HYGRID

FLEXIBLE HYBRID SEPARATION SYSTEM FOR H2 RECOVERY FROM NG GRIDS

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WP2 – Industrial Requirements Definition

D.2.2
Definition of the reference case

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Dissemination Level		
PU	Public	X
PP	Restricted to other programme participants (including the Commission Services)	
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CO	Confidential, only for members of the consortium (including the Commission Services)	
CON	Confidential, only for members of the Consortium	

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

Content

1. EXECUTIVE SUMMARY (3 pages max. all points)

1.1. Description of the deliverable content and purpose

This document aims to collect information about the composition of the hydrogen-natural gas sources in terms of definition of pollutants and typical amount. The definition of pollutants is very important since they can damage the recovery process both for the membranes and the sorbents. This report also summarizes the costs required for the traditional separation system based on the PSA unit in terms of purity, pressure and costs required.

The reference case is used for a first comparison between the PSA unit and the hygrid system in terms of costs and energy demand. The flow coming from the grid consists in 10% H_2 and 90% CH_4. The total flow is equal to 6246.1 mol/h while the operative conditions that were considered are equal to 8 bar and 25 °C.

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

The main current traditional separation systems for hydrogen recovery coming from a hydrogen-methane stream are the PSA unit and the cryogenic system. The electric consumption related to both these techniques are high due to the compression for the first system [11] and due to the low temperatures at which the second one needs to work [12]. Especially for a low hydrogen concentration in the stream, these two systems are not economically feasible. The HyGrid project has the purpose to separate the hydrogen with a lower electric consumption and cheaper capital costs.

1.3. Deviation from objectives

The deliverable has been delayed because of additional calculations required to accommodate the suggestions of the different partners. Anyway, this delay does not impact on the other deliverables in the other WPs (only D23 will be affected).

1.4. If relevant: corrective actions

The D2.3, based on this deliverable, will be delayed by 1 month.

2. INTRODUCTION

2.1. The importance of hydrogen

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 problem related to the traditional power plants is the great exergetic losses due to the mechanical conversions. To overpass the modern efficiencies of the traditional conversions systems it is 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.

3. HYDROGEN NATURAL GAS SOURCES

Limits to impurities in the natural gas-hydrogen sources are necessary by technical and safety issues. Contaminants in the grids could decrease the efficiency of the membrane and the electrochemical separator.

3.1. Poisoning of palladium-silver membranes

Contaminants such as sulphur, chlorine and arsenic chemically react with palladium leading to a collapse of the membrane. In particular

1. Poisoning of sulphur compounds: Pd-coated membranes could rapidly be destroyed after exposure to a gas stream containing hydrogen sulphide and the poisoning effects are irreversible.
2. Poisoning of CO: the presence of CO in a feed gas stream could cause a decrease in the hydrogen permeation flux because the adsorbed CO displaces the adsorbed hydrogen and further blocks H_2 adsorption sites. Moreover, this reduction becomes more significant at low temperature or high CO concentration. CO is adsorbed on the Pd surface blocking available dissociation sites for H_2.

For a better behaviour of the palladium membrane, the natural gas- hydrogen sources should be with a maximum amount of sulphur and CO equal to 10 ppm [6].

3.2. Poisoning of EHP

According to scientific studies the membranes of the electrochemical separator can be poisoned by sulphur compounds such us H_2S and SO_2.

1. PBI membranes

   When the PBI cell is exposed to 1 ppm of H_2S or SO_2, the performance of the cell decreases up to 2% but any poisoning effect is fully reversed when the cells are exposed to neat air. If the amount of H_2S is up to 5 ppm, the efficiency decreases more than 5.2% of the initial current density but when the cell was exposed to air, the performances came back to the original ones. The problems started when the cell was exposed to 10 ppm of H_2S or SO_2, in that cases the efficiency could not come back to the previous. It is important that the natural gas-hydrogen sources coming from the grid has a maximum sulphur impurity equal to 10 ppm [7] since EHP cells contain precious metal-based catalysts like Pt that are susceptible to poisoning.

2. Sulfonated fluorocarbon-based membrane

   The same results were obtained for the PEM membranes. To avoid poisoning the maximum amount of impurities in the system should be 10 ppm of H_2S and SO_2.

4. PSA UNIT

4.1. Introduction

The Pressure Swing Adsorption technology is based on a physical binding of gas molecules to adsorbent material. The respective force acting between the gas molecules and the adsorbent material depends on the gas component, type of adsorbent material, partial pressure of the gas component and operating temperature. The separation of adsorption is based on the different adsorption forces between a given adsorbent material and different gas component. Based on technical adsorbent applications a typical sequence of adsorption forces is shown in Figure 1.

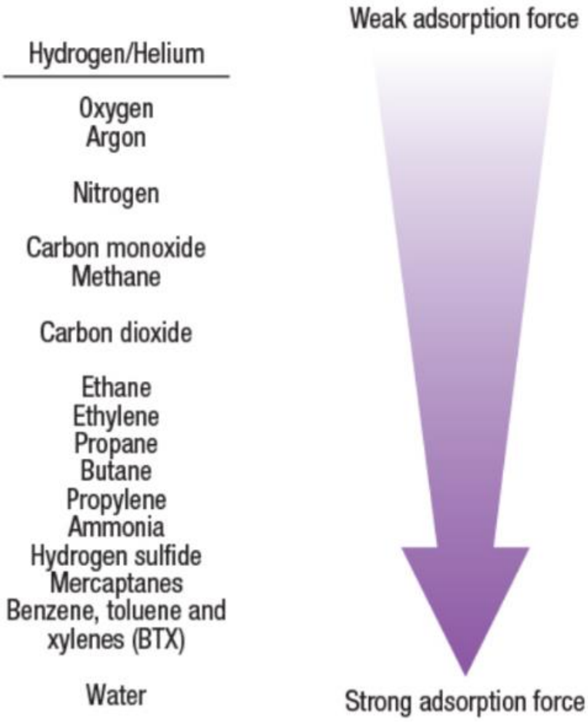


Figure 1. Adsorption forces [6]

The strength of such a surface interaction depends on the nature of both the solid adsorbent and the fluid adsorbate. Consequently, different substances adsorb with different affinities. Such a selectivity provides the basis to achieve separation in adsorption separation processes, such as Pressure Swing Adsorption. If the fluid-surface interactions involve weak forces, such as van der Waals, we observe physical adsorption or physisorption. In contrast, if the forces are strong and involve electron transfer, the phenomenon is called chemisorption. Adsorbent regeneration is an important aspect of adsorption separation processes. A given adsorbent has a finite solute uptake capacity from the free fluid phase and must be cleaned for re-utilization. Thus, the adsorption phenomena should be reversible. Such reversibility is economically achieved in case of physisorption compared to chemisorption. Based on the principle of adsorption and adsorbent regeneration, adsorption separation processes are designed to operate in a cyclic manner. Often at least two fixed-bed adsorbers are provided, such that one is used for adsorption while the other is being regenerated.

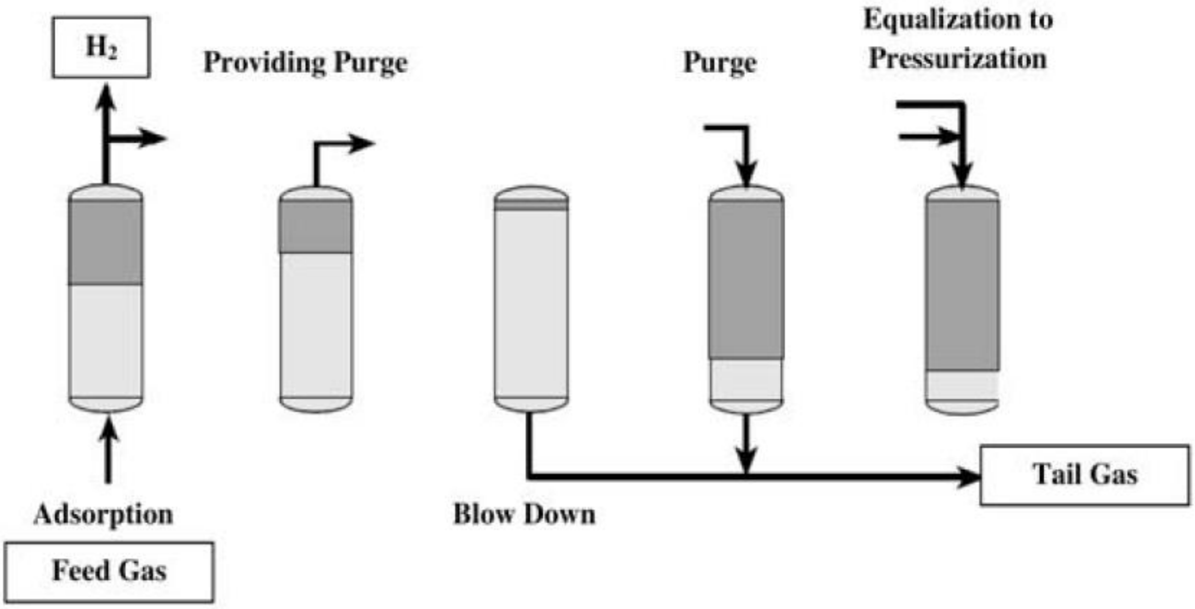


Figure 2. A schematic diagram of PSA industrial plant for H_2 recovery [6].

Temperature swing adsorption (TSA): In this process bulk separation of a mixed gas is achieved by repeating adsorption at a lower temperature and desorption at a higher temperature. The cyclic operation in this case typically takes a rather long time because of a relatively large time constant of heat transfer due to poor thermal conduction in the adsorbent packed bed.

Pressure Swing Adsorption (PSA): In this process, bulk separation of a mixed gas is achieved by repeating adsorption at a higher pressure and desorption at a lower pressure. In this case, the step time for desorption is of the same order of magnitude as that of the adsorption (sometimes even smaller). Hence, this process enjoys shorter cycle time and more productivity compared to TSA, and thus, is preferred.

As can be seen from Table 1 hydrogen recovery for a mixture of 25% hydrogen and 75% methane is very low due to experimental limitations. According to the results, the purity as well the recovery of hydrogen when the inlet percentage of hydrogen is few, decrease. One of the main disadvantage of the PSA unit is that for low quantity of hydrogen, the power consumption required for separating hydrogen from methane with a high purity and recovery is too costly [12].

Figure 3 shows the effect of an adsorption pressure on performances for H_2/CH_4 systems under a 0.22 l/min purge rate. The H_2 purity declines rapidly below about 8 atm while recovery declines almost linearly with pressure. The decline of recovery is mostly due to the loss of H_2 in the feed end during countercurrent depressurization. Therefore, when the operating pressure ratio is high, it is desirable to incorporate higher amount of adsorption bed to obtain good recovery, even if the capital cost will increase.

Table 1. Purity and H_2 recovery as function of feed composition [6]

Run no.	Feed composition	P (bar)	T (K)	H_2 recovery (%)	Purity (% H_2)
1	50% H_2/50% CH_4	5.8	303.15	39.6	99.8
2	40% H_2/60% CH_4	5.8	303.15	26.0	98.1
3	25% H_2/75% CH_4	5.8	303.15	12.1	83.7
4	50% H_2/50% CH_4	4.5	303.15	47.7	88.7
5	50% H_2/50% CH_4	7.2	303.15	27.8	99.9
6	50% H_2/50% CH_4	8.6	303.15	25.4	99.9
7	50% H_2/50% CH_4	5.8	303.15	15.4	99.8
8	50% H_2/50% CH_4	5.8	303.15	31.0	99.7
9	50% H_2/50% CH_4	5.8	303.15	41.9	86.8
11	50% H_2/50% CH_4	5.8	303.15	57.1	81.1
12	50% H_2/50% CH_4	5.8	303.15	69.8	73.2
13	50% H_2/50% CH_4	5.8	303.15	72.3	88.9
14	50% H_2/50% CH_4	5.8	303.15	54.0	96.3
15	50% H_2/50% CH_4	5.8	313.15	34.3	96.6
16	50% H_2/50% CH_4	5.8	323.15	35.6	92.6

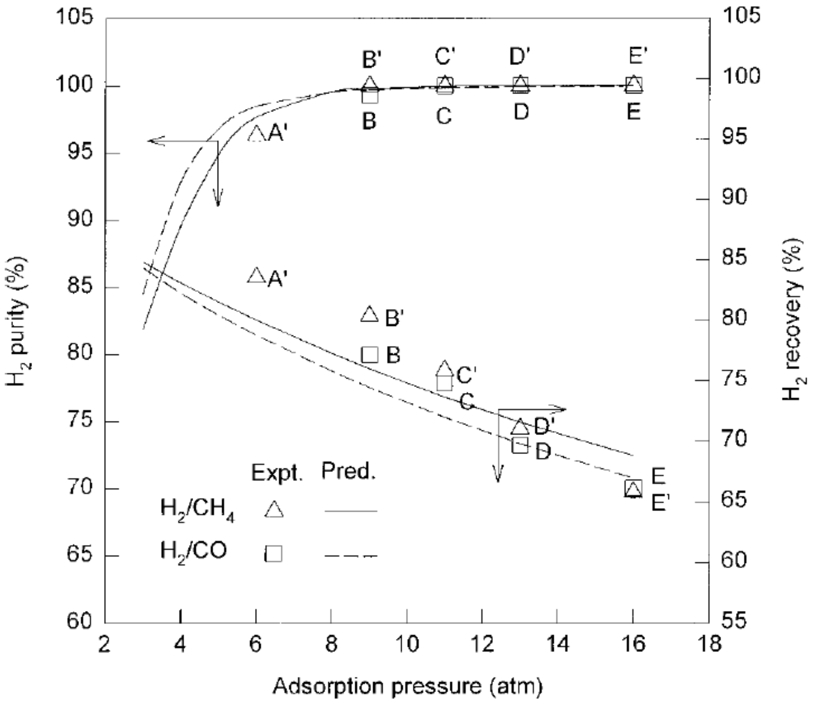


Figure 3. Effects of adsorption pressure on H_2 purity and H_2 recovery [6]

An Aspen simulation was carried out to demonstrate the main disadvantages of the pressure swing adsorption unit in terms of electrical costs due to compression and the not economically feasibility of the systems for hydrogen content less than 10%. Two different configurations of the PSA have been studied. The first one considers only one bed while the second one has five columns. The schematic representation of the first system is shown in Figure 4.

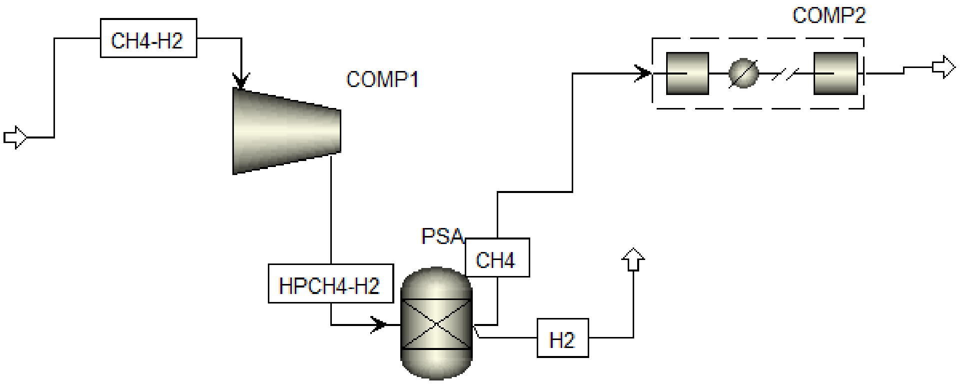


Figure 4. Aspen modeling for PSA unit

In order to obtain a hydrogen purity of 99.97%, a pressure of 16 bar is required at the inlet stream. The system is obtained based on the assumption that increasing the cycle time it is possible to obtain the hydrogen recovery required. The initial condition for the methane coming from the grid is 8 bar. The values of feed and hydrogen recover are shown in table 2. A second compressor is required to obtain the methane at the same pressure of the grid. The energy consumption is associated to the compressors in which all the methane need to be compressed in the first one up to 16 bar and in the second one until 8 bar. In the first case only one stage compressor is used since the pressure ratio is equal to 2, while in the second case a multistage compressor is used since the pressure ratio is equal to 8. Four stages are used with an inter-cooler that help the methane to reach 120 ºC after every stage. The total electric consumption obtained from the system is equal to 19.41 kWh/kg$_{H2}$. The first compressor has an electric consumption equal to 4.625 kW while the second compressor of 15.59 kW.

Table 2. Flow, temperature and pressure conditions in before and after the components of the system.

stream	H_2 flow [mol/h]	CH_4 flow [mol/h]	temperature [°C]	pressure [bar]
feed in the compressor	624.61	5621.49	25	8
feed in the PSA	624.61	5621.49	60	16
total hydrogen recovered	520.84	0.156	120	8

The targets of electricity consumption and cost required are higher than the target request from the HyGrid system. The PSA unit is quite efficient, and it can separate gases with an extremely high purity, but the costs required, and the power consumptions request can be justified only if the stream to be separated is high. For large size plant the use of PSA makes sense while for small system the use of PSA is too costly [13]. Another main disadvantage of the PSA unit is that the purity and the recovery of the hydrogen decrease with the percentage of hydrogen at the inlet stream. To obtain high recovery, it is necessary to incorporate many PSA units and the capital cost will not be repaid for small systems. The PSA unit cannot be economical feasible for small systems.

An Aspen simulation with 5 beds was carried out to demonstrate the main disadvantages of the pressure swing adsorption unit in terms of electrical costs due to compression and the not economically feasibility of the systems for hydrogen content less than 10%. The schematic representation of the system is shown in Figure 5.

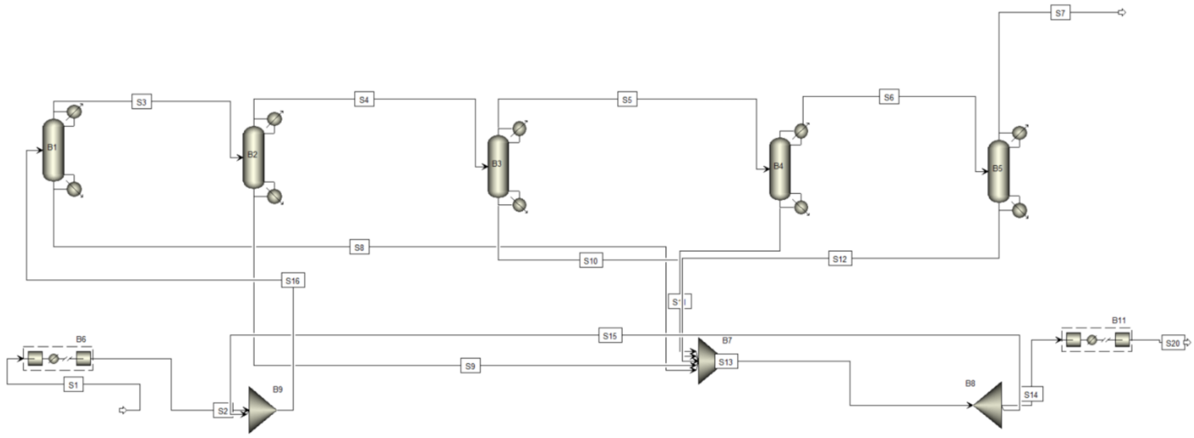


Figure 5. Aspen modeling for PSA unit.

To obtain a hydrogen purity of 99.999%, a pressure of 25 bar is required at the inlet stream to guarantee the pressure difference of each columns including the pressure drops. The stream is then sent to five different columns in series to increase the purity and the hydrogen recovery factor of the system. The first column has a pressure difference of 8 bar, the second one of 6 bar, the third one of 5 bar, the fourth one of 4 and the last one of 2 bar. When the adsorption pressure is higher it is possible to reach higher purity but lower hydrogen recovery factor. For this reason, a recirculation of the gas is essential for reaching the target of HRF and purity. A second compressor is required to obtain the methane at the same pressure of the grid. The energy consumption is due to the compressors in which all the methane need to be compressed in the first one up to 25 bar and in the second one until 8 bar. In both cases a multistage compressor is used since the pressure ratio is equal to 3.125 in the first and 8 in the second. Four stages are used with an inter-cooler that help the methane to reach 80 ºC after every stage. The first compressor has an electric consumption equal to 6.393 kW while the second compressor of 14.244 kW. The total electric consumption is equal to 20.213 kWh/kg$_{H2.}$

Table 3. Flow, temperature and pressure conditions in before and after the components of the system

stream	H_2 flow [mol/h]	CH_4 flow [mol/h]	temperature [°C]	pressure [bar]
feed in the compressor	624.61	5621.49	25	8
feed in the PSA	624.61	5621.49	80	25
total hydrogen recovered	510.437	0.000510	80	8

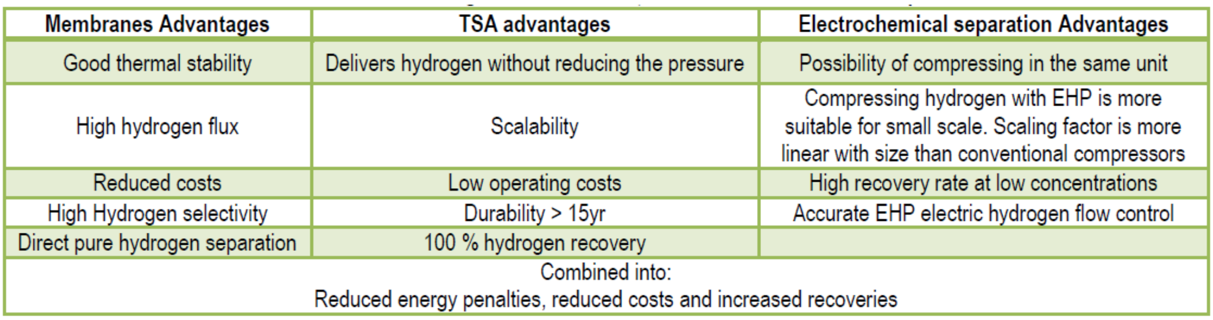
The result obtained with the simulation of five column PSA is similar to the simulation with only one column (19.41 kW/kg$_{H2}$ e 20.213 kW/kg$_{H2}$). The description in terms of flow and pressure are in Table 3. The targets of electricity consumption and cost required are higher than the target required from the HyGrid system in both the configuration. The main difference is related to the purity obtained. With five stages PSA it is possible to reach a very high purity compared to only one stage.

5. HYGRID SYSTEM

5.1. Advantages

The new concept will combine membrane separation and electrochemical hydrogen separation for hydrogen separation and TSA for the final hydrogen purification. Membranes or EHP taken alone would be able to separate hydrogen from NG streams, however they would be too costly and with low efficiency. The OPEX costs for hydrogen separation using only the electrochemical compressor is equal to 0.54 €/kg$_{H2}$, doubles the target of HyGrid. On the other hand, the smart combination and sizing of the three technologies will allow obtaining high recoveries of hydrogen at very low costs. This new concept will thus combine the advantages of high temperature membranes, TSA and electrochemical separation as reported in Table 4.

Table 4. Combined advantages of membrane, TSA and electrochemical separator.



Membranes Advantages	TSA advantages	Electrochemical separation Advantages
Good thermal stability	Delivers hydrogen without reducing the pressure	Possibility of compressing in the same unit
High hydrogen flux	Scalability	Compressing hydrogen with EHP is more suitable for small scale. Scaling factor is more linear with size than conventional compressors
Reduced costs	Low operating costs	High recovery rate at low concentrations
High Hydrogen selectivity	Durability > 15yr	Accurate EHP electric hydrogen flow control
Direct pure hydrogen separation	100 % hydrogen recovery	
Combined into: Reduced energy penalties, reduced costs and increased recoveries		

5.2. Modeling

To check the feasibility of the HyGrid system in accordance with the targets request from the project, an aspen model of the overall system was carried on. The first consideration is related to the fact that using a high amount of sweep gas requires an important quantity of heat supplied. At the same time, it is possible to obtain only one membrane module due to the presence of the sweep gas that allow a high hydrogen permeation with a small amount of area request. The schematic representation of the system is shown in Figure 6.

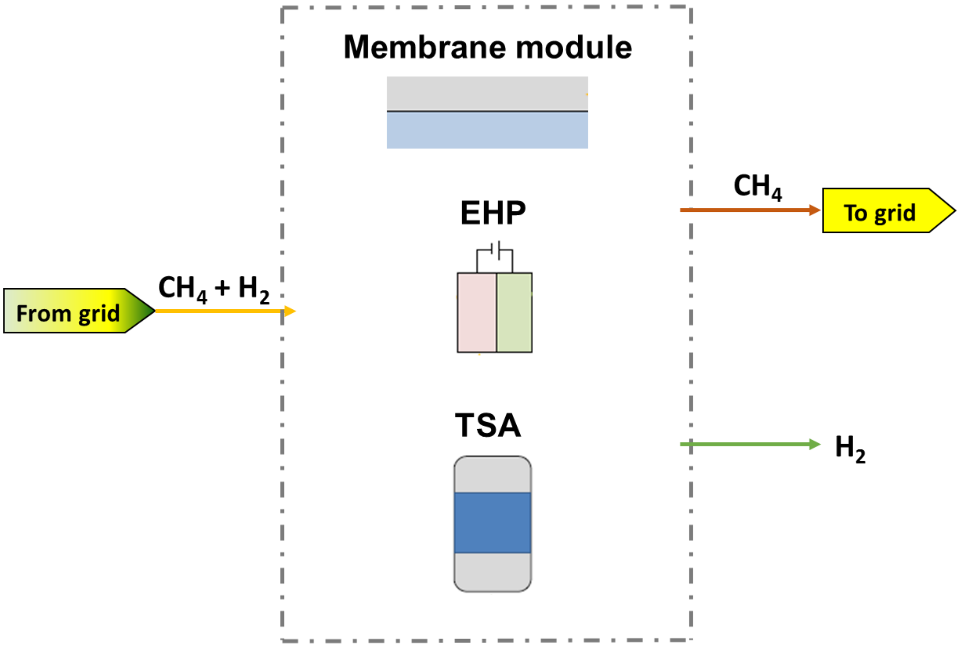


Figure 6. Aspen modeling for HyGrid system; layout confidential.

The heat consumption required to evaporate the steam is equal to 22 kW that need to be supplied. The total heat required from the system is equal to 28 kW. On the other side, the total electrical consumption for both components is 6.3 kWh/hgH_2.

For the electrochemical pump in the simulation was not considered any specific membrane but the unit is considered only as a simple separator in which the hydrogen can pass while the methane not. The purity assumed is equal to 100%. The main assumption for the TSA is that all the water content is removed while the amount of humidity in the inlet stream depends on the temperature that the cooler is reaching and depending on the conditions, it is possible to decrease it to have a less amount of water going to the TSA. In the simulation no real sorbents were considered but the TSA is considered as a simple separator in which the hydrogen is purified from the humidity. For the case considered the water content in the inlet stream is 3% v/v. The hydrogen separated in the EHP is pressurized depending on the conditions of the electrochemical pump. In order to obtain hydrogen at 1 bar, the electric consumption of the EHP is 3.8 kWh/kg$_{H2}$ while for reaching 200 bar the electric consumption is 5.8 kWh/kg$_{H2}$. The final pressure of the hydrogen depends on the application for which is used after. The only two components that require electric consumption are the EHP and the compressors. A final consumption of 2.6 kWh/kg$_{H2}$ is found from all these assumptions.

Other HyGrid system layouts have been studied to decrease the heat consumption request from the system while obtaining a high purity. In one configuration it is possible to achieve a final hydrogen purity of 99.97% with an electric consumption of 4.6 kWh/kg$_{H2}$ while the total heat consumption is equal to 10 kW. The electric consumption is lower than the target required from HyGrid project. The total hydrogen produced is equal to 26.23 kg/day at 8 bar and 77 ºC.

6. CONCLUSIONS

The main purpose of the report consists in showing the advantages of HyGrid system compared to the reference case for hydrogen separation. The PSA unit is a mature technology in the industrial market but its feasibility for a stream composed of low hydrogen content is arguable. The electric consumptions due to the compressors is around 34.83 kW that means 33.43 kWh/kg$_{H2}$ far from the targets required in HyGrid.

On the other hand, the HyGrid system for hydrogen separation coming from a methane-hydrogen stream with a low content of hydrogen seems to be feasible. From the cases analyzed, the electric consumptions are less than 5 kWh/kg$_{H2}$. In Table 5 is shown the comparison between electric consumption for PSA unit for high plant, small plant, and two different HyGrid system configuration and the target of the project.

Table 5. Comparison between PSA and HyGrid system in terms of electric consumption.

System	Electric consumption [kW/kg_{H2}]
PSA unit for small plant	19.41
PSA unit for large plant	33.43
HyGrid configuration A	2.6
HyGrid configuration B	4.6
HyGrid target	5

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