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 (3 pages max. all points)

1.1. Description of the deliverable content and purpose

This document aims to describe the high pressure setup built in Tue university of Eindhoven for the experimental tests with membranes. The setup has been debugged and the membrane has been tested up to 15bar.

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 and due to the low temperatures at which the second one needs to work. 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

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

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. MEMBRANE 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.

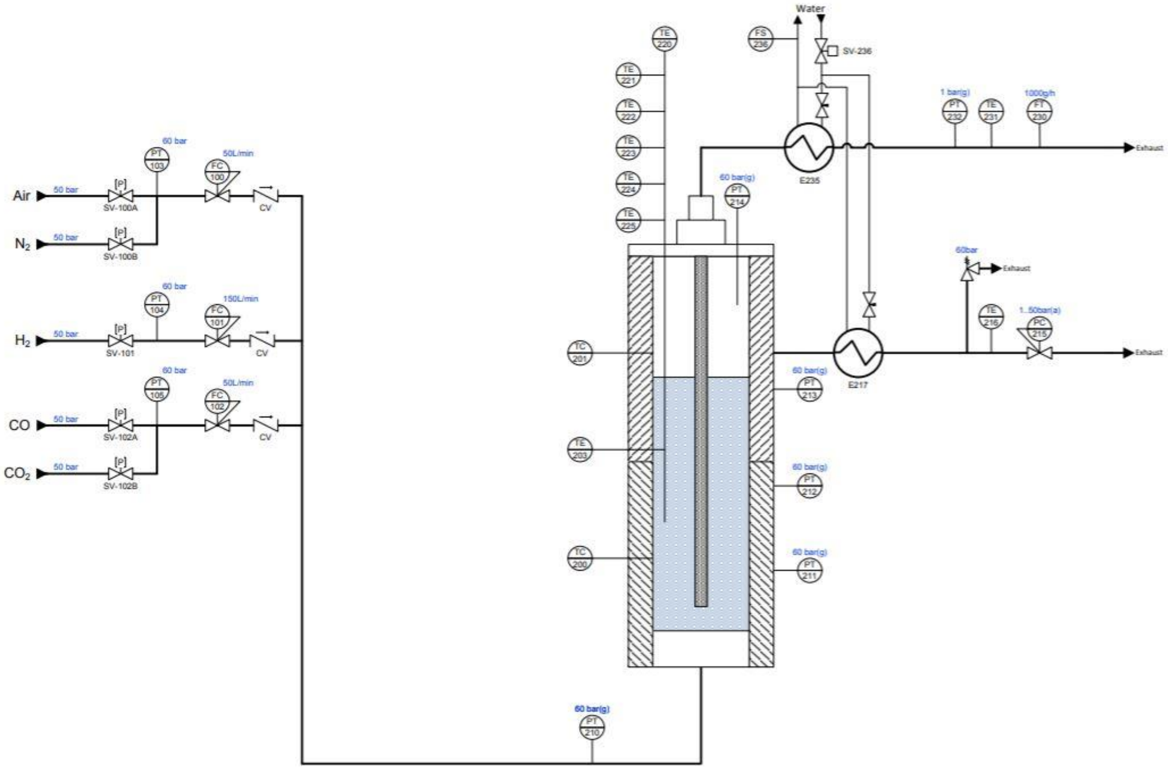


Figure 1 Schematic representation of the high permeation setup

4. MEMBRANE TESTS

4.1. Pure gas tests

The sealing of Pd-Ag membranes have been realized through graphite ferrules and Swagelok connectors [1][2]. 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 [3]. 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 [4].

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 [5].

The transport mechanism for carbon molecular sieve membranes takes place according to one of three mechanisms [6]–[8]: 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 [9]. 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).

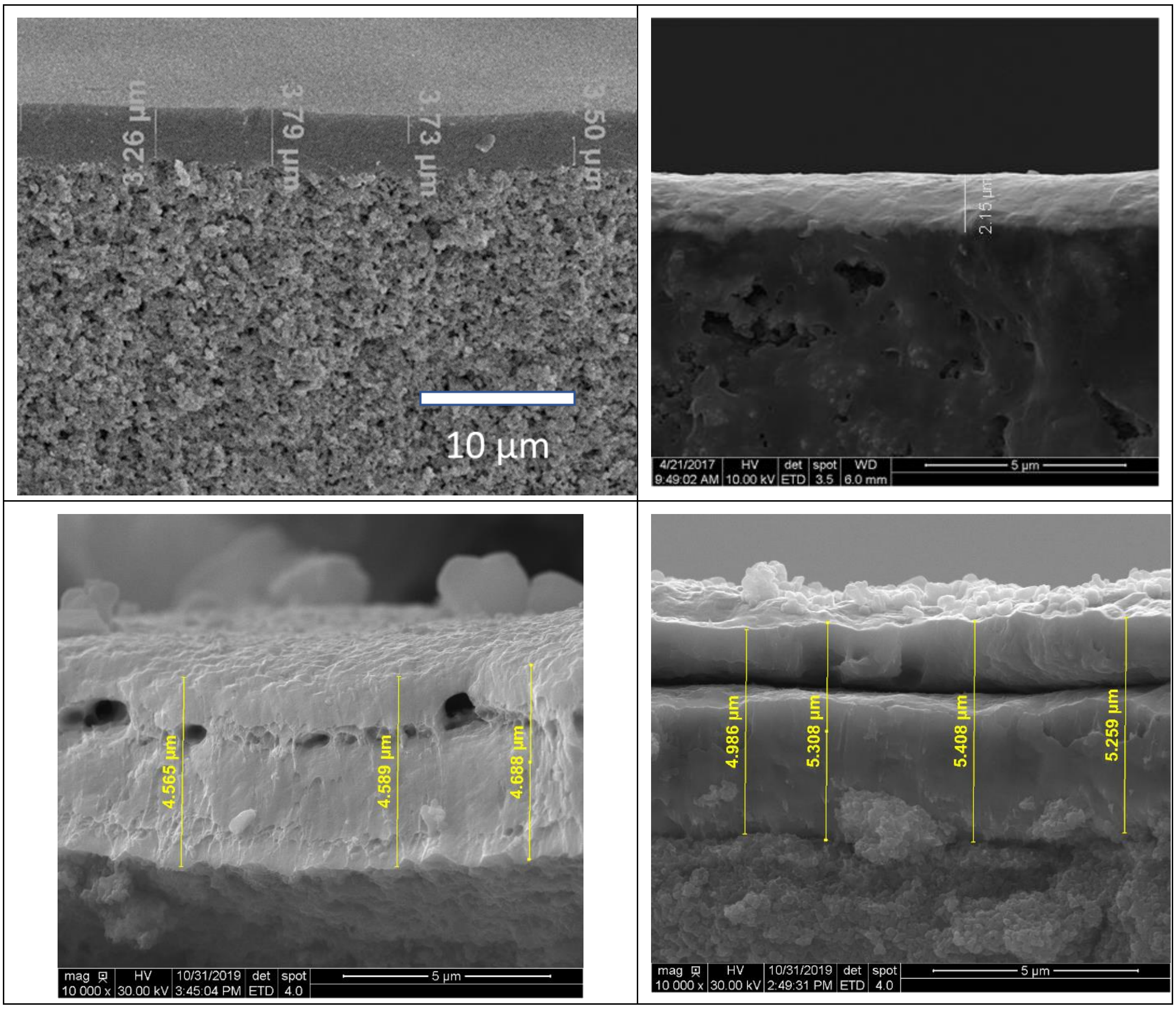


Figure 2. Scanning electron microscopy CMSM1 on the left top side, Pd3 on the right top side, Pd1 on the bottom right side and Pd2DS on the bottom left side

Table 1 Hydrogen permeance, at 400 °C for Pd-Ag and 20 C for CMSM and 1 bar pressure difference, and selectivity for the membranes tested

Membrane code	Membrane type	H_2 permeance [mol/s/m^2/Pa]	Pressure exponent [-]	H_2 selectivity [-]
Pd1	Pd-Ag	$1.18\cdot10^{-6}$	0.66	24300
Pd2DS	Pd-Ag	$1.35\cdot10^{-6}$	0.63	65200
Pd3	Pd-Ag	$4.36\cdot10^{-6}$	0.58	4280
CMSM1	CMSM	$7.02\cdot10^{-8}$	1	527
CMSM2	CMSM	$5.23\cdot10^{-8}$	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).

Figure 3 shows the hydrogen flow rate of Membrane CMSM1 at different hydrogen partial pressure difference with hydrogen concentration from 5 to 100% at the inlet side for a H_2-CH_4 mixture. Vacuum has been applied to the permeate side. According to the results, no mass transfer limitation is observed since at the same hydrogen partial pressure it is possible to recover the same hydrogen flow rate independently from the inlet hydrogen concentration. Carbon membranes do not suffer from mass transfer limitations because the membrane has a much lower hydrogen permeation compared to Pd-Ag membranes due to the different permeation mechanisms.

It is an interesting result, especially considering that it is well known from literature, that Pd-Ag membranes suffer from concentration polarization effects especially when working at very low inlet hydrogen content and high pressure [10], [11].

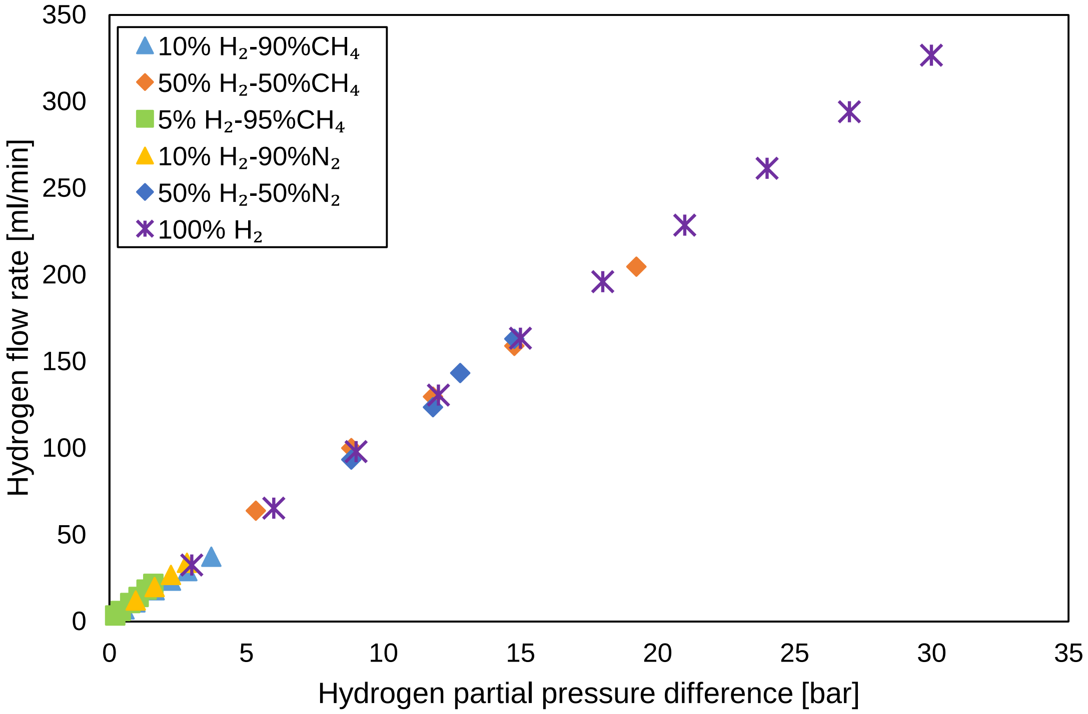


Figure 3. Hydrogen flow rate at different hydrogen partial pressure difference when working with different inlet hydrogen concentration with carbon molecular sieve CMSM 1 at a working temperature of 20 °C

Experimental hydrogen flow rates as a function of the partial pressure of H_2 performed with Pd2DS, have been reported in Figure 4. At lower inlet hydrogen concentrations more pronounced mass transfer limitations are observed, as expected. The differences between the value, obtained with pure gas and those obtained with gas mixtures becomes more relevant at 10% H_2 content which is the lowest hydrogen concentration tested. As observed in Figure 4, the pressure plays a negative role on the concentration polarization effect. Indeed, at higher total pressure difference, the mass transfer limitation increases due to the higher flow through the membrane and the higher recovery of hydrogen. These tests were performed for a H_2-CH_4 mixtures at 400 °C.

For a proper description of the Pd-Ag membrane behaviour when working with mixtures, a model which includes concentration polarization in the retentate side was developed and used. The equations of the model are described in our previous work [12]. The experimental results in the presence of the gas mixture of Figure 4, and in pure hydrogen at different temperatures, shown in Figure 5, have been used for the validation of the model. Figure 6 shows a comparison between the hydrogen flux measured in the experiments and the simulation results from the membrane model with and without mass transfer limitations. The continuous lines indicate the model results without mass transfer limitations, while the dotted lines represent the model results when accounting for concentration polarization. The lines are not linear as the model also computes the depletion of hydrogen along the membrane separator.

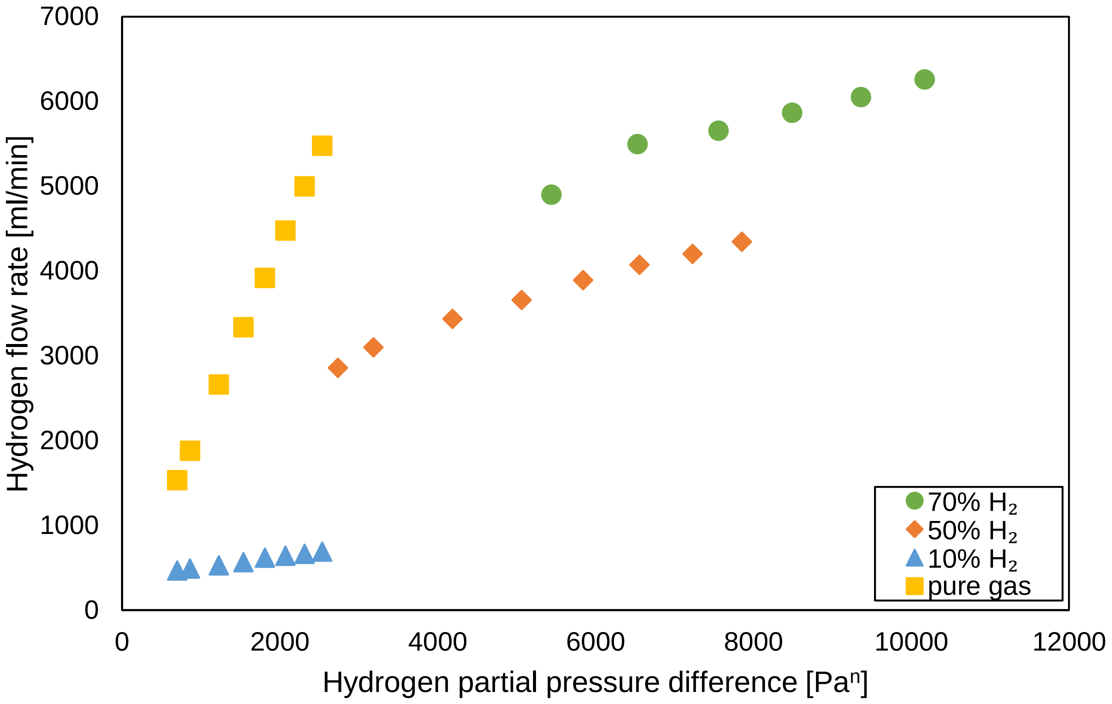


Figure 4. Hydrogen flow rate at different hydrogen partial pressure difference when working with different inlet hydrogen concentration in H_2 - CH_4 mixture with Pd2DS membrane at 400 °C

The results reported in Figure 6 clearly show that the concentration polarization is a very important phenomena that the model is able to capture, and thus the results in this case match very well with the experimental results. The model also well describes the hydrogen purity as shown in Figure 7, where the small deviations observed are attributed to the experimental error of the analytical instrument (GC).

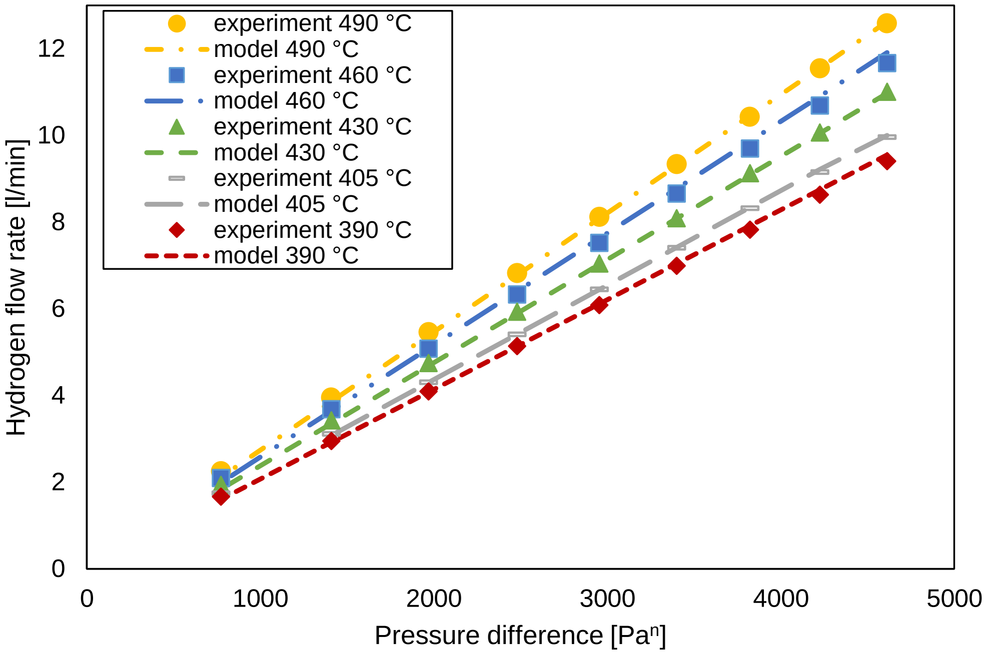


Figure 5. Comparison between experimental and modelled results in pure gas tests at different operating temperature with Pd2DS membrane

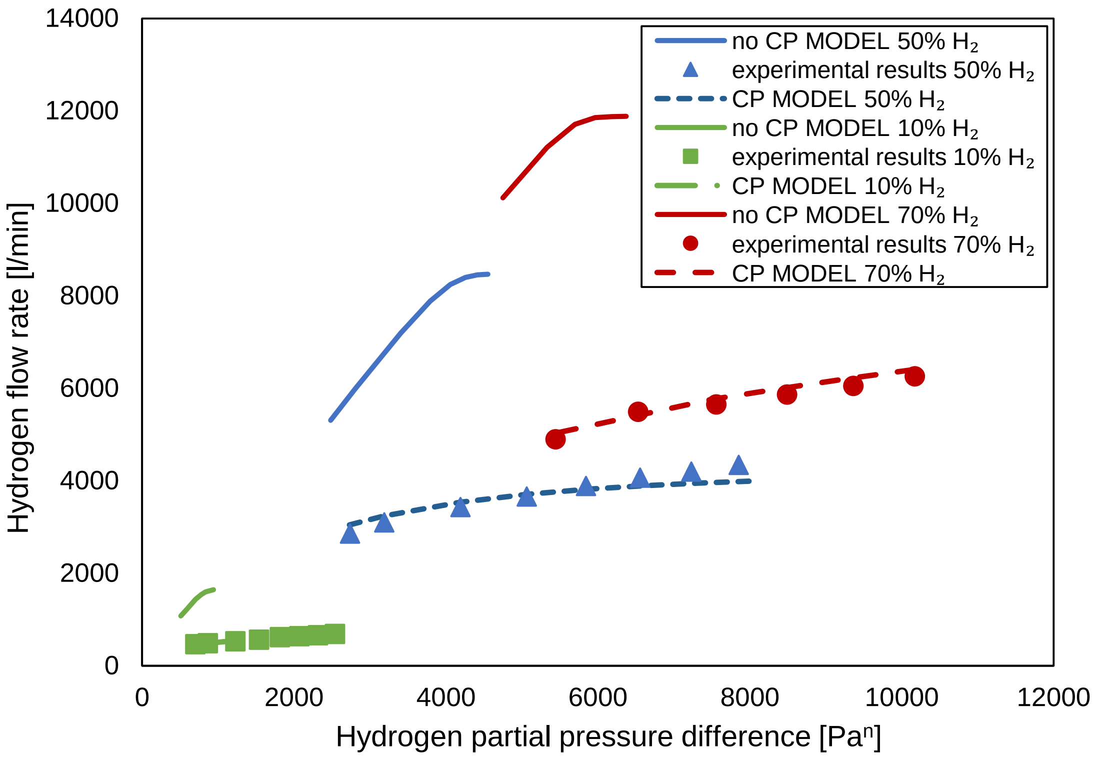


Figure 6. Comparison between hydrogen flux from experimental and modelled results in mixture tests at different hydrogen inlet content; continuous line to described ideal case and dotted line includes mass transfer limitation at a working temperature of 400 °C

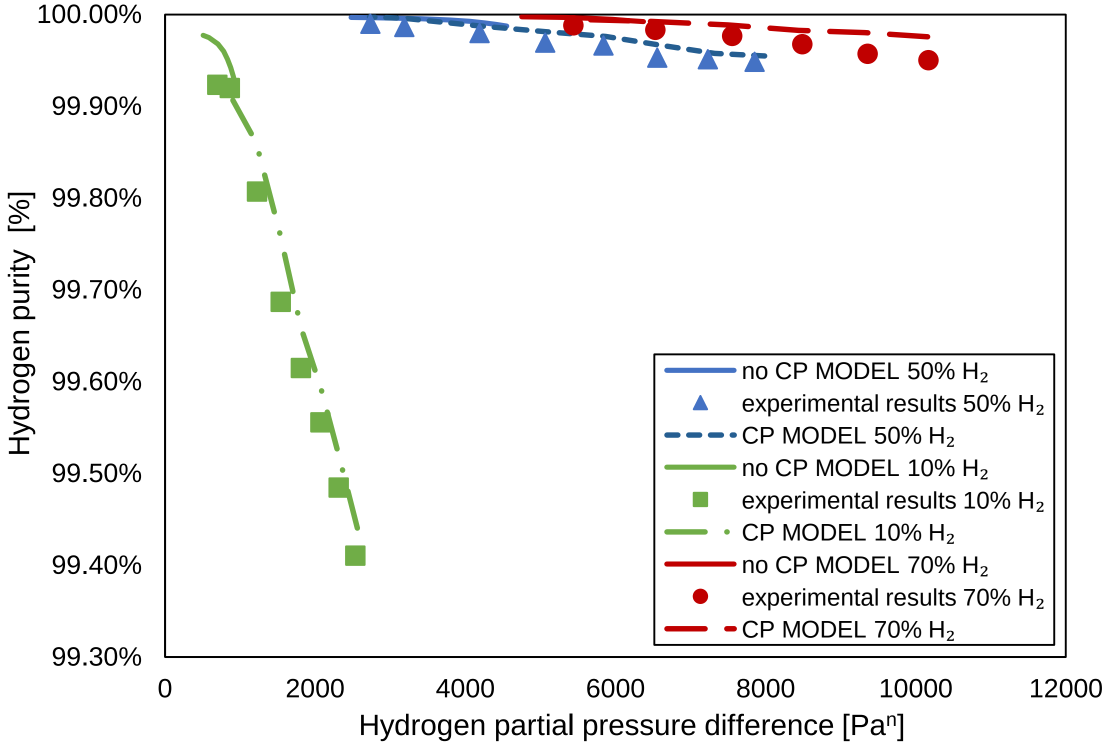


Figure 7. Comparison between hydrogen purity from experimental and modelled results in mixture tests at different hydrogen inlet content; continuous line to described ideal case and dotted line includes mass transfer limitation at a working temperature of 400 °C

In Figure 8, the hydrogen partial pressure profile at the bulk retentate and at the retentate membrane surface is depicted, for the simulation obtained with the model. A 10% H_2 - 90% CH_4 mixture at different pressures (40, 30 and 20 bar) was considered with the Pd2DS Membrane for the simulations. There is a relevant difference between the hydrogen partial pressure at the bulk and at the membrane surface, especially at higher retentate pressures. The retentate hydrogen partial pressure at the bulk represents the ideal pressure difference responsible for the expected driving force in case no mass transfer limitation is observed. On the other hand, the hydrogen partial pressure at the surface in the retentate side is the real driving force faced by the membrane. The relevant discrepancy observed can justify the decrease in hydrogen permeation observed in Figure 6 between the results from the ideal simulation and experiments.

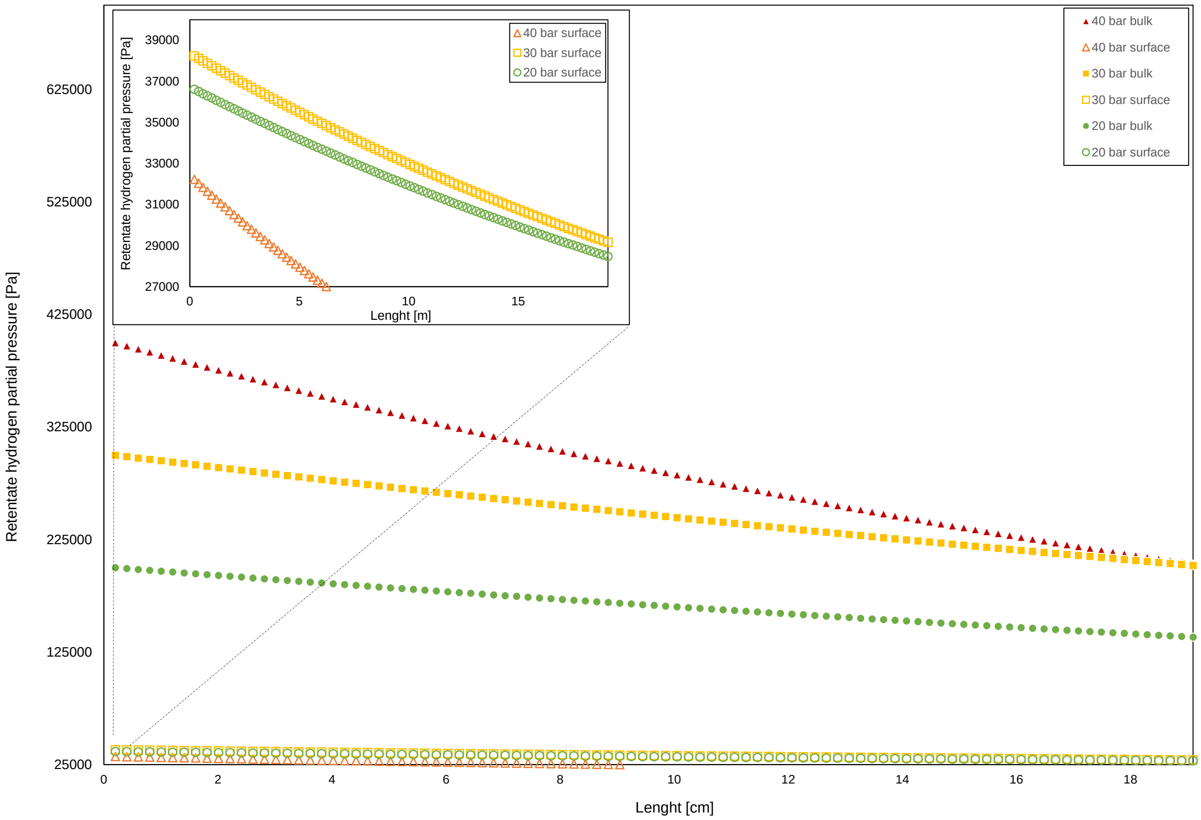
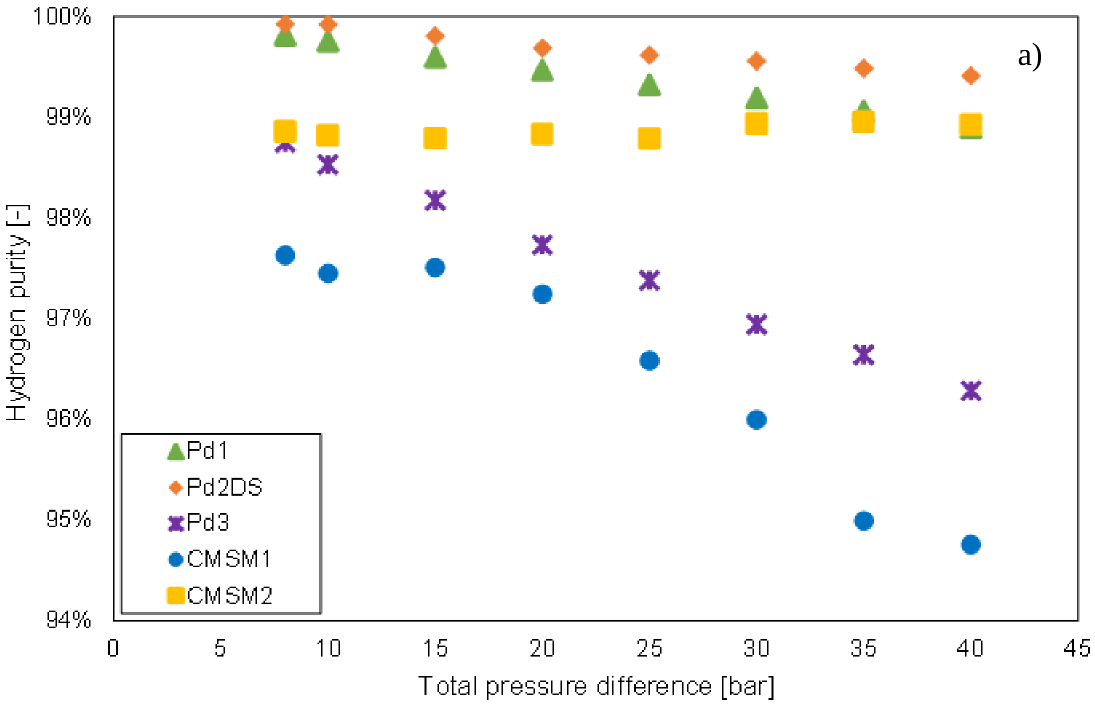


Figure 8. Hydrogen partial pressure profile at the bulk and at the surface at 40, 30 and 20 bar for a mixture of 10% H_2 – 90% CH_4 with Pd2DS membrane at 400 °C

H_2-CH_4 mixtures tests with 10 and 50% H_2 concentration in the feed were performed with the Pd-Ag and carbon molecular sieve membranes for a proper comparison of the hydrogen purity at a distinct pressure difference along the membrane. The retentate pressure was varied from 8 to 40 bar, while the permeate pressure has been kept at 150 mbar with a vacuum pump. The operating temperature, when working with Pd-Ag membrane, is 400 °C, while in case of carbon molecular sieve membranes 20 °C is considered.

In Figure 9 a), the results for 10% H_2 - 90% CH_4 in the inlet mixture is depicted for all the five membranes considered. Pd1 and Pd2DS show the highest hydrogen purity, respectively of 97.76% and 98.83%, as expected from the single gas tests reported in Table 1. The values of purity are remarkable, especially in the case of 10% hydrogen concentration at the inlet retentate. It is interesting to note the decrease in the hydrogen purity with increased pressure when Pd-Ag membranes are considered. This can be explained by the dependency of the permeation flux of hydrogen with pressure (around 0.6), and the flux of contaminants, which increases linearly with pressure through the sealings or pinholes.

At 40 bar in the retentate side, the CMSM2, shows the same hydrogen purity as Pd1, even if its H_2/N_2 selectivity in pure gas tests is remarkably lower (1200 vs 24000). Moreover, the trend of hydrogen purity of CMSM2 is almost constant with the pressure difference. The extremely high purity of CMSM is explained considering the membrane is saturated with water and no contaminant-gas adsorption takes place even at high pressure. Another important consideration is the lower purity results of Pd3, compared to CMSM2. On the other hand, CMSM1 shows even lower hydrogen purity compared to all the previous membranes and the purity decreases with the total pressure difference. It is evident the contaminant gas gets adsorbed on the membrane surface at very high pressure causing the purity to decrease. CMSM1 has been carbonized at 500 °C and has a higher content of amino groups; it is interesting to investigate the effect of the temperature of carbonization and the amount of nitrogen in the membrane on the permeation properties of the CMSM. Concluding, the CMSM seems competitive to Pd-Ag membranes when working at high pressure and low hydrogen content in the feed.



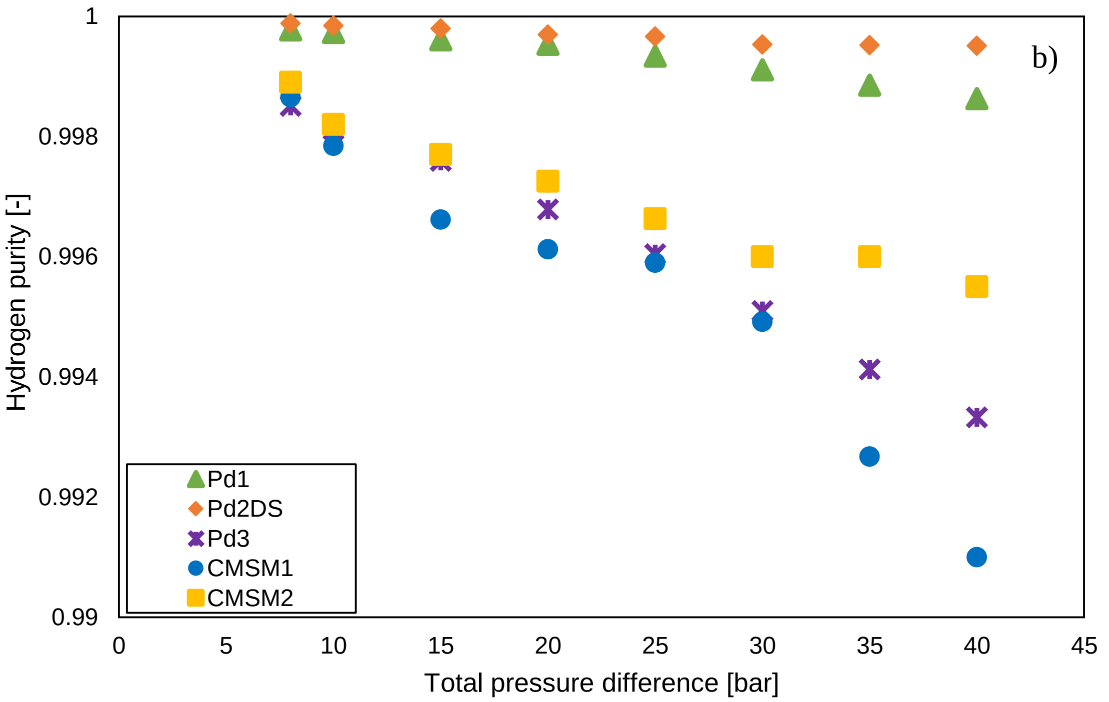


Figure 9 a). Hydrogen purity at different total pressure difference with Pd1, Pd2DS, Pd3, CMSM1 and CMSM2 with a mixture of 90% CH4 and 10% H_2 (Pd-Ag membranes 400 °C; CMSM 20 °C) b). Hydrogen purity at different total pressure difference with Pd1, Pd2DS, Pd3, CMSM1 and CMSM2 with a mixture of 50% CH4 and 50% H2 at 400 °C

The similar results are depicted in Figure 9 b) for a mixture of 50% H_2 - 50% CH_4 at different total pressure differences. Similar observations as described previously for the 10% H_2 content case can be made here for Pd1 and Pd2DS. The final purity is higher than the previous case because the initial mixture is richer in hydrogen. CMSM1 has a lower purity than Pd-Ag membranes. In terms of purity, CMSM are less competitive than Pd-Ag membranes when the separation involves higher hydrogen content in the feed.

The results confirm that carbon molecular sieve membranes become technically competitive with Pd-Ag membranes in specific conditions of purity and hydrogen content. The next sections will assess whether supported CMSM are also competitive with Pd-based membranes from an economic point of view.

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. Since the mechanism of permeation in both types of membranes is different, the effect of high pressure and composition of the binary gas on the permeation properties and cost of hydrogen production were analysed. Concentration polarization effect is observed with Pd-Ag membranes, especially at high pressure and low hydrogen content, while CMS membranes do not suffer from this effect. Indeed, no reduction in hydrogen permeance is shown between pure gas and mixture permeation tests with the latter membranes. A model accounting for concentration polarization has been validated with experimental results in pure gas and mixtures, to determine the membrane area needed in 10 and 50% H_2 mixtures to separate 25 kg/day of hydrogen.

Hydrogen permeation measurements with 10% H_2 - 90% CH_4 and 50% H_2 - 50% CH_4 mixtures were performed at 400 °C for Pd-Ag membranes and 20 °C for carbon molecular sieve membranes to compare the hydrogen permeance and purity. For the case of lower hydrogen content, very high purities are reached with the more selective carbon molecular sieve membrane, being the preferred strategy when working at high pressures (> 30 bar).

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