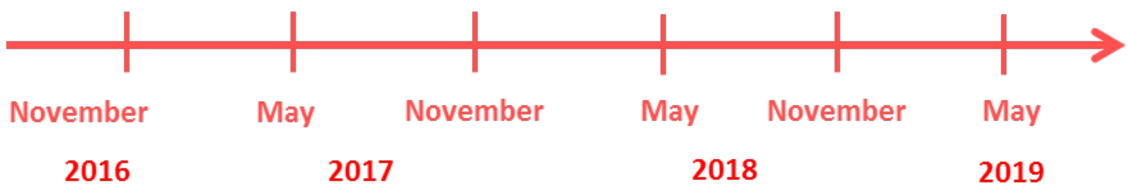
Flexible Hybrid separation system for H2 recovery from NG Grids

Newsletter – Issue 2 – August 2017



Editorial

Welcome to this second HyGrid newsletter. HyGrid is a three year project targeting the development of a high performance, cost effective separation technology for the direct separation of pure hydrogen from natural gas grids. Three different technologies - membrane separation, electrochemical separation and temperature swing adsorption - will be combined in a new separation system to decrease the total cost of hydrogen recovery. The new separation & purification system will increase the value of hydrogen blended into the natural gas grid.

The present newsletter is the second release and it is presenting the progress on the project and highlighting information related to the R&D fields addressed. Hope you will find the info in this newsletter interesting. On our website www.hygrid-h2.eu you will find public presentations, all the public deliverables of the project and many other interesting news. Stay tuned!

In this Issue:

What is HyGrid?

The concept

One of the main problems for the implementation of the hydrogen based economy is the transportation from production centres to the end user both industries and population. To solve this problem, besides the in-situ production of hydrogen, the use of the existing Natural Gas network has been proposed for storing and distributing hydrogen. However, cost effective separation technologies for direct separation of hydrogen from the natural network should be developed for separating and purifying the hydrogen to match the end user requirements.

The HyGrid project proposes an integral solution for developing of an advanced high performance, cost effective separation technology for direct separation of hydrogen from natural gas networks. By using a novel membrane based hybrid technology combining three technologies integrated in a way that enhances the strengths of each of them (Figure 1): membrane separation technology is employed for removing H_2 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, pure hydrogen production (ISO 14687) will be obtained.

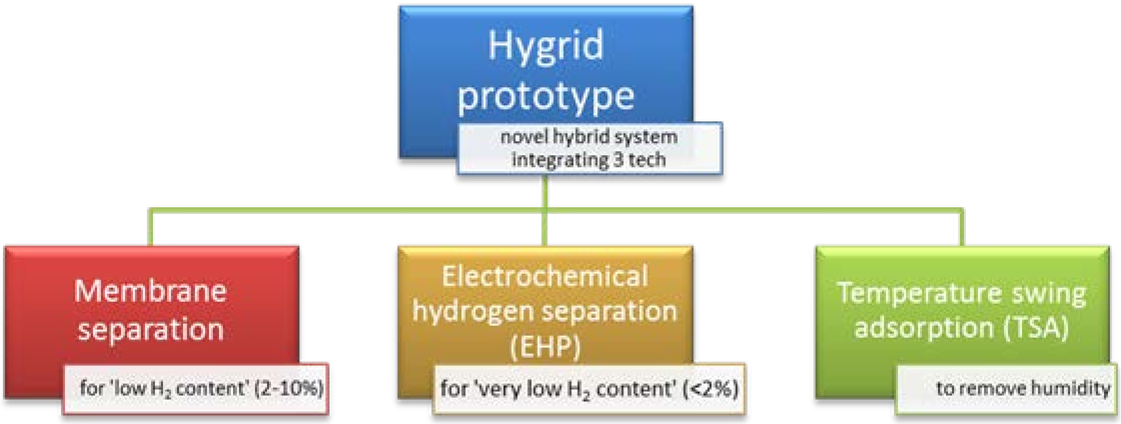


Figure 1. HyGrid concept

The new separation & purification system will 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. In addition, it will reduce cost, and therefore increase the use of hydrogen from very dilute hydrogen streams in energy and transport applications. On the other side, 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.

Project objectives

The HyGrid project will develop, build and demonstrate at industrial relevant condition a novel advanced high performance, cost effective separation technology for the direct separation of pure hydrogen from natural gas grids. In particular, by combining the three different technologies (membrane separation, electrochemical separation and temperature swing adsorption) the total cost of hydrogen recovery will be decreased. The project targets a pure hydrogen separation system with power and cost of < 5 kWh/kg$_{H2}$ and < 1.5 €/kg$_{H2}$. The pilot will be designed for the separation and purification of >25 kg/day of hydrogen (ISO 14687).

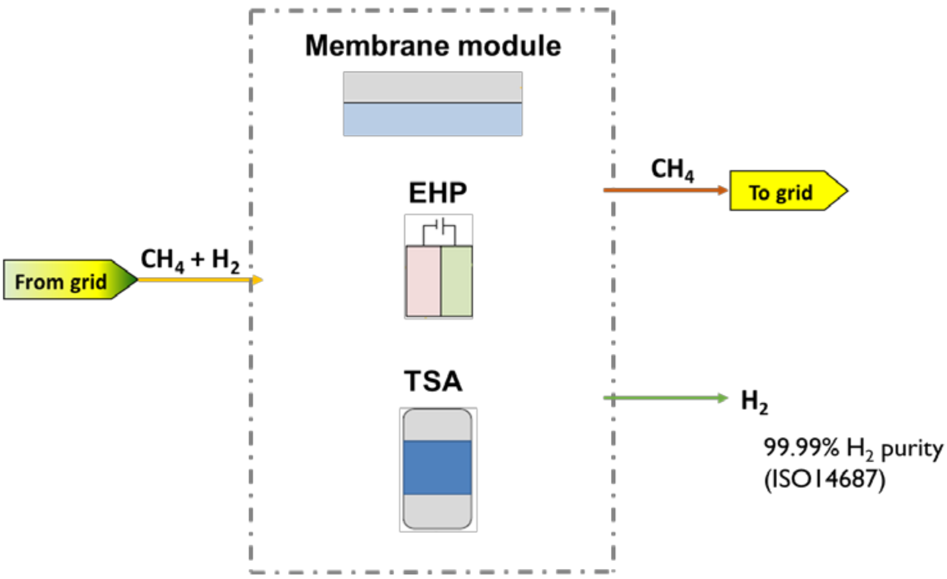


Figure 2. System schematic layout

The main objectives of the HyGrid project are:

- Design, develop, demonstrate and optimise an advanced hydrogen separation system for the production of at least 25 kg/day of hydrogen as per ISO 14687 from low (2-10%) and very low (<2%) H_2 blends in natural gas grids

- Development of stable, high performance and long durability membranes for hydrogen recovery from low (2-10%) hydrogen content streams.

- Development of more stable sealing methods for the membranes at moderate temperatures and reductive atmospheres.

- The further development of EHP for hydrogen recovery from very low (<2%) concentration streams.

- The further development of TSA for water removal from hydrogen/water streams.
- The integration of the new membranes, TSA and EHP in novel hybrid system to achieve high recoveries with low energy penalties.
- 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 analysis through a Life Cycle Assessment of the complete chain.
- Dissemination and exploitation of the results.

Partnership

The HyGrid consortium consists of 7 European organizations from 4 countries (Netherlands, Spain, Italy and Switzerland). HyGrid gathers the complete chain of expertise reaching the critical mass necessary to achieve the objectives of the project. The consortium brings together multidisciplinary expertise of material development (electrochemical separation, sorption and membranes), chemical and process engineering, modelling (from thermodynamics to unit operation modelling to system integration), membranes modules and reactors development, LCA and industrial study, innovation management and exploitation.

Figure 3. European partnership in HyGrid

Project structure

The HyGrid project structure is subdivided in ten work packages (see the simplified scheme below) following the focus on the development of novel (longer and more stable) membranes for H_2 separation, electrochemical separation and TSA for hydrogen separation from natural gas grids. Furthermore, the project will give a robust proof of concept, validation and assessment of the novel hybrid separation technology. The synergies between the partners are also visible in the scheme. Therefore, the work structure is based on the following work packages

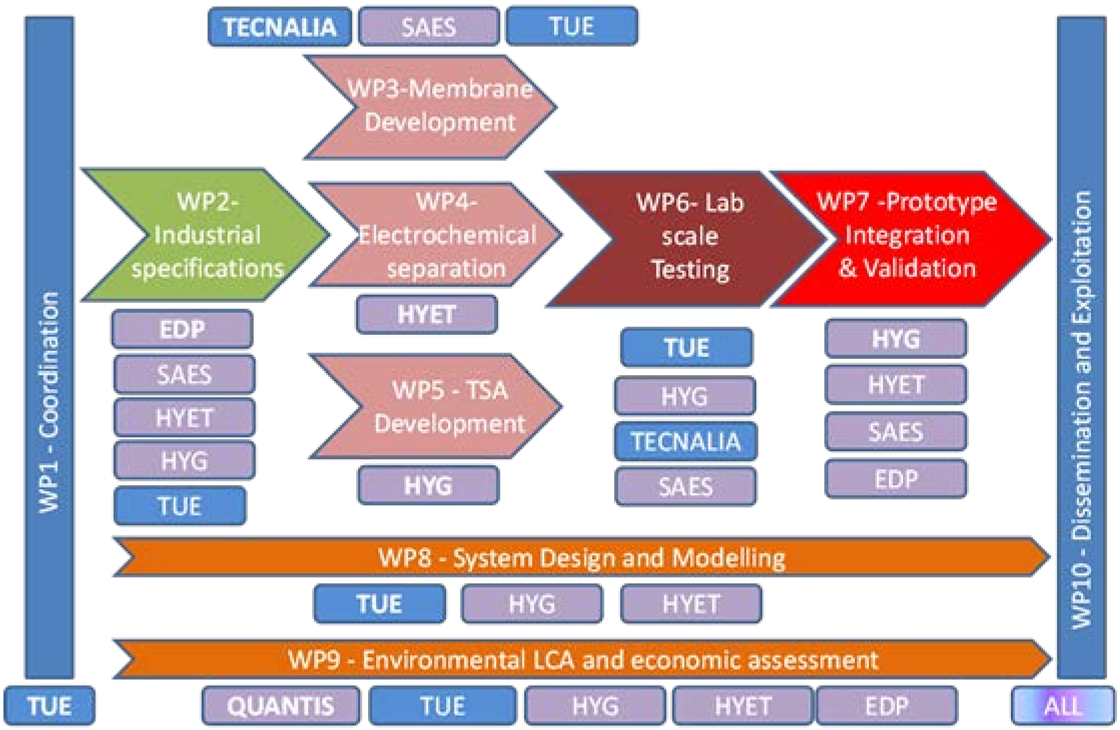


Figure 4. Work structure and synergies between partners.

Latest news from the project

The latest new on different WP activities are now reported:

Membranes development

TECNALIA is developing two types of membranes for hydrogen separation in the frame of the HyGrid project: carbon molecular sieve membranes (CMSM) and Pd-based membranes. CMSM are produced by the carbonization of thermosetting polymers coated onto porous alumina supports in non-oxidizing environment. Three types of membranes have been prepared and delivered to the partners for lab-scale testing:

- Thin Pd-Ag (3-5 µm thick) membranes supported onto porous ceramic and metallic tubes.
- Ultra-thin Pd-Ag (<3 µm thick) membranes supported onto porous ceramic tubes.
- Thin composite-carbon membranes (~3 µm thick) supported onto porous ceramic tubes.

While the problem of sealing is already solved when using metallic porous support welded to dense metallic tubes, leak-free sealing should be improved when using ceramic porous support. Two approaches are considered in the frame of the HyGrid project. On one side, SAES is developing joining techniques for having the ceramic support already welded to dense tubes (metallic dense tubes at the end side. On the other side, finger-like ceramic supports are used as support for reducing the number of sealing.

Electrochemical hydrogen separation development

The main objective of this task is the development of a hydrogen purifier (EHP) prototype for the recovery of the hydrogen from low concentration streams ($H_2 \leq 2$ %) to be integrated in the final hybrid separation/purification prototype. The development of electrochemical hydrogen separation carried out by HyET has produced first results on:

- Set up of theoretical model for EHP stack and system design.
- Low temperature membrane material screening for the EHP.
- High temperature membranes.
- Exploratory testing of several separator plate flow field geometries to maximize hydrogen recovery from H_2/CH_4 mixture.
- New EHP stack design prototype completed.
- System electronics for smart EHP stack operation algorithms

Temperature Swing Adsorption development

In the last twelve months HYGEAR finished the assembly of the TSA test station and started testing the drying capacity of different drying agents. Different operational conditions, such as temperature, pressure, carrier gas etc. were tested to find the most optimal regeneration procedure. Using the test results the developed theoretical TSA model was evaluated and updated. Here after the model was used to define the process flow diagram (PFD) for the TSA module. The required instrumentation was defined corresponding to the selected optimal operational adsorption and regeneration mode. The final step was to build a concept 3-dimensional model of the 25 kg hydrogen per day TSA unit. Currently selection of the key components is in progress.

Below Figure shows the process flow diagram developed for the TSA module.

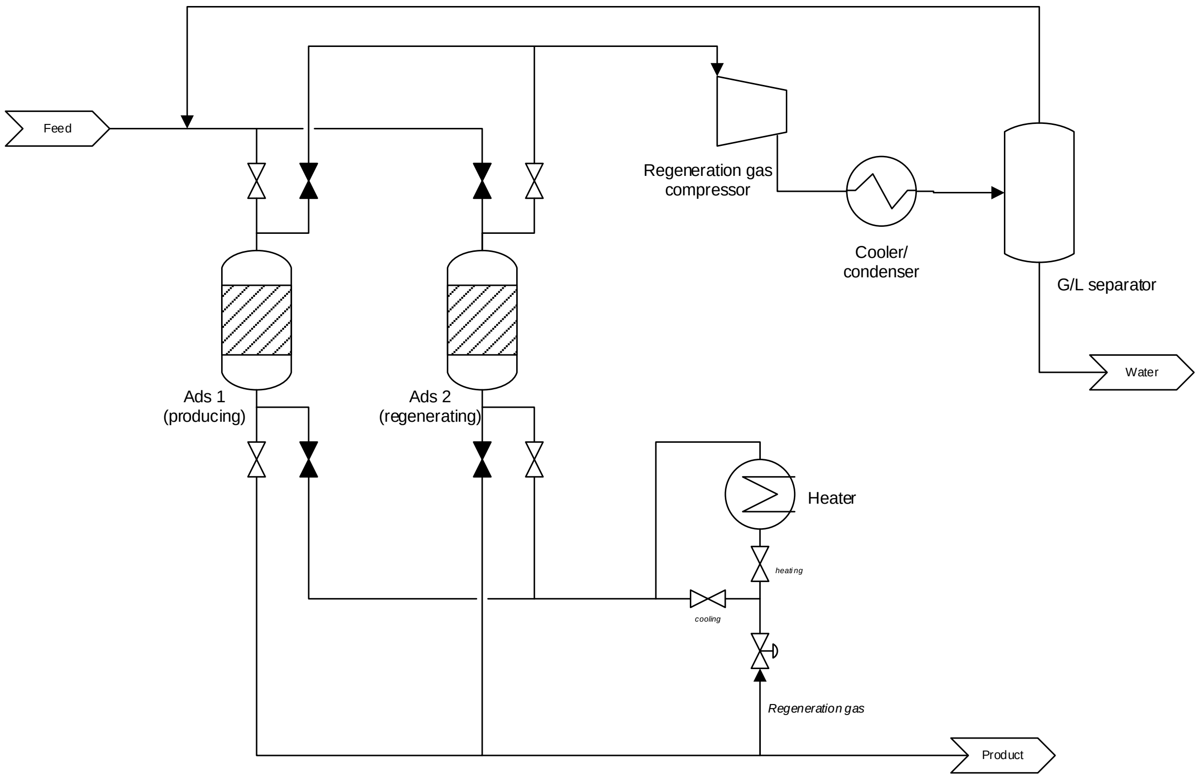
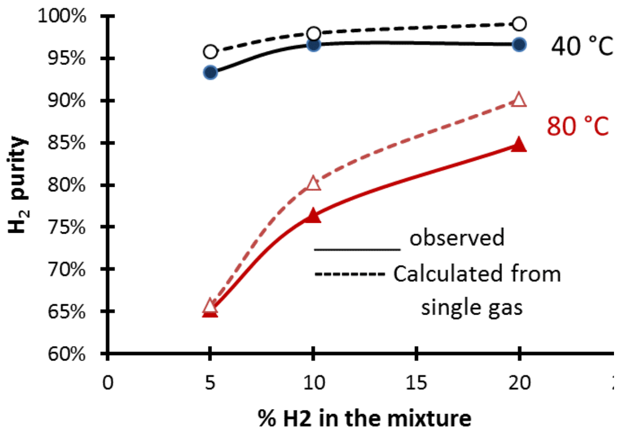


Figure 5. The process flow diagram of the TSA.

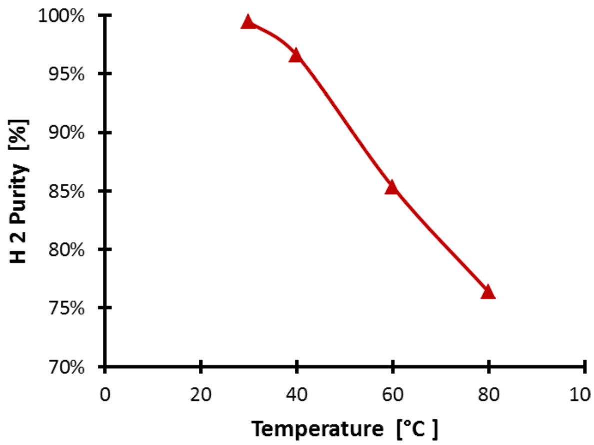
Lab scale testing

Lab scale testing work package objective is the design and building of the lab scale rig for testing the membranes, the sorbents and the electrochemical compressor in the hybrid system. The membrane module will be able to withstand 400 °C at a pressure of up to 50 bar to be able to test various separation scenarios (while even higher pressures will be tested at lab scale). The aim is to test the concept at the minimum scale required to ensure that the process works for industrially relevant conditions. First test results obtained on the membranes and sorbent are detailed hereafter.

Mixed gas permeation tests of one of the delivered carbon membranes have been conducted at TU/e. The H_2 purity of the permeate stream has been measured by Gas Chromatography as a function of the H_2 content (ranging between 5 and 20) in the H_2-CH_4 feed mixture and at 40 and 80 °C at 7.5 bara total pressure and applying vacuum in the permeate. The results are presented in Figure 6-a. H_2 purities ranging from 93.3 to 96.7 have been obtained at 40 °C at a H_2 content between 5 and 20%; and H_2 purities ranging from 65.2 and 84.8 % at 80 °C at the same H_2 content range. At 40 °C, the H_2 purities calculated using the single gas tests results are somehow larger than the experimentally measured H_2 purities probably due to the competition of both gases to the pore. Then, an additional test has been performed with the same carbon membrane at 10% H_2 content of H_2-CH_4 feed mixture and varying the temperature between 30 and 80 °C (see Figure 6-b). At 30 °C a H_2 purity of 99.4% has been obtained.



(a)



(b)

Figure 6. H_2 purity in the permeate of a supported carbon membrane (code: 302-N): (a) as a function of H_2 content in feed stream and at 40 and 80 °C, (b) as a function of temperature and at 10% H_2 content in the feed mixture.

Pd-Ag ultra-thin ceramic supported membranes have been tested at different operative conditions in order to study the hydrogen recovery factor (HRF) and hydrogen purity. The main objectives of the tests are the determination of hydrogen-nitrogen permselectivity, hydrogen permeance and nitrogen flux with the pressure. Later on, of the amount of sweep gas has been changed in order to understand the influence on the hydrogen permeation. As it is possible to see in Table 1, the hydrogen flux for the ultra-thin membranes is much higher compare to conventional Pd-Ag membrane with ceramic support. The weak point of the ultra-thin membranes is the selectivity due to the thin layer deposition and to the sealing. Since the palladium layer is very thin, the torque force that is possible to apply is around 4 N*m in order not to peel off the membrane.

Table 1. Hydrogen permeation and ideal permselectivity at 400 °C

	Hydrogen permeation [mol/s/m^2/Pa]	Ideal permselectivity H_2/N_2 (1bar)
E633	$6.27 \cdot 10^{-6}$	580.00
E635	$7.70 \cdot 10^{-6}$	252.21
E689	$7.78 \cdot 10^{-6}$	433.07

After pure gas tests, experiments are carried out with mixture and sweep gas. Nitrogen has been used as sweep gas. The experiments have been carried out with a mixture of methane and hydrogen. The amount of sweep gas has been changed from 0.3 to 1 l/min in order to study the influence of the sweep gas with the hydrogen permeation. In Figure 7, the results have been described. When the sweep gas is increased, the driving force is higher due to the hydrogen partial pressure. The influence of the sweep gas decreases when the amount of sweep gas is higher. It means there is an upper limit for which, when the sweep gas is increased, the hydrogen permeation cannot be higher anymore.

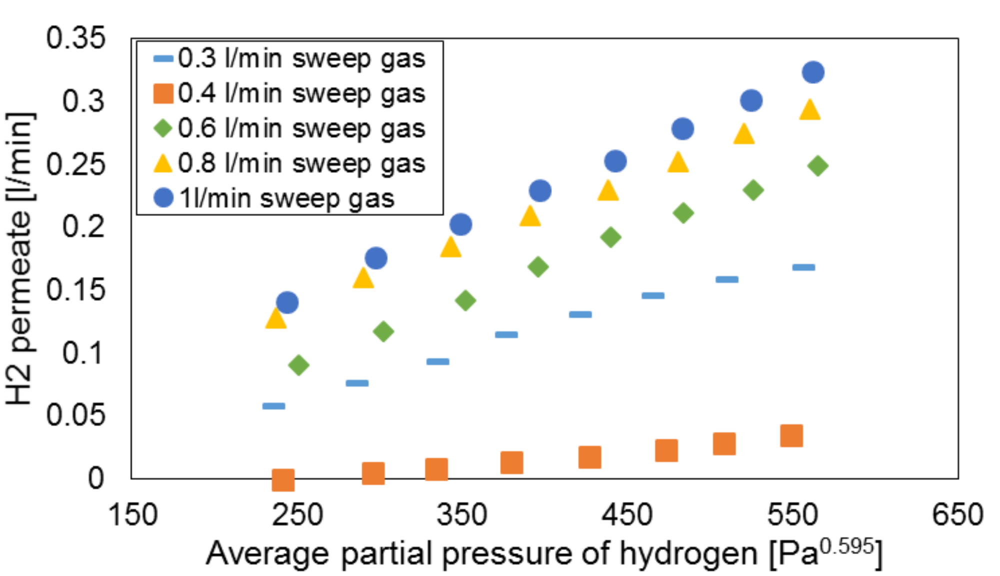


Figure 7. Sweep gas contribution to hydrogen permeation with the pressure

For the sorbents of the temperature swing adsorption, isotherm cycles have been done in a thermogravimetry system in order to measure the adsorption capacity. Zeolite 4A, zeolite 13X, modified zeolite and silica beads have been tested. According to isothermal adsorption, when the temperature is lower, the adsorption capacity is higher as it is possible to see in Figure 8. The sorbents considered are zeolite 13X.

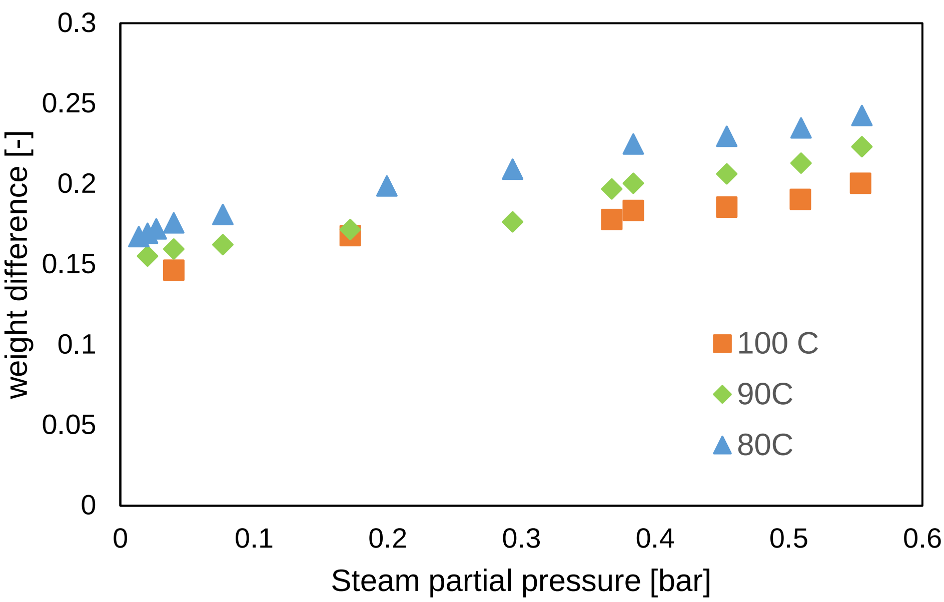


Figure 8. Adsorption capacity as function of steam partial pressure

System modelling and simulation

An aspen plus simulation has been modelled in order to find the best configuration in terms of optimization of the system in accordance with the targets of the project. The membrane module is described by a delphi7 model that takes into account the mass transfer limitation in the retentate side. The electrochemical hydrogen compressor is described by a matlab model that includes energy and mass balances. The main parameters influencing the modelling are the total pressure, amount of sweep gas used, the type of membrane used, the number of membranes and the hydrogen recovery factor from the electrochemical hydrogen compressor. As it is possible to see in Figure 9 when the pressure of the grid is increased, the membrane area required is lower while the hydrogen purity decreases. The membrane considered in the simulation is a metallic supported membrane.

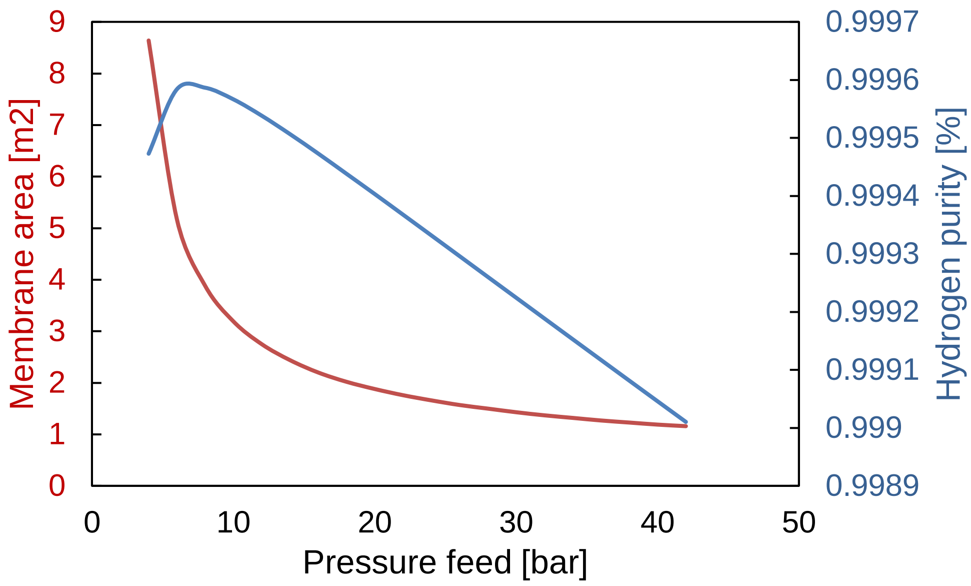


Figure 9. Membrane area required and hydrogen purity as function of the pressure feed for a metallic supported membrane

Environmental and economic assessment

The environmental and economic assessment of the new hydrogen recovery systems developed within the HyGrid project will be also evaluated. The aim is not only to assess the developed technologies against current hydrogen recovery systems, but also to try and guide the design of the investigated technologies towards more environmentally friendly solutions. The core methodology which will be used to achieve this is life cycle assessment (LCA), a quantitative environmental assessment tool which estimates the environmental impacts of products or services looking at their entire life cycle.

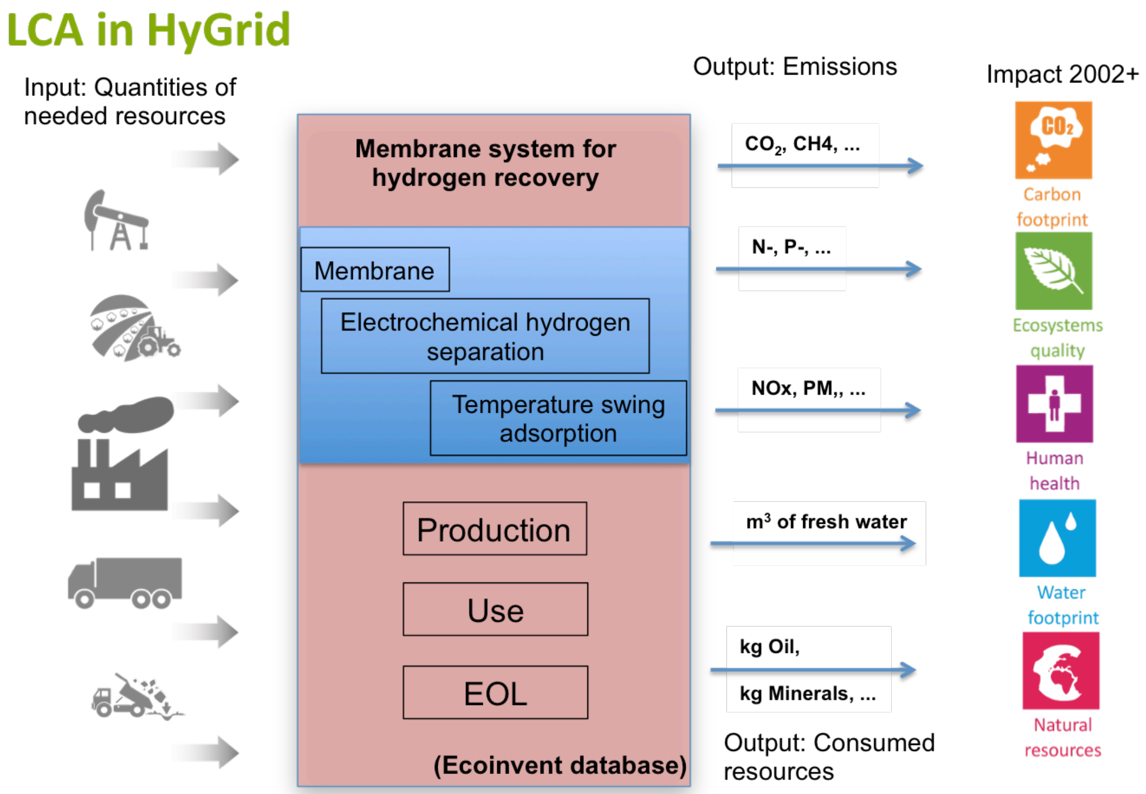


Figure 10. LCA approach

During the first 12 months, the activity has been focused on understanding the key aspects of the membrane systems which will be developed in HyGrid in order to prepare the framework for their environmental and economic assessment. In technical LCA terms, this corresponds to developing the goal and scope of the study which is the task defined for the first year of the project. This will require, amongst other things, to clearly define what different systems will be analysed, what precise system boundaries will be used for the study and what reference technology the HyGrid system will be compared to. Pressure swing adsorption was identified as a suitable reference technology for the project. A first analysis of available LCA literature for the reference system against which the developed hydrogen recovery system will be compared was conducted. In addition, the LCA methodology has been presented and discussed with the project partners at the M12 meeting. A key part of this project will be the data collection phase, since data from different project partners will be required to model the life cycle of the membrane systems. In any case, it is expected that the largest part of the data collection will occur during the second and third year of the project.

Highlights

Third European Workshop on Membrane reactors: Membrane Reactors for Process Intensification

On 9 and 10 March 2017, the Third European Workshop on Membrane Reactors took place in Villafranca di Verona (Italy). More than 85 people coming from all around Europe and from Russia, Pakistan and Philippines attended what proved to be a very productive and stimulating meeting. The Book of Abstracts and presentation can be downloaded at this link: http://www.fluidcell.eu/content/workshops.

There were 17 scientific presentations, 3 round tables, poster sessions and a company visit (ICI). The scientific presentations were given by both academics and industry representatives, on the following themes:

1. Fundamentals of membrane reactors
2. Process design and applications
3. Industrial applications of Membrane Reactors

The Workshop was very successful in terms of attendance but also in terms of discussions and interactions between academia and industry. It was very stimulating to try to find a compromise between what the academia wants (basically study the more fundamental aspects of membrane reactors) and what the Industry wants (a reliable working system, even if not the best in terms of performance).

Different aspects related to the scale-up and operation of membrane reactors were discussed, and it was common opinion of industrial participants that we are now facing in most cases some technical problems that can be more easily solved when working together, especially using the expertise of industrial partners (for example for the sealing of membranes).

It was also interesting to see how the application of membrane reactors could open new markets for industries working on filtrations and porous supports.

There was also a large consensus on the requirement of standards for membrane (reactor) testing, as many groups test membranes in different conditions and for different times. One good outcome of the workshop will thus be a document for standardization of membrane testing to be used as reference for the coming projects.

The natural next step is to start to collect information on running projects on membrane reactors to organize the next Workshop. Two projects are already identified, but more need to be contacted. It was also mentioned that the organization of a common exploitation/dissemination workshop can be included as default in the writing of new proposals on membrane reactors.

PROMECA Workshop 2017:
Energy Analysis and Modelling of Membrane Reactors
November 16th, 2017, Chieti Scalo - Italy

KT – Kinetics Technology will host the 1st PROMECA Workshop on Energy analysis and modelling of Membrane Reactors. The focus will be on structured catalytic membrane reactors for process intensification in hydrogen production. Selected presentation will be given on detailed modelling, process design and industrial applications of membrane reactors.

The workshop will be part of the first transfer of knowledge event of the PROMECA project (www.promecaproject.com), contributing to the increase of knowledge, skills, and competitiveness in the European Community of membrane reactors.

Dissemination activities, publications and presentations:

HyGrid public presentations as well as open access articles and public reports are available online in the dissemination section of the project website: www.hygrid-h2.eu.

Peer reviewed articles:

1. Margot A. Llosa Tanco, David A. Pacheco Tanaka. Recent Advances on Carbon Molecular Sieve Membranes (CMSMs) and Reactors. Processes 2016, 4, 29; doi:10.3390/pr4030029.

2. A.M. Gutierrez, J.R. Arraibi, M.A. Llosa Tanco, J. Zúñiga, J.L. Viviente, L. García Gómez. Development of carbon molecular sieve Membranes for the use of renewable gases, biomethane and hydrogen in natural gas networks. Proceeding of the International Gas Union Research Conference 2017 (IGRC2017). Rio de Janeiro, Brazil (24-26/05/2017).

Other dissemination activities:

1. M. Nordio, F. Gallucci, M. van Sint Annaland, V. Spallina. *Flexible Hybrid separation system for Hydrogen recovery from Natural gas Grids*. Dutch membrane meeting (2016). Poster

2. Naturgas. *Una industria energéticamente sostenible.* Newspaper El Correo – Innovation section. Bilbao, Spain (1st June 2016).

3. Martijn J.J. Mulder, Peter J. Bouwman. The need for High Temperature Proton Exchange Membranes for electrochemical hydrogen purification and compression. EMEA workshop 2016. Bad Zwischenahn, Germany (27-29/06/2016). Poster.

4. A.M. Gutierrez, Flexible Hybrid separation system for H2 recovery from Natural Gas Grids (HyGrid). GERG Meeting with DG ENERGY, Brussels, Belgium (06/02/2017). Oral

5. F. Gallucci, J.L. Viviente. Flexible Hybrid separation system for H2 recovery from NG Grids. Third European Workshop on Membrane reactors: Membrane Reactors for Process Intensification (MR4PI2017). Villafranca di Verona, Italy (9-10/03/2017). Poster.

6. Marco Succi, Giorgio Macchi. Pd Supported Membrane Hydrogen Purifier: a comparison with other technologies. Third European Workshop on Membrane reactors: Membrane Reactors for Process Intensification (MR4PI2017). Villafranca di Verona, Italy (9-10/03/2017). Poster.

7. A.M. Gutierrez. Hidrógeno en redes de gas natural. Fronteras Tecnológicas en Generación de Electricidad, Energías Renovables e Hidrógeno Whorshop. Madrid, Spain (26/04/2017). Oral

8. A.M. Gutierrez, J.R. Arraibi, M.A. Llosa Tanco, J. Zúñiga, J.L. Viviente, L. García Gómez. Development of carbon molecular sieve Membranes for the use of renewable gases, biomethane and hydrogen in natural gas networks. International Gas Union Research Conference 2017 (IGRC2017). Rio de Janeiro, Brazil (24-26/05/2017). Poster.

9. M. Succi, G. Macchi, E. Fernandez, J. Melendez, J. L. Viviente, D.A Pacheco Tanaka. Advancement in Palladium Membranes Hydrogen Purification. 6th European PEFC and Electrolyser Forum. Lucerne, Switzerland (4-7/07/2017). Poster

10. D.A. Pacheco Tanaka, M.A. Llosa Tanco, J. Medrano, J. Melendez, E. Fernández, M. Nordio, F. Gallucci. Preparation and hydrogen permeation studies of ultra-thin Palladium (≈1 micrometer) and carbon membranes from mixtures containing low concentration of hydrogen (< 30%). 13th International Conference on Catalysis in

Membrane Reactors (ICCMR13). Houston (Texas), USA (10-13/07/2017). Oral presentation: Key note.

11. M. Nordio, M. Van Sint Annaland, F. Gallucci, V. Spallina, M. Mulder, L. Raymakers, P. Bouwman. Electrochemical Compressor for Hydrogen Separation in a Small Scale Hybrid System. 13th International Conference on Catalysis in Membrane Reactors (ICCMR13). Houston (Texas), USA (10-13/07/2017). Oral presentation.

12. M. Nordio, J. Meléndez, E. Fernández, M. Van Sint Annaland, D.A. Pacheco Tanaka, F. Gallucci. Ultra-thin palladium-silver membranes for pure hydrogen production and separation: modelling and effect of sweep gas. 13th International Conference on Catalysis in Membrane Reactors (ICCMR13). Houston (Texas), USA (10-13/07/2017). Oral presentation.

13. M. Nordio, J. Meléndez, D.A. Pacheco Tanaka, M. Mulder, P. Bouwman, L. Raymakers, M. Van Sint Annaland, F. Gallucci. Hybrid separation system for hydrogen recovery from natural gas grids. 10th World Congress of Chemical Engineering (WCCE10). Barcelona, Spain (1-5/11/2017). Oral presentation.

Upcoming events

29 July – 4 August 2017	11th International Congress on Membranes and Membrane Processes (ICOM 2017), San Francisco, CA USA http://www.icom2017.org/
23-25 October 2017	5th International Conference and Expo on Separation Techniques Paris, France http://separationtechniques.conferenceseries.com/
16 November 2017	Workshop On Membrane Reactors organised by PROMECA Chieti (Italy) www.promecaproject.com
23 -24 November 2017	FCH JU Programme Review Days 2017 Brussels, Belgium http://www.fch.europa.eu/page/programme-review-2017
14-16 March 2018	European Hydrogen Energy Conference 2018 Málaga, Spain http://www.ehec.info/
20-23 May 2018	International Conference on Chemical Reaction Engineering Firenze Fiera, Florence, Italy http://www.aidic.it/iscre25/

28-29 May 2018	20th International Conference on Inorganic Membranes and Applications (ICIMA 2018), Tokyo, Japan
17-22 June 2018	22nd World Hydrogen Energy Conference (WHEC2018) Rio de Janeiro, Brazil. http://www.whec2018.com/
18-22 June 2018	15th International Conference on Inorganic Membranes, ICIM2018 Dresden, Germany https://www.icim2018.com/
25-29 June 2018	27th World Gas Conference, Washington DC, USA http://wgc2018.com/
9-13 July 2018	Euromembrane 2018 Valencia, Spain http://www.euromembrane2018.org/
6-7 August2018	20th International Conference on Inorganic Membranes (ICIM 2018), Vancouver, Canada http://waset.org/conference/2018/08/vancouver/ICIM
November 2018	FCH JU Programme Review Days 2018 Brussels, Belgium http://www.fch.europa.eu/
2-7 June 2019	8th World Hydrogen Technology Convention (WHTC 2019) Tokyo, Japan http://whtc2019.jp/
8-11 July 2019	14th International Conference on Catalysis in Membrane Reactor (ICCMR14) Eindhoven, The Netherlands

HyGrid in figures:

- *7 partners (2RES, 2 IND, 3 SME)*
- *4 countries*
- *2,847,710 € project (2,527,710 € EU funded)*
- *Start May 2016*
- *Duration: 36 months*

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More information on HyGrid (including a non-confidential presentation of the project) is available at the project website: www.hygrid-h2.eu

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