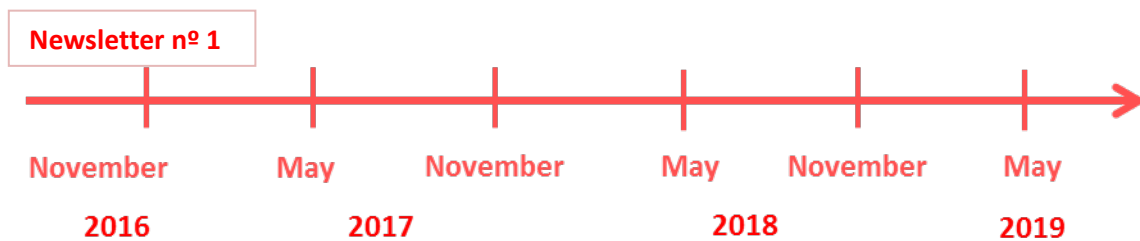


Flexible Hybrid separation system for H2 recovery from NG Grids

Newsletter – Issue 1 – 2nd half 2016



Editorial

Welcome to this first 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 first release of the biannual letter that will be published by HyGrid 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?	2
Latest news from the project.....	5
Highlights	11

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 H₂ from the “low H₂ content” (e.g. 2-10 %) followed by electrochemical hydrogen separation (EHP) optimal for the “very low H₂ 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.

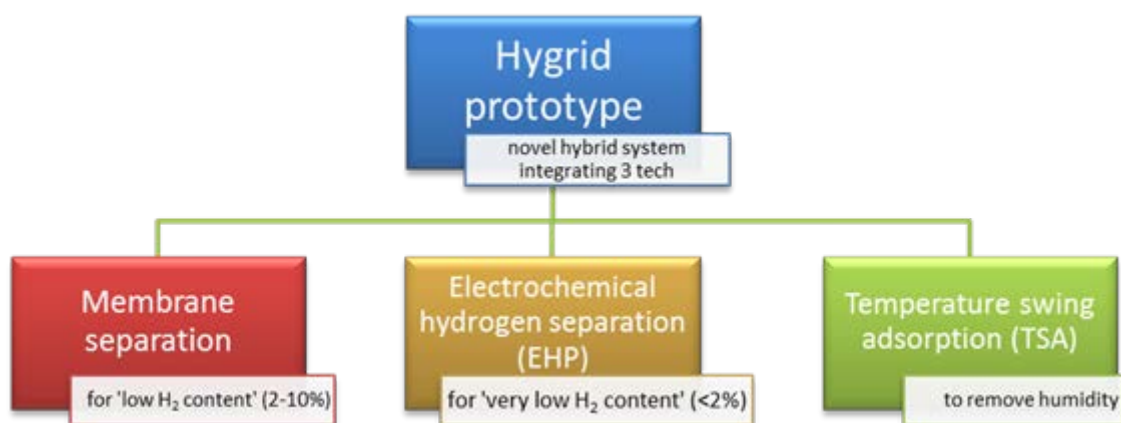


Figure 1. HyGrid concept

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 $< 5 \text{ kWh/kg}_{\text{H}_2}$ and $< 1.5 \text{ €/kg}_{\text{H}_2}$. The pilot will be designed for the separation and purification of $>25 \text{ kg/day}$ of hydrogen (ISO 14687).

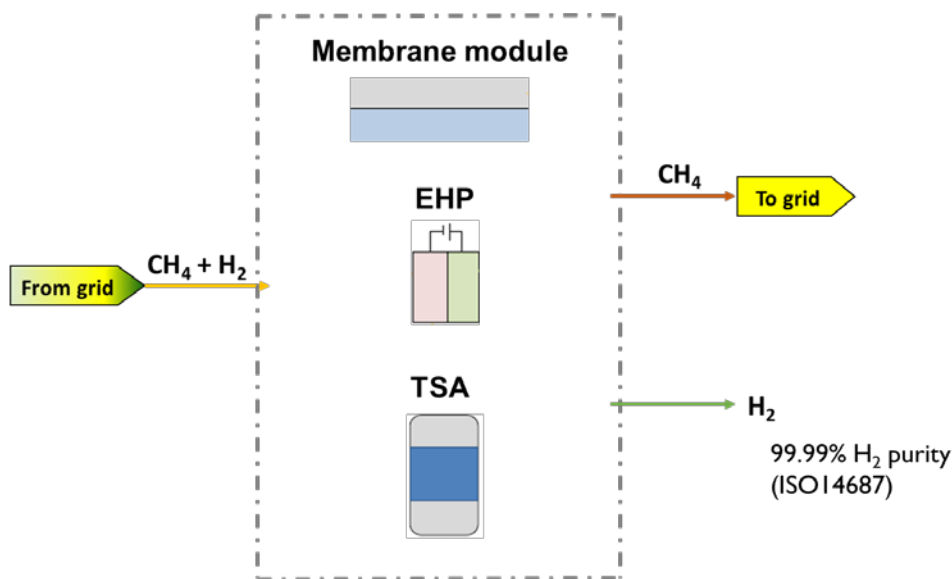


Figure 2. System schematic layout

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 H₂ from low concentration streams (2% -10%) up to 99.99% H₂ 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 H₂ 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

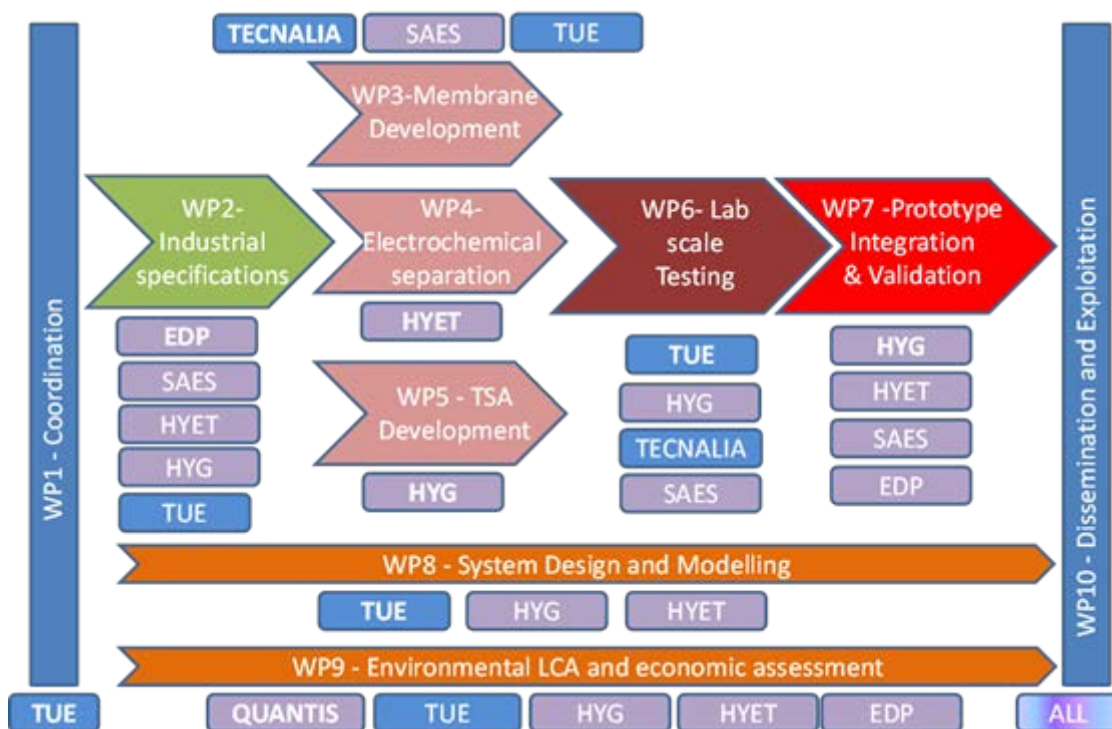


Figure 4. Work structure and synergies between partners.

Latest news from the project

The latest new on different WP activities are now reported:

Industrial specifications

Along the last six months the state-of-the-art separation systems for hydrogen separation & purification from natural gas blends have been analysed. Both process parameters and constraints of the different separation technologies have been assessed. Moreover, the natural gas conditions and properties along the grid infrastructure have been identified as well as the impact of adding hydrogen to the natural gas grid. Additionally, industrial specifications for the new HyGrid separation system have been further detailed. On the other side, a reference case has been defined. The reference case is used for a first comparison between the PSA unit and the HyGrid system in terms of costs and energy demand. First aspen models of the new concept have been carried out in order to check the feasibility to fulfil the targets.

The natural gas infrastructure could be used to transport hydrogen from production to delivery points blended with natural gas. However, the maximum hydrogen allowed into natural gas pipelines is in the range 2 to 10% depending on the end-users existing in the grid and maybe lower. The main impacts of the hydrogen injection in the natural gas grid that have been reviewed are summarised in the Figure 5. However, further studies are needed for a complete assessment of the impact of the hydrogen content in the grid as well as in the gas infrastructure installation and other components. Short reports are available in the HyGrid website (<http://www.hygrid-h2.eu/content/publications>).

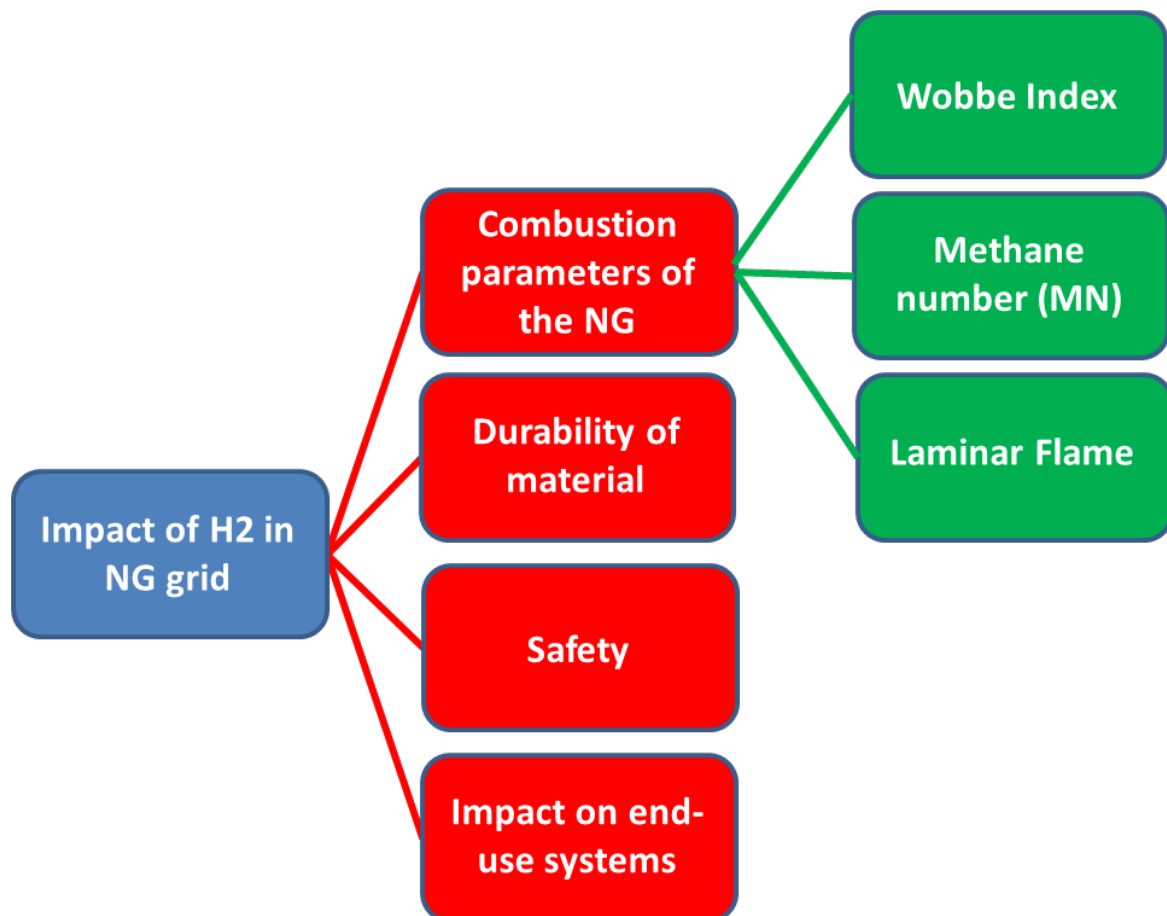


Figure 5. Impact of the hydrogen injection in the natural gas grid.

According to the standard ISO 14687 on the Hydrogen fuel specifications, the hydrogen gas fuel shall be classified according to different types and grade designations in accordance with its appliances (Table 1). For each type and grade the standard is defining limiting characteristic on the H₂ purity and impurities.

Table 1. Hydrogen gas classification and applications

Type	State	Grade	Application
I	Gaseous	A	internal combustion engines/fuel cells for transportation; residential/commercial appliances
		B	industrial fuel, for use e.g. in power generation or as a heat energy source
		C	aircraft and space-vehicle ground support systems
		D	gaseous hydrogen fuel for PEM fuel cell road vehicle systems
		E	gaseous hydrogen fuel for PEM fuel cell stationary appliance systems

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. This process generates micropores with tunable pore size and pore size distribution. First generation of CMSMs (15 cm long) have been developed onto 200 nm pore size alumina porous tubular support (Figure 6-a) and delivered to carry out permeation test.

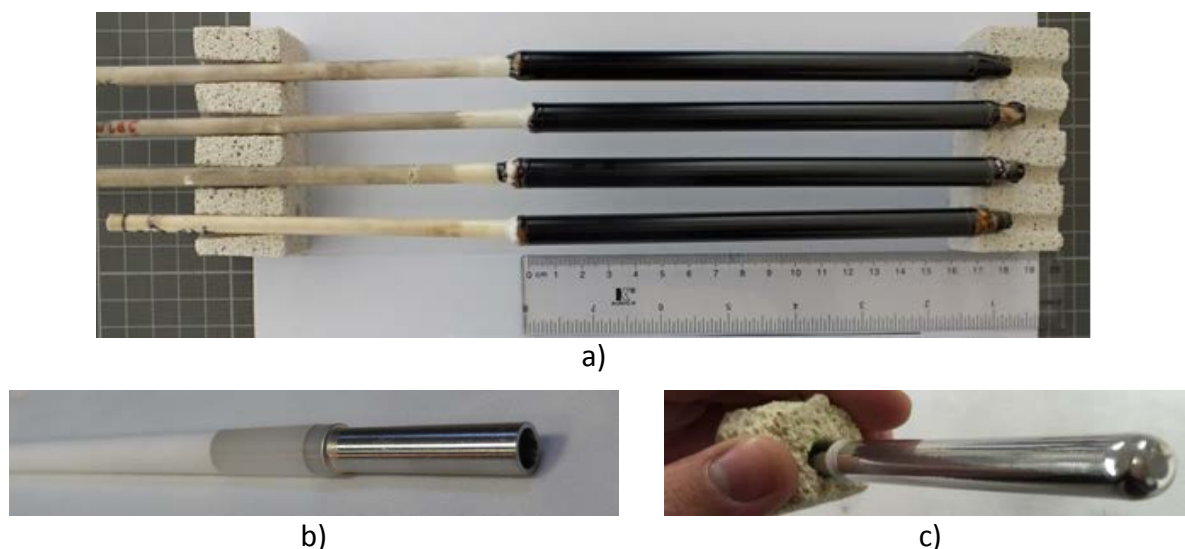


Figure 6. First generation of membranes and joining developments: a) carbon molecular sieve membranes (CMSM), b) ceramic porous support joined to a metallic dense tube and c) Pd-based membranes using a finger-like ceramic porous support.

On the other side, first batch of highly permeable hydrogen selective supported Pd-based membranes onto ceramic porous have been also developed considering two different selective layers thicknesses ($\sim 4 \mu\text{m}$ and between $1\text{-}2 \mu\text{m}$). However, leak free sealing is a requisite to have high pure membranes. 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, Figure 6-b). On the other side, finger-like ceramic supports are used as support for reducing the number of sealing (Figure 6-c).

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
- Exploratory testing of several separator plate flowfield geometries to maximize hydrogen recovery from H_2/CH_4 mixture.
- First version of higher H_2 output stack design for dedicated, combined hydrogen purification / compression (current compressor stack in figure below).
- System electronics for smart EHP stack operation algorithms



Figure 7. Current HyET compressor stack

Temperature Swing Adsorption development



Figure 8. TSA station at HyGear

Main objective of this task is the design, construction and testing of the TSA prototype before its integration in the final hybrid separation/purification prototype. In the first year HyGear is mainly involved in material selection for the gas drying module and test rig design at lab-scale for sorbent material testing. Different drying adsorbents have been selected and they will be tested in terms of gas drying capacities. The results will be used to validate the adsorption and desorption model. On the other side, the test rig for lab-scale tests has been already designed and assembly of the test rig is close to completion. Finally, first TSA process flow designs of the drying module prototype have been prepared

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. The flanged design will allow changing the type of hydrogen selective membranes designed and produced in the project.

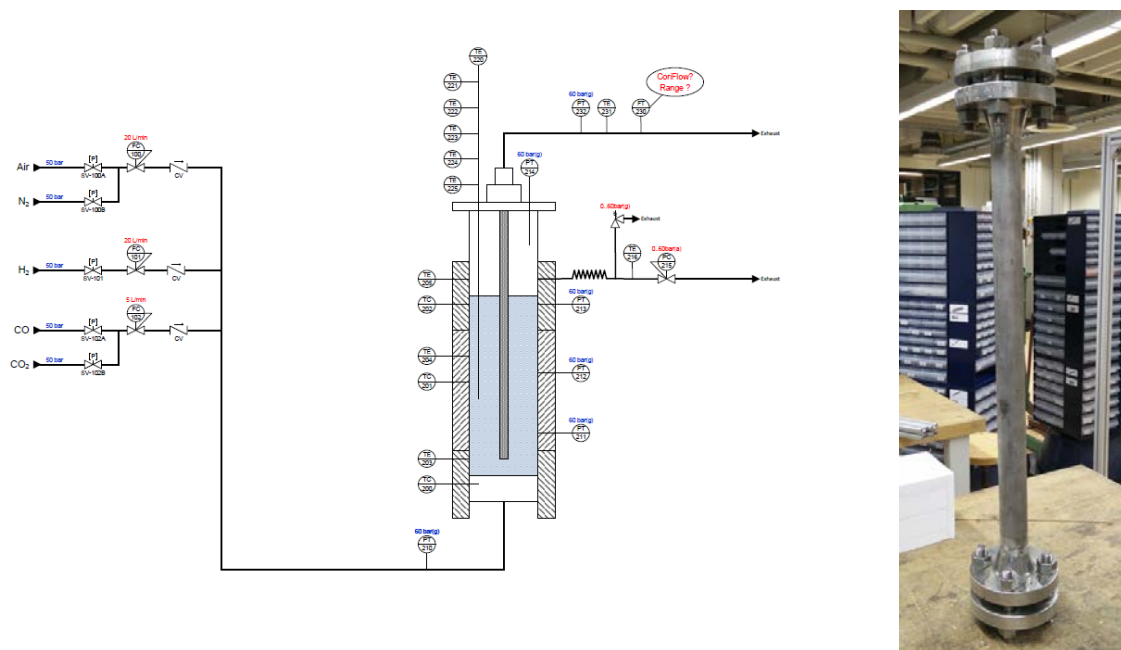


Figure 9. Membrane module layout (TU/e)

The first six months were focused on designing and building of the reactor for the membrane (Figure 9). The membrane sealing will be evaluated at different operative conditions, changing the hydrogen concentration, the amount of sweep gas, the temperature and the pressure. The sorbents for the temperature swing adsorption will be analysed in the thermogravimetric analysis setup to check the optimum type of particles in order to adsorb all the humidity left in the hydrogen stream. Several different samples of drying agents were received from HyGear for testing. Isotherm adsorption and desorption will be carried out to reproduce the temperature swing adsorption cycle. The electrochemical compressor will be tested with methane-hydrogen mixture to analyse the electric consumption required for low hydrogen content.

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.

LCA in HyGrid

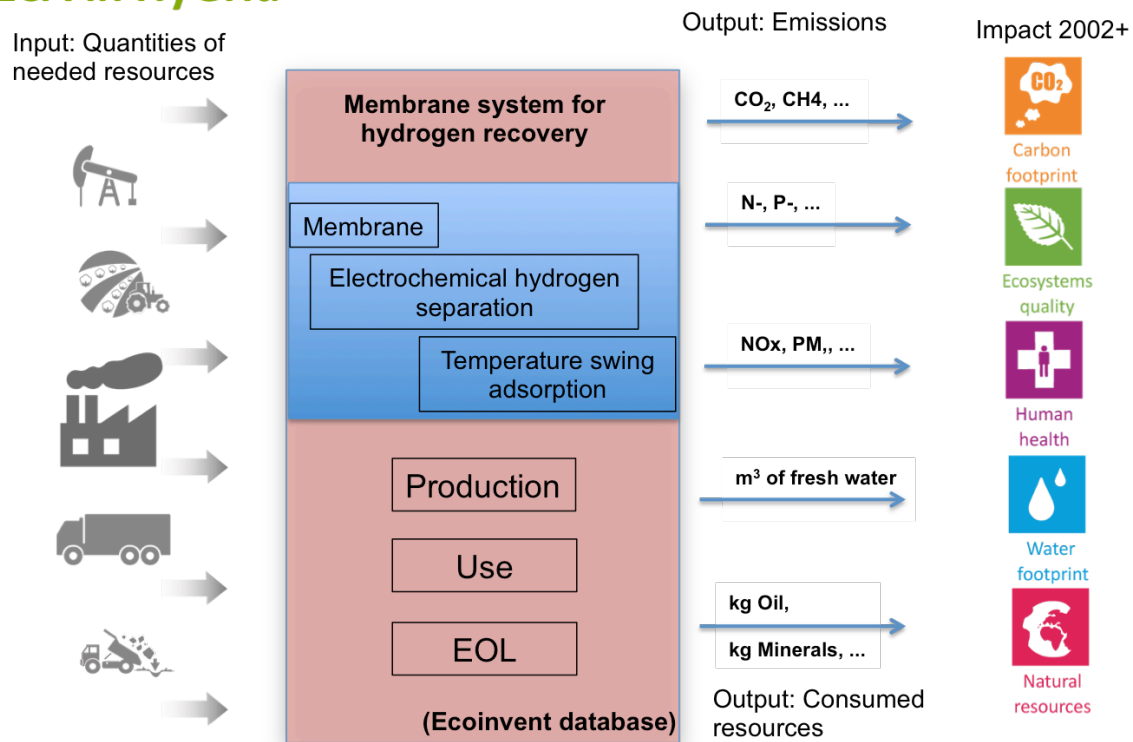


Figure 10. LCA approach

During the first six 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. While the first two points are still being addressed, pressure swing adsorption was identified as a suitable reference technology for the project. 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. While it is expected that the largest part of the data collection will occur during the second and third year of the project, first exchanges on the materials tested for the temperature swing adsorption unit have already begun between Quantis (the work package leader) and HyGear.

Highlights

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

Villafranca di Verona, Italy, March 9-10, 2017

This conference continues the previous workshops on membrane reactors. The first workshop was organised back in November 2012 (Italy) and was entitled “Pd-based membranes and reactor scale-up”. The second workshop, “Catalytic Membrane Reactors: what’s next” was held in April 2015 in the Netherlands. This third one is jointly organised by BIONICO, FERRET, FluidCELL, MEMERE, and ROMEO, 5 major European projects on membrane reactors.

The event will be held at the Hotel Expo Verona. Further information on the event and registration can be found online: <http://www.fluidcell.eu/content/workshops>.

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.

Other dissemination activities:

1. Maria Nordio, Fausto Gallucci, Martin Sint Annaland, Vincenzo 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.

Upcoming events

- 5 – 8 December 2016** 9th IMSTEC, International Membrane Science and Technology Conference, Adelaide Convention Centre, Australia
<http://www.imstec.com.au/>
- 29 – 30 December 2016** 18th ICCB 2016, International Conference on Biofuels and Bioenergy, Paris, France
<https://www.waset.org/conference/2016/12/paris/ICBB/home>
- 8-11 January 2017** ILSEPT - 3rd International Conference on Ionic Liquids in Separation and Purification Technology, Kuala Lumpur, Malaysia
<http://www.ilsept.com/>
- 23 – 25 January 2017** 10th Annual European Gas Conference, Vienna, Austria
<http://www.europeangas-conference.com/>
- 31 January – 2 February 2017** 7th International Conference on "Fundamentals & Development of Fuel Cells, Stuttgart, Germany
<http://www.nerghy.eu/>
- 13-17 February 2017** AMTA/AWWA Membrane Technology Conference & Exposition, Long Beach, California, USA
<http://www.awwa.org/conferences-education/conferences/membrane-technology.aspx>
- 24 February 2017** Biogas Italy 2017, Rome, Italy
<http://www.biogasitaly.com/>
- 9-10 March 2017** Third European Workshop on Membrane reactors: Membrane Reactors for Process Intensification.
Villafranca di Verona, Italy, March 9-10, 2017
<http://www.fluidcell.eu/content/workshops>
- 10 – 11 May 2017** 4th REGATEC 2017, International Conference on Renewable Energy Gas Technology, Italy
<http://regatec.org/>
- 12 – 15 June 2017** 25th EUBCE 2017, European Biomass Conference & Exhibition, Stockholm, Sweden
<http://www.eubce.com/home.html>
- 2 – 5 July 2017** 7th WHTC World Hydrogen Technologies Convention, Prague, Czech Republic
<http://www.whtcprague2017.cz/>
- 10 – 13 July 2017** 13th ICCMR, International Conference on Catalysis in Membrane Reactors, Houston, USA
<http://iccmr.tamu.edu/>

29 July – 4 August 2017	11 th International Congress on Membranes and Membrane Processes (ICOM 2017), San Francisco, CA USA http://www.icom2017.org/
25-29 June 2018	27 th World Gas Conference, Washington DC, USA http://wgc2018.com/
28-29 May 2018	20 th International Conference on Inorganic Membranes and Applications (ICIMA 2018), Tokyo, Japan
6-7 August 2018	20 th International Conference on Inorganic Membranes (ICIM 2018), Vancouver, Canada http://waset.org/conference/2018/08/vancouver/ICIM
2018	22 nd WHEC. World Hydrogen Energy Conference 2018, Rio de Janeiro, Brazil
2019	8 th WHTC World Hydrogen Technology Convention 2019, Tokyo, Japan

HyGrid in figures:

- ↪ 7 partners (2 RES, 2 IND, 3 SME)
- ↪ 4 countries
- ↪ 2,847,710 € project (2,527,710 € EU funded)
- ↪ Start May 2016
- ↪ Duration: 36 months
- ↪ Key milestones:
 - ↪ January 2018 – Electrochemical purification pilot ready
 - ↪ April 2018 – Membrane module prototype ready
 - ↪ June 2018 – TSA ready for integration
 - ↪ October 2018 – Pilot scale prototype ready for testing

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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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Disclosure:

The present document reflects only the author's views, and neither the FCH-JU nor the European Union is liable for any use that may be made of the information contained therein.