HYGRID

FLEXIBLE HYBRID SEPARATION SYSTEM FOR H2 RECOVERY FROM NG GRIDS

FCH-2 GRANT AGREEMENT NUMBER: 700355

Start date of project: 01/05/2016 **Duration: 3 years**

WP2 – Industrial Requirements Definition

D.2.3
HyGrid pre-commercial scale plant report

Topic:	Development of technology to separate hydrogen from low-concentration hydrogen streams
Funding scheme:	Research and Innovation Action
Call identifier:	H2020-JTI-FCH-2015-1

Due date of deliverable: 31-10-16	**Actual submission date:** 25-11-16	**Reference period:** 01-04-2016-06-09-17
Document classification code (*): HYGRID-WP2-D23-TUE-22072016-v02.docx		**Prepared by (**):** MARIA NORDIO (TUE)

Version	DATE	Changes	CHECKED	APPROVED
v0.1	06-09-17	First Release	TUE	Fausto Gallucci
V0.1	06-09-17	Corrected format	TUE	FGallucci

Project funded by the FCH-2 JU within the H2020 Programme (2014-2020)		
Dissemination Level		
PU	Public	X
PP	Restricted to other programme participants (including the Commission Services)	
RE	Restricted to a group specified by the consortium (including the Commission Services)	
CO	Confidential, only for members of the consortium (including the Commission Services)	
CON	Confidential, only for members of the Consortium	

(*) for generating such code please refer to the Quality Management Plan, also to be included in the header of the following pages

(**) indicate the acronym of the partner that prepared the document

Content

1. EXECUTIVE SUMMARY

1.1. Description of the deliverable content and purpose

This document aims to define the potential market applications in terms of possible final consumers of the hydrogen produced.

1.2. Brief description of the state of the art and the innovation brought

The main hydrogen consumers are the chemical industry that uses 4.3 millions of ton per year. One of the possible application for HyGrid project in the electricity production in order to supply the energy missing from the renewable sources. A preliminary configuration for a case in which 50 and 250 kg/day of hydrogen are request, is described in detail.

1.3. Deviation from objectives

The deliverable was delayed one month following the delay of the previous deliverable (D2.2).

1.4. If relevant: corrective actions

There are no deviations.

1.5. If relevant: Intellectual property rights

N/A

2. INTRODUCTION

Global drivers for a sustainable energy visions of our future centre on the need to:

1. Reduce global emissions
2. Ensure security of energy supply
3. Create a new industrial and technology energy base crucial for our economic prosperity

Hydrogen is an attractive alternative to fossil fuels. Part of his attraction is that it can be produced from different resources, both renewable and non-renewable. Hydrogen can then be utilized in high-efficiency power generation system, including fuel cells for vehicular transportation and electricity distribution generation. One of the main problems related to the conventional power plants is the great exergy losses due to the thermal conversions. To overcome the efficiencies of the traditional conversions systems it is thus necessary to avoid the conversion process based on the combustion of the fuel. Since the fuel cell allow the direct conversion of chemical energy in electricity, they are promising systems that could reach higher efficiencies.

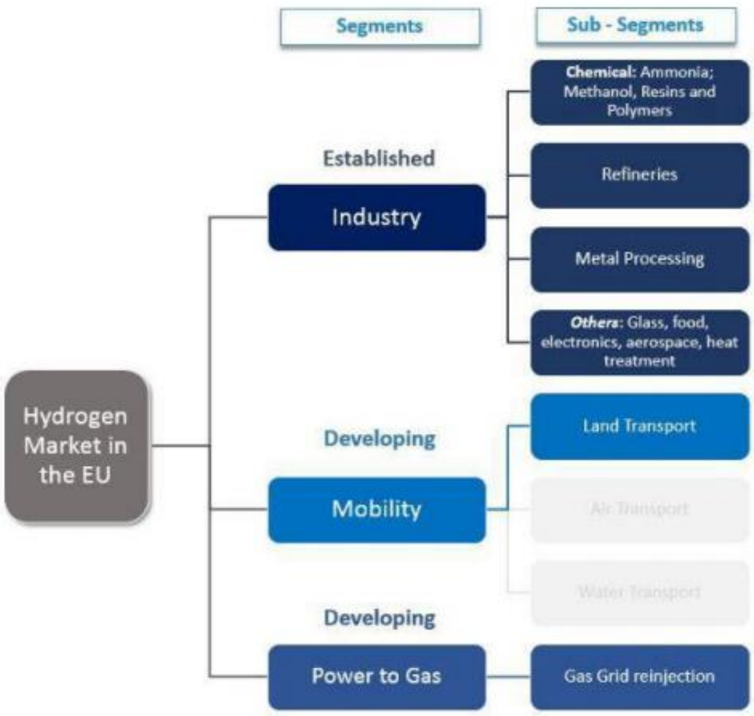
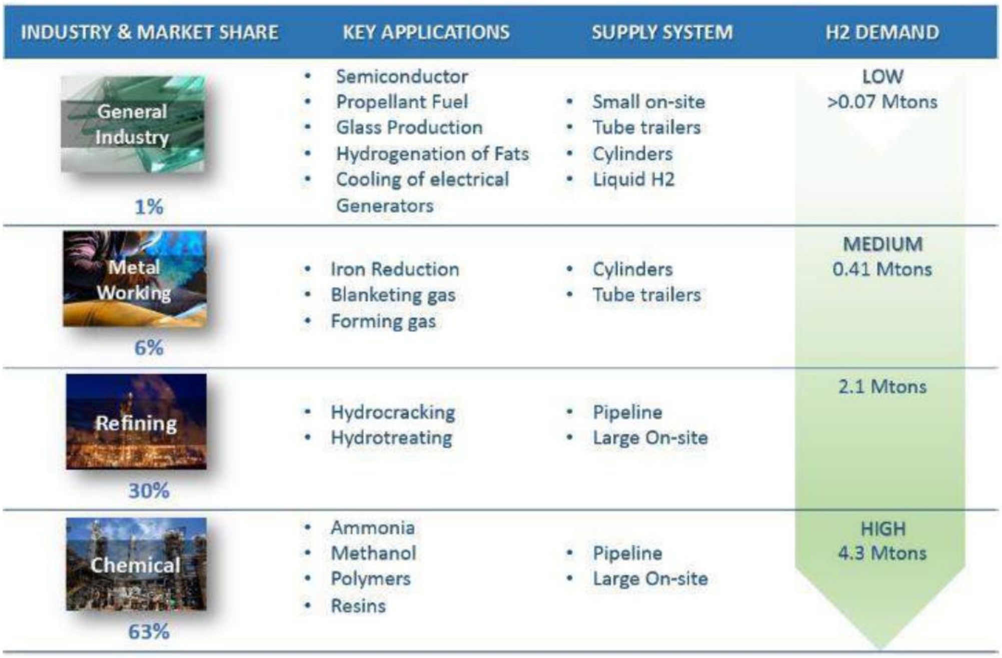


Figure 1 Hydrogen market segments [1]

In Europe there are three different market segments for hydrogen: industry, mobility and power to gas. The first one is already established while the others are developing as it is possible to see in picture 1.

3. POTENTIAL MARKET APPLICATIONS

Hydrogen market can be divided in industry, mobility and power to gas. The industrial sector represent more than 90% of today's hydrogen consumption. The main segments of the industry are chemical, refineries, metal processing and heat treatment for electrical generation. The chemical sector is the most important hydrogen consumer, accounting for 63% of the market share equal to 4.3 million of tons per year among the European Union, followed by the refinery sector which account for the 30% of the market share as shown in Figure 2.



INDUSTRY & MARKET SHARE	KEY APPLICATIONS	SUPPLY SYSTEM	H2 DEMAND
General Industry 1%	• Semiconductor • Propellant Fuel • Glass Production • Hydrogenation of Fats • Cooling of electrical Generators	• Small on-site • Tube trailers • Cylinders • Liquid H2	LOW >0.07 Mtons
Metal Working 6%	• Iron Reduction • Blanketing gas • Forming gas	• Cylinders • Tube trailers	MEDIUM 0.41 Mtons
Refining 30%	• Hydrocracking • Hydrotreating	• Pipeline • Large On-site	2.1 Mtons
Chemical 63%	• Ammonia • Methanol • Polymers • Resins	• Pipeline • Large On-site	HIGH 4.3 Mtons

Figure 2 Industry sector snapshot [1]

The main problem of the chemical sector is the huge amount of hydrogen required that cannot be feasible for HyGrid system.

3.1 Most promising potential application

The hydrogen separated from the Hygrid system could be used as energy carrier for electricity production for the cases in which the renewable are not available. One of the main problems of the electrical grid is the fact that the renewable sources have the priority to be fed in the grid but since they are not predictable, the conventional power plants should supply the missing electricity when they are not available. One possible solution involves the transformation of the hydrogen in electricity through the fuel cells. Considering a hydrogen production target of the project of 50-250 kg/day, the energy that could be supplied is ranging from 37 to 189 kW_e based on a preliminary assessment in which it was considered that from 1 Nm^3/h of hydrogen it is possible to obtain 1.6 kW.

4. PURITY LEVEL

Hydrogen purity level varies with industry segment and has a direct impact on the costs of production of hydrogen to meet a certain market requirement. The hydrogen quality verification level is determining depending on the state of the hydrogen: liquid or gaseous as described in table 1 and 2.

Table 1. Gaseous hydrogen level qualification [1]

GASEOUS (Type I)		
Quality Verification Level	Typical Uses	Hydrogen purity
B	General industrial applications	99.95%
D	Hydrogenation and water chemistry	99.99%
F	Instrumentation and Propellant	99.995%
L	Semiconductor and specialty applications	99.999%

Table 2. Liquid hydrogen level qualification [1]

LIQUID (Type II)		
Quality Verification Level	Typical Uses	Hydrogen purity
A	Standard Industrial, fuel and standard propellant	99.995%
B	High Purity: industrial, fuel and Propellant	99.999%
C	Semiconductor	99.9997%

The level of purity required in the fuel cells is normally 99.97% but the performances of the fuel cell increases for higher purity.

5. PRELIMINARY CONFIGURATION FOR THE SELECTED APPLICATION

An aspen modelling was carried on in order to define a preliminary configuration for the overall system in which the selected application need between 50 and 250 kg/day of hydrogen. The initial assumptions are:

- Hydrogen purity of 99.97%
- Total HRF of 83%
- Minimum hydrogen flow of 50 kg/day
- Maximum hydrogen flow of 250 kg/day
- Electric consumption of 5 kWh/kg_{H2}

Since the amount of hydrogen request is high, it is not possible to reach the target of purity only with one membrane module but it is necessary to have two membranes in the system. The grid is considered at the pressure of 8 bar because this value of pressure is able to optimize the system in terms of membrane area and purity of hydrogen.

A schematic representation of the preliminary configuration is shown in Figure 3 in which it is possible to see a membrane modules, a TSA and the EHP.

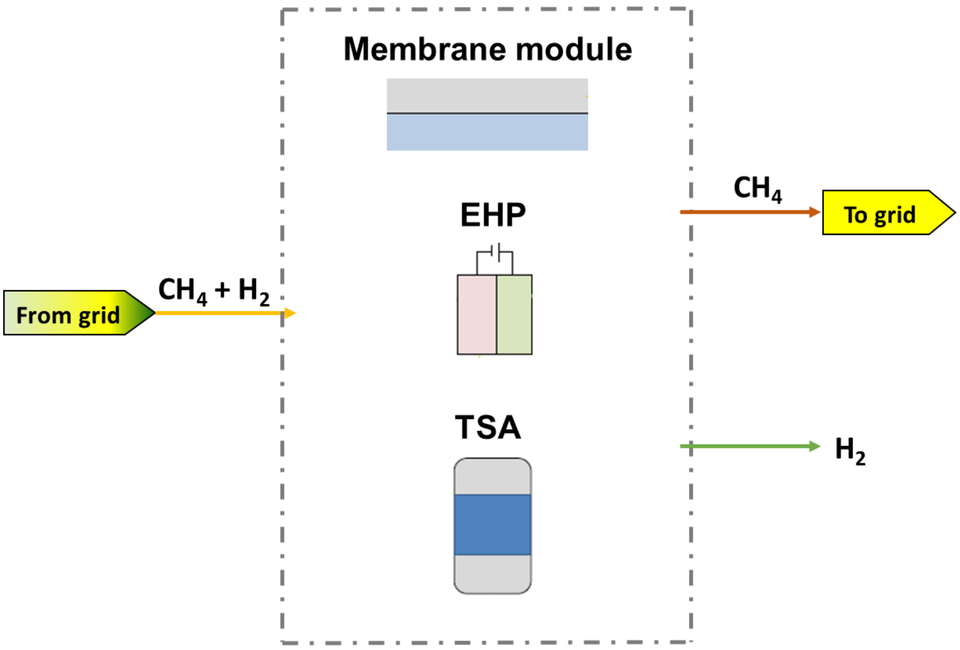


Figure 3 Schematic representation of the preliminary configuration for the selected application. The real layout of the system is confidential.

In order to obtain a minimum final hydrogen flow of 50 kg/day, the feed coming from the grid should be equal to 1200 mol/h of H_2 and 10800 mol/h of CH_4. A palladium-silver membrane is considered with a metallic support. The characteristics of the membrane are defined as followed: the selectivity depends on the partial pressure according to the equation 1.

$$S = \frac{((p_{H2,ret}^{0.5} - p_{H2,perm}^{0.5}) * \mathrm{P} + \mathrm{Q} * (p_{H_{2,ret}} - p_{H_{2,perm}}))}{\mathrm{Q} * (p_{N_{2,ret}} - p_{N_{2,perm}}))} \qquad equation\ 1$$

In which $p_{H_{2,ret}}$, $p_{H_{2,perm}}$ are respectively the partial pressure of the hydrogen in the retentate side and in the permeate side. P is the permeability equal to $10^{-6} \frac{mol}{s*Pa*m^2}$ and Q is the parameter related to the leakages and it should be calculated experimentally. For this simulation the value of Q is taken from [4] and is equal to $5.7 * 10^{-12} \frac{mol}{s*Pa*m^2}$. The area required is obtained as consequences of the hydrogen permeate from the first two membranes in order to obtain an HRF of 80%.

The mixture is sent to the electrochemical compressor in which it is necessary to recover at least 81.7 mol/h of hydrogen in order to respect the target of flow. In the EHP it is possible to recover 86.5 mol/h of hydrogen with a ratio between hydrogen outlet and hydrogen inlet equal to 0.5. The EHP is simulated only considering that the ratio between the hydrogen at the outlet and the hydrogen at the inlet should not overpass 50%. The electric consumption request from the compressor is equal to 3.24 kW. The total electric consumption for the electrochemical compressor is equal to 0.7 kW. The permeate is sent to the temperature swing adsorption after cooling down the stream in order to remove all the humidity. In the inlet of the TSA the amount of humidity considered is equal to 2.3% v/v and for this simulation the assumption used is that all the water is removed in the TSA unit. The amount of humidity in the stream going to the TSA depends on the temperature at which the cooler is working. If necessary is possible to decrease it in order to have less humidity at the inlet of the TSA. In this preliminary simulation no real sorbents were considered and the heat consumption has not been yet defined. The final total electric consumption is equal to 2.18 kWh/kg_{H2} that is lower than the target request for the HyGrid system. The heat consumption is mainly due to the high quantity of steam that is necessary as sweep gas. The total heat consumption required in the system is equal to 13 kW and in terms of consumption for kg of hydrogen produced is 6.21 $kWh/kg_{H2.}$

The same calculations were carried on in order to study a system able to produce 250 kg/day of hydrogen. For this configuration the initial feed is equal to 5800 mol/h of hydrogen and 52200 mol/h of methane. The methane grid is at 8 bar.

The methane impurities increase with the area but if the sweep gas is used, it is possible to increase the hydrogen permeation through the membrane with the same amount of methane and the purity level will increase. The heat consumption associated to the evaporation is really high and the total heat consumption will increase in an important way.

The electric consumption associated to the compressor is of 16 kW considering an outlet pressure of 8 bar. While the consumptions for the electrochemical pump since the hydrogen permeating is 0.86 kg/h, is equal to 3.27 kW considering a final pressure of 1 bar. The total consumption is of 3.053 kWh/kg_{H2}.The heat consumption due mainly to the heaters for evaporating the sweep gas is equal to 8.64 kWh/kg_{H2} that is equal to the heat supplied burning 1% of the methane in the grid. The stream is sent to a cooler and to the TSA for removing all the humidity. Since the effect of the steam on the hydrogen permeation is not negative, [7] the humidity in the inlet of the second membrane is not removed. No real sorbents are considered in the simulation since the temperature swing adsorption is considered as a simple separator in which the main assumption consists in the possibility to remove all the water content.

5.1 Case with a level purity of 99.999%:

Since the efficiency of the fuel cells increase when the purity of hydrogen is higher, a last case was studied in order to obtain 50 kg/day of hydrogen with a purity level of 99.999%.

The initial feed is equal to 1200 mol/h of hydrogen and 10800 mol/h of methane.The ideal selectivity of the membrane is equal to 200000 while the permeability is $10^{-6}\frac{mol}{Pa*s*m^2}$. The area of the membrane is equal to 3.5 m^2. The HRF after the first membrane is equal to 75% because to separate more it is necessary to have a bigger area but the impurities become too higher and the purity level request would not be reachable. The assumption that was done consists in the possibility to recover more than 2% from the EHP without decreasing the ratio between hydrogen at the outlet and at the inlet of the electrochemical separator.

The stream is cooled down and sent to a TSA unit in order to obtain pure hydrogen. The EHP is simulated considering a simple separator without modeling a real ionic membrane in the system. The outlet pressure of the EHP is considered at 1 bar since in this application, the hydrogen is sent to the fuel cell that works at 1 bar. The electrical consumption of the EHP is equal to 3.8 kWh/kg_{H2} for an outlet pressure of 1 bar. Since the hydrogen passing through the electrochemical compressor is equal to 0.342 kg/h, the electrical consumption associated to it is equal to 1.3 kW_e. The consumption due to the compressor is equal to 3.6 kW and the final electrical consumption is equal to 2.8 kWh/kg_{H2}.The heat consumption mainly due to the evaporation of the water for obtaining steam as sweep gas is equal to 13.6 kWh/kg_{H2}.

6. CONCLUSIONS

From these cases the main purpose was to shown the preliminary configuration that should be built for the selected application of 50 and 250 kg/day of hydrogen produced. In both the configurations it is possible to see that the target for the HyGrid project are respected with a hydrogen purity of 99.97% and an electric consumption that is much less than the target of 5 kWh/kg_{H2}. The different configurations in terms of number of membranes and amount of sweep gas where necessary, need to be selected depending on the quantity of hydrogen to produce for the specific application.

From the last case the main purpose was to show the preliminary configuration of a HyGrid system that can separate 50 kg/day of hydrogen with a purity equal to 99.999%. The main problem is related to the high heat consumption required in the system. In order to decrease the area of the membrane and the impurities of methane that could pass through it, a high amount of sweep gas is used. The second issue consists in the assumption that even if the amount of hydrogen that could be separated through the EHP is increased, the ratio between hydrogen at outlet and inlet is considered around 60%. The maximum obtained until now is 50% but one of the task of WP4 is the possibilities to increase the ratio until 60%. Moreover the electrical consumption associated to it is respectable of the target required from the project. The last question is related to the high amount of sweep gas used while the real effect of it need to be studied in detail. The main advantage is the small size request for the membrane area due to the sweep gas used.

REFERENCES

[1] Zoulias, E. I., Glockner, R., Lymberopoulos, N., & Tsoutsos, T. (2004). Integration of hydrogen energy technologies in stand-alone power systems analysis of the current potential for applications, 1–31. https://doi.org/10.1016/j.rser.2004.10.001

[2] Ahmad, R., & Buttle, F. (2017). Customer retention : a potentially potent marketing management strategy Customer retention : a potentially potent marketing management strategy, *4488* (September). https://doi.org/10.1080/096525400010011466

[3] Thomassen, M., Sheridan, E., & Kvello, J. (2010). Journal of Natural Gas Science and Engineering Electrochemical hydrogen separation and compression using polybenzimidazole (PBI) fuel cell technology. *Journal of Natural Gas Science and Engineering*, *2*(5), 229–234.

[4] Hao, Y., Nakajima, H., Yoshizumi, H., & Inada, A. (2016). ScienceDirect Characterization of an electrochemical hydrogen pump with internal humidifier and dead-end anode channel. *International Journal of Hydrogen Energy*, *41*(32), 13879–13887. https://doi.org/10.1016/j.ijhydene.2016.05.160

[5] Gallucci, F., Fernandez, E., Corengia, P., & Sint, M. Van. (2013). Recent advances on membranes and membrane reactors for hydrogen production. *Chemical Engineering Science*, *92*, 40–66. https://doi.org/10.1016/j.ces.2013.01.008

[6] Nigel P. Brandon, D. T. (2005). *Fuel cell compendium*. (J. of P. Sources, S. S. Ionics, A. C. B. Environmental, C. Today, C. O. in S. S. and M. Science, I. J. of H. Energy, C. E. and Processing, Eds.).

[7] Helmi, A., Fernandez, E., Melendez, J., Alfredo, D., Tanaka, P., Gallucci, F., & Annaland, M. V. S. (n.d.). Fluidized Bed Membrane Reactors for Ultra Pure H 2 Production — A Step forward towards Commercialization. https://doi.org/10.3390/molecules21030376

[8] Fernandez, E., Antonio, J., Melendez, J., Parco, M., Luis, J., Sint, M. Van, Tanaka, D. A. P. (2016). Preparation and characterization of metallic supported thin Pd – Ag membranes for hydrogen separation. *Chemical Engineering Journal*, *305*, 182–190. https://doi.org/10.1016/j.cej. 2015.09.119

[9] Lee, H. K., Choi, H. Y., Choi, K. H., Park, J. H., & Lee, T. H. (2004). Hydrogen separation using electrochemical method, *132*, 92–98.