Flexible Hybrid separation system for H_2 recovery from NG Grids

HyGrid

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

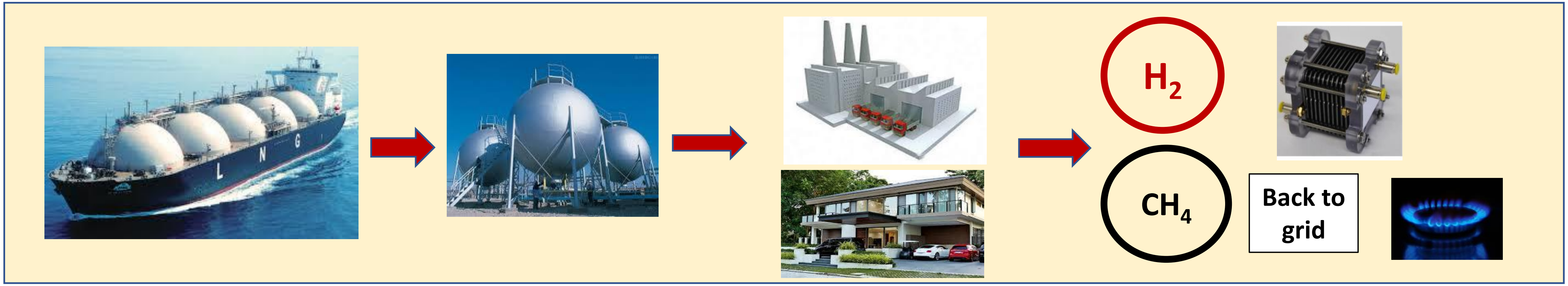
Duration: ~5 years. Starting date: 01-May-2016
Contact: Fausto Gallucci (F.Gallucci@tue.nl)

The project leading to this application 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, Hydrogen Europe and Hydrogen Europe research.

Summary

Use the natural gas network to store and distribute H_2

Blend hydrogen (10 %) with NG

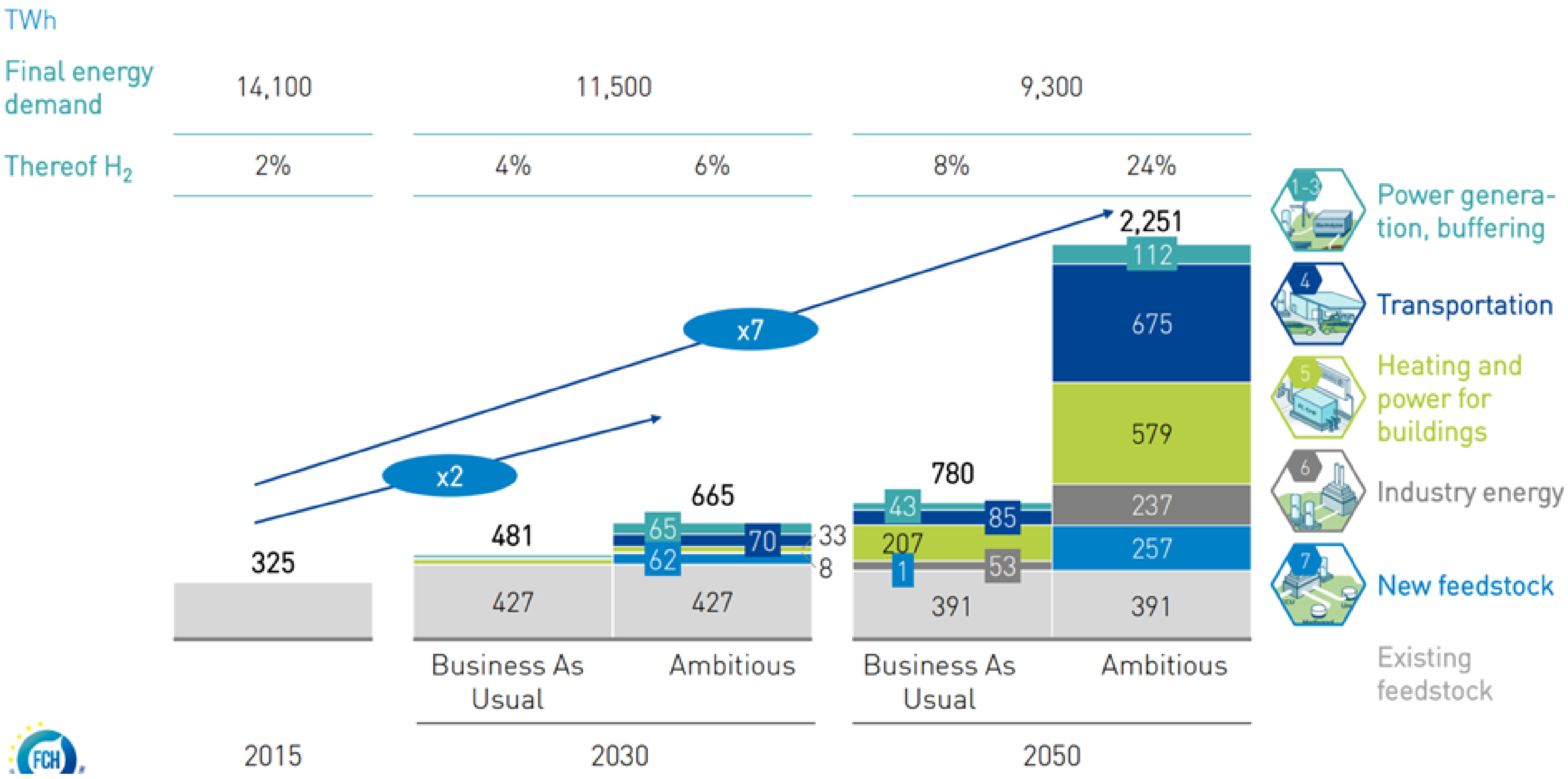


HyGrid **aims** at developing of an advanced **high-performance**, cost-effective separation technology for **direct separation of hydrogen from natural gas networks.**

The project targets a pure hydrogen separation system with **power** and **cost** of **< 5 kWh/kgH2** and **< 1.5 €/kgH2**. A pilot designed for **>25 kg/day** of hydrogen will be built and tested at industrially relevant conditions (TRL 5)

Introduction

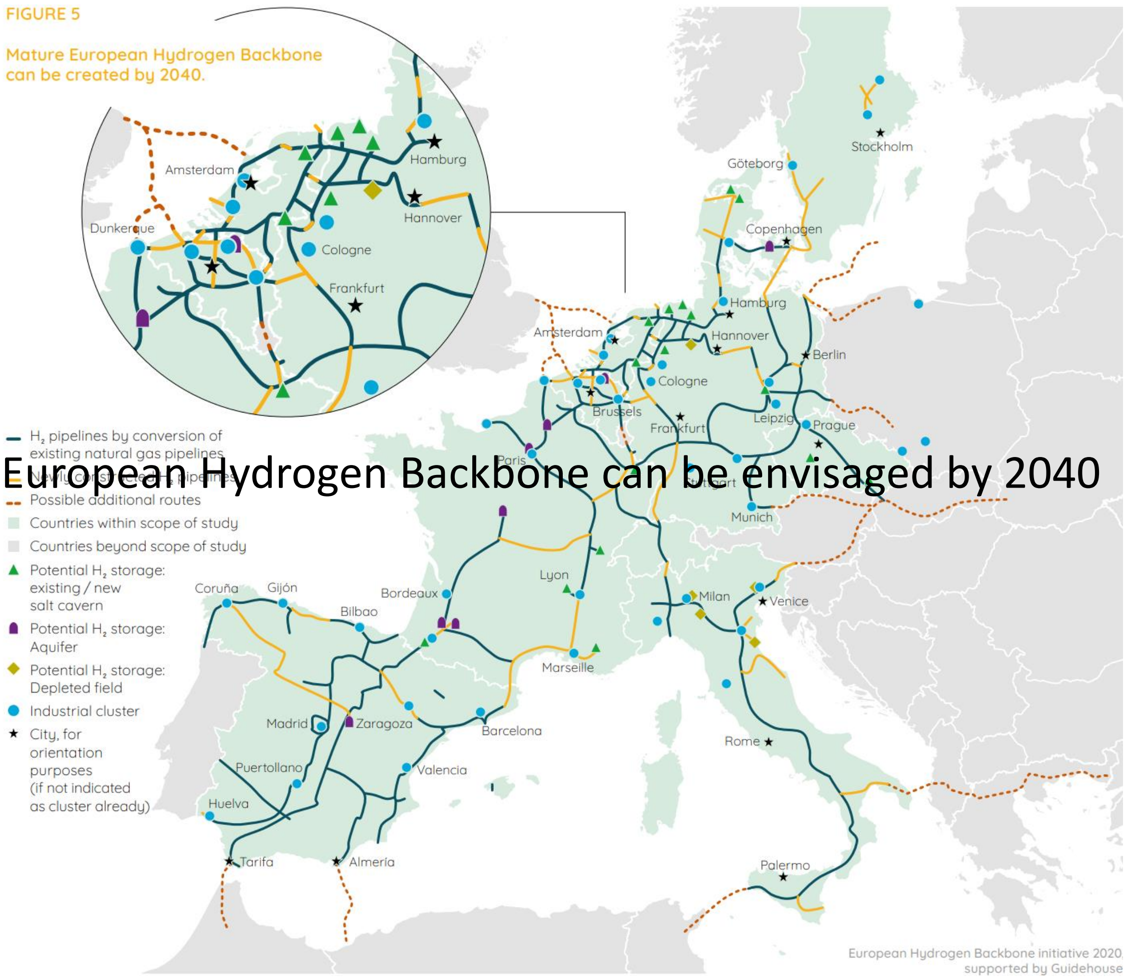
Estimated hydrogen consumption in the EU in 2030 and 2050 per sector



https://www.fch.europa.eu/sites/default/files/20190206_Hydrogen%20Roadmap%20Europe_Keynote_Final.pdf

Introduction

Hydrogen gas network envisaged by 2040 stretching out to most European countries with links to North Africa



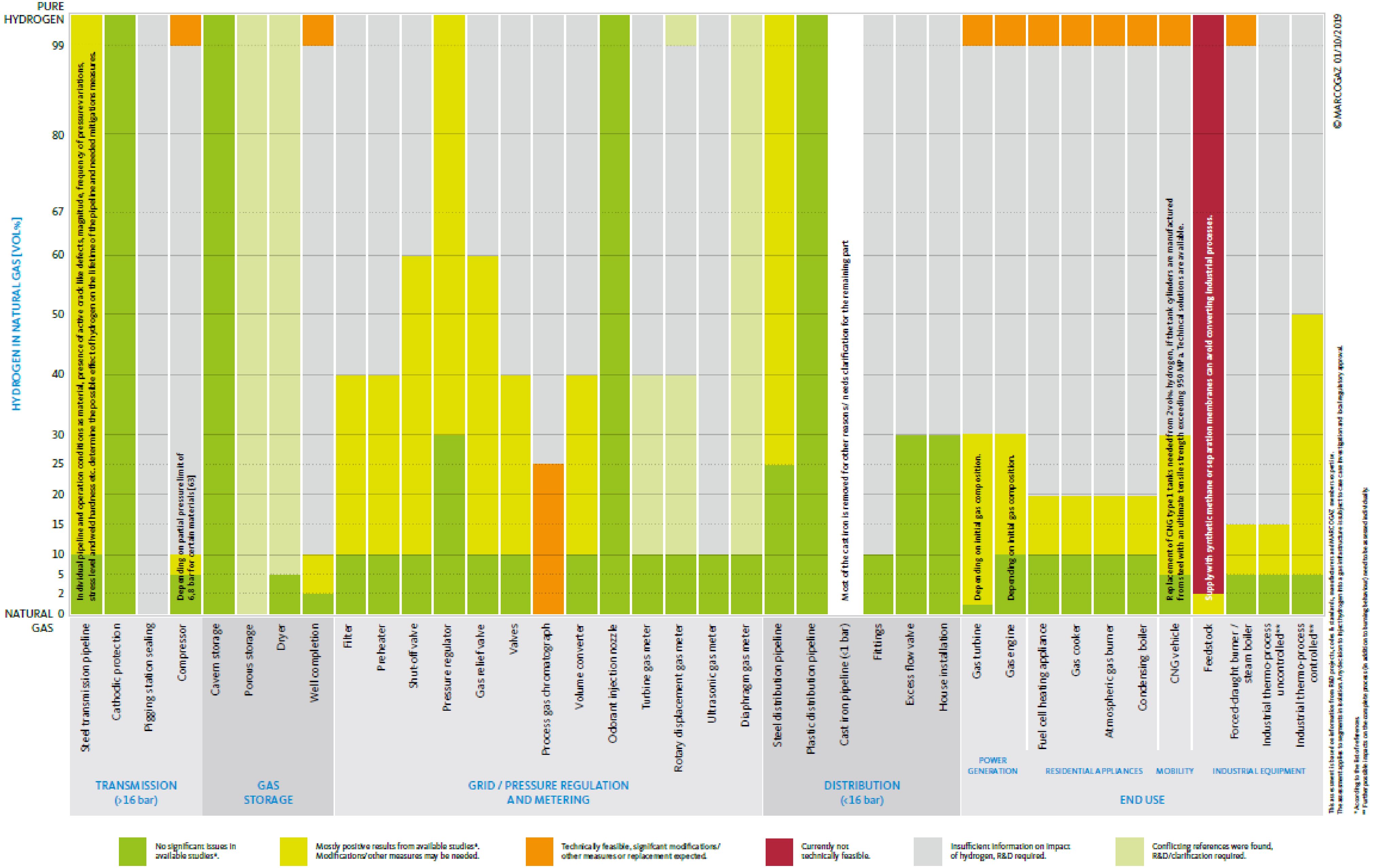
European Hydrogen Backbone can be envisaged by 2040

https://gasforclimate2050.eu/wp-content/uploads/2020/07/2020_European-Hydrogen-Backbone_Report.pdf

Introduction

Overview of available test results and regulatory limits for hydrogen admission into the existing natural gas infrastructure and end use

https://www.hydrogeneurope.eu/wp-content/uploads/2021/05/ENTSOG_GIE_HydrogenEurope_QandA_hydrogen_transport_and_storage_FINAL.pdf



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).

Project objectives

Membranes

H2
2- 10 %

Carbon

Palladium

tecnalia Inspiring Business

Electrochemical Hydrogen Purification (EHP)

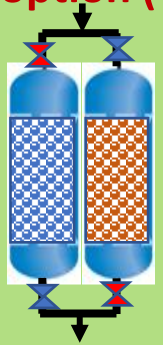
H2
< 2%

HyET Hydrogen Efficiency Technologies

Temperature Swing Adsorption (TSA)

HYGEAR

Remove humidity

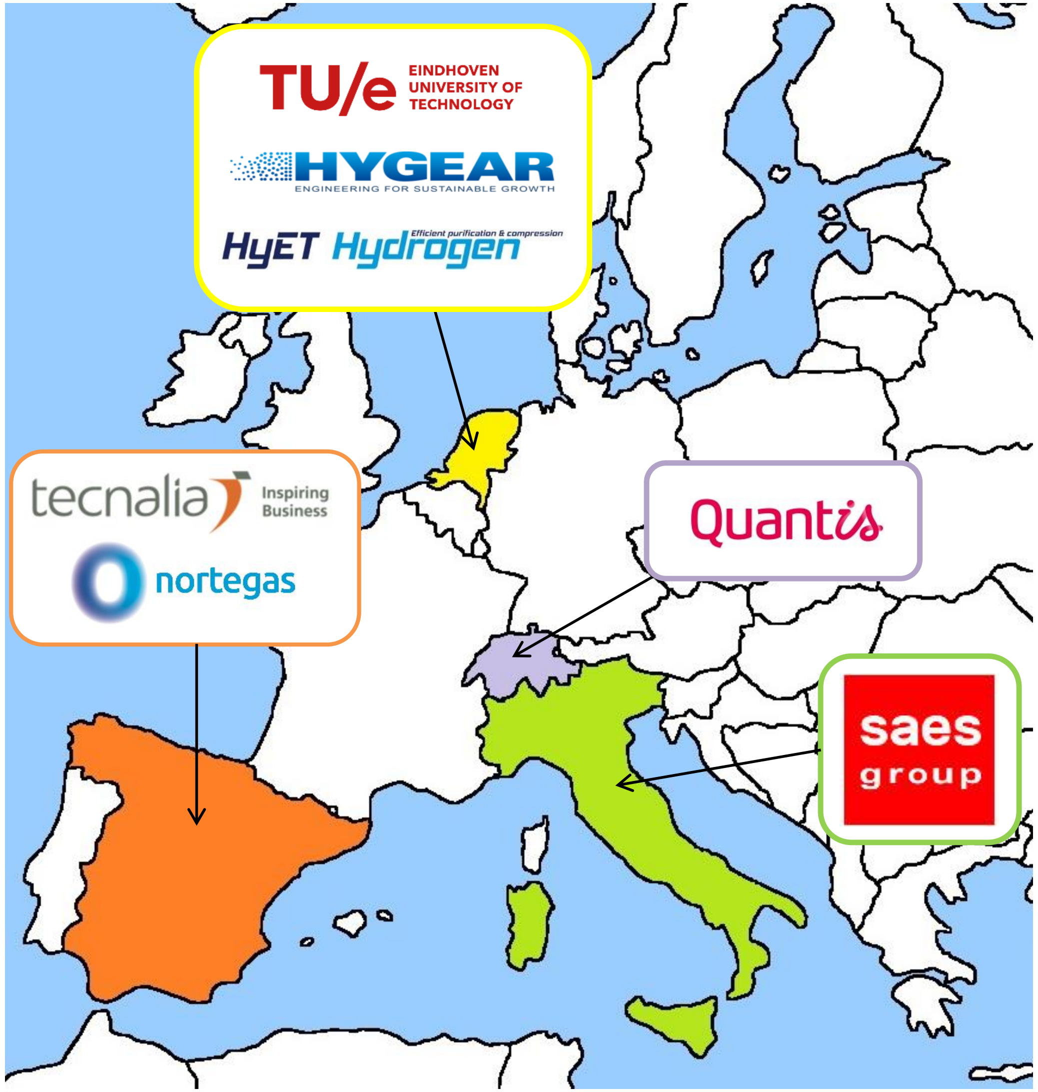


- Development of a hydrogen separation system capable of targeting low (2-10%) and very low (<2%) H_2 blends in natural gas.
  - Membranes for H_2 recovery from low hydrogen content streams (2-10%).
  - EHP for H_2 recovery from very low concentration streams (<2%) .
  - TSA for water removal from hydrogen/water streams.
- Technical validation of the novel modules at lab scale.

Project objectives

- 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.

Consortium



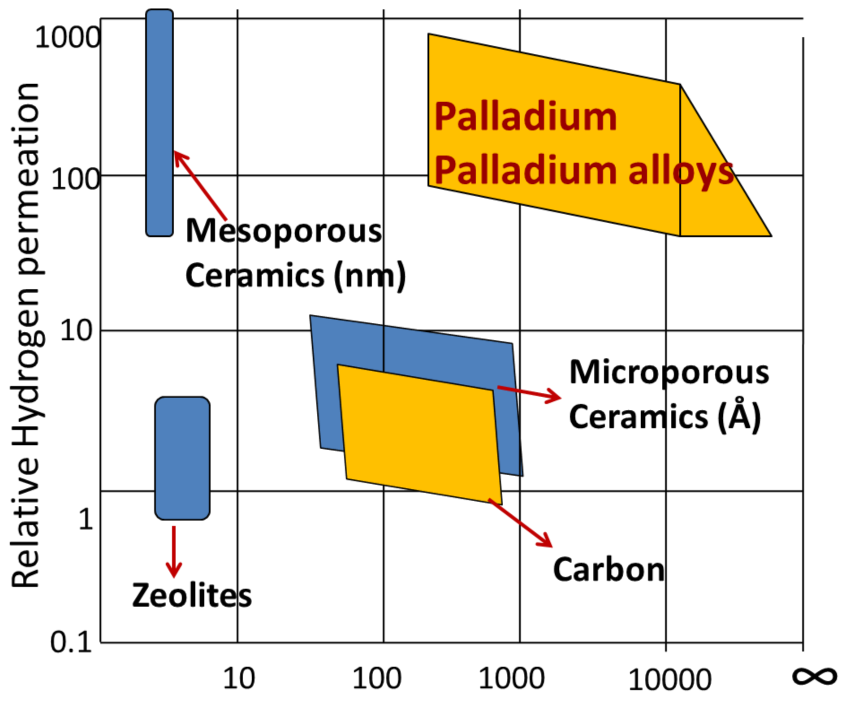
Multidisciplinary and complementary team: 7 European organisations from 4 countries: 2 research institutes and 5 industries (3 SME) in different sectors (from materials development to membrane modules and separation systems, etc.).

1. TU/e: Project Coordinator, lab scale testing & modelling, system modelling, energy analysis. Design and manufacture membrane module prototype.
2. TECNALIA: Dissemination Manager. Pd-based and CMSMs membranes developer, Design and manufacture membrane module prototype (including membranes).
3. HYG: TSA, HyGrid prototype integration (membrane separator, EHP and TSA, BoP) and testing, business case.
4. SAES: Membrane sealing.
5. 5 HYET: Exploitation Manager. Electrochemical hydrogen purification (lab-scale and prototype)
6. 6 QUANTIS: Sustainability assessment (LCA and LCC)
7. 7 NORTEGAS: Industrial specifications

Membrane 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

Permation of H_2 against H_2/N_2 selectivity

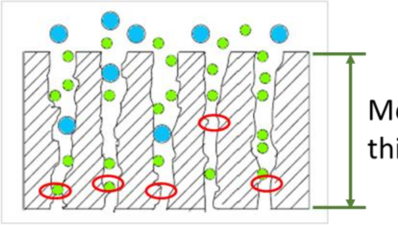


H_2/N_2 selectivity

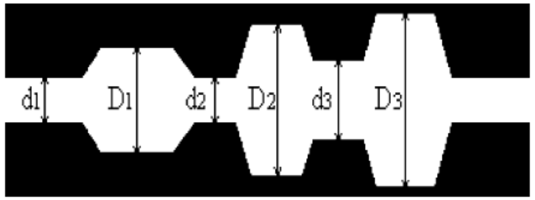
- **Pd-based membranes** for the medium to the lowest Natural Gas Grid pressures.
- **Carbon Molecular Sieve membranes** for the high-pressure range.
- Membrane **module for the prototype**.

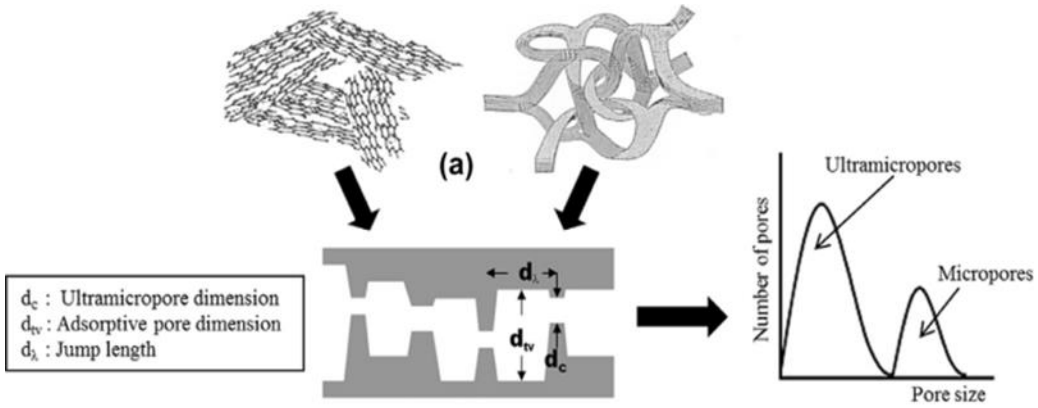
Membrane development:
Carbon Molecular Sieve membranes

Transport mechanism

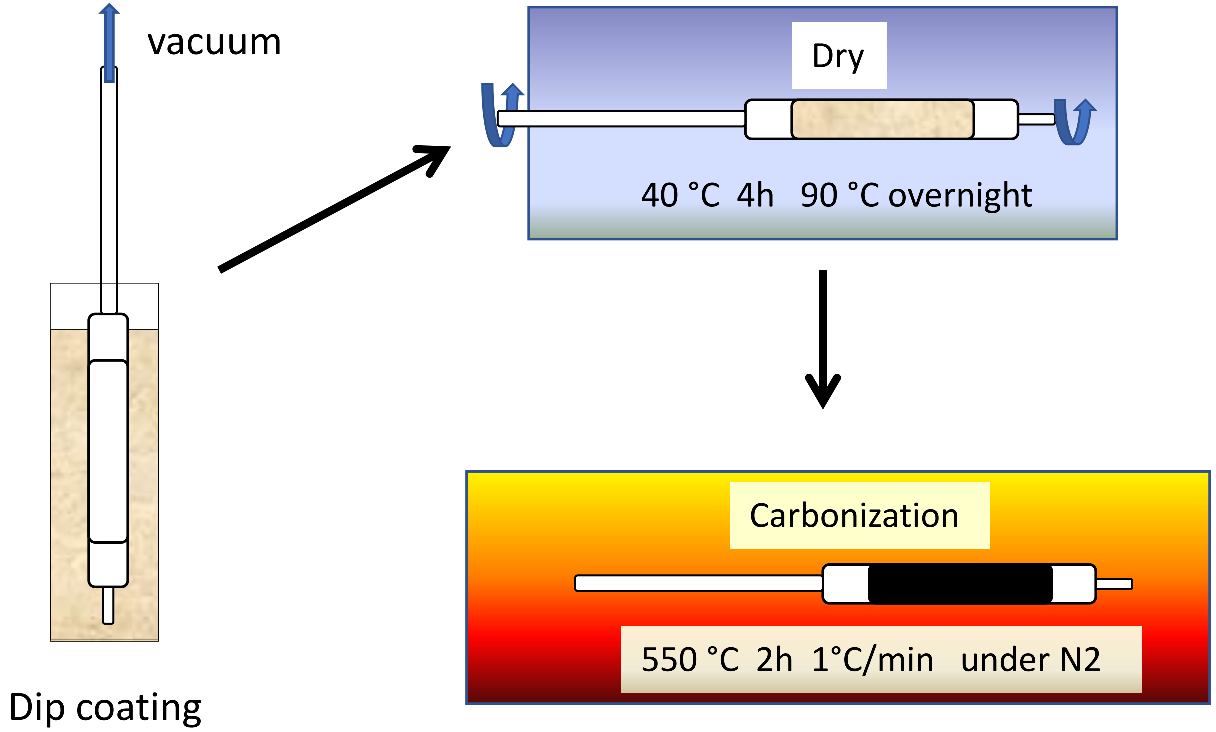


Nanopores + constrictions

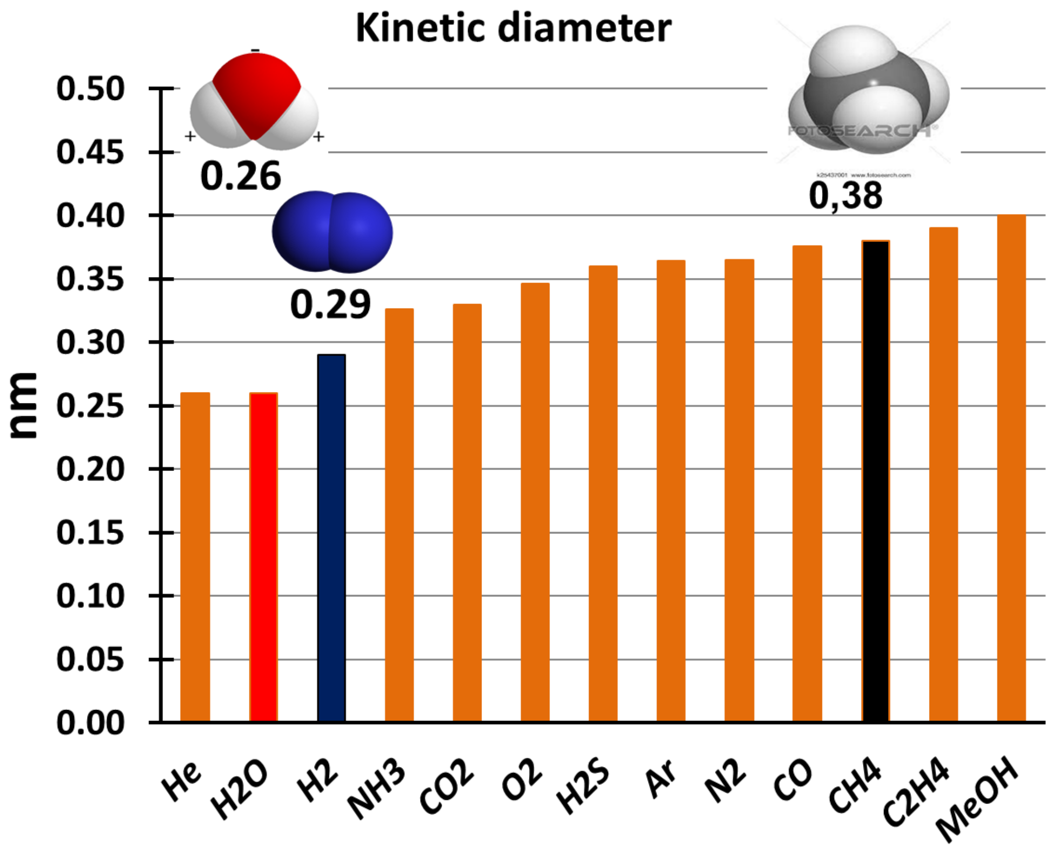


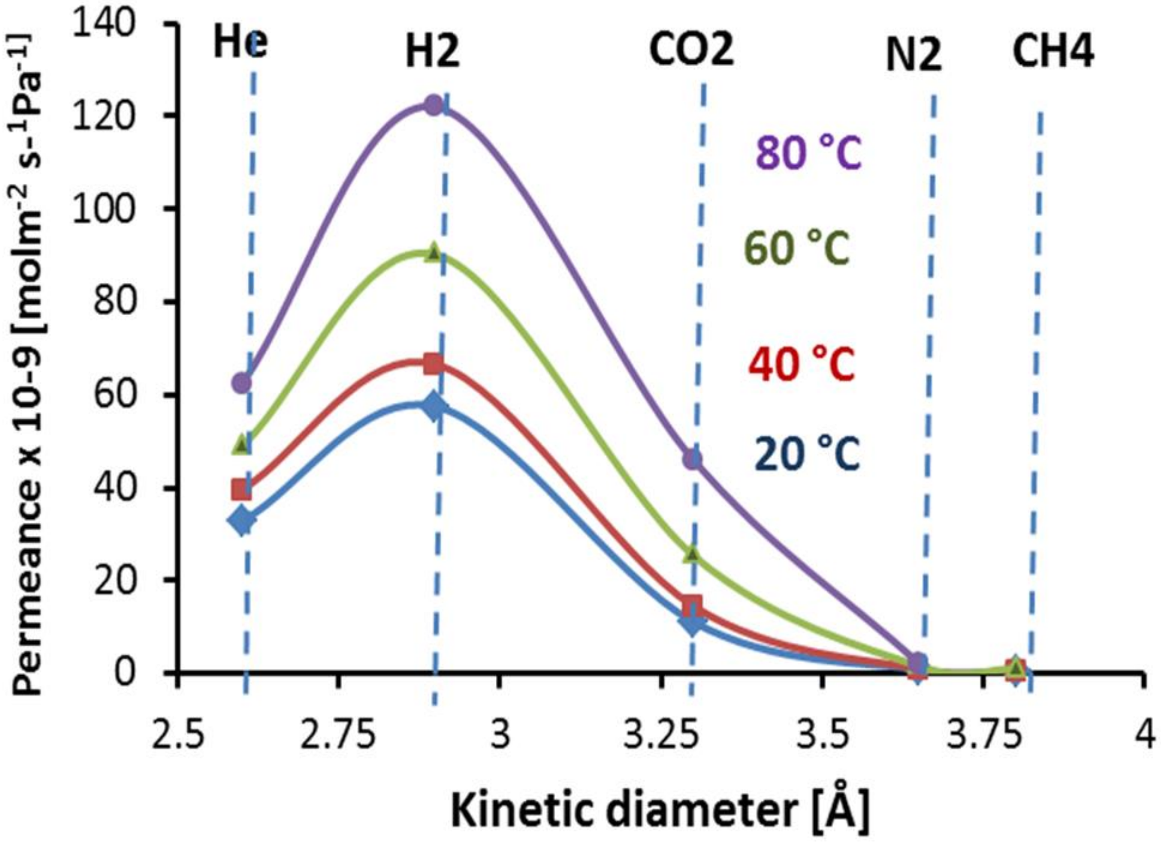


Preparation of composite Al_2O_3 – CMSM



Membrane development:
Carbon Molecular Sieve membranes

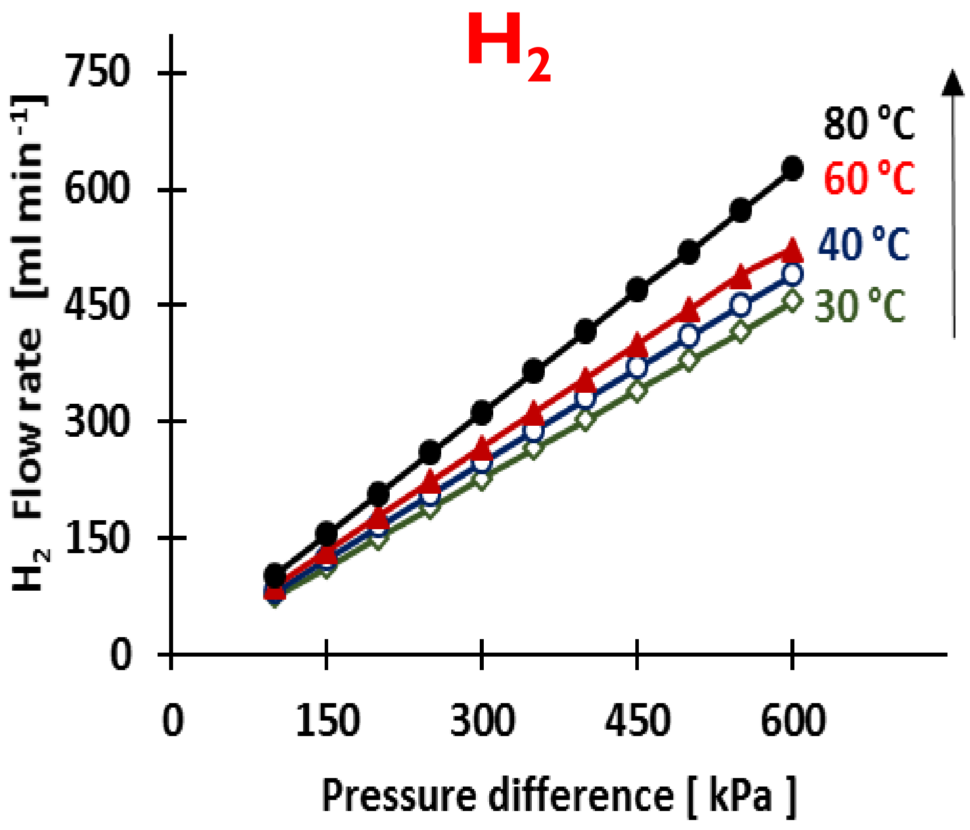


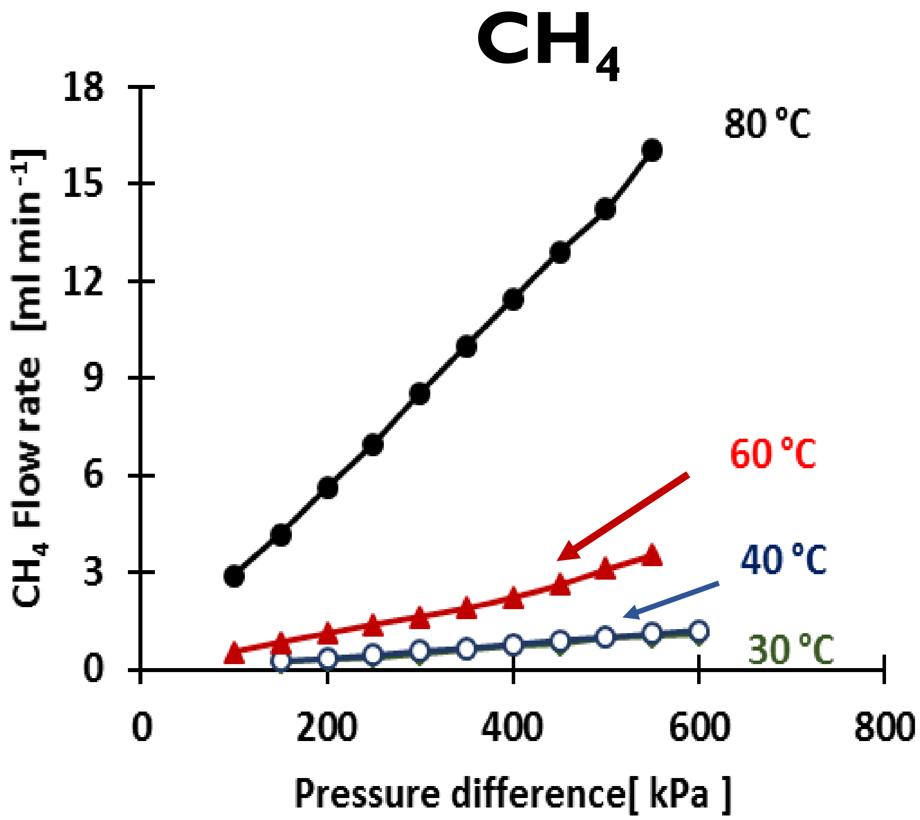


Membrane development: Carbon Molecular Sieve membranes

H_2 and CH_4 single gas permeation

Activated at 100 °C

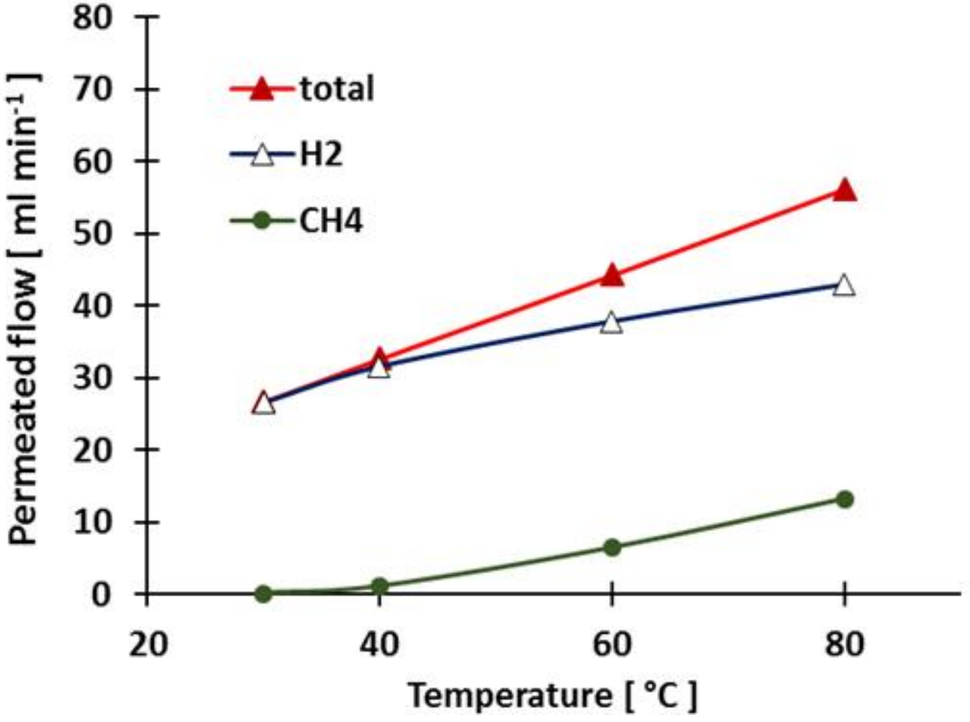


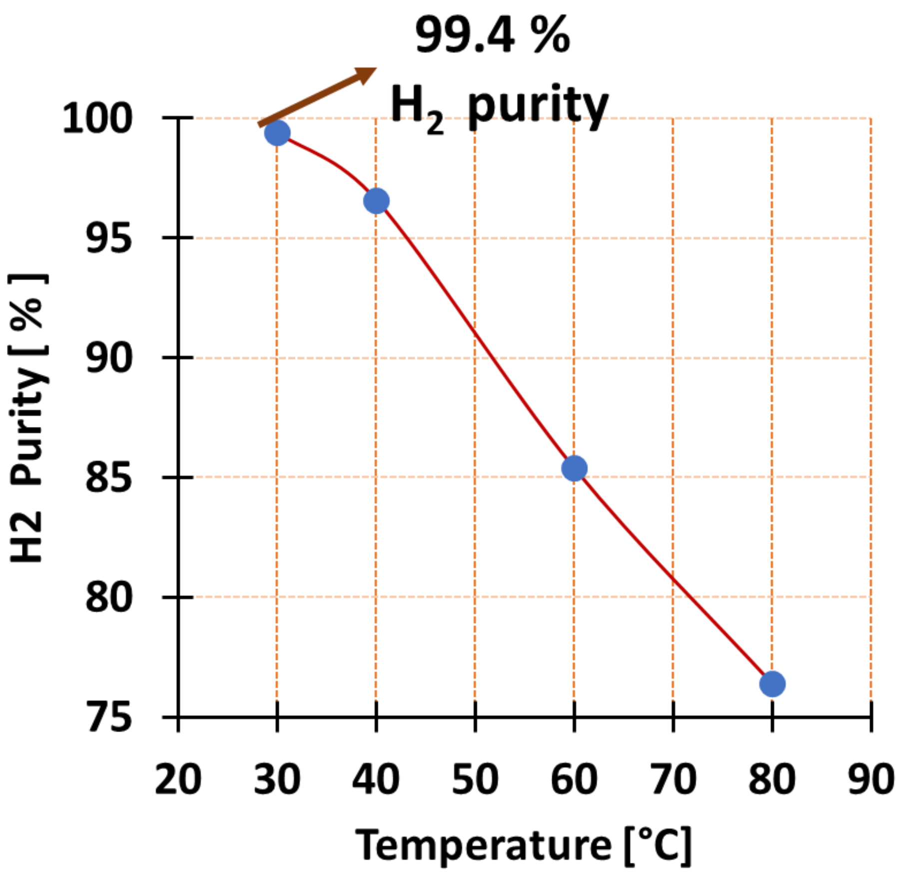


Membrane development: Carbon Molecular Sieve membranes

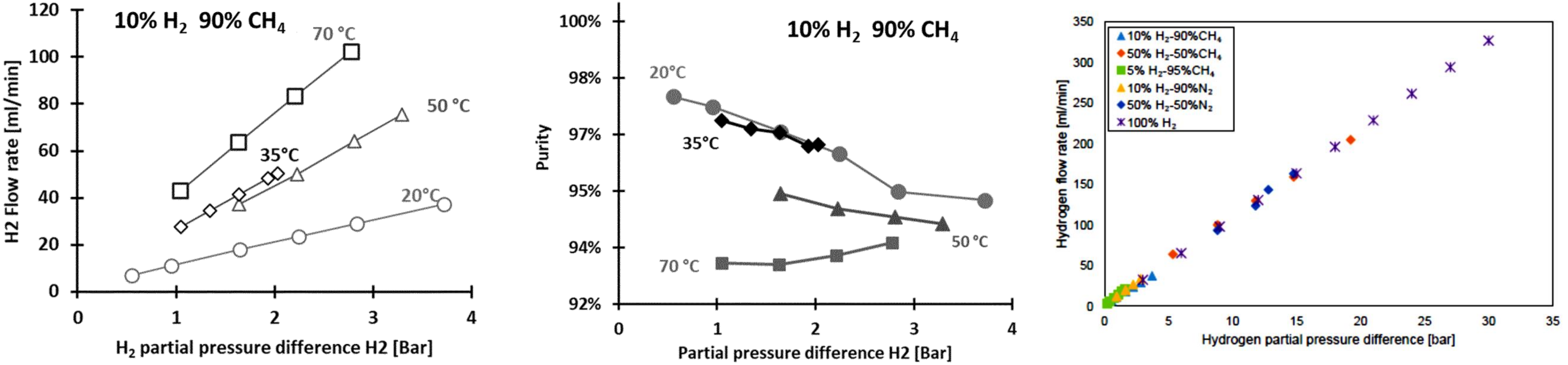
10% H_2 / 90% CH_4 gas mixture permeation at various temperatures

P inlet 7.5 bar,
P Permeated 0.01 bar

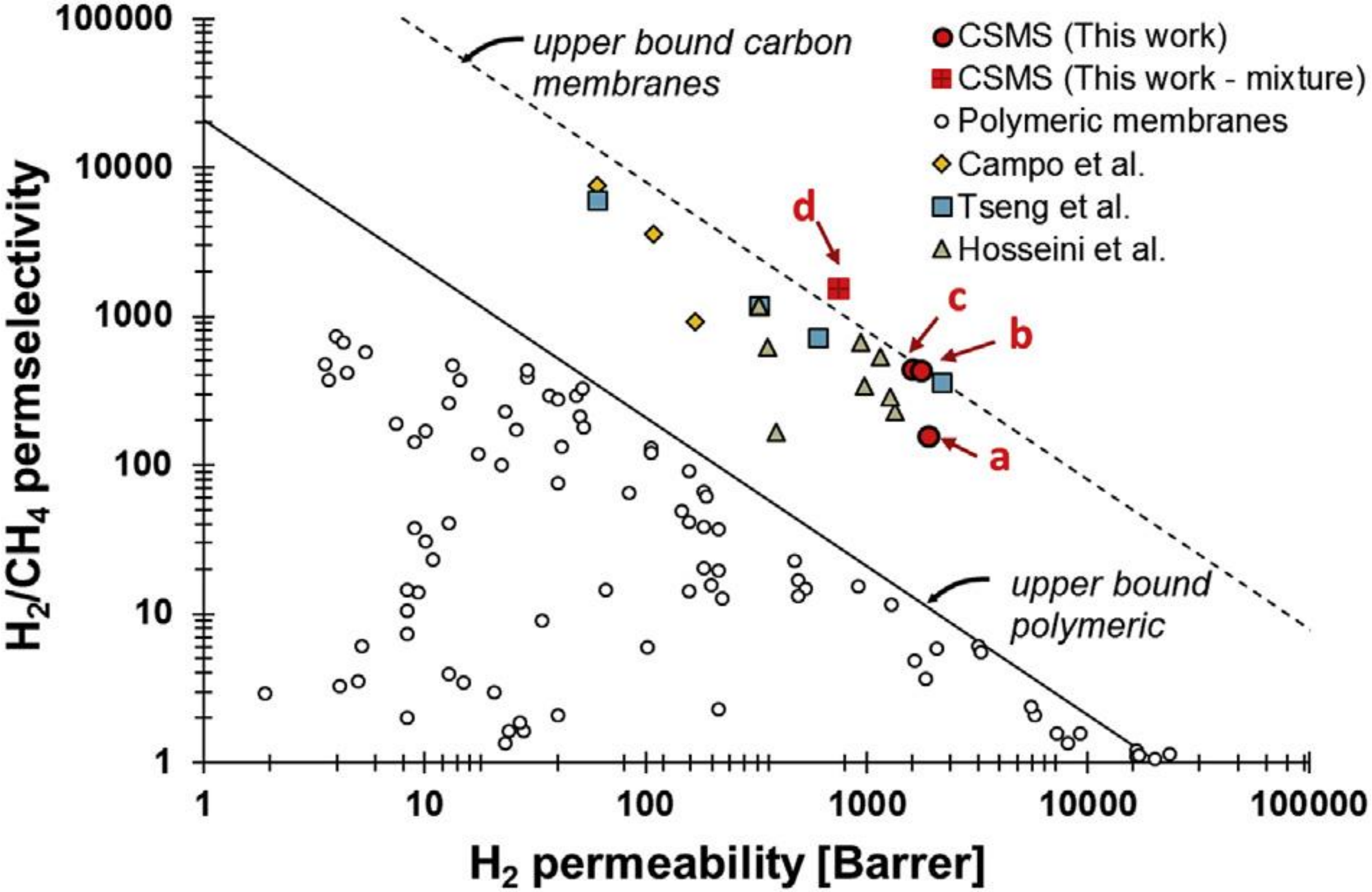




Membrane development:
Carbon Molecular Sieve membranes

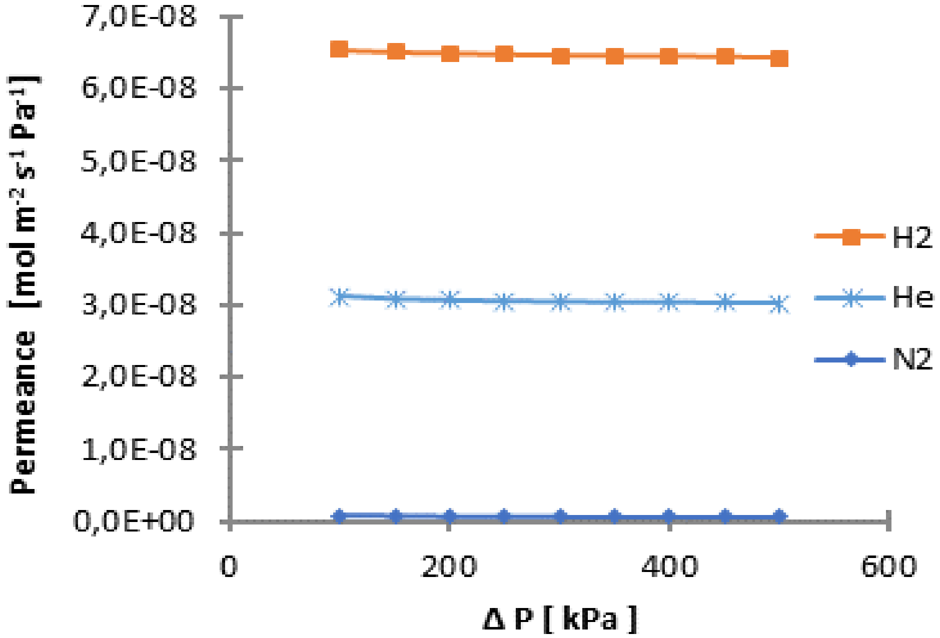


Membrane development:
Carbon Molecular Sieve membranes



Membrane development:
Carbon Molecular Sieve membranes

- 40 cm long CMSMs developed



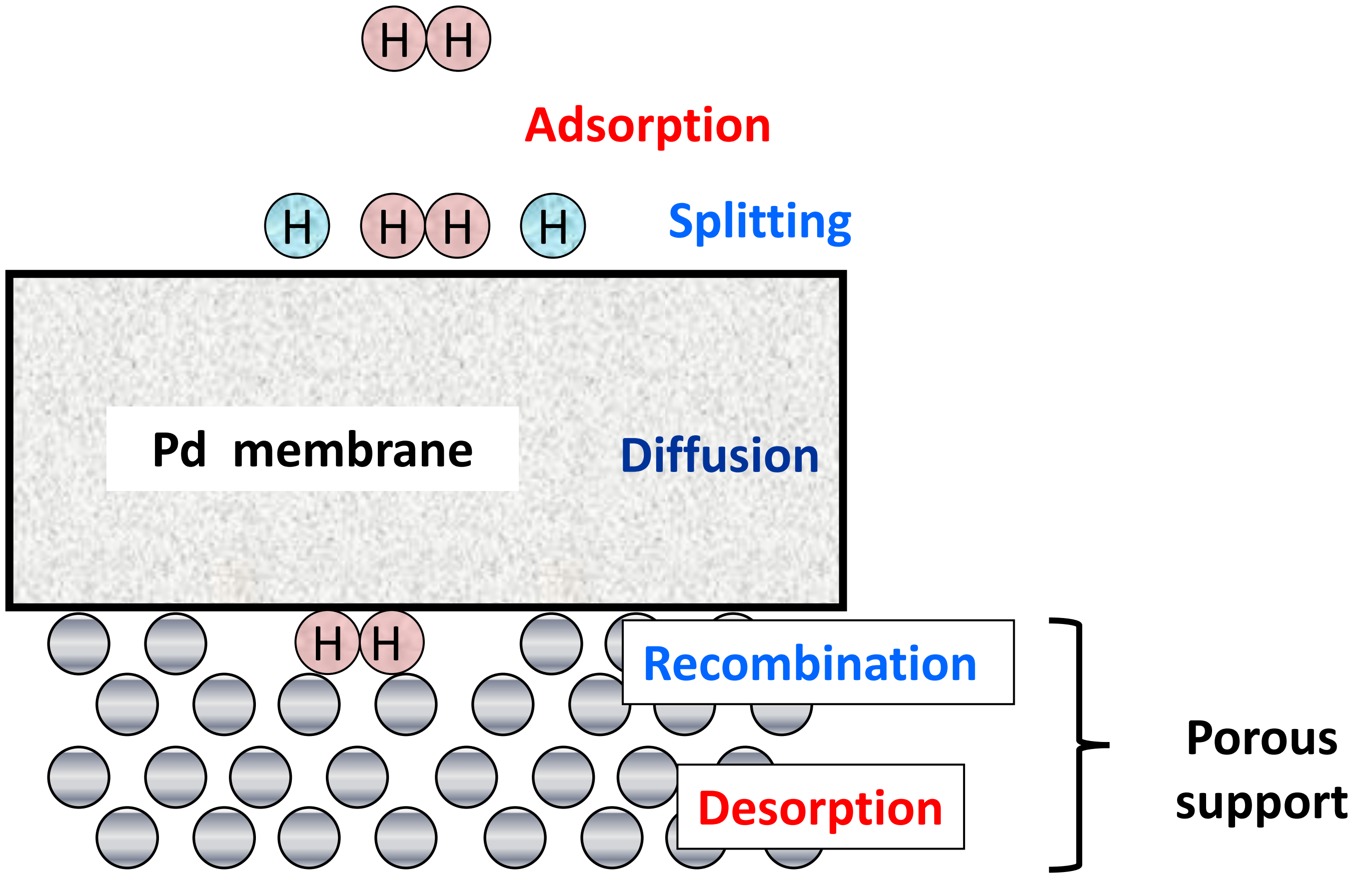
Membrane development: Ceramic supported Pd-based membrane

H_2 permeation in Pd membranes

Thin membranes

-Surface interference
- H_2 splitting

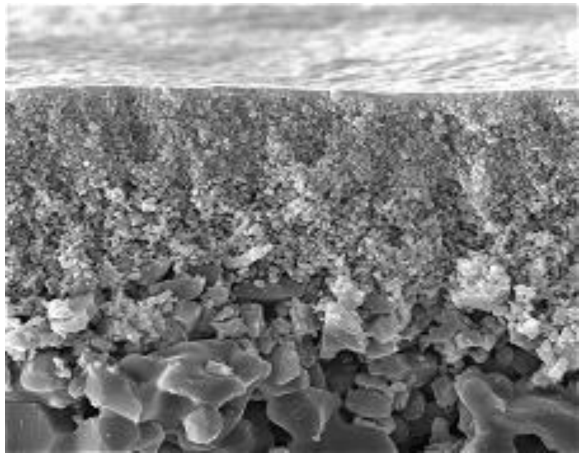
resistance of support



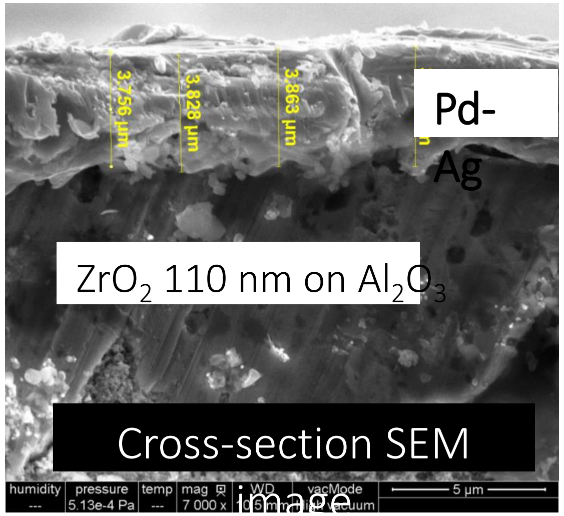
Membrane development:
Ceramic supported Pd-based membrane

<u>Porous Support:</u>

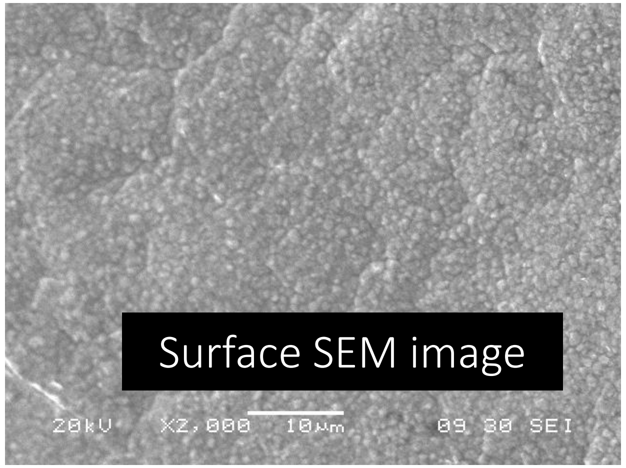
- Supplied by Rauschert
- 100nm pore size Al_2O_3



<u>Pd-Ag membrane layer deposition by Electroless Plating technique</u>



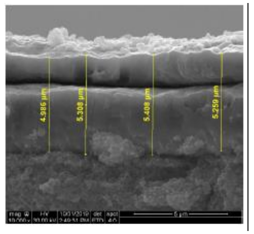
- ~4 µm thick Pd-Ag membrane

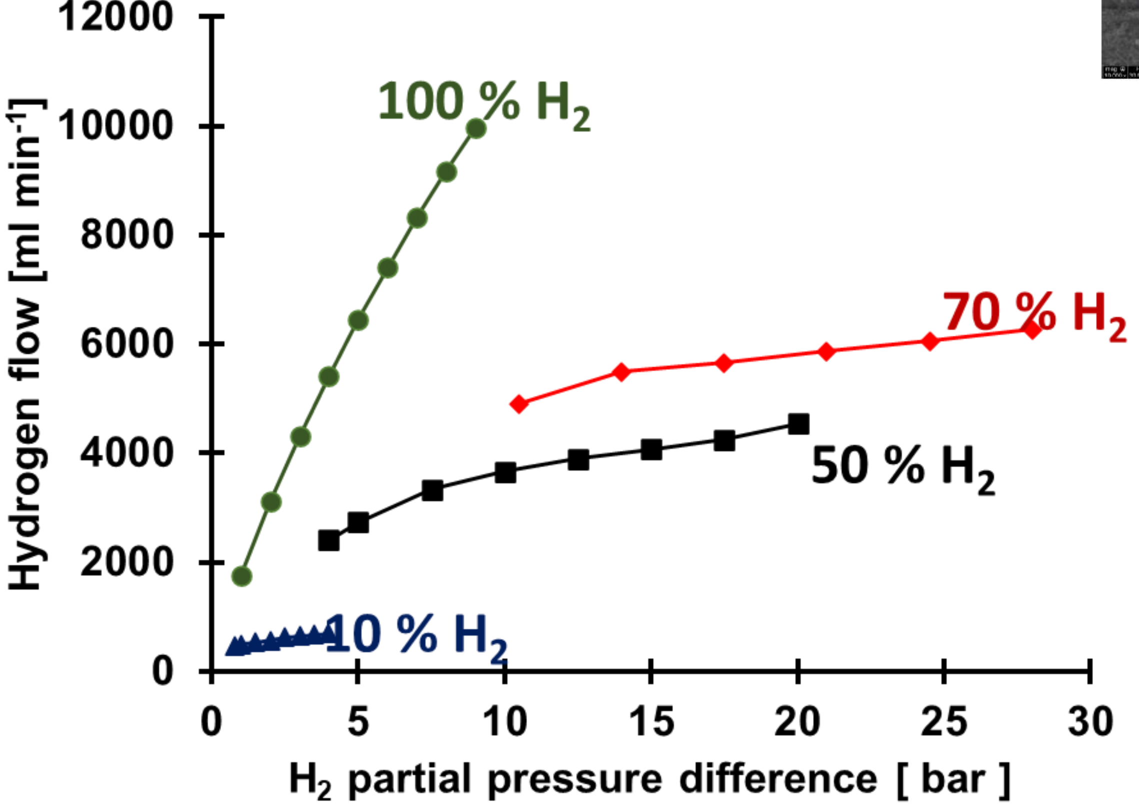


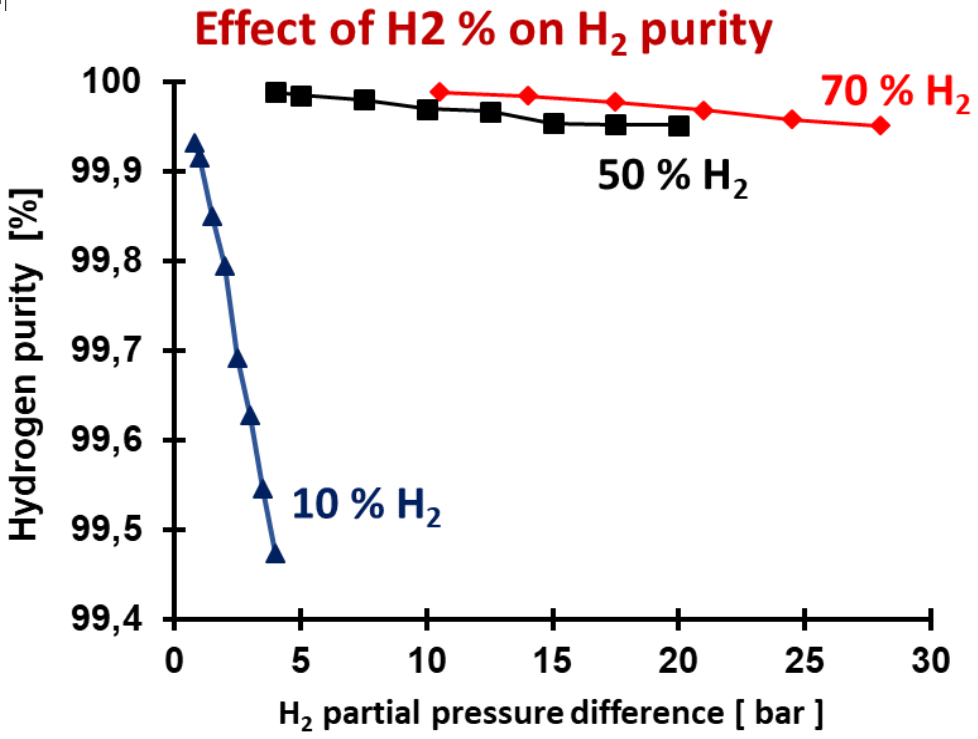
tecnalia Inspiring Business

Membrane development:
Ceramic supported Pd-based membrane

Pd-Ag double skin



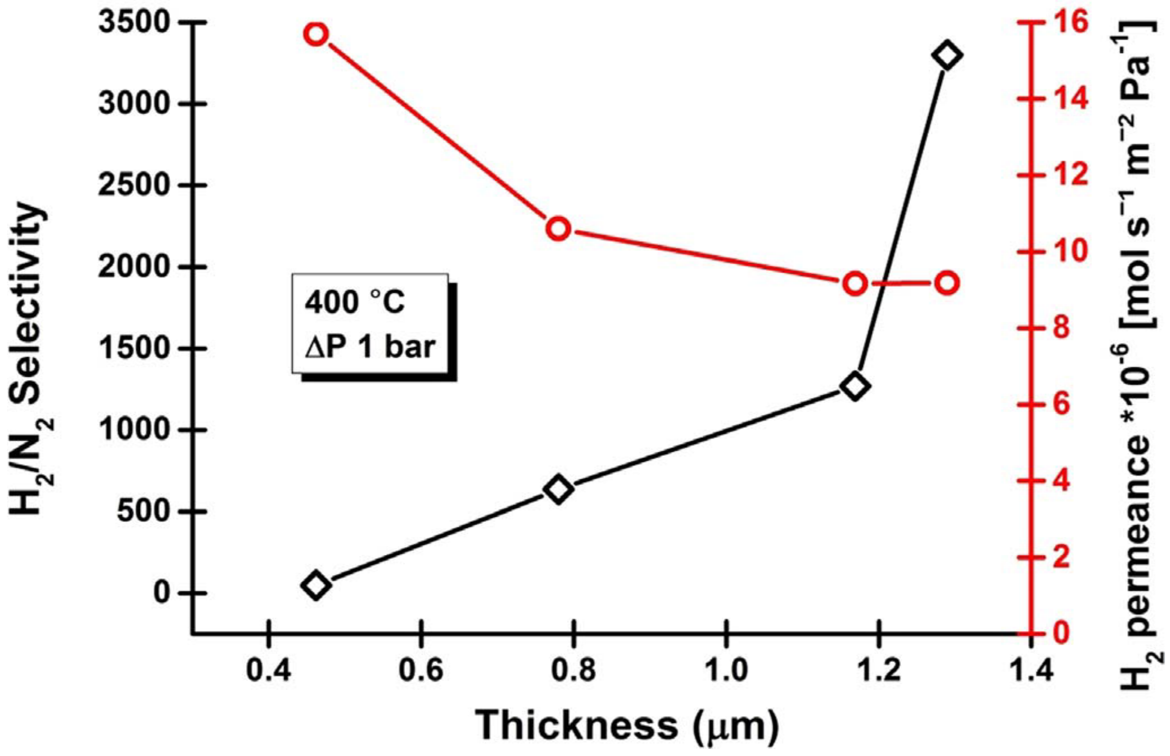




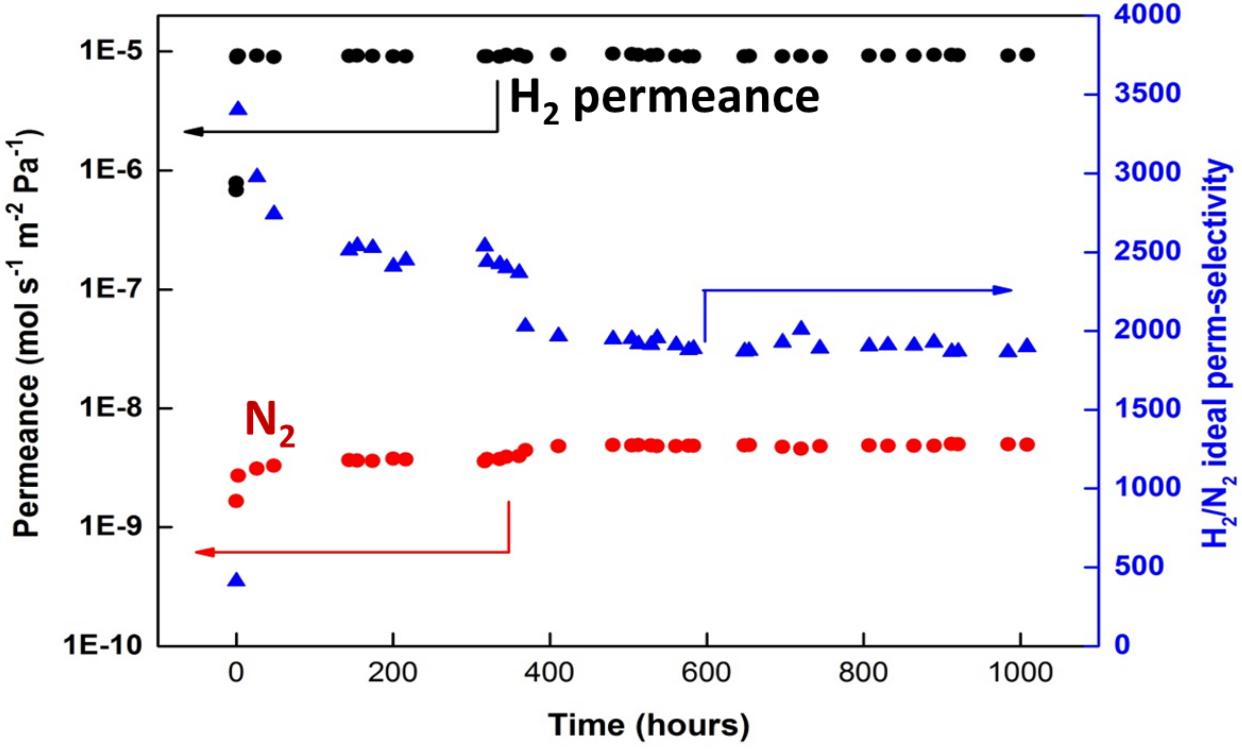
HyGrid

Membrane development: Ceramic supported Pd-based membrane

Previous project (FluidCELL)



1.3 μm PdAg at 400 °C, 1 barg

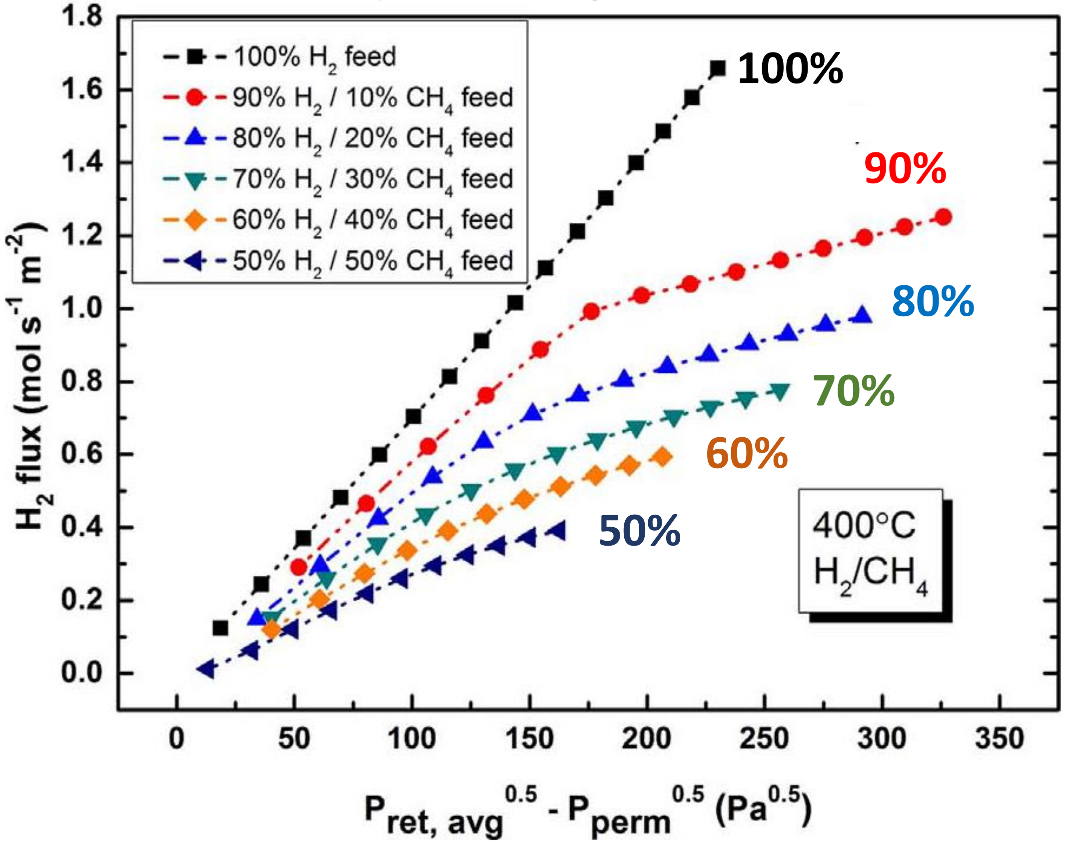


J. Melendez et al. J. Membr. Sci 528 (2017) 12-23

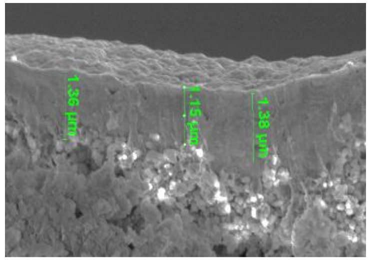
Membrane development:
Ceramic supported Pd-based membrane

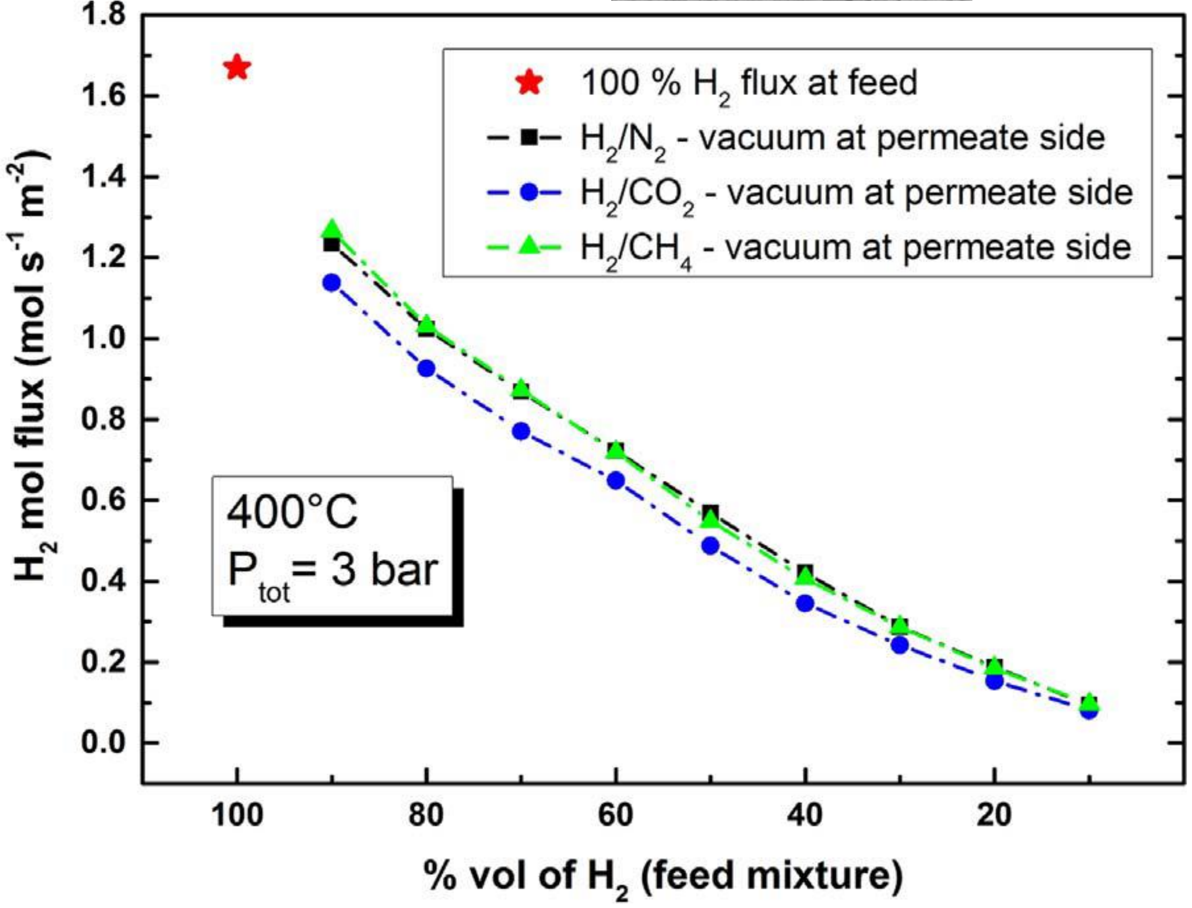
Previous project (FluidCELL)

0.8 µm PdAg



1.3 µm PdAg





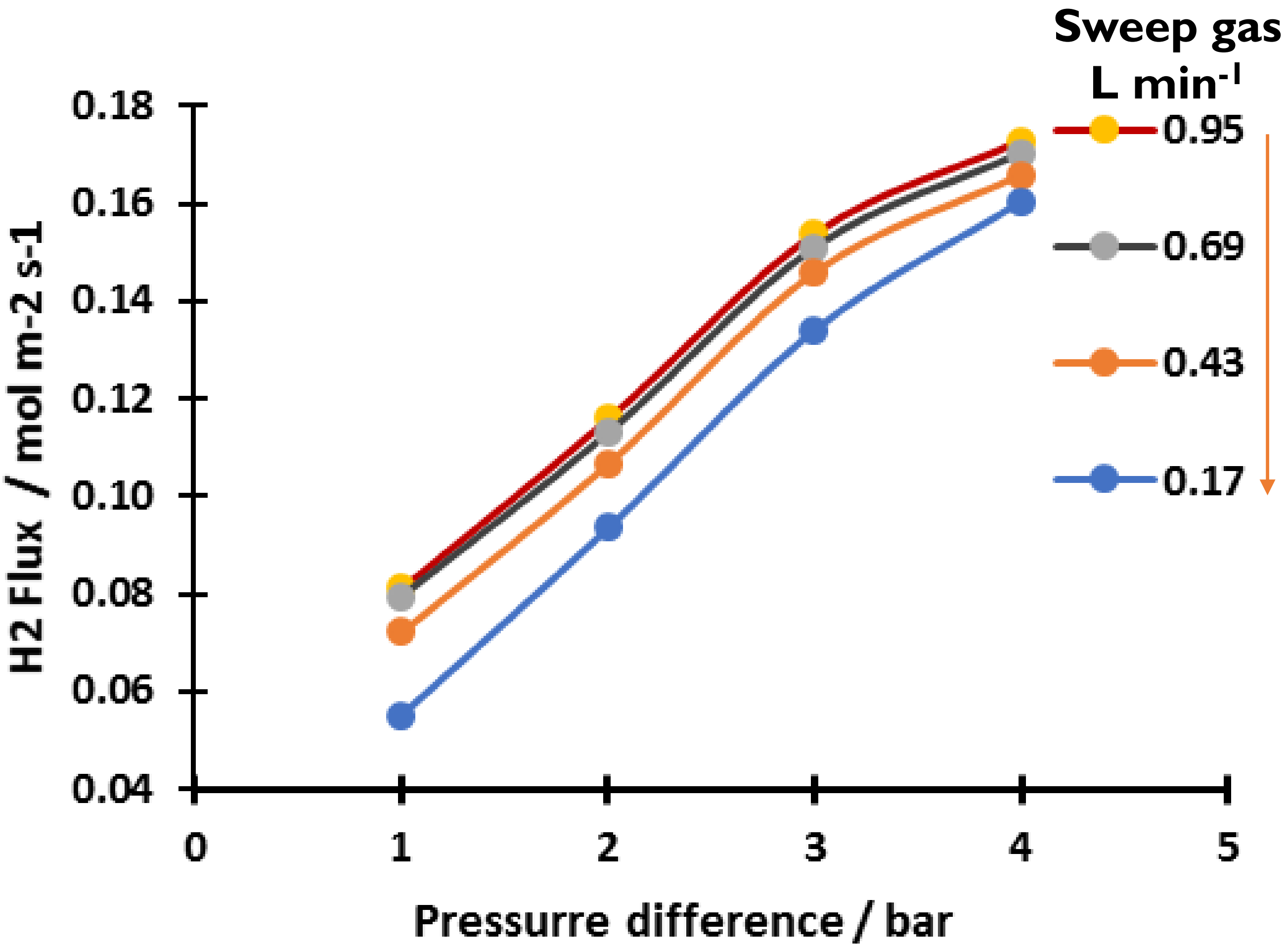
J. Melendez… J. Membr. Sci 528 (2017) 12-23

Membrane development:
Ceramic supported Pd-based membrane

Effect of the sweep gas flow in the H_2 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-like



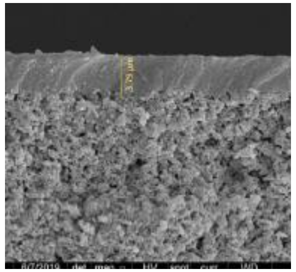
M Nordio et. Al International Journal of Hydrogen Energy 44 (2019) 4228

Membrane development:
CMSMs vs Ceramic supported Pd-based membranes

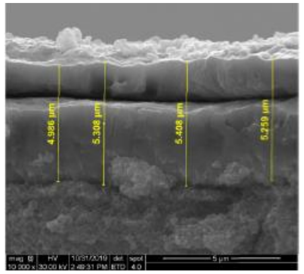
Single gas permeation

	Thickness µm	H2 permeance Mol m^{-2} s^{-1} Pa^{-1} X 10^{-7}	H_2/CH_4 Ideal selectivity
Pd- Ag membranes 400 °C			
Pd1	4-5	11.8	24300
Pd2 DS	4-5	13.5	**65200**
Pd3	**2-3**	43.6	4280
Carbon molecular sieves membrane 20 °C			
CM2	4.2	0.52	**1020**

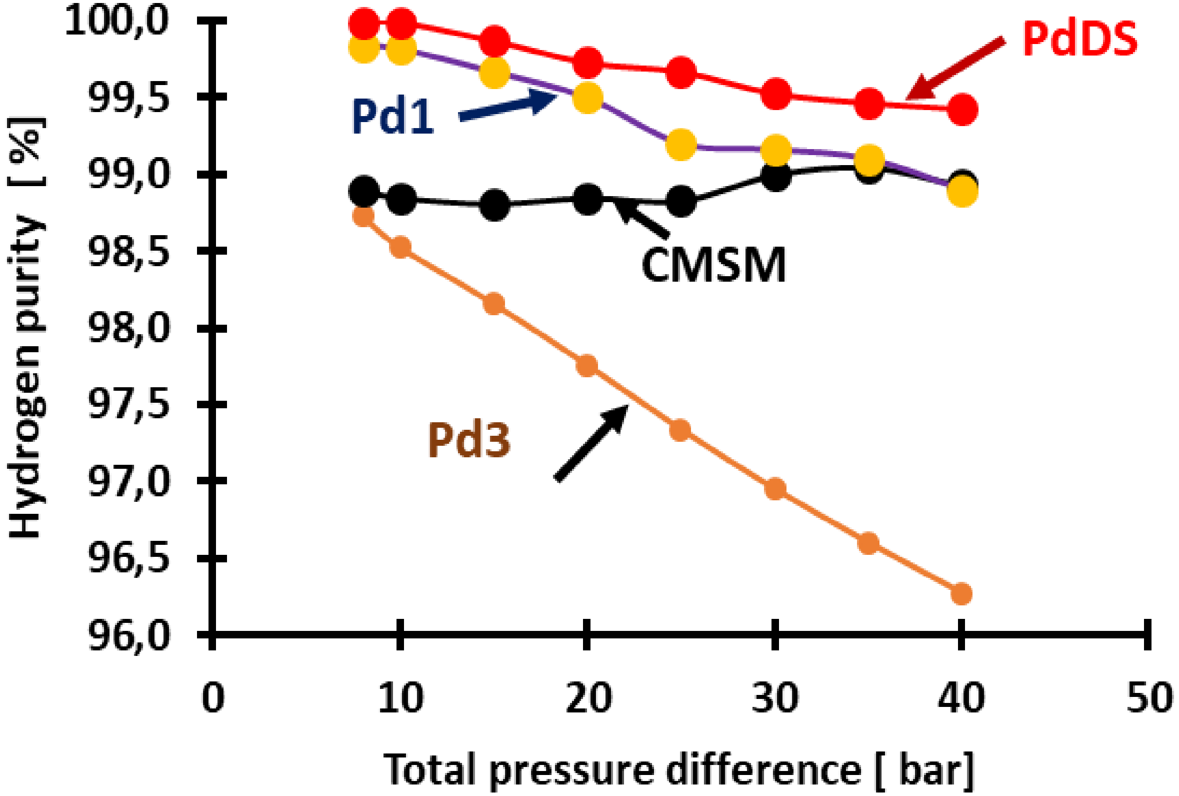
Pd 1 and 3



Pd 2 DS



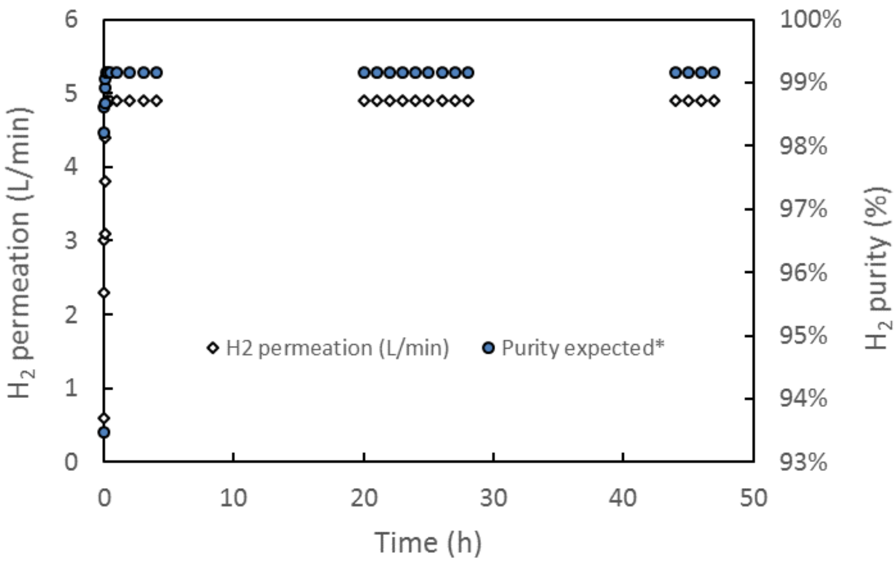
H_2 Purity 10 % H_2 90% CH_4



Membrane development:
Membranes for the membrane module prototype

- 66 Pd-Ag supported membranes
- Electroless plating
- Finger-like or open-end alumina supports
- Average length: ~43.5 cm long
- Membrane area: ~1,26 m^2

Membrane development:
Membrane module prototype – integration and FAT

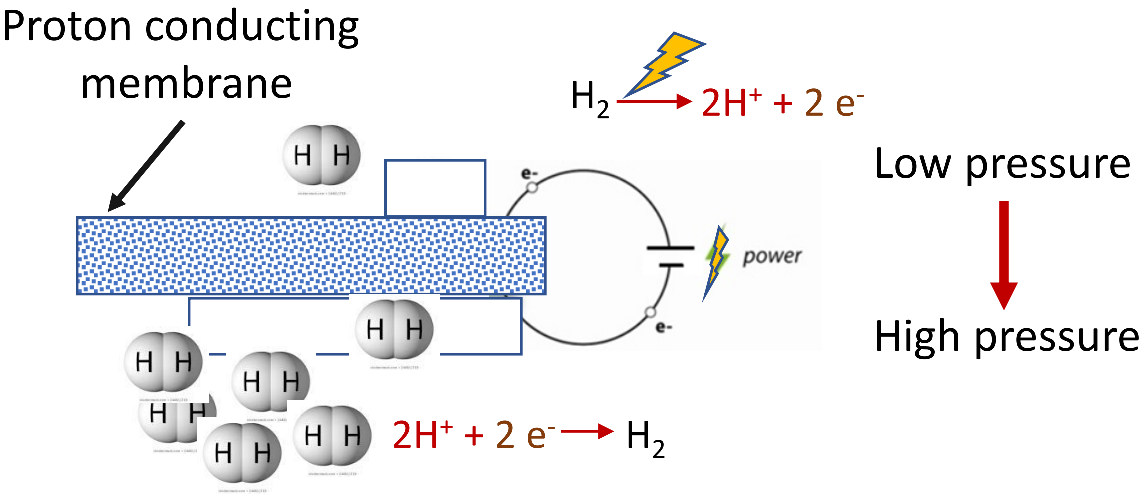


Electrochemical hydrogen separation development: Objectives

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.

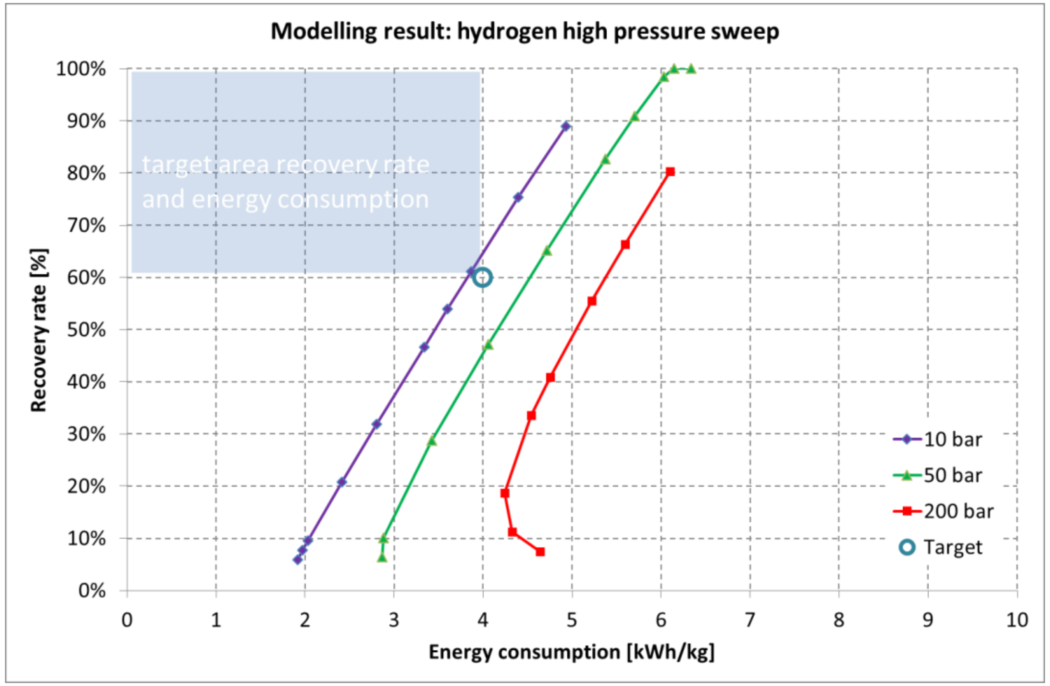
Electrochemical hydrogen separation development: Concept



Electrochemical hydrogen separation development: Modelling

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



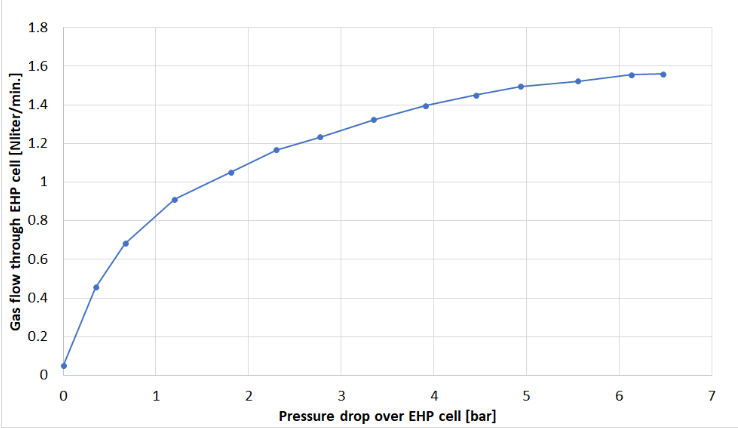
- Conclusion: Meeting the KPIs for EHP is possible with the right number of cells, operating temperature, membrane and pressure for hydrogen concentration in the feed gas between 2 and 10%

Electrochemical hydrogen separation development: 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



Electrochemical hydrogen separation development: Prototype

- dedicated EHP system has been engineered, built, and tested successfully in the complete HyGrid system
- capable of processing 85 Nm^3/h of a gas mixture containing H_2
- The system contains two full-size stacks of 144 cells each
- The system was capable of extracting 65 mol H_2/h or 3.1 kg H_2/day from the gas mixture at less than 4 kWh/kg H_2, which is the energy demand target of the EHP stacks.
- Operation of up to 199 mol H_2/h or 9.6 kg H_2/day has been tested with an energy demand close to 4 kWh/kg H_2 where 53% of the hydrogen in the feed gas was recovered by the EHP sub-system alone.

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.

Temperature Swing Adsorption development: TSA strategy and sysing

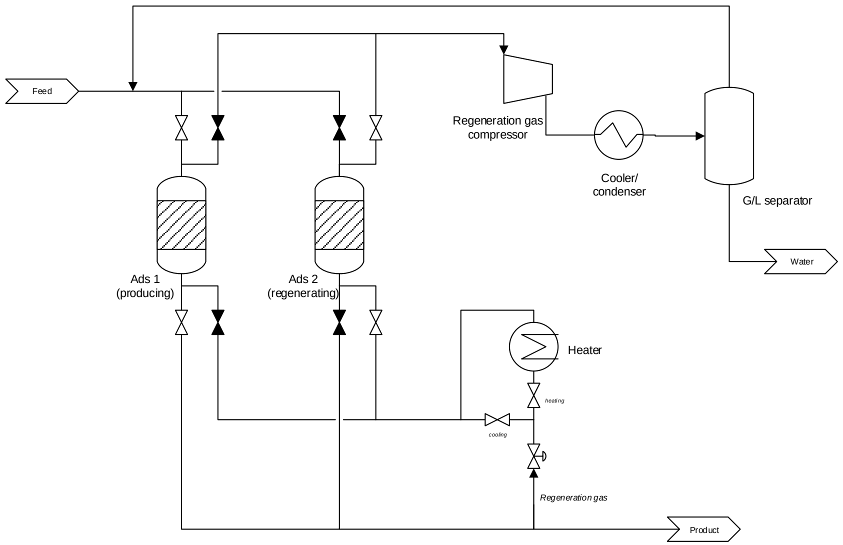
Sorbent materials tested:

- 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

Temperature Swing Adsorption development: Prototype

- Prototype TSA:
  - Process flow diagram defined
  - Operational safety assessed
  - Control strategy implemented
  - Prototype assembly ready



PFD prototype TSA

Prototype TSA assembly

Lab-scale testing: Objective

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

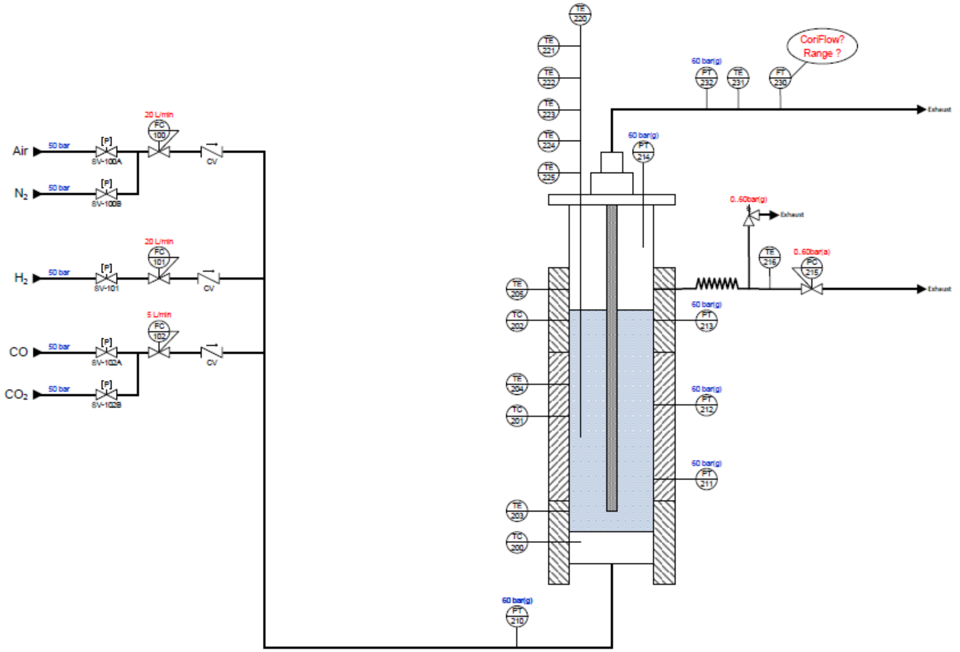
- Investigate the recovery of the membrane system at different pressures and different concentrations of hydrogen.
- Sorbents for the TSA selected will be further studied in TGA experiments to evaluate the cyclic sorbent capacity and adsorption isotherms.
- Evaluation of different configurations to identify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

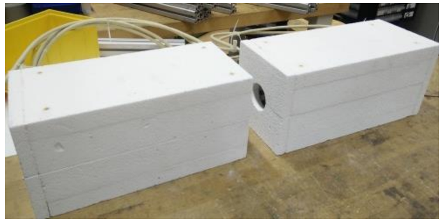
Lab-scale testing: Objective

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

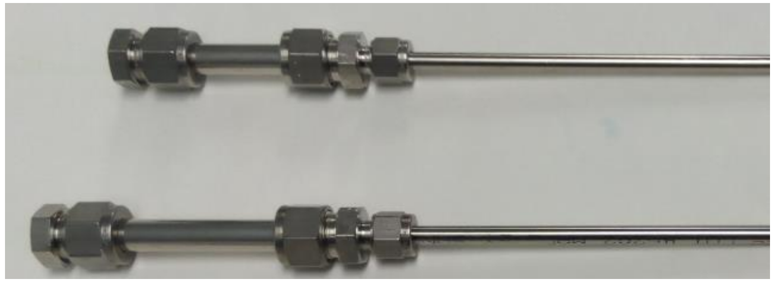


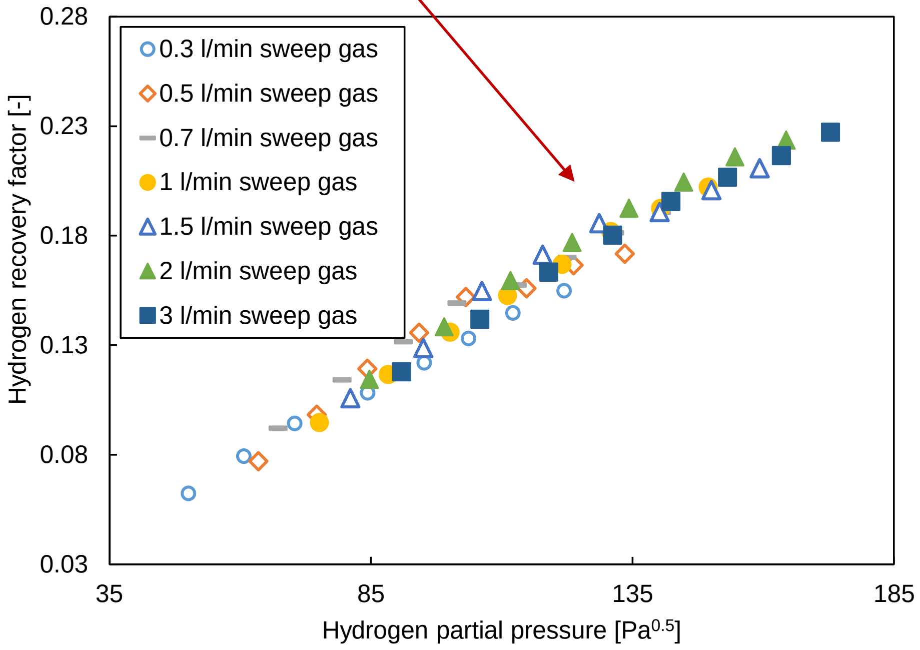


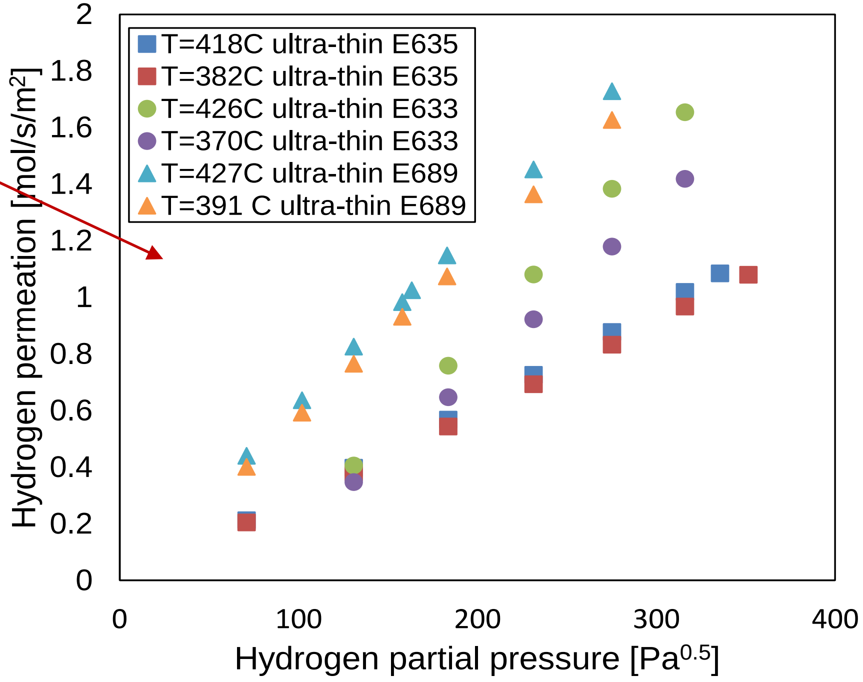
Lab-scale testing:
Testing of membranes and sorbents

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

- Temperature and pressure
- Type and amount of sweep gas

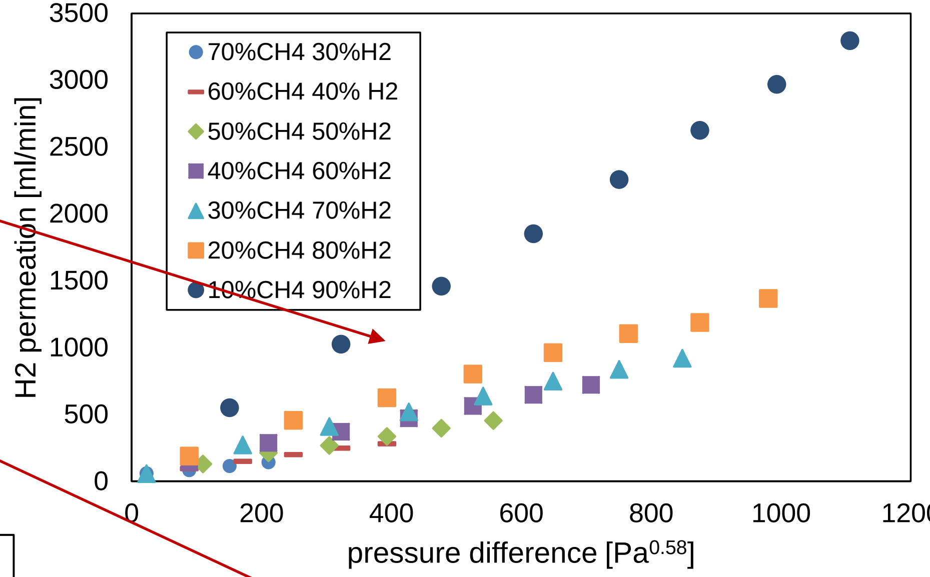


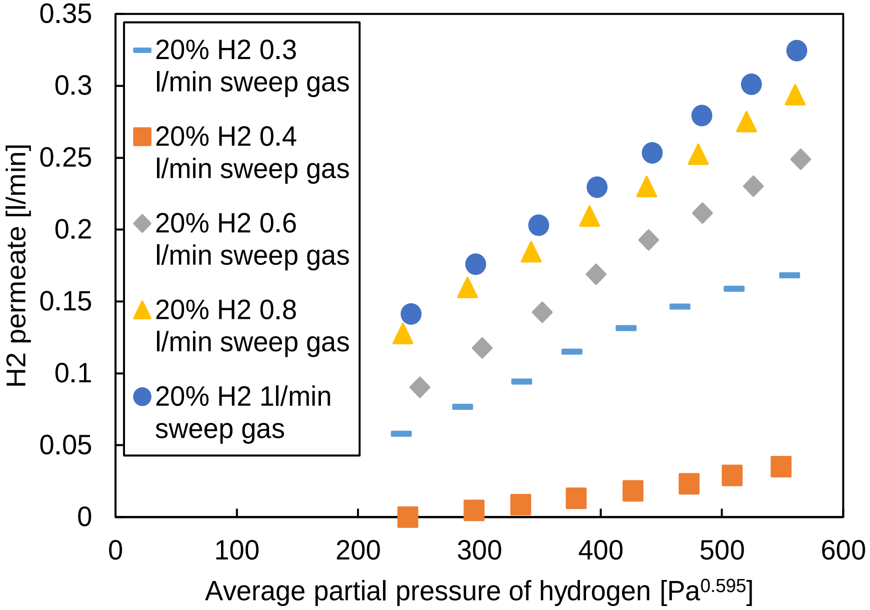


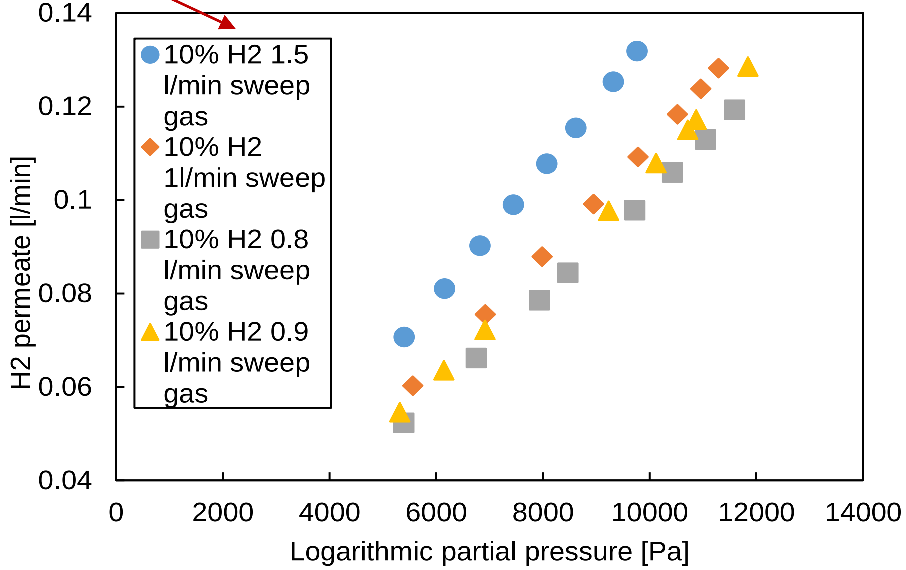


Lab-scale testing:
Testing of membranes and sorbents

- Changing H2 concentration
- Changing H2 concentration with sweep gas

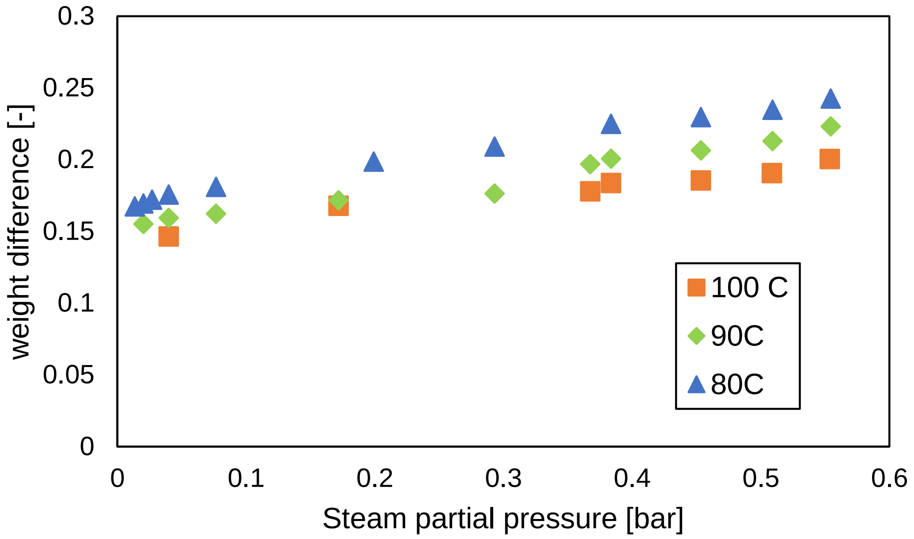


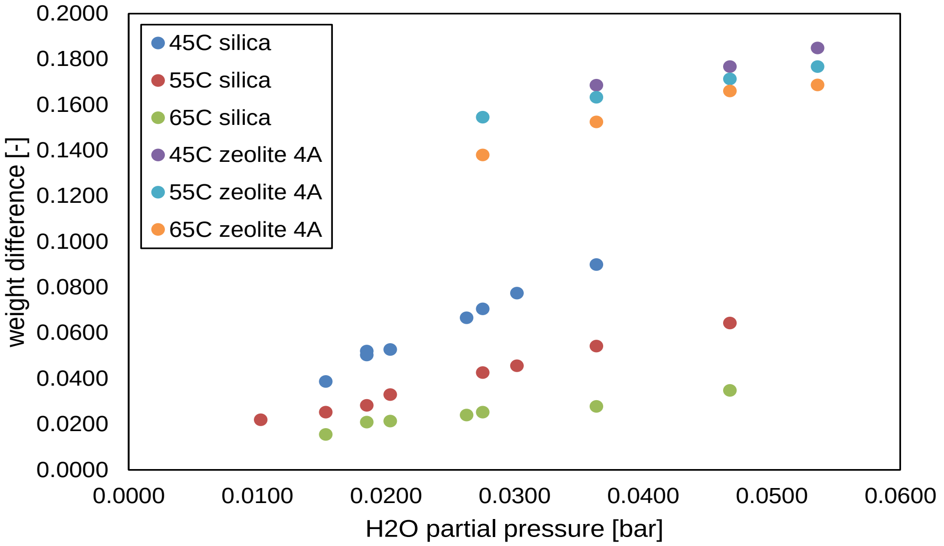




Lab-scale testing: Testing of membranes and sorbents

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.

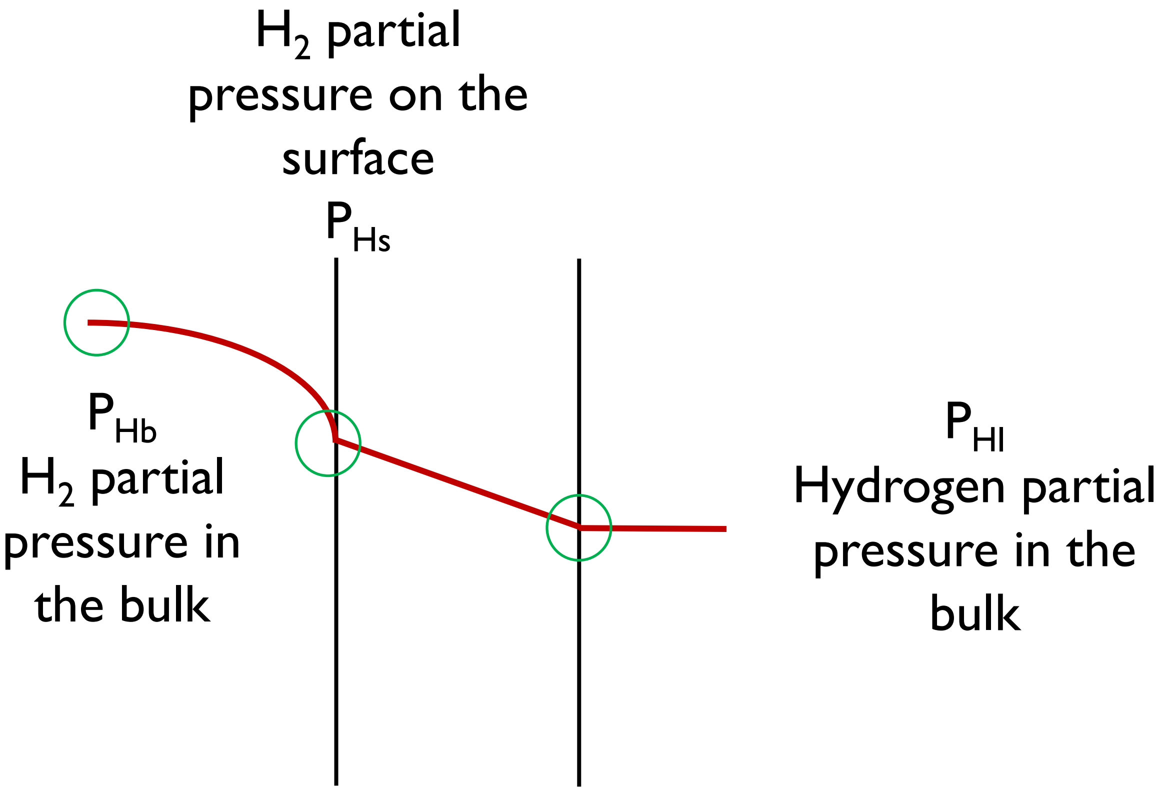
System modelling and simulation: Objectives

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

System modelling and simulation: 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:

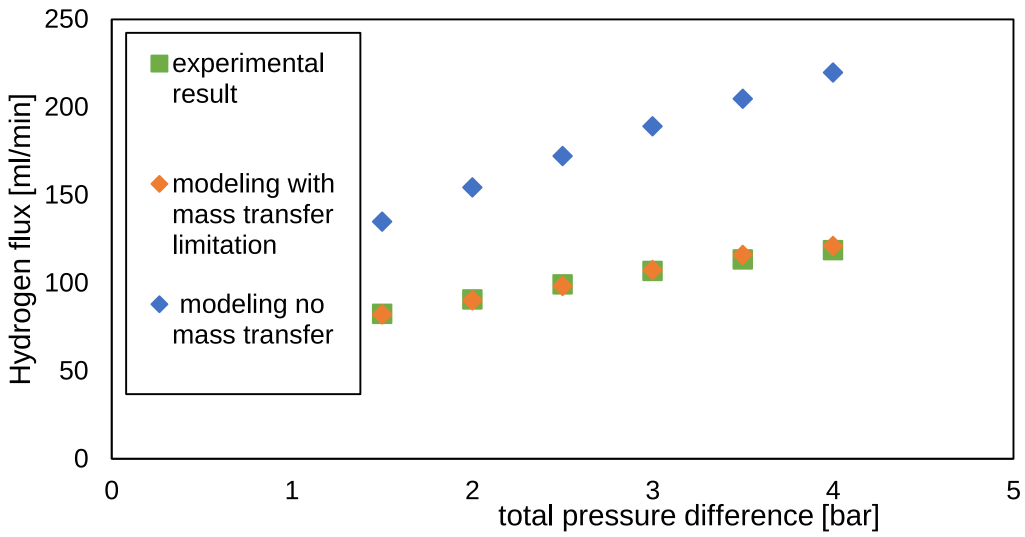
- Retentate side
- Porous support
- Permeate side

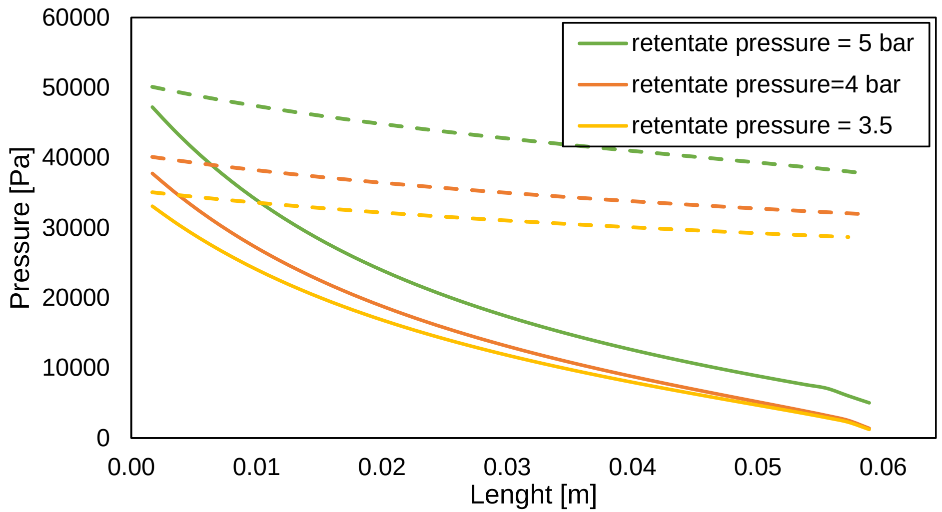
System modelling and simulation: Membrane modelling

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

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

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



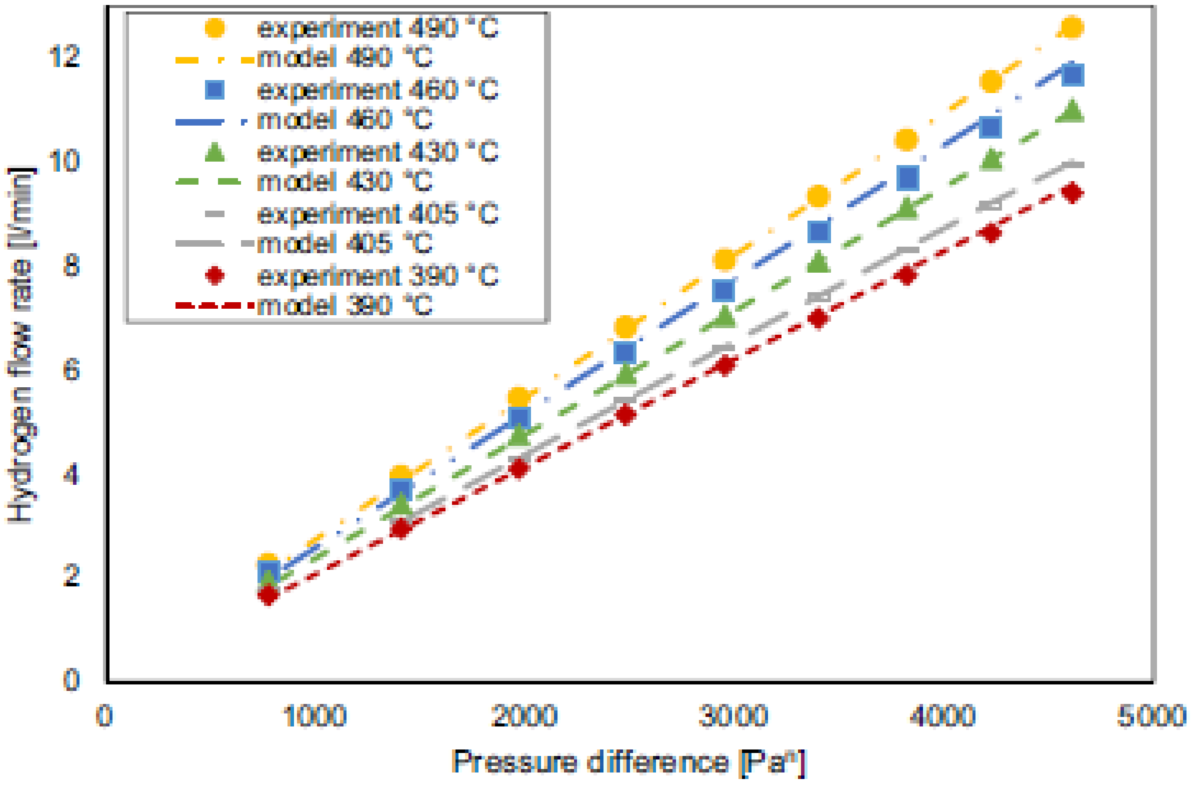


- - - - Retentate partial pressure

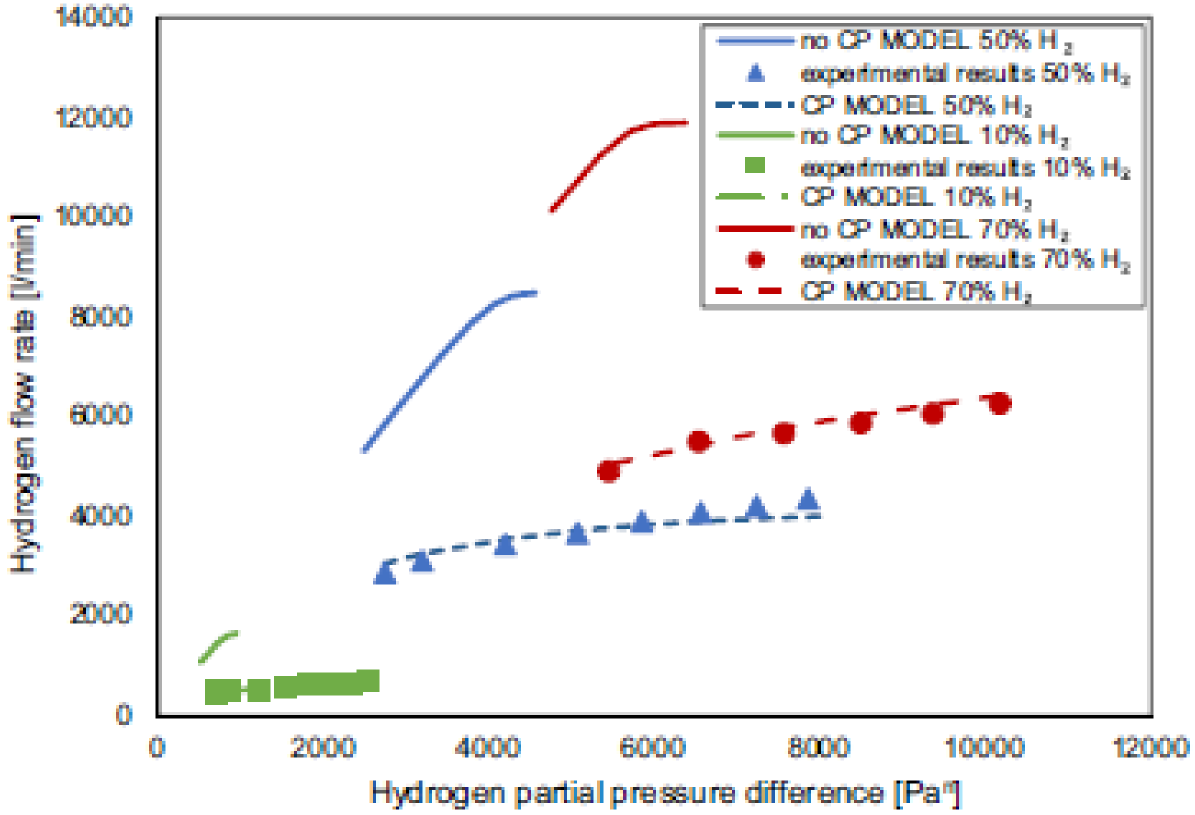
—— Surface partial pressure

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

System modelling and simulation: Membrane modelling



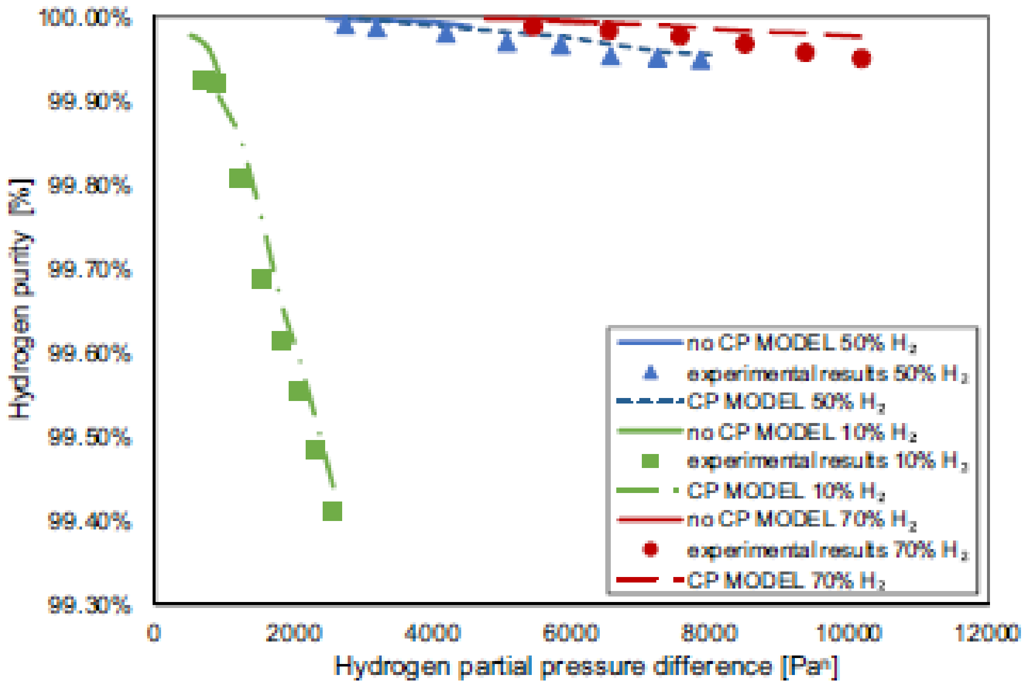
Experimental and modelled results in pure gas tests at different operating temperature with Pd2DS membrane.



Hydrogen flux from experimental and modelled results in mixture tests at different hydrogen inlet content; continuous line to described ideal case and dotted line includes mass transfer limitation at a working temperature of 400 °C.

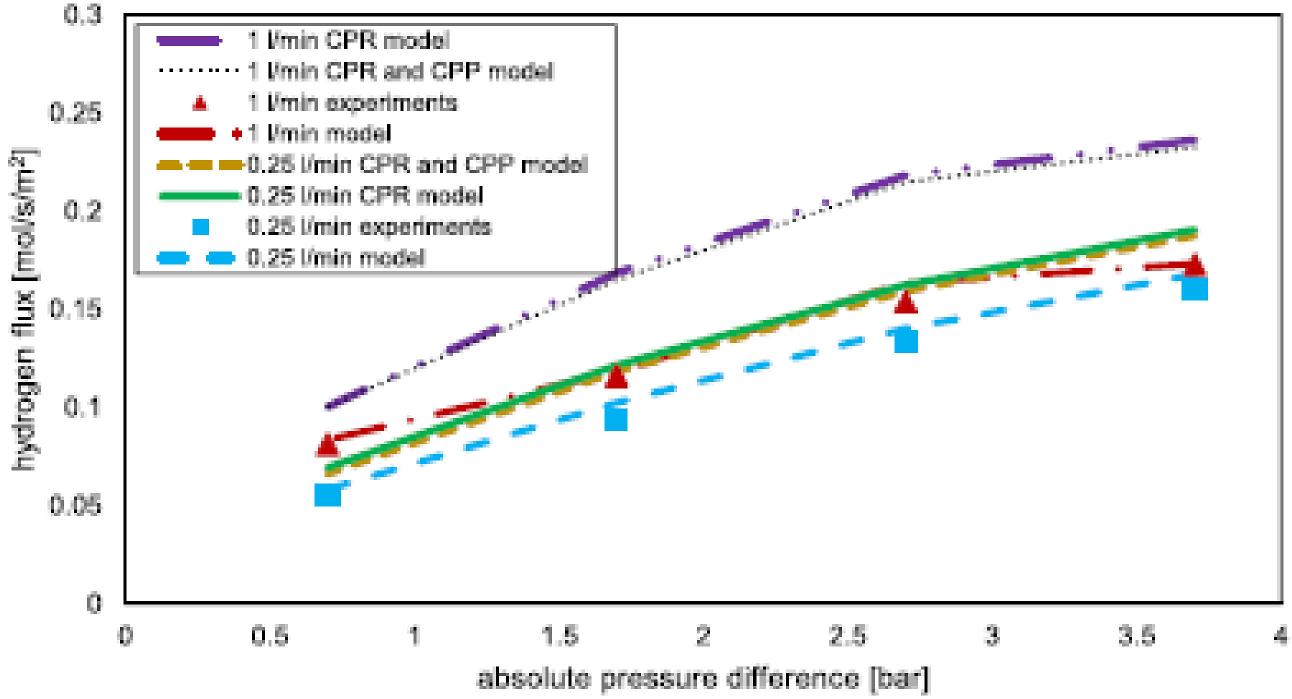
M. Nordio et al. Int J Hydrogen Energy 45 (2020) 28876-28892

System modelling and simulation: Membrane modelling



Hydrogen purity from experimental and modelled results in mixture tests at different hydrogen inlet content; continuous line to described ideal case and dotted line includes mas

M. Nordio et al. Int J Hydrogen Energy 45 (2020) 28876-28892

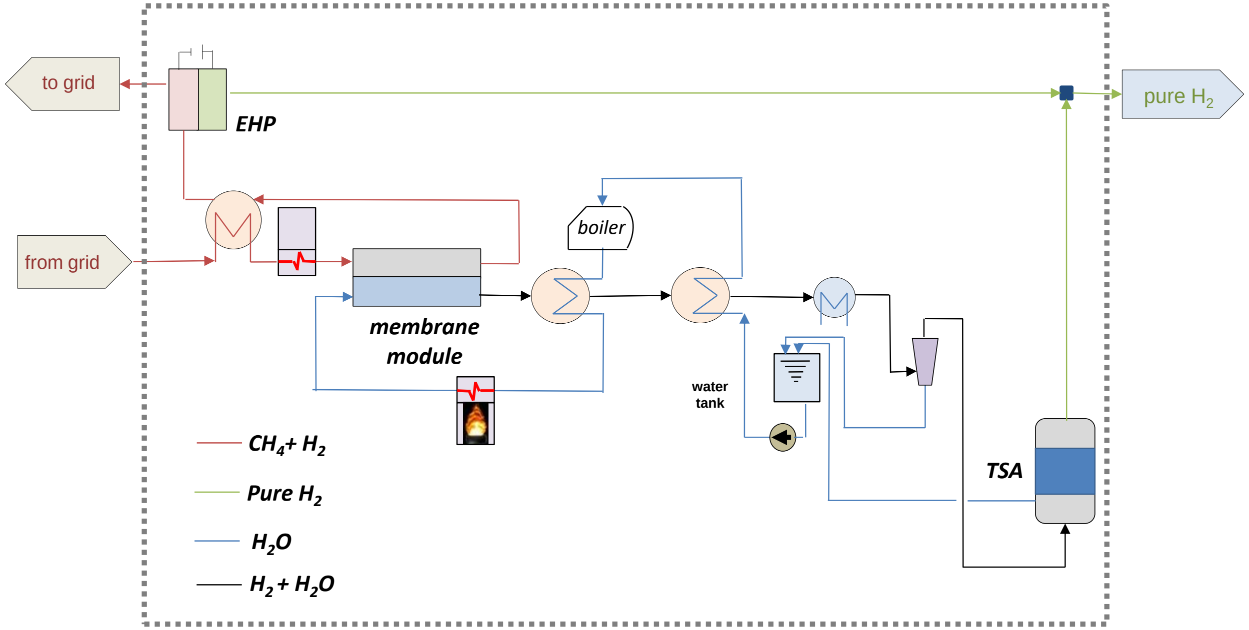


Comparison between experimental and modeling results for a mixture of $CH_{4/}H_2$ with nitrogen as sweep gas. The sweep gas is 0.25 l/min.

M. Nordio et al. Int J Hydrogen Energy 44 (2019) 4228-4239

System modelling and simulation: Simulation of then HyGrid system

- The validated models have been used for carrying out optimization of different plant configurations:
  - several membranes modules are used in series or parallel,
  - with or without electrochemical separator or TSA,
  - and different other combinations.
- All these configurations have been compared in terms of efficiencies and costs and the results used for a optimizing the prototype for the next scale.
- These optimizations have helped identifying the costs of hydrogen separation for different separation scales.



System modelling and simulation: Simulation of then HyGrid system

Two different configuration has been modelled to optmize the targets required

First case: two membrane modules

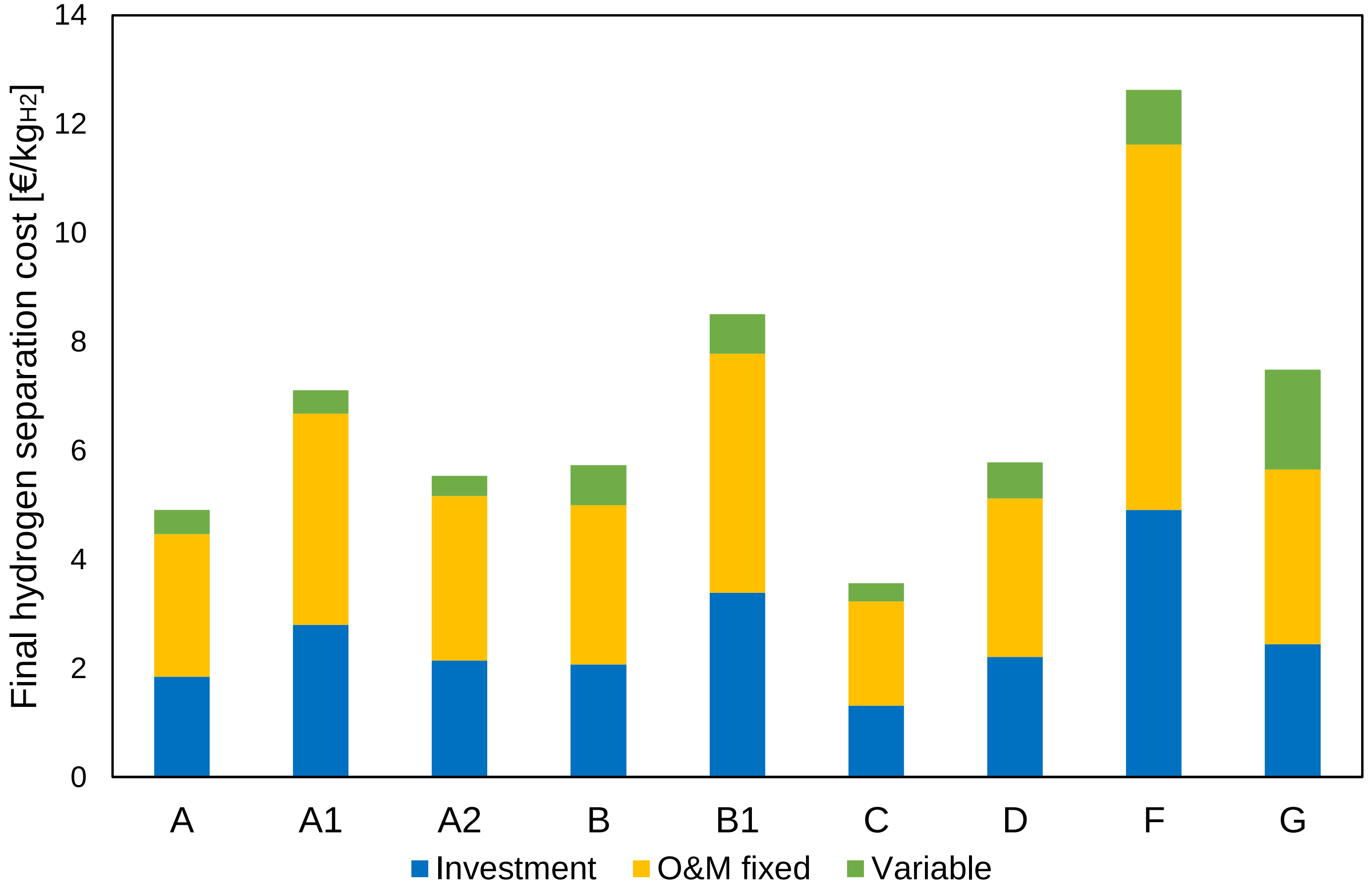
Total electric consumption	3.9	kWh/kgH_2	<	5	kWh/kgH_2	✓
Total hydrogen separated	27.26	kgH_2/day	>	25	kgH_2/day	✓
purity	99.98	%	>	99.97	%	✓
HRF	90	%	>	85	%	✓
Total membrane area	3.33	m^2				

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				

System modelling and simulation: Simulation of then HyGrid system

Costs breakdown of different configurations for small scale (25 kg/day) hydrogen separation unit.



Prototype integration and validation: Design specifications HyGrid demo

- Prototype design, incl. membrane separator and EHP
  - Feed stock: 90 Nm^3 (NG + 10vol% H_2) / h
  - Operating pressure NG blend: 8 bar(g)
    - Pressure drop NG < 100 mbar(g)
  - Overall Hydrogen Recovery Factor: 65% (membrane dev. will increase this) → NG spec. current users (industrial / automotive) not yet met
  - H_2 product ambient pressure
    - Product flow approx. 12 kg H_2 / day
    - Product dew point (controlled) : < - 56 ° C (after TSA)
    - Temperature H_2 : 12 – 15 ° C
- System is self operating (controlled by PLC : 24/7 operation)
  - Operational temperature membrane module: 400 ° C
  - Operational temperature EHP system: 35 ° C
  - Adsorption temperature TSA; 12 – 15 ° C; desorption temperature < 200 ° C
- Demonstration system CE certified

Prototype integration and validation: Development of demo ready

- Demo separation module:
  - Mass and heat balance study
  - P&ID prototype separation and drying module
  - Assembly prototype separation module
  - Integration with TSA
- Next steps: testing HyGrid demonstration unit

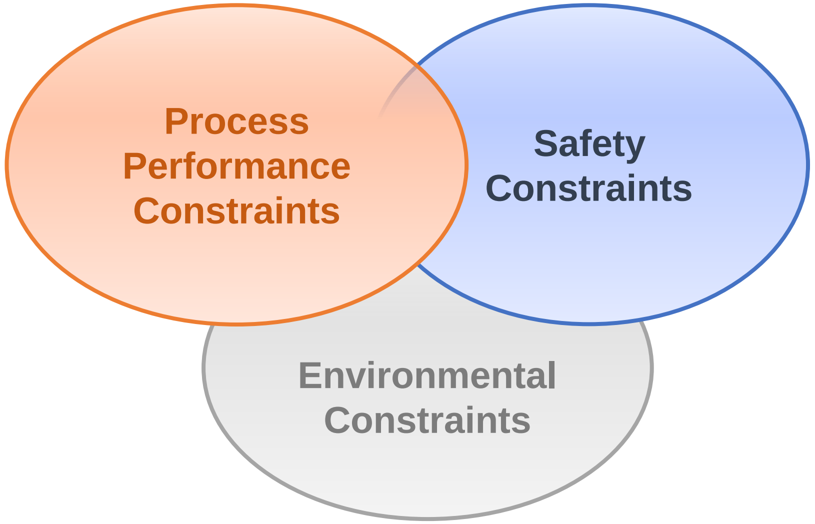
Prototype integration and validation: Main lessons learned from testing

- HyGrid demonstration testing:
  - HyGrid demonstration plant operated successfully
  - Prototype capable of extracting 12-13 kg H_2 /day from NG/H_2 mix
  - Contaminants in natural gas appear to influence separation of H_2 by EHP and membrane separator
  - Loss of eff. EHP when processing NG/H_2 mix partially reversible
  - Product purity and stability of separation systems in NG need to be increased for commercialisation
  - Product dewpoint by TSA is met, and;
  - Commercial system will be able to remove H_2 from NG at $<$ 5 kWh /kg H_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

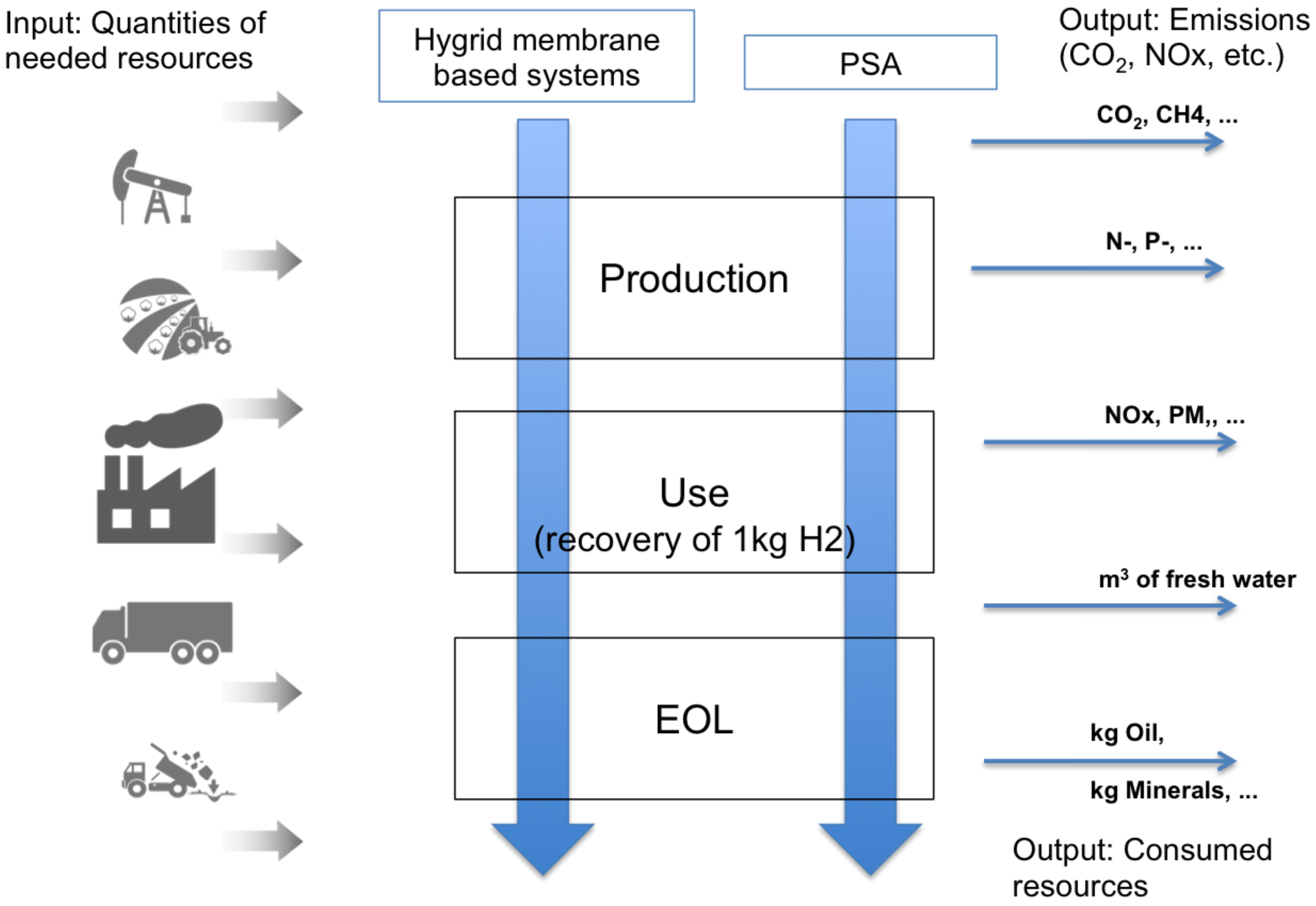


Environmental LCA and economic assessment: Goal and scope definition

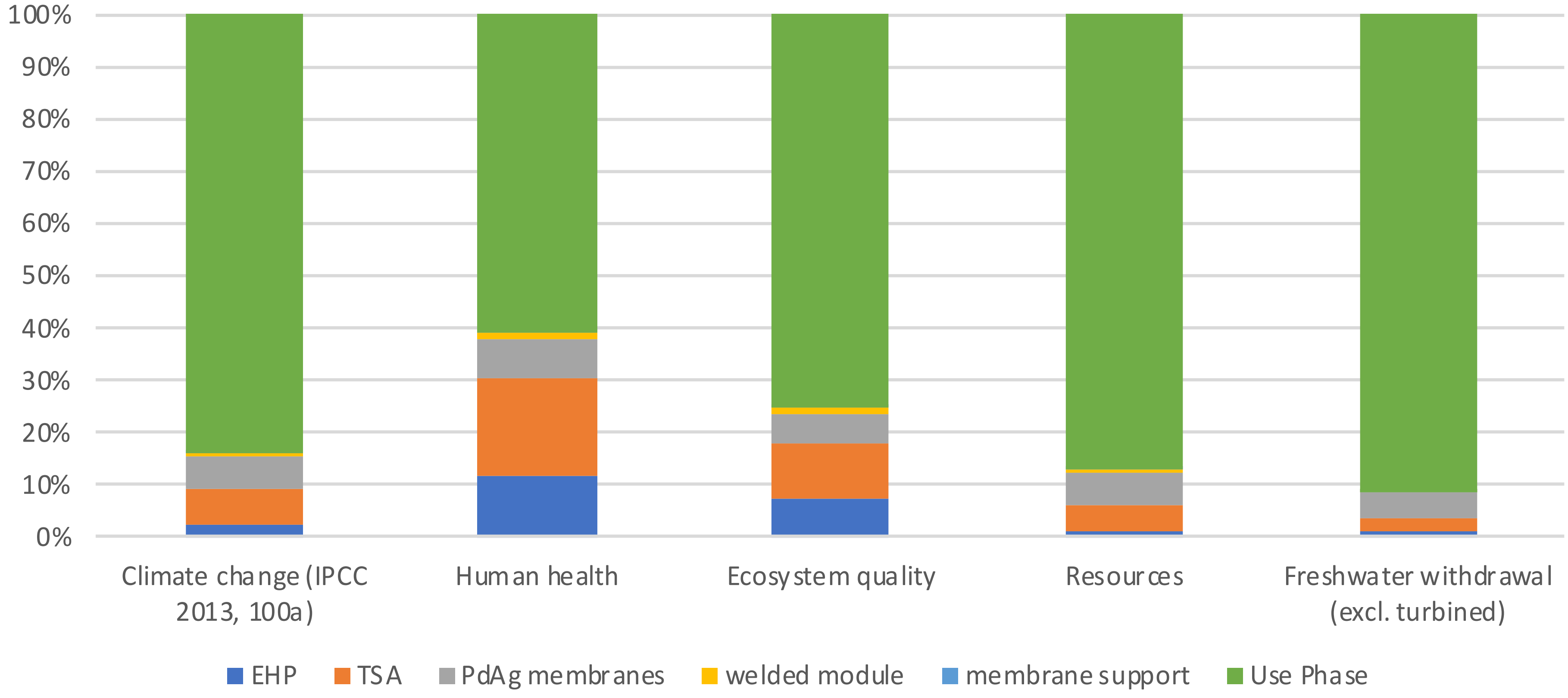
- Overall, the main questions analysed during the goal and scope development include:
  - What is the aim of the study?
  - What is the function of the analysed system?
  - What systems exactly are going to be analysed?
  - What reference system/ technology will we compare our system against?
  - What are the system boundaries of the analysed product?
  - What environmental indicators will be calculated?
  - What is the data availability for the study?
- 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)*

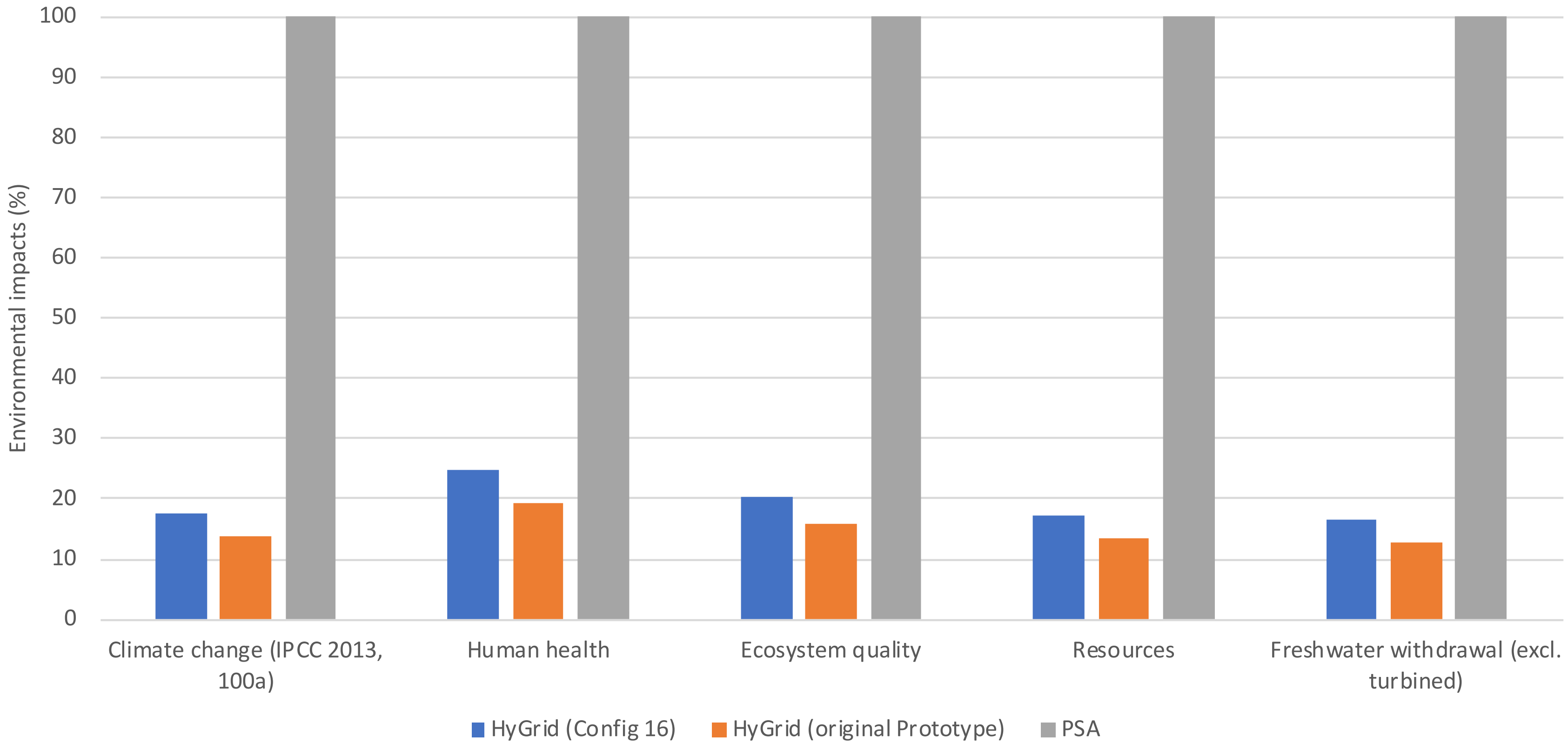
Environmental LCA and economic assessment: System boundaries



Environmental LCA and economic assessment: Preliminary results



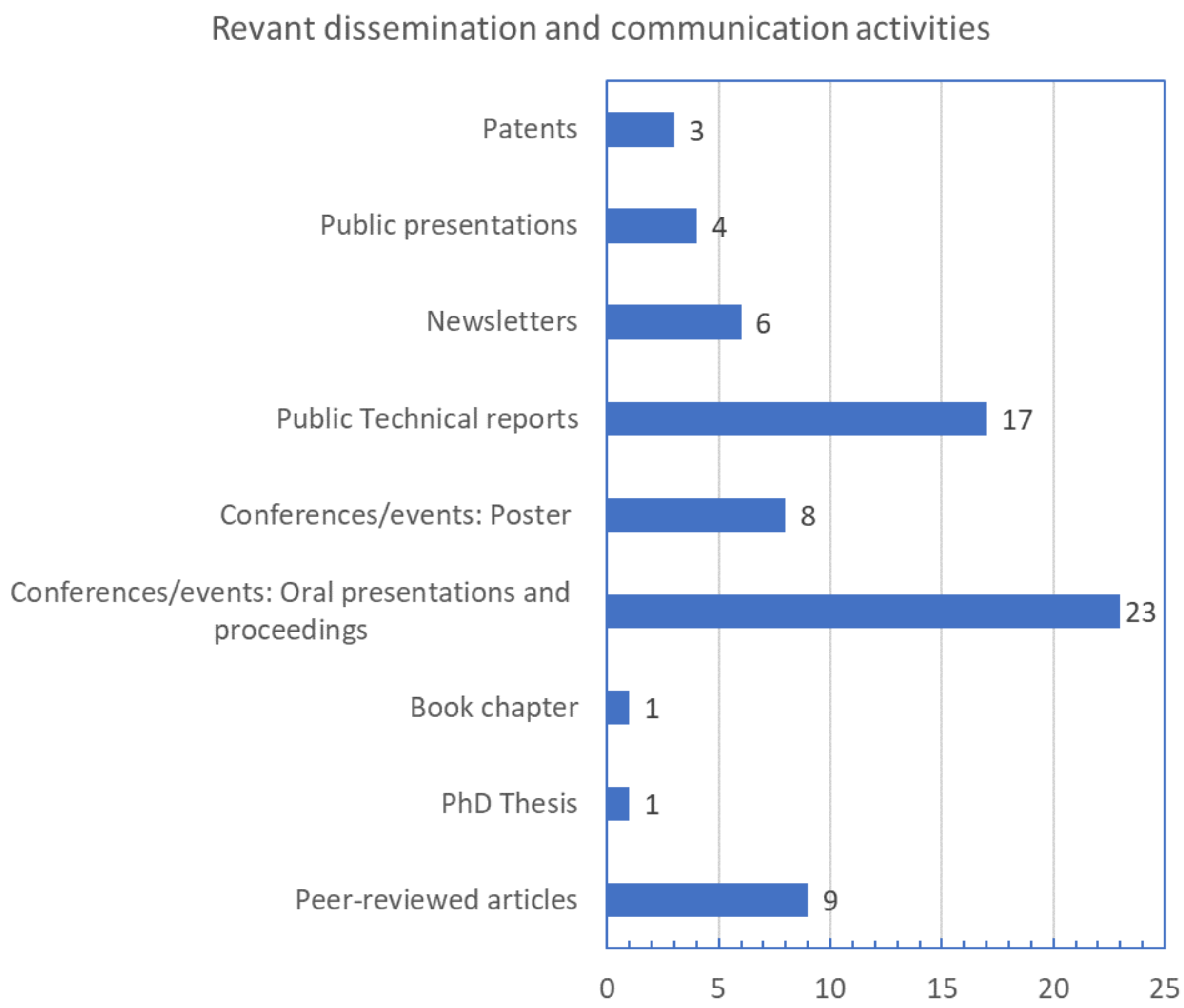
Environmental LCA and economic assessment: Preliminary comparison with the results



Environmental LCA and economic assessment: Business case

- Strong European increase in hydrogen use for
  - Industry, FCEV and Hydrogen Refuelling Stations from 2025 expected
- After 2040 hydrogen dedicated network available:
  - (H_2 backbone) connecting to Middle East and North Africa
- H_2 trucking economically, safety and environmentally not friendly
- H_2 in NG poses difficulties to local end-users
  - HyGrid market evolves at NG and H_2 fuelling stations
  - Possible retail price of H_2 estimated
  - Costs of removing H_2 from NG for NG fuelling negligible
  - After 2040 market will still exist in remote areas not connected to H_2 net
- A risk matrix is also presented; high priority needs to be given to adapting (inter)national norms regarding the presence of hydrogen in natural gas
  - Local incentives in EU for H_2 transportation in NG pipeline exist
  - (Inter)national policymakers need to adapt soon for market creation
- Strategies for future commercialisation and deployment targets have been addressed

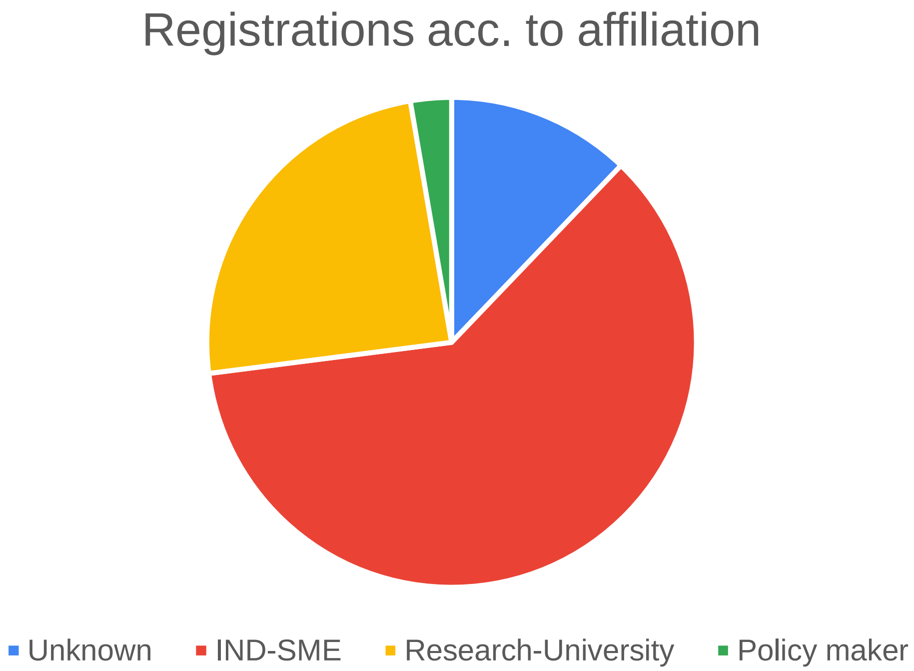
Dissemination and exploitation



- Public web site: https://www.hygrid-h2.eu/
- 3 patents:
  - WO/2020/122709: Method for low hydrogen content separation from a natural gas mixture.
  - WO2020106152A1: Cell plate assembly for a solid-state compressor, solid-state compressor and method for operating a solid-state compressor.
  - WO 2021/116319 A1: Carbon molecular sieve membrane and its use in separation processes.
- One spin-off company from TECNALIA and TUE on Pd-based membranes and membrane reactors created in 2019: Hydrogen Onsite, S.L. (H2SITE, (https://www.h2site.eu/en/).

Dissemination and exploitation: Final workshop HyGrid

Flexible Hybrid Separation System for H_2 Recovery from Natural-Gas Grids



- Online workshop June 24th , 2021
  - Over 70 registrations
  - 38 Attendees
  - 7 Presentations by project partners and invited speaker

Flexible Hybrid separation system for H_2 recovery from NG Grids

HyGrid

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

Thank you for your attention

Contact: Fausto Gallucci (F.Gallucci@tue.nl)

The project leading to this application 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, Hydrogen Europe and Hydrogen Europe research.