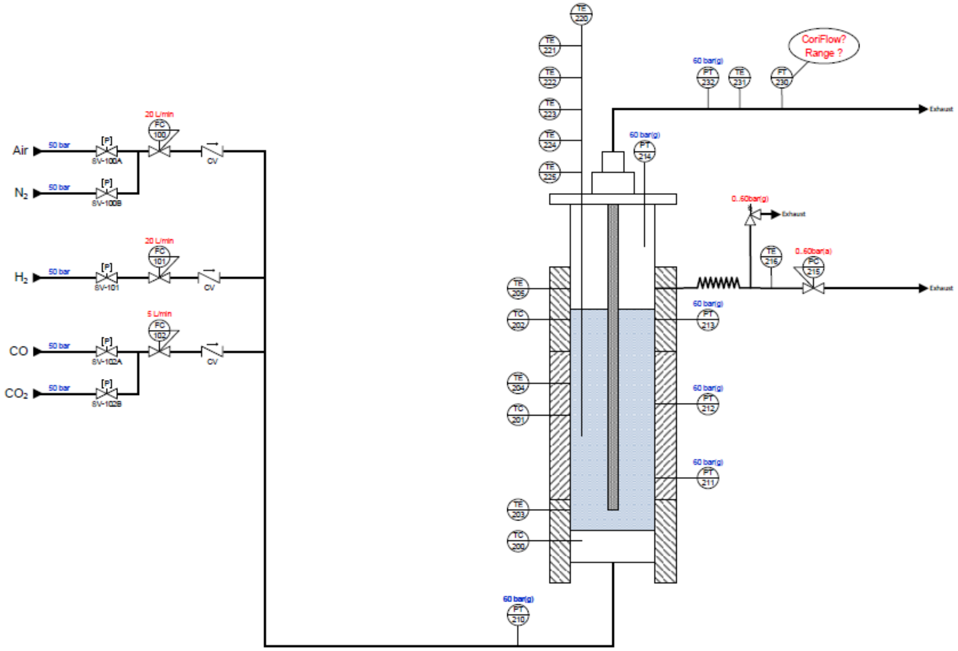
The present publication reflects only the author's views and the FCH JU and the Union are not liable for any use that may be made of the information contained therein.

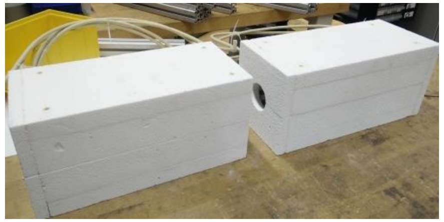
Design and building of the lab scale rig

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

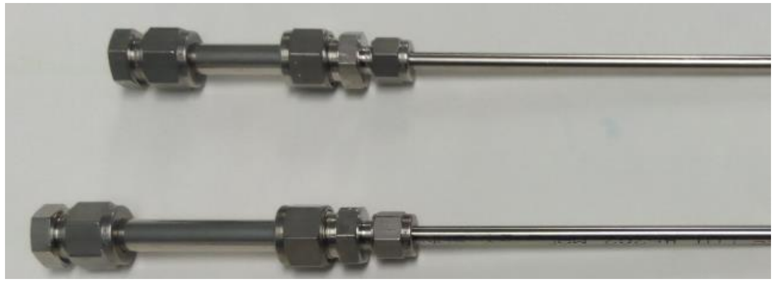


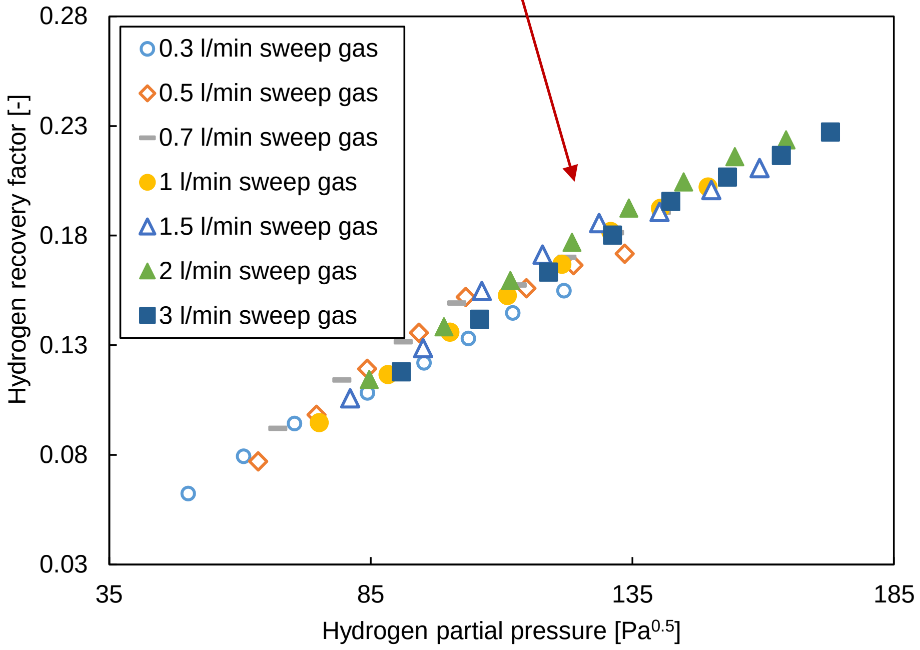


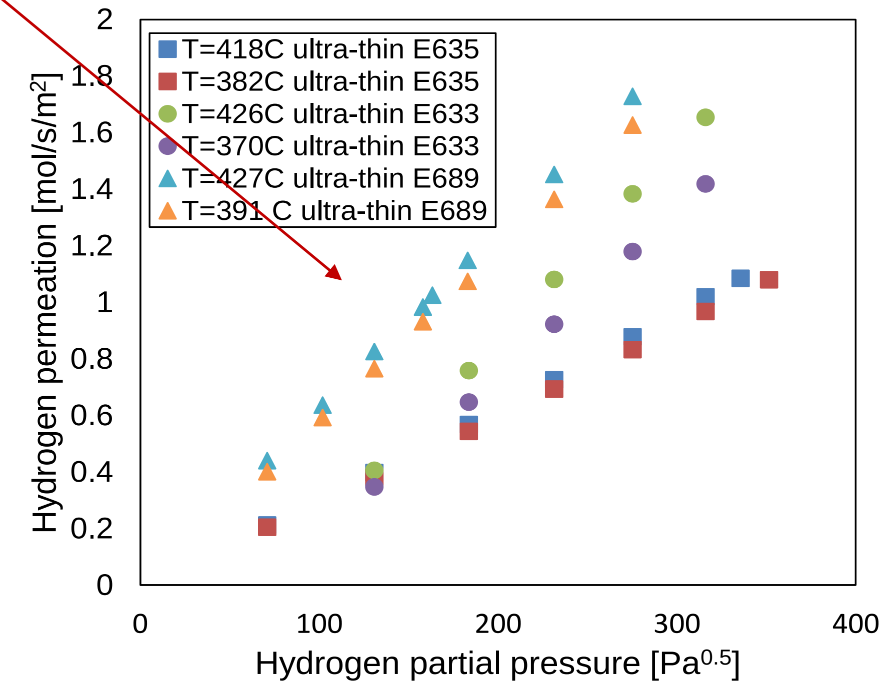
Testing of membranes and sorbents

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

- Temperature and pressure
- Type and amount of sweep gas



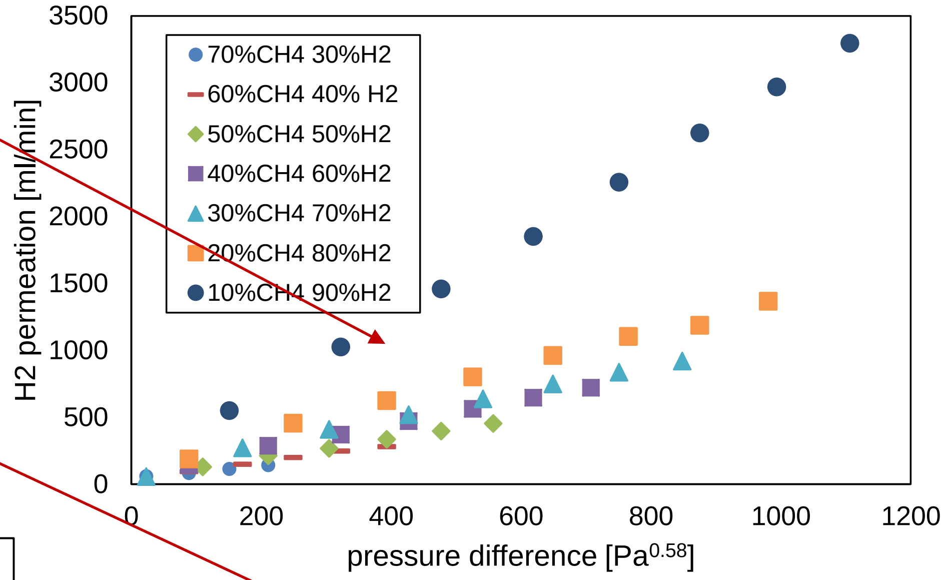


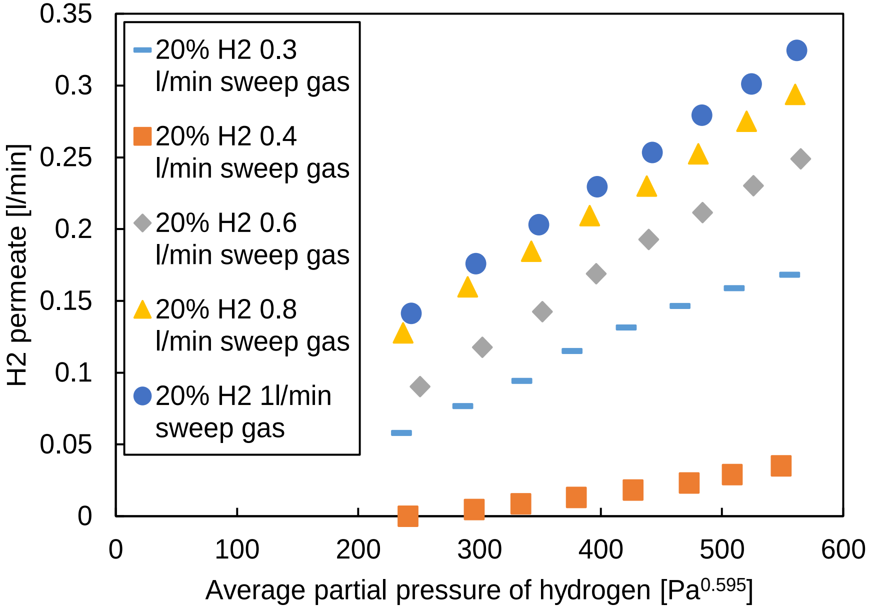


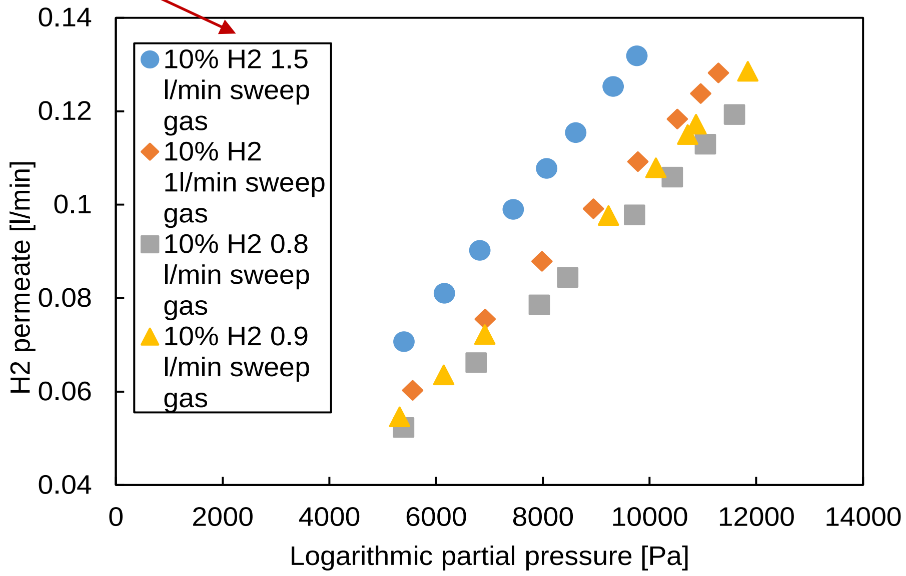
Testing of membranes and sorbents

- Changing H2 concentration

- Changing H2 concentration with sweep gas

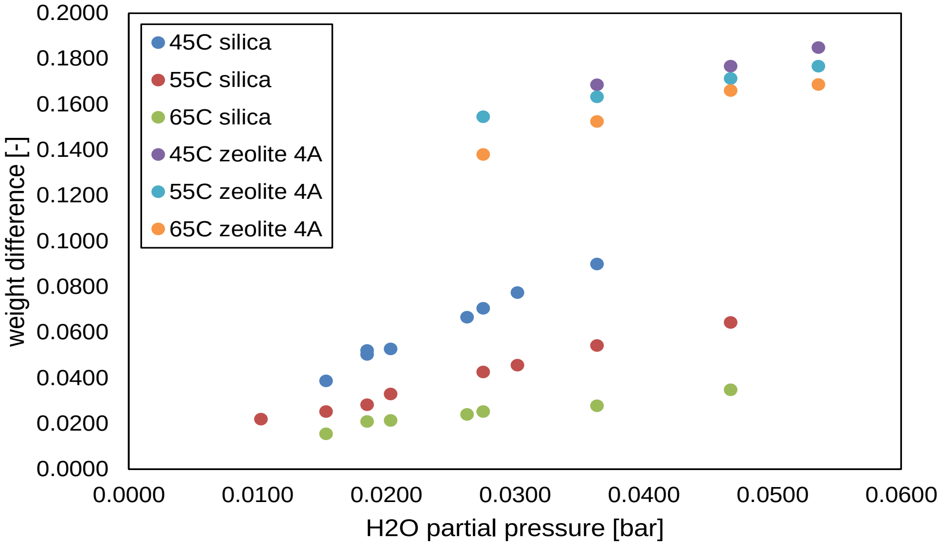


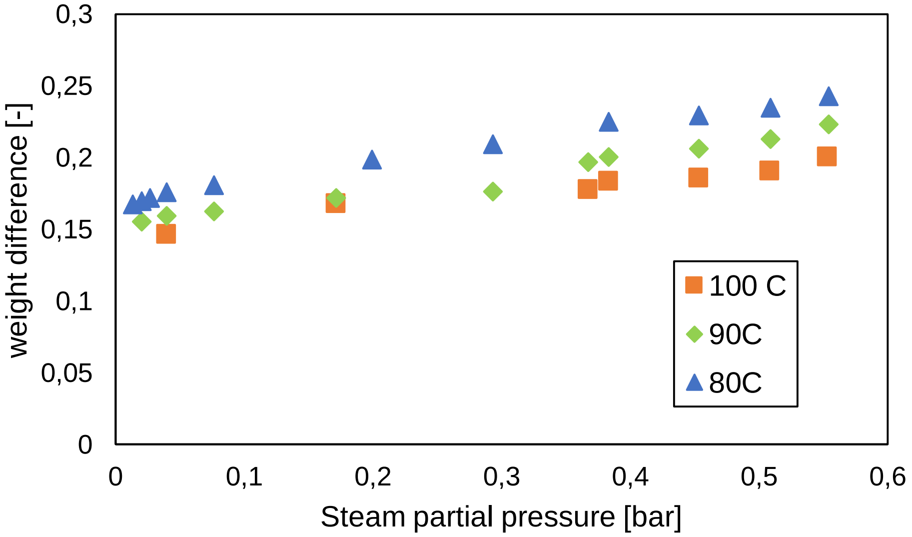




Testing of membranes and sorbents

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

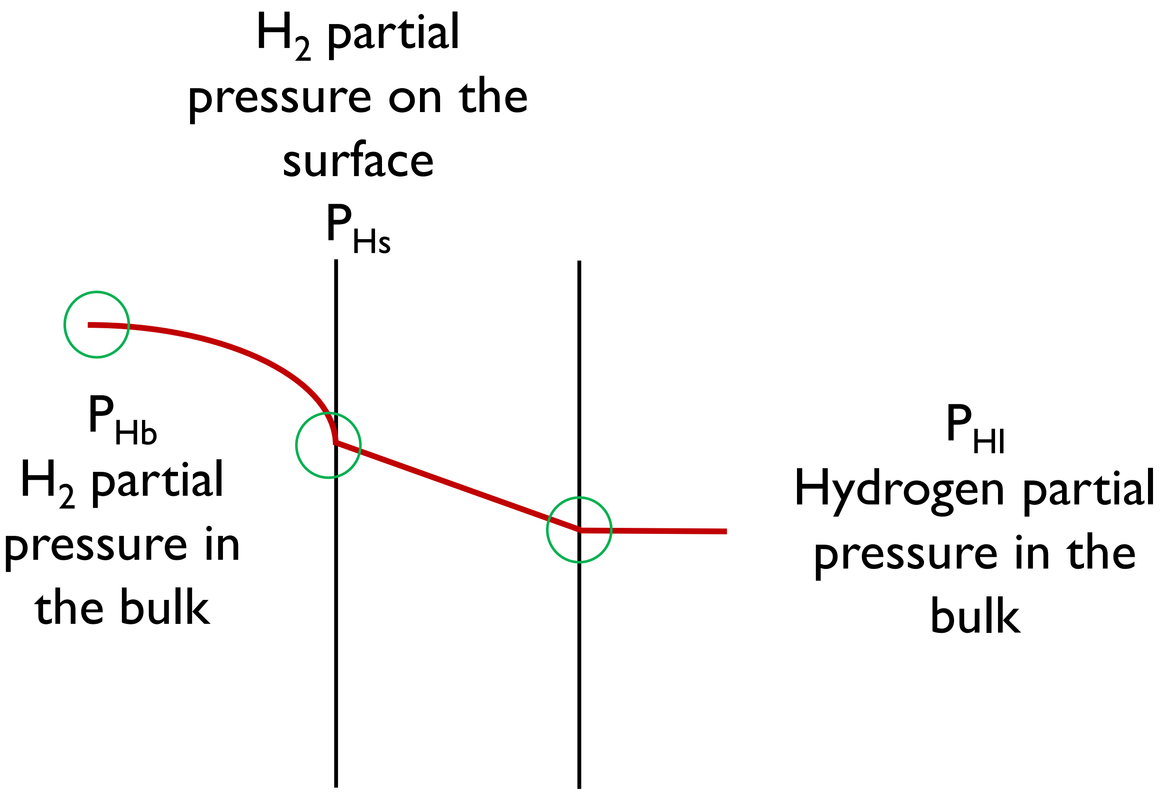
Objectives:

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:

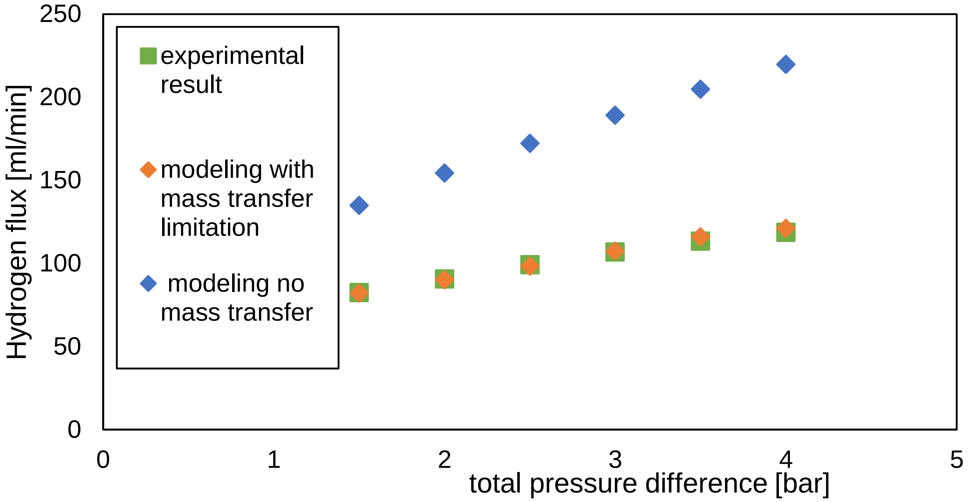
- Retentate side
- Porous support
- Permeate side

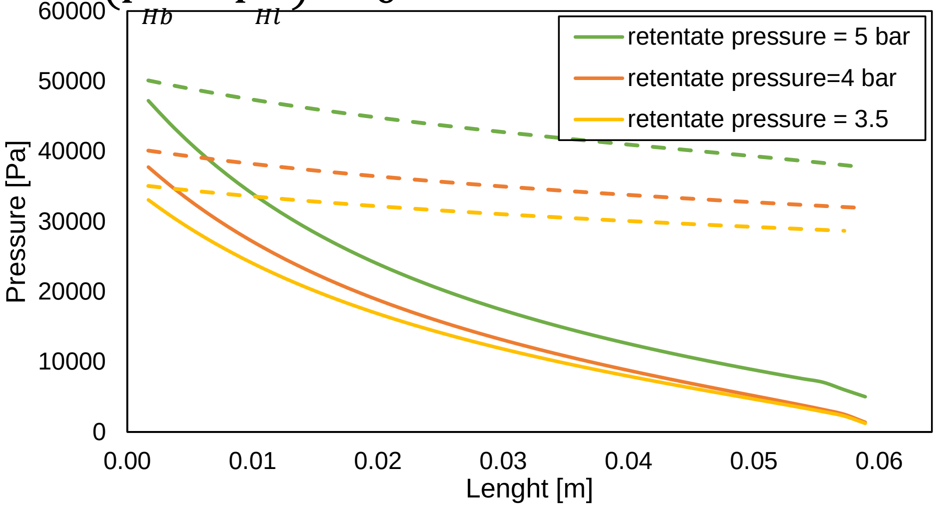
Membrane modelling

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

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

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





- - - - - Retentate partial pressure

——— Surface partial pressure

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

s and the FCH JU and the Union
are not liable for any use that may be made of the information contained therein.

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				

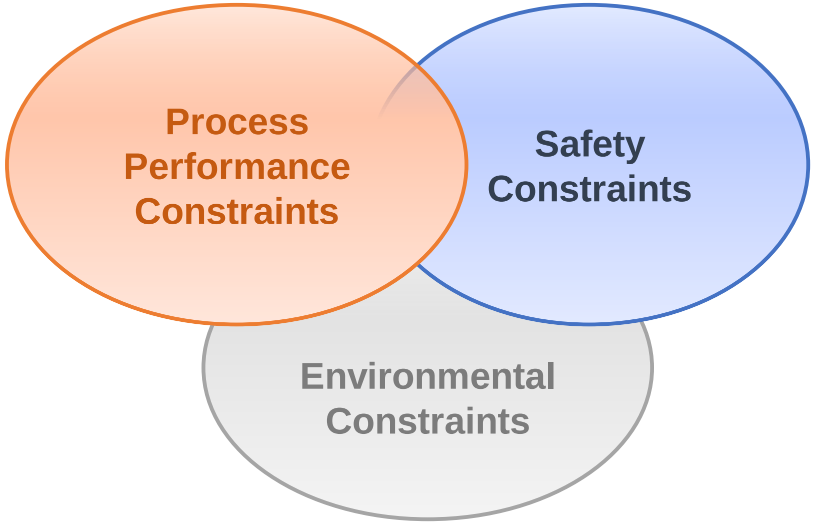
Second case: one membrane module

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

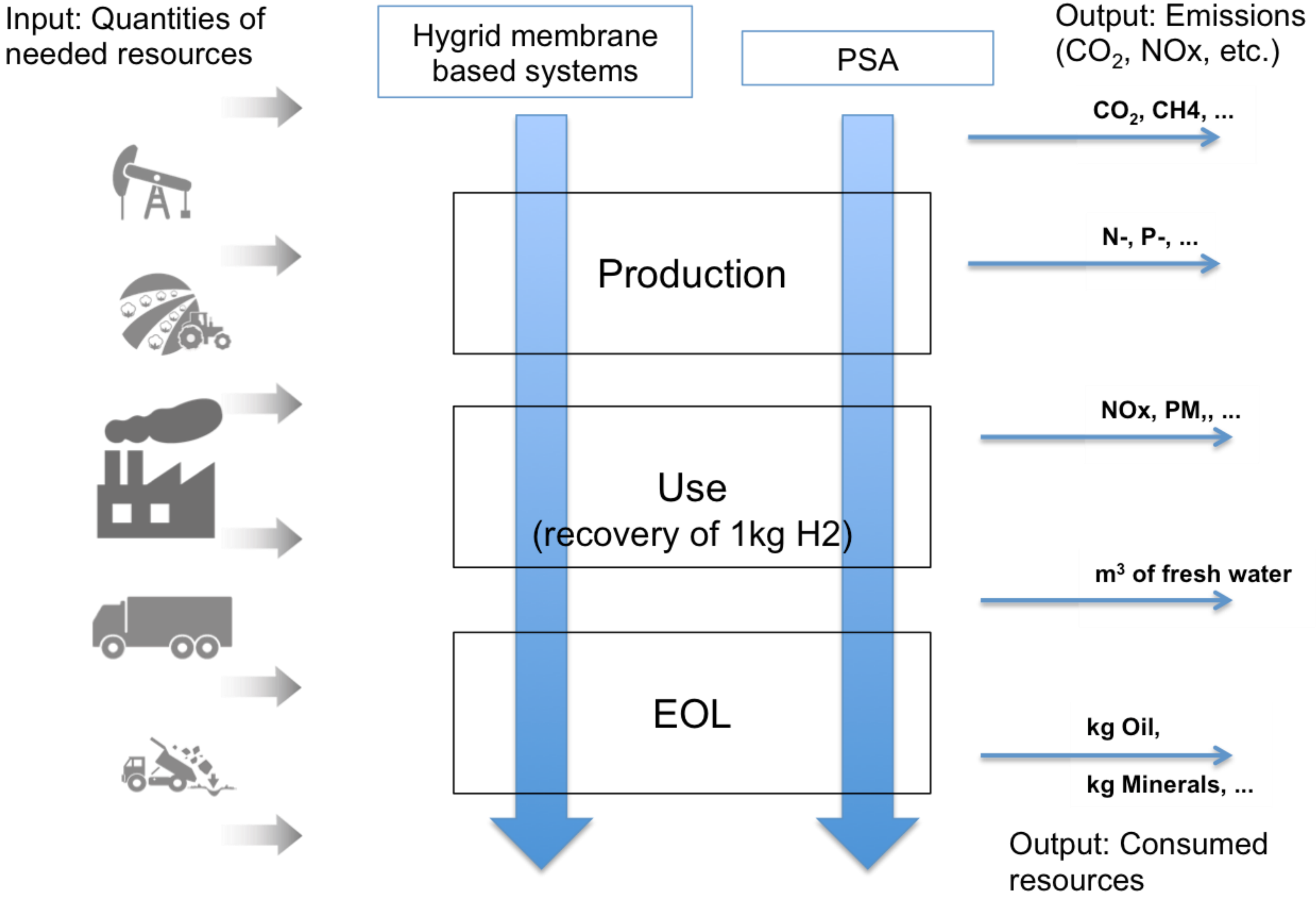
- Functional unit:

  "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



Prototype integration and validation

- 75 PdAg finger-like membranes have been manufactured (≈ 45 cm long, 14/7 o.d/i.d)
- Assemble the membranes in the module (TU/e & Tecnalia)
- Send the module to Hygear
- Construct and assemble the hydrogen recovery pilot plant including controls
- Testing and assessment of hydrogen recovery pilot plant

Flexible Hybrid separation system for H2 recovery from NG Grids

HyGrid

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