HYGRID

FLEXIBLE HYBRID SEPARATION SYSTEM FOR H2 RECOVERY FROM NG GRIDS

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Dissemination Level		
PU	Public	X
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Content

1. EXECUTIVE SUMMARY

1.1 Description of the deliverable content and purpose

This document aims to describe the experimental results with Pd-Ag and carbon molecular sieve (CMS) membranes at the prototype operating conditions for a description of the membrane performance which are expected in the final system.

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

Pd-Ag and CMS membranes have been intensively studied in literature at different operating conditions even if those membranes have not been tested at high pressure. The operating conditions of the prototype were selected: 400 °C and 8 bar for Pd-Ag membranes and 20, 50 and 70 °C at 8 bar for CMSMs. When working with CMSMs it is important to keep the membrane humidified to improve the membrane selectivity. The obtained results will be adopted to validate a model and perform a techno-economic evaluation required in WP8.

1.3. Deviation from objectives

There are deviations related to the disclosure of the information for publishing the paper on the work related to this document.

1.4. If relevant: corrective actions

There are no deviations.

1.5. If relevant: Intellectual property rights

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2. INTRODUCTION

The choice of the membrane type to use in a membrane reactor must consider both performance and cost. Pd-Ag membranes are highly selective to hydrogen and allow the production of a pure hydrogen stream. However these membranes suffer from H_2 embrittlement cracking during thermal cycling and surface contamination by sulphur-containing species. Moreover they are expensive so a cheaper solution is strongly needed.

Carbon molecular sieve membranes are becoming an alternative solution to the high costs of Pd-Ag membranes. Carbon membranes, which composed of microporous, amorphous high-carbon materials, have emerged as promising materials for the gas separation applications because of their characteristics such as superior thermal resistance, chemical stability in corrosive environments, high gas permeance, and excellent selectivity compared to available polymeric membranes. They have been proved to be very effective for various applications, such as purification of gaseous blend, dehydration of fine chemical products and natural gas processing in order to replace the other traditional processes for the purpose of cost and energy saving [1]. So far, polymer-based membranes are among the most popular material used in the industries, but in many cases, their poor temperature and chemical stabilities greatly limit their applications, and the demands for the inorganic gas-permselective membranes are increasing. Through adsorption and molecular sieving mechanism, the carbon membranes are particularly useful in gas separation, and the excellent separation may be achieved even between gases with almost similar molecular size. However, they suffer greatly from low permeability and poor mechanical strength in industrial applications. The aim of this work is to compare the performance of Pd-Ag and carbon molecular sieve membranes at the same pressure.

3. SETUP

A schematic representation of the permeation setup is depicted in Figure 1. The membrane is sealed to the flange of the reactor and is located in the middle of the reactor. Process gases are fed to the shell side of the membrane. The permeate side is at atmospheric pressure when pure gas tests are performed and at vacuum conditions when tests with gas mixtures are carried out. The inlet of the retentate side is controlled through a back-pressure regulator (Bronkhorst). The reactor is placed in an electrically heated oven, where the membrane and the process gases are heated to the operating temperature. Two thermocouples are located at the retentate side of the membrane to measure the temperature of the retentate. An acquisition and control system regulates the main process parameters, such as temperature and pressure, interfaced with a computer. Digital soap bubble flow meters (Horibastec) have been used for the pure gas measurements and a micro-GC from Agilent model 490 for analyzing the mixture to evaluate the hydrogen purity.

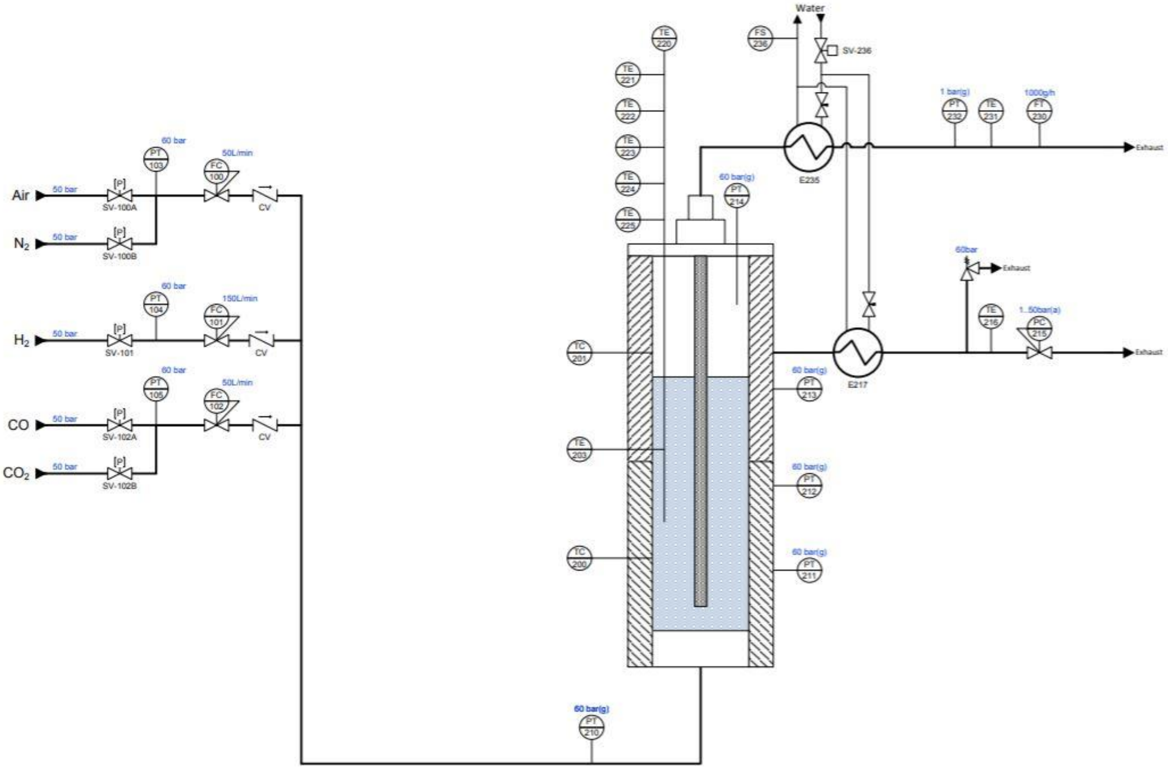


Figure 1 Schematic representation of the high permeation setup

The sealing of Pd-Ag membranes has been realized through graphite ferrules and Swagelok connectors [2], [3]. The sealing is checked for leakages, and if no leakages are detected, the membrane has been installed in the reactor and the N_2 permeation has been tested at room temperature to measure the membrane leakages at 10 bar. Afterward, when working with Pd-Ag membranes, the reactor was heated up to 400 °C with a rate of 2 °C/min under a nitrogen atmosphere to avoid embrittlement and possible pinhole formation [4]. The N_2 flow rate is measured during the heating of the reactor to detect possible leakages. Theoretically, if the leak points are between 2-50 nm, the N_2 permeation should decrease with increasing the temperature because of the Knudsen mechanism of permeation. Once the reactor reaches the desired temperature, the membrane is activated by feeding the reactor with air at atmospheric pressure for 2-3 minutes. This step can increase the permeance with 25-90% compared to non-activated membranes, because the impurities present on the surface of the Pd layer (due to the chemicals used during membrane preparation) are burned off in the presence of oxygen.

Finally, the set-up is left under a hydrogen atmosphere until the permeance becomes steady. This operation could last some hours up to a few days, depending on the type of membrane.

When the H_2 permeation rate has become stable, hydrogen and nitrogen permeation tests are performed under pure hydrogen and a pure nitrogen environment. The permeate pressure is fixed at 1 bar (atmospheric pressure), except for the vacuum case, in which 150 mbar has been used, while the retentate pressure has been varied between 8 and 40 bar. The temperature of the reactor is changed between 380 and 480 °C. When working with carbon membranes, the reactor is kept at 20 °C. In case of pure gas tests, atmospheric pressure is applied to the permeate side [5].

4. MEMBRANE TESTS

4.1. Pure gas tests

The sealing of Pd-Ag membranes have been realized through graphite ferrules and Swagelok connectors [2][6]. The sealing is checked, and if no leakages are detected, the membrane has been installed in the reactor and the N_2 permeation has been tested at room temperature to measure the membrane leakages at 10 bar. Afterward, when working with Pd-Ag membranes, the reactor was heated up to 400 °C with a step of 2 °C/min under a nitrogen atmosphere to avoid embrittlement and possible pinhole formation [4]. The N_2 is measured during the heating of the reactor to detect leaks. Theoretically, if the leak points are between 2-50 nm, the N_2 permeation should decrease with increasing the temperature because of Knudsen mechanism of permeation. Once the reactor reaches the desired temperature, the membrane is activated by feeding the reactor with air at atmospheric pressure for 2-3 minutes. This step can increase the permeance with 25-90% compared to non-activated membranes because the impurities present on the surface of the Pd layer (due to the chemicals used during membrane preparation) are burned off in presence of oxygen.

Finally, the set-up is left under hydrogen atmosphere until the permeance is steady. This operation could last some hours up to a few days, depending on the different types of membranes.

When the H_2 permeation is stable, hydrogen and nitrogen permeation tests are performed under pure hydrogen environment and a pure nitrogen environment. The permeate pressure is fixed at 1 bar (atmospheric pressure), except for the vacuum case in which 150 mbar has been used, while the retentate pressure was 8 bar. The temperature of the reactor is changed between 380 and 480 °C.

When working with carbon membranes, the reactor is kept at 20 °C. In case of pure gas tests, atmospheric pressure is applied in the permeate side [7].

4.2. Mixture tests

H_2-CH_4 mixture tests have been carried out as a function of the hydrogen molar fraction in the feed and of the pressure at the retentate side. The inlet hydrogen mole fraction is varied between 10 and 50%, while the total retentate pressure is 8 bar. Vacuum is applied in the permeate side with a pressure of 150 mbar. The purity of the permeated hydrogen is measured for all the experiments with a micro GC.

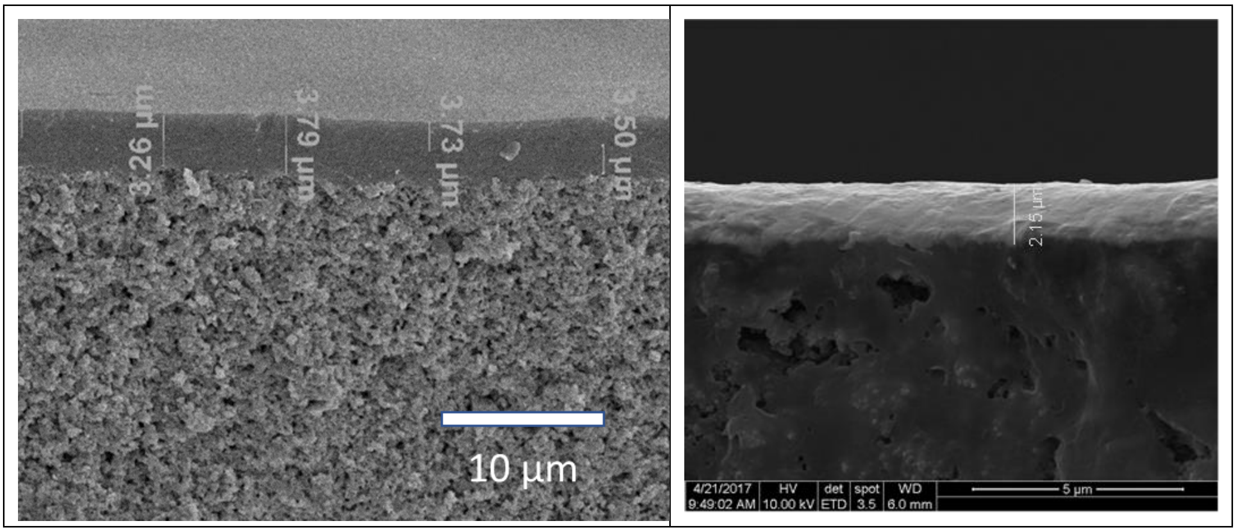
The main aim of the experimental tests is to compare the hydrogen flux obtained from Pd-Ag and CMS membranes for a proper estimation of the required membrane area and thus the costs to separate the same amount of hydrogen with a Pd-Ag or a CMS membrane. Indeed, the experimental results in the presence of gas mixtures, have been used to validate a model for the description of the membrane behaviour at different pressures and hydrogen concentrations.

5. RESULTS

The measured hydrogen permeance and ideal perm-selectivity for each membrane are listed in Table 1, while in Figure 2 the membrane thickness is shown through scanning electron microscopy analysis. According to the results, Membrane Pd3 has a high hydrogen permeance and a lower selectivity due to the thinner membrane layer, as shown in Table 1 Pd2DS has a high permeance and an extremely high selectivity for a ceramic supported Pd-Ag membrane. The ceramic layer covers the defects that are present in the very thin Pd layer. The difference in hydrogen pure gas permeance is quite remarkable between Pd-Ag membranes, which is in the order of 10^{-6} mol/s/m^2/Pa, and carbon molecular sieve membranes of 10^{-8} mol/s/m^2/Pa. The reason is due to their different permeation mechanisms. In the case of Pd membranes, hydrogen molecules react selectively with palladium metal producing hydrogen atoms (Pd acts as catalyst for the splitting) which cross the membrane due to the difference in the partial pressure of hydrogen on both sides of the membrane [8].

The transport mechanism for carbon molecular sieve membranes takes place according to one of three mechanisms [9]–[11]: Knudsen diffusion dominates for the largest pores, molecular sieving for the smallest. Molecular sieving is often referred to as a configurational diffusion, and it is an activated diffusion like surface selective flow. For Knudsen diffusion to take place, the lower limit for the pore diameter is usually set to d > 20 Å. However, it has recently been discussed how Knudsen diffusion may contribute to transport even in smaller pores [12]. The driving force for separation according to a selective surface diffusion is basically the difference in the concentration of the adsorbed phase of the diffusing components. This means that a large driving force can be attained even with a small partial pressure difference for the permeating component. Molecular sieving is the dominating transport mechanism where carbon membranes are applied; the pore size is usually within the range between 3-5 Å.

It is worth noting the remarkable difference in selectivity between Pd1 and Pd3 which are both Pd-Ag membranes with a different Pd layer thickness. Indeed, Pd3 shows a higher hydrogen permeance compared to Pd1 and Pd2DS. The hydrogen selectivity of CMSM1 and CMSM2 are lower than Pd-Ag membranes because the carbon membrane layer is porous, enabling the contaminant gas to permeate in case the molecule diameter is smaller than the membrane pore size and also because of the difference in temperature of permeation, 400 and 20 °C, respectively (in Pd membranes, the selectivity decreases with the temperature).



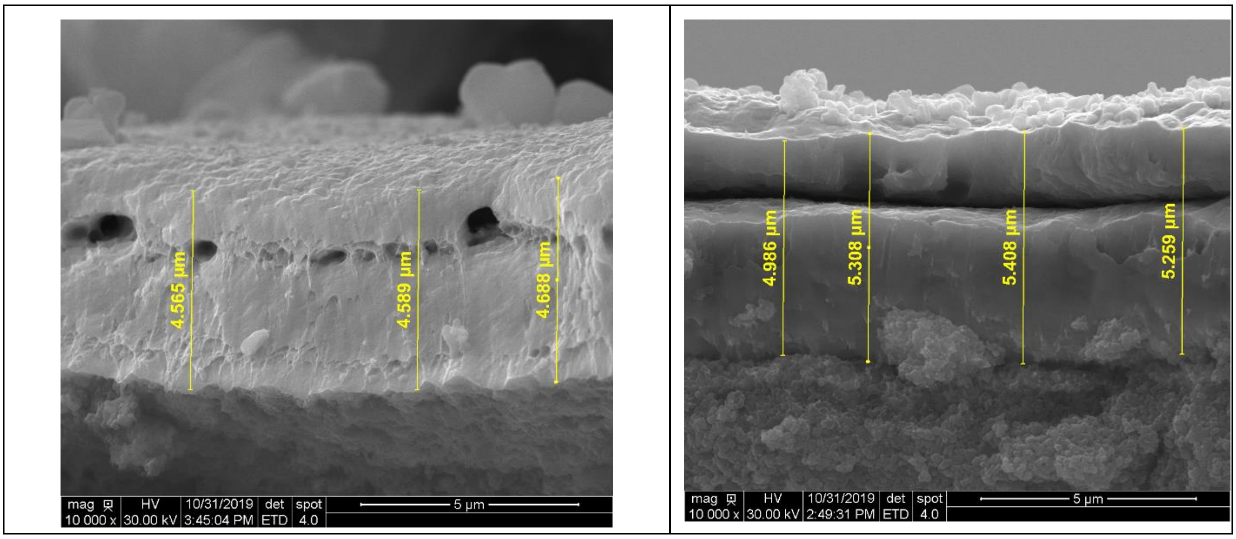


Figure 2. Scanning electron microscopy CMSM1 on the left top side, Pd3 on the right top side, Pd1 on the bottom right side and Pd2DS on the bottom left side

Table 1 Characteristics of the membranes tested

Membrane code	Membrane type	H_2 permeance [mol/s/m^2/Pa]	Pressure exponent [-]	H_2 selectivity [-]
Pd1	Pd-Ag	$1.18 \cdot 10^{-6}$	0.66	24300
Pd2DS	Pd-Ag	$1.35 \cdot 10^{-6}$	0.63	65200
Pd3	Pd-Ag	$4.36 \cdot 10^{-6}$	0.58	4280
CMSM1	CMSM	$7.02 \cdot 10^{-8}$	1	527
CMSM2	CMSM	$5.23 \cdot 10^{-8}$	1	1020

It is worth noting the remarkable difference in selectivity between Pd1 and Pd3 which are both Pd-Ag membranes with a different Pd layer thickness. Indeed, Pd3 shows higher hydrogen permeance compared to Pd1 and Pd2DS. The hydrogen selectivity of CMSM 1 and 2 are lower than Pd-Ag membranes because the carbon membrane layer is porous, enabling the contaminant gas to permeate in case the molecule diameter is smaller than the membrane pore size and also to the temperature of permeation 400 and 30 °C respectively (in Pd membranes, the selectivity decreases with the temperature).
Those membranes have been tested at 8 bar in presence of H_2-CH_4 mixture to study the hydrogen flux and purity. Experimental tests with Pd-Ag membranes have been performed at 400 °C, while for CMSM at 20 °C. The results are depicted in Figure 2. Pd1and Pd2DS show better performance in terms of purity and flux compared to CMSM1 and CMSM2. On the other hand, CMSM1 and CMSM2 have higher purity than Pd3 which is the ultra-thin Pd-Ag membrane.

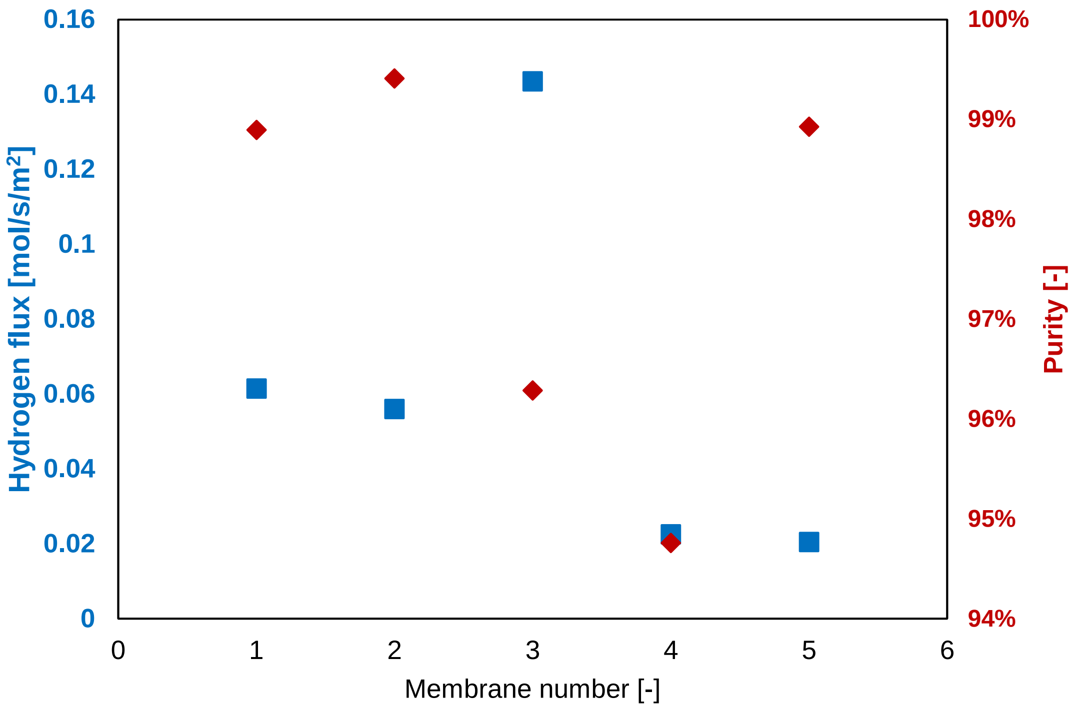


Figure 3 Comparison between Pd1, Pd2DS, Pd3, CMSM1 and CMSM2 in presence of H_2-CH_4 mixture at 8 bar

A techno-economic evaluation is required to properly choose the membrane which optimize the hydrogen purity and the final separation cost. This evaluation is provided in D8.5.

6. CONCLUSIONS

Three supported Pd-Ag membranes (thin, double skin and ultra-thin) and two Al-CMSM have been investigated for the separation of hydrogen from blends in the natural gas grids.
Hydrogen permeation measurements with 10% H_2 - 90% CH_4 were performed at 400 °C for Pd-Ag membranes and 20 °C for carbon molecular sieve membranes to compare the hydrogen flux and purity. When working at low pressures, Pd-Ag membranes are performing better than CMSM. It is interesting to perform experimental tests at higher pressures and evaluate the separation costs to further understand the convenience of Pd-Ag or CMS membranes.

7. REFERENCES

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