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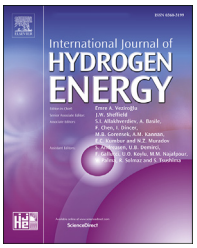

# Comparison between carbon molecular sieve and Pd-Ag membranes in $H_2$-$CH_4$ separation at high pressure

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## HIGHLIGHTS

- Three supported Pd−Ag and two Al-CMSM membranes have been compared.
- A model accounting for concentration polarization has been validated with experimental results.
- the final cost to separate 25 kg/day of hydrogen has been calculated.
- A sensitivity analysis has also been performed for a complete economic evaluation.

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## ABSTRACT

From a permeability and selectivity perspective, supported thin-film Pd−Ag membranes are the best candidates for high-purity hydrogen recovery for methane-hydrogen mixtures from the natural gas grid. However, the high hydrogen flux also results in induced bulk-to-membrane mass transfer limitations (concentration polarization) especially when working at low hydrogen concentration and high pressure, which further reduces the hydrogen permeance in the presence of mixtures. Additionally, Pd is a precious metal and its price is lately increasing dramatically. The use of inexpensive CMSM could become a promising alternative. In this manuscript, a detailed comparison between these two membrane technologies, operating under the same working pressure and mixtures, is presented.

First, the permeation properties of CMSM and Pd−Ag membranes are compared in terms of permeance and purity, and subsequently, making use of this experimental investigation, an economic evaluation including capital and variable costs has been performed for a separation system to recover 25 kg/day of hydrogen from a methane-hydrogen mixture. To widen the perspective, also a sensitivity analysis by changing the pressure difference, membrane lifetime, membrane support cost and cost of Pd/Ag membrane recovery has been considered. The results show that at high pressure the use of CMSM is to more economic than the Pd-based membranes at the same recovery and similar purity.

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## Introduction

Currently, environmental concerns regarding climate change are driving the world towards the search of clean and sustainable energy sources. In this scenario, hydrogen has a great potential to become a key factor in the operation and design of future energy systems. As a fuel and as an energy carrier, the use of hydrogen holds multiple benefits including carbon-free emissions when oxidized (water), the possibility of being produced from different feedstocks (fossil fuels, natural gas, coal, biomass, water) and versatile methods of transport and storage [1]. However, the production of high-quality hydrogen streams requires purification of hydrogen from gas mixtures. In this context, membrane technology has shown up as a promising option to conventional separation technologies (cryogenic distillation and adsorption) offering advantages in terms of energy efficiency, small process footprint and low environmental impact [2].

This work was carried out under the European project HyGrid (flexible hybrid separation system for hydrogen recovery from natural gas grids). The key objective of the HyGrid project is the design, scale-up and demonstration at industrially relevant conditions a novel membrane based hybrid technology for the direct separation of hydrogen from natural gas grids. The idea behind the project is the possibility to take advantage of the wide natural gas grid infrastructure to store and distribute hydrogen present in low concentration blended gas. Then, at the end-users one would separate the hydrogen using various techniques, among the membranes.

The choice of the membrane type to be used in a membrane module must consider both performance and costs. 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 at low temperatures and high pressure as well as surface contamination by sulphur-containing species, requiring cleaning steps of the feed gas and high temperature during separation. Studies over the past decades has shown that the resistance towards the Pd4S formation can be improved by alloying with Au, however, de Nooijer et al. [3] demonstrated it is not sufficient to limit the effects of inhibition and structural changes of the membrane. Furthermore, Pd is an expensive noble metal, which encourages the search for cheaper solutions.

Carbon molecular sieve membranes (CMSM) are becoming an alternative to the high costs of Pd–Ag membranes due to their much lower costs and the fact that they can operate at low temperatures, where Pd–Ag membranes suffer from instabilities or low permeabilities. CMSM, 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, lower cost and proven stability at high feed pressures (up to 69 bar) [4–7].

The properties of CMSM are affected by many factors, such as carbonization temperature history, gas atmosphere and pre- or post-treatments. In addition, one of the most important factors to obtain high performance CMSM is the choice of the precursor. CMSM based on polyimide [8], phenolic resin [9], polyfurfuryl alcohol [10] and cellulose [11], have been previously reported. Phenolic resins are desirable precursors to prepare CMSMs, since they present the advantage of being inexpensive and possess high carbon yield [9], withstanding elevated temperatures without losing their shape. They are very stable, with a high glass transition temperature, decomposing before achieving their melting point, assuring this way a resultant defect-free carbon structure. Phenolic resins are the product of the poly-condensation reaction of phenol with formaldehyde; their structure and properties depend on the formaldehyde/phenol ratio (F/P), catalyst, pH and temperature. There are two forms of phenolic resins: resol and Novolac. Resol resins are the product of basic catalysis in excess of formaldehyde (F/P > 1). Resol resins are not stable because the polymerization reaction continues with the time due to the presence of reactive methylol groups in the resin and their properties will depend on the basic catalysts used during their preparation. Novolac resins are obtained in acidic media and the amount of formaldehyde is lower, usually with an F/P of ca. 0.75–0.85. Novolac resins have no reactive methylol groups in their molecules and therefore, without hardening groups, are incapable of condense with other molecules on heating; to complete the condensation reaction, it is necessary to add formaldehyde and/or amine to achieve the cross-linking. The phenolic resins have the hydroxyl group that makes the membrane hydrophilic. The CMSM of this work was prepared from Novolac resin and nanoparticles of boehmite (precursor of alumina) were added before carbonization, enhancing the hydrophilicity.

Through adsorption and molecular sieving mechanisms, the CMSMs are particularly useful in gas separation, and separation can be achieved even between gases with almost similar molecular size. However, in comparison with Pd-based membranes CMSMs suffer greatly from relatively low permeance. A number of studies on hydrogen separation with CMSM have been addressed in literature. Shusen et al. [12] reported the preparation of asymmetric CMSMs from the pyrolysis of thin self-supporting films of a thermosetting phenol-formaldehyde resin (50–100 μm average thickness) followed by controlled oxidation of only one side of the film. Separation factors of 23.6 and 10.6 (based on single gas permeation studies) for the $H_2/N_2$ and $O_2/N_2$ gas pairs were reported at ambient temperatures. In 1994, Jones and Koros [13] prepared

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hollow fiber carbon membranes based on polyimide precursors with good productivity for air separation. In the following years several other researchers continued using polyimides to further understand the heat treatment parameters and improving the performances of CMSM. Good results concerning other separations $H_2/N_2$, $He/N_2$, $CO_2/N_2$ were also obtained with this type of precursor [4].

Therefore, this manuscript aims to compare and discuss the advantages/disadvantages of CMSM compared to Pd–Ag membranes from a performance and economic point of view for the separation of $H_2$ from $H_2$–$CH_4$ mixtures. The techno-economic analysis is performed at different operating temperatures because the idea is to compare two different membrane types at similar hydrogen purity. Indeed at the same operating temperature of Pd–Ag membrane, the CMSMs have lower hydrogen selectivity. Therefore at the same temperature, the hydrogen separation cost would be extremely lower for CMSM compare to the considered operating temperature but the separation system would not be efficient.

In this manuscript, an in-depth analysis of the behaviour of composite alumina-CMSM and supported thin-film Pd–Ag membranes operating at high pressure in a mixture containing hydrogen is presented. First, the influence of concentration polarization on the Pd–Ag membranes and the Al-CMSMs has been studied at different hydrogen feed concentrations. Subsequently, based on these experimental results, an economic evaluation has been carried out calculating the costs to separate hydrogen from a $H_2$–$CH_4$ mixture for a membrane module with a capacity of 25 kg/day when integrating Pd–Ag or molecular sieve membranes.

## Experimental

### *Membranes*

#### *Pd–Ag membranes*

Asymmetric tubular alumina supports with an inner diameter of 7 mm and with a selective layer on the outside (O.D. 14 mm and 10 mm) were provided by Rauschert Kloster Veilsdorf and used for both Pd–Ag membranes and CMSMs.

Three Pd–Ag selective membranes were deposited onto 500 mm long, 14 mm diameter modified alumina tubes with an outside pore size of 100 nm using the simultaneous (Pd and Ag) electroless plating technique already reported [14]. For these membranes, different plating times were set to obtain different selective layer thicknesses and thereby different permeation properties. Indeed, Pd1 and Pd2DS were prepared with a 5 h deposition process, while Pd3 was prepared with 2 h deposition. After the co-deposition step, the metallic layers were annealed at 550 °C for 4 h by exposing the membrane to a 10% $H_2$/90% $N_2$ gas mixture, as reported in [15]. One of the prepared Pd–Ag membranes was turned into a double-skin membrane following the procedure described by Arratibel et al. [16]. Pd3 is an ultra-thin Pd–Ag ceramic supported membrane.

#### *CMSMs*

The CMSMs were prepared on alumina supports of 10 mm diameter with 200 nm pore size by the method of one dip-dry-carbonization step, reported before [17,18]. The composition of the dipping solution was: NNovolac resin (13 wt%), formaldehyde (2.4 wt%), ethylenediamine (0.4 wt%), boehmite (as precursor of alumina 0.8 wt%) in N-methyl-2-pyrrolidone (NMP). CMSM1 and CMSM2 were carbonized at 550 °C and 600 °C, respectively, under $N_2$ using a heating rate of 5 °C/min until 100 °C and 1 °C/min to reach the carbonization temperature.

To perform the experimental tests in the presence of $H_2$–$CH_4$ mixtures, the three Pd–Ag membranes (one of them as a double-skin configuration) and two CMSMs were cut and sealed using Swagelok® connectors and graphite ferrules, following the procedure previously reported in [19] and also proven in several further works [20,21].

For further references, membrane coded as Pd1 and Pd3 are Pd–Ag ceramic supported membranes. Pd2DS is a double-skin Pd–Ag ceramic supported membrane, while CMSM1 and CMSM2 are CMSM. In Table 1 a more detailed description of the membranes is provided in terms of length, membrane layer thickness, support size and type.

One of the main properties of these membranes is the functionality, which comes from the polymer precursor. Hydroxyl and unsaturated groups are the main groups that are expected to be present in the membranes.

Fourier Transformed Infrared Spectroscopy (FTIR) is a powerful tool for both qualitative and quantitative analysis of molecule bonds. Moreover, the use of FTIR for carbon membrane analysis has been reported by several authors previously in the open literature [18,22,23].

FTIR is a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas (in this case the sample is solid). The difference between FTIR and a dispersive spectrometer is that FTIR collects high-spectral-resolution data over a wide range, whereas a dispersive spectrometer measures the intensity over a narrow range of wavelengths at a time. This results in a better quantitative accuracy of the FTIR. This technique allows quantifying the bonds present in the sample. Specifically, hydroxyl groups, insaturations, and carbonyl groups are the functionalities expected to be present in the samples. Experiments are carried out using an Agilent Cary 630 FTIR with a ZnSe Diffuse module for powder samples analysis. The membrane layers are previously ground and then diluted with KBr powder. The resulting mixture contains 5% (w/w) of carbon membrane material.

The final plots are obtained by subtracting the KBr spectrum to the diluted samples, normalizing the signal intensity for all plots and, finally, converting the absorbance into transmittance.

### *Permeation setup*

A schematic representation of the permeation setup is depicted in Fig. 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

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**Table 1 – Membranes parameters.**

| Membrane code | Membrane type | Length [mm] | Support size OD/ID [mm] | Layer thickness [μm] |
|---|---|---|---|---|
| Pd1 | Pd–Ag | 220 | 14/7 | 4–5 |
| Pd2DS | Pd–Ag DS | 191 | 14/7 | 4–5 |
| Pd3 | Pd–Ag | 90 | 14/7 | 2–3 |
| CMSM1 | CMSM | 130 | 10/7 | 3.5 |
| CMSM 2 | CMSM | 145 | 10/7 | 4.2 |

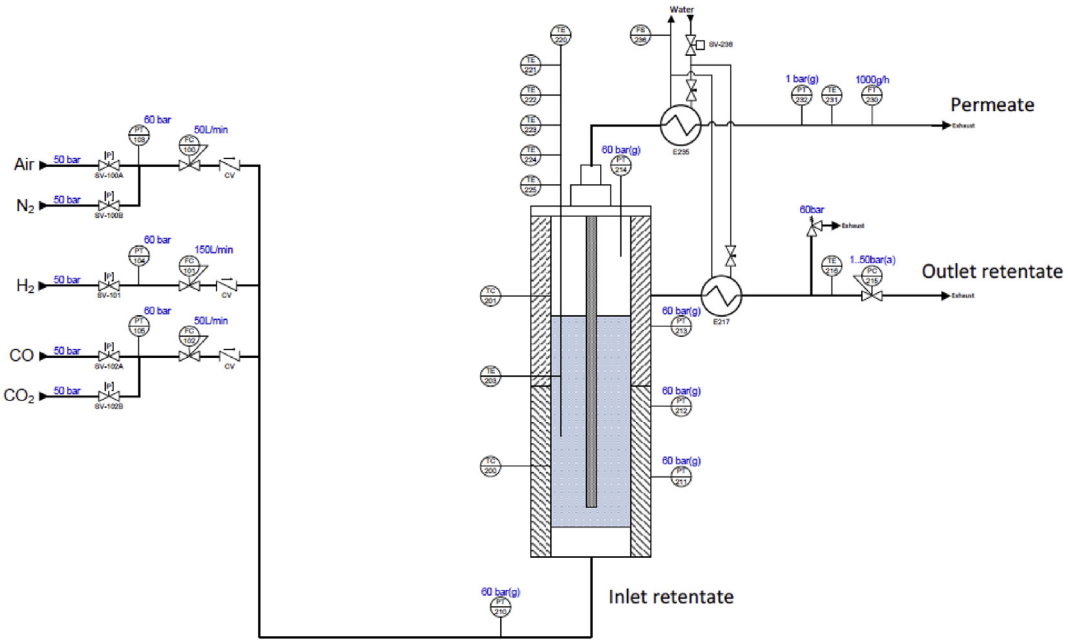


**Fig. 1 – Schematic representation of the high permeation setup.**

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.

### *Pure gas tests*

The sealing of Pd–Ag membranes have been realized through graphite ferrules and Swagelok connectors [24,25]. 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 [26]. The $N_2$ is measured during the heating of the reactor to detect leaks. Once the reactor reaches the desired temperature, the membrane is activated by feeding the reactor with air at atmospheric pressure for 2–3 min. 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 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 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 the case of pure gas tests, atmospheric pressure is applied in the permeate side [17].

### *Mixture tests*

$H_2$–$CH_4$ mixture tests have been carried out as a function of the hydrogen molar fraction in the feed and the pressure at the retentate side. The inlet hydrogen mole fraction is varied between 10 and 50%, while the total retentate pressure is changed from 8 to 40 bar. Vacuum is applied in the permeate

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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.

## Results and discussion

### *Membranes performance*

The measured hydrogen permeance and ideal perm-selectivity for each membrane are listed in Table 2, while in Fig. 2a 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 2. Pd2DS has a high permeance and an extremely high selectivity for a ceramic supported Pd–Ag membrane. The ceramic layer, deposited on top of the Pd 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 CMSM of $10^{-8}$ mol/s/m$^2$/Pa. The reason is due to their different permeation mechanisms and different operating temperatures. In the case of Pd membranes, hydrogen molecules react selectively with palladium metal producing hydrogen atoms (Pd acts as a catalyst for the splitting) which cross the membrane due to the difference in the partial pressure of hydrogen on both sides of the membrane [27]. The transport mechanism for CMSM takes place according to one of three mechanisms [18,28,29]: Knudsen diffusion dominates for the largest pores, molecular sieving for the smallest. (i) Molecular sieving is often referred to as a configurational diffusion, and it is an activated diffusion like surface selective flow. (ii) 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 [30]. (iii) The driving force for separation according to a selective surface diffusion is 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 and 5 Å.

In Fig. 2 b), the FTIR results are depicted. These functional groups are responsible of the functionality of the membranes and have an effect on the separation mechanism. As expected, the functional groups present in all the carbon membranes are O–H bonds, C–O bonds and C=C un-saturations that were originally present in the Novolac resin structure. Analysing the FTIR spectrum from high to low wave lengths, it is possible to notice: broad signal at 3400 mm corresponds to the O–H bond stretching, the two peaks located at 2920 mm and 3040 mm are the C–H bonds stretching. The C–H stretching that gives a signal below 3000 mm comes from aromatic rings. Moreover, aromatic C=C stretch peaks are detected at 1610 mm and 1460 mm, followed by the 1240 mm C–O signal. Finally, below 900 mm, the IR energy is absorbed by the C–H and C=C bending movements [31].

Zhang et al. proposed a pure Pd membrane supported on $Al_2O_3$ with a membrane layer thickness of 3 μm Pd3 has similar thickness but is a Pd–Ag alloy membrane. As expected, Pd–Ag alloy membranes have higher hydrogen permeance than pure Pd membranes [33,34]. 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. It is interesting to observe that the double-skin Pd–Ag ceramic supported membrane (Pd2DS) has doubled the $H_2/CH_4$ selectivity as compared to Pd1 even the $H_2$ permeance of Pd2DS is slightly higher than Pd1. The difference in the perm-selectivity can be explained considering the sealing plays an important role on the leaking contribution. The sealing of Pd2DS is less affected by leakages. The variance between Pd1 and Pd2DS in hydrogen permeance could depend on different percentage of Pd and Ag. The $H_2$ permeance of the Pd2DS is slightly higher than the Pd1. 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). Moreover CMSM2 is more selective than CMSM1 thanks to the thicker membrane layer. $H_2/CH_4$ selectivity of CMSM1 and CMSM2 is remarkable compared to literature studies [35].

**Table 2 – Hydrogen permeance, at 400 °C for Pd–Ag and 20 °C for CMSM and 1 bar pressure difference, and selectivity for the membranes tested and for pure Pd* composite membrane based on Zhang et al. work [32].**

| Membrane code | Membrane type | $H_2$ permeance [mol/s/m$^2$/Pa] | Pressure exponent [–] | $H_2/CH_4$ 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 |
| Zhang et al. | Pd | $2.45 \cdot 10^{-6}$ | n.d. | 700 |

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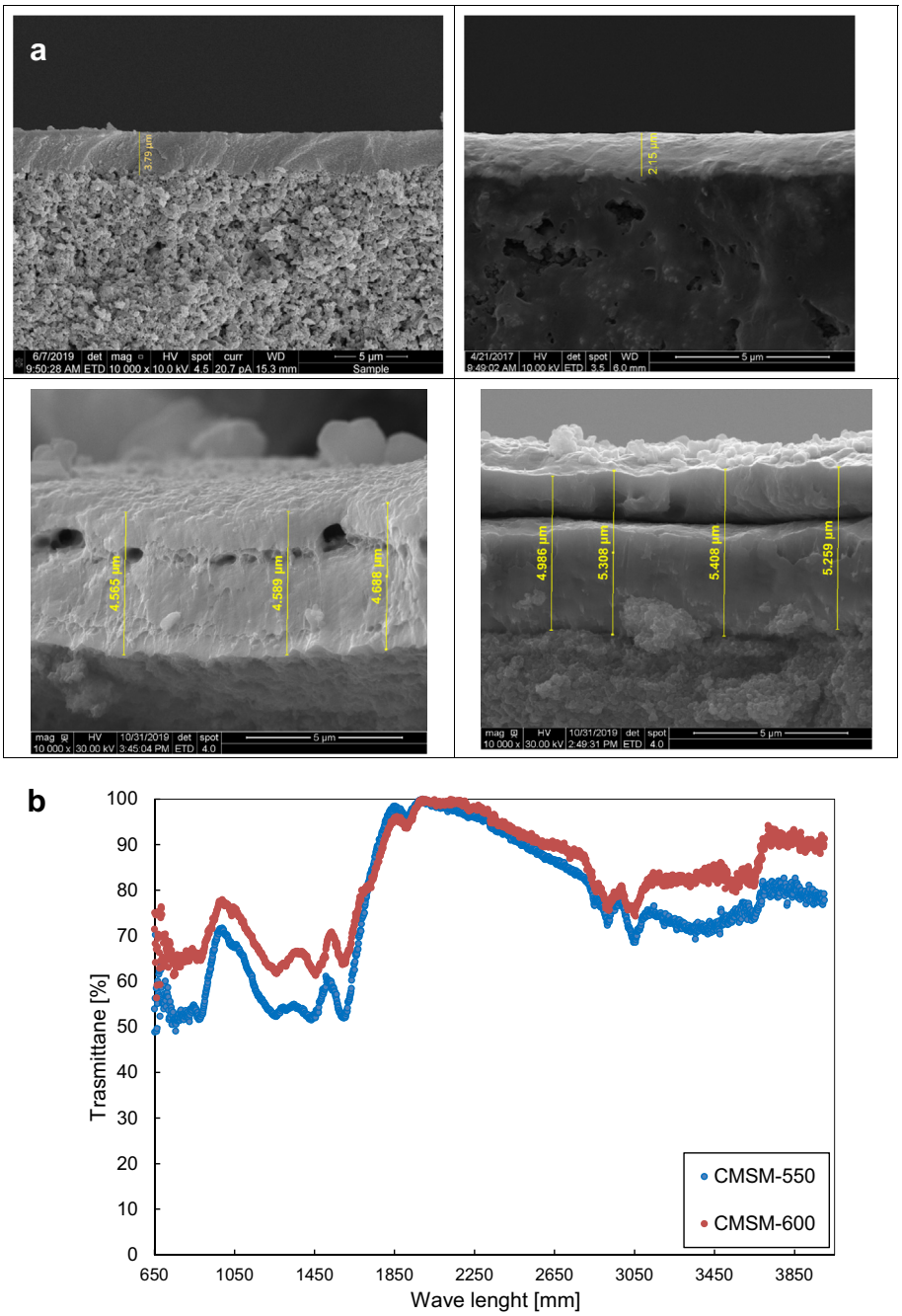


**Fig. 2 – a) Scanning electron microscopy CMSM1 on the left top side, Pd3 on the right top side, Pd1 on the bottom right side and Pd2DS on the bottom left side. b) FTIR of CMSM-550 and CMSM-600.**

Fig. 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 the literature, that Pd–Ag membranes suffer from concentration polarization effects especially when working at very low inlet hydrogen content and high pressure [36,37].

Experimental hydrogen flow rates as a function of the partial pressure of $H_2$ performed with Pd2DS, have been reported in Fig. 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 become more relevant at 10% $H_2$ content which is the lowest hydrogen

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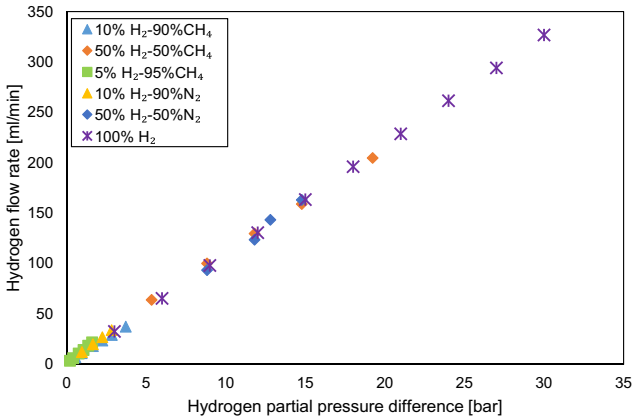


**Fig. 3 – Hydrogen flow rate at different hydrogen partial pressure difference when working with different inlet hydrogen concentration with carbon molecular sieve CMSM 1 at a working temperature of 20 °C.**

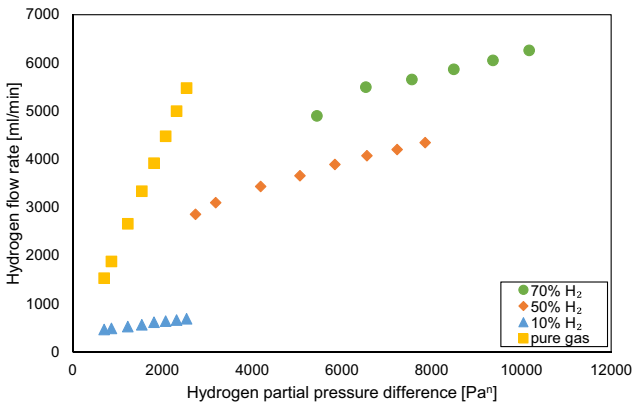


**Fig. 4 – Hydrogen flow rate at different hydrogen partial pressure difference when working with different inlet hydrogen concentration in $H_2$–$CH_4$ mixture with Pd2DS membrane at 400 °C.**

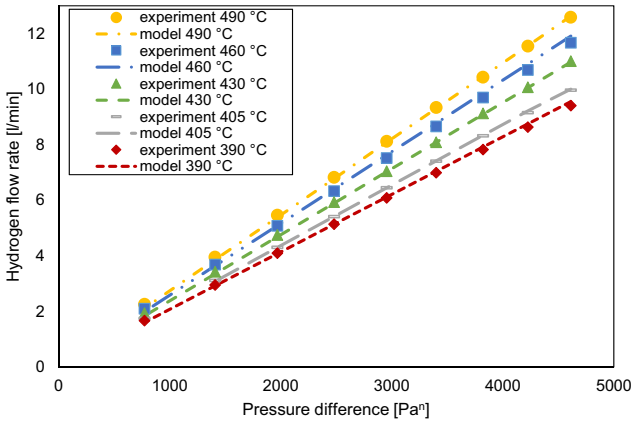


**Fig. 5 – Comparison between experimental and modelled results in pure gas tests at different operating temperature with Pd2DS membrane.**

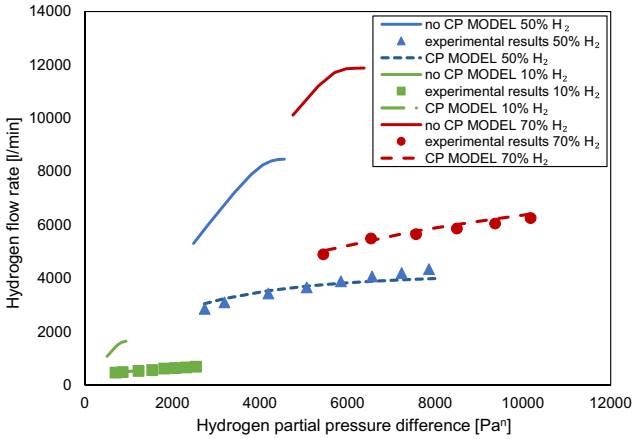


**Fig. 6 – Comparison between hydrogen flux from experimental and modelled results in mixture tests at different hydrogen inlet content; continuous line to described ideal case and dotted line includes mass transfer limitation at a working temperature of 400 °C.**

concentration tested. As observed in Fig. 4, the pressure plays a negative role in 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 [38–40]. The experimental results in the presence of the gas mixture of Fig. 4, and pure hydrogen at different temperatures, shown in Fig. 5, have been used for the validation of the model. Fig. 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.

The results reported in Fig. 6 clearly show that the concentration polarization is a very important phenomenon that the model can 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 Fig. 7, where the small deviations observed are attributed to the experimental error of the analytical instrument (GC).

In Fig. 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

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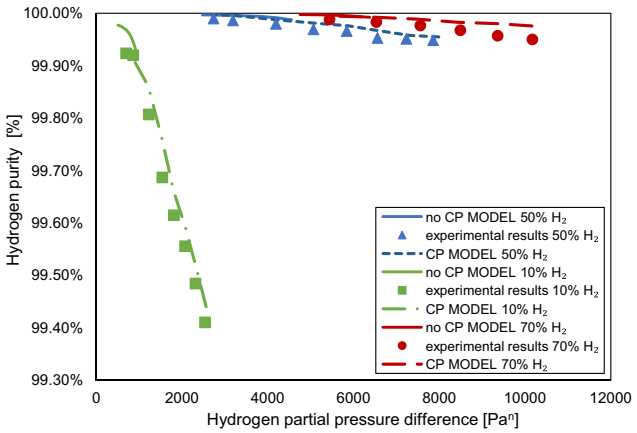


**Fig. 7 – Comparison between hydrogen purity from experimental and modelled results in mixture tests at different hydrogen inlet content; continuous line to described ideal case and dotted line includes mass transfer limitation at a working temperature of 400 °C.**

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 the case of CMSM 20 °C is considered.

In Fig. 9a), 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 2. The values of purity are remarkable, especially in the case of 10% hydrogen concentration at the inlet retentate. It is interesting to note a reduction in the hydrogen purity when increasing the pressure with Pd–Ag membranes. This can be explained by the dependency of the permeation flux of hydrogen with pressure (around 0.6, see Table 2) 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 $H_2/CH_4$ selectivity in pure

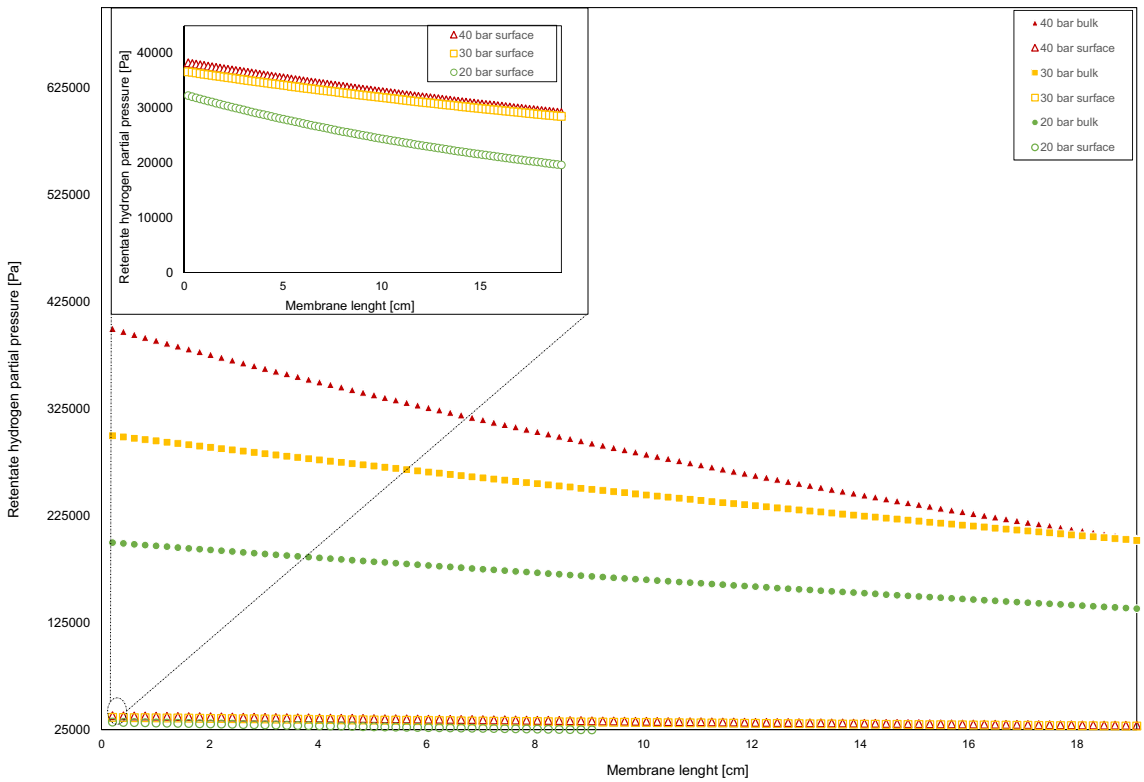


**Fig. 8 – Hydrogen partial pressure profile at the bulk and at the surface with the membrane length at 40, 30 and 20 bar for a mixture of 10% $H_2$ – 90% $CH_4$ with Pd2DS membrane at 400 °C.**

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 Fig. 6 between the results from the ideal simulation and experiments.

$H_2$–$CH_4$ mixtures tests with 10 and 50% $H_2$ concentration in the feed were performed with the Pd–Ag and CMSM for a gas tests is remarkably lower (1200 vs 24000). Moreover, the trend of the 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. Water adsorption causes a decrease in gas permeance, increasing the $H_2$ purity towards methane thanks to the smaller molecule size of hydrogen. Another

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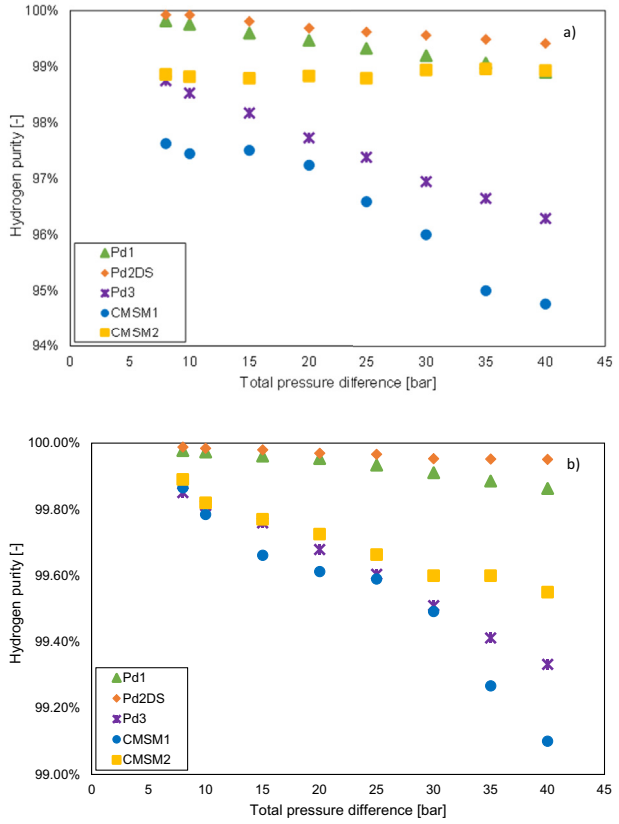


**Fig. 9 – a). Hydrogen purity at different total pressure difference with Pd1, Pd2DS, Pd3, CMSM1 and CMSM2 with a mixture of 90% $CH_4$ and 10% $H_2$ (Pd–Ag membranes 400 °C; CMSM 20 °C) b). Hydrogen purity at different total pressure difference with Pd1, Pd2DS, Pd3, CMSM1 and CMSM2 with a mixture of 50% $CH_4$ and 50% $H_2$ at 400 °C.**

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

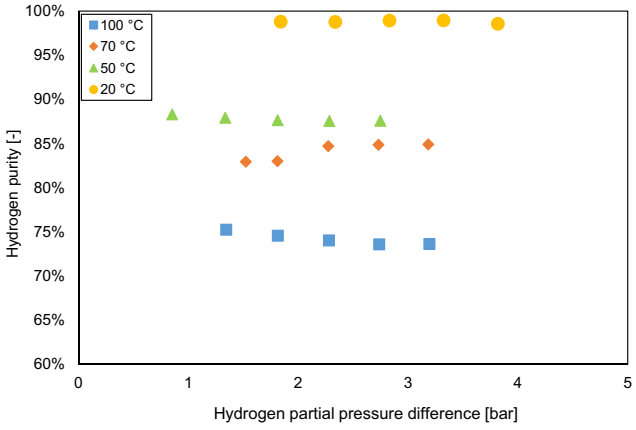


**Fig. 10 – Hydrogen purity at different hydrogen partial pressure difference when working at different temperatures with CMSM2 in presence of 10% $H_2$ – 90% $CH_4$.**

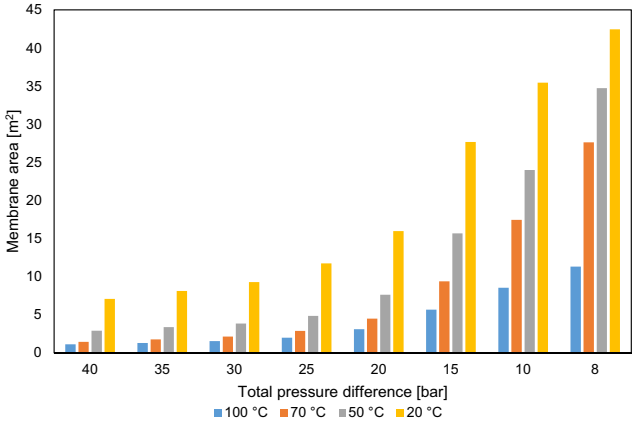


**Fig. 11 – Membrane surface area required to separate 25 kg/day of hydrogen from 10% $H_2$ to 90% $CH_4$ mixture at different total pressure difference when working at different temperatures with CMSM2.**

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. The pore size of CMSM2 is smaller than CMSM1 as it was observed by the perm-selectivity in Table 2; the adsorption of water reduces the pore size allowing mainly hydrogen to permeate when the initial pore size is small enough as in CMSM2. CMSM1 has been carbonized at 550 °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.

Similar results are depicted in Fig. 9b) for a mixture of 50% $H_2$ - 50% $CH_4$ at different total pressure differences. Comparable observations as described previously for the 10% $H_2$

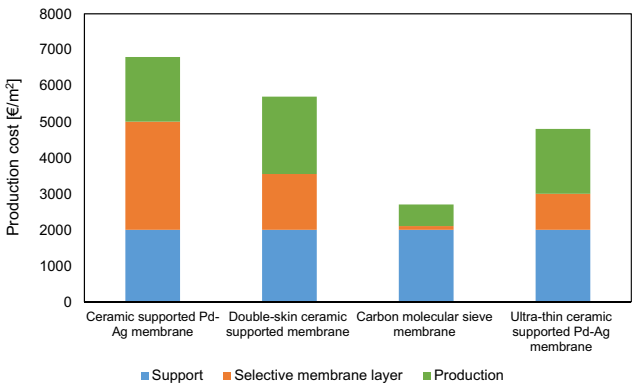


**Fig. 12 – Membrane production cost for the different membranes type considered including support, selective membrane layer and production costs [43].**

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**Table 3 – Economic evaluation assumptions.**

| Capital costs (CAPEX) | |
|---|---|
| Plant component | Cost |
| Component A | A |
| Component B | B |
| Component C | C |
| Component D | D |
| BEC (Bare erected costs) | A+B+C+D |
| Container cost | 12000 € |
| Transportation cost | 4000 € |
| Assembly cost | 5000 € |
| Contingency cost | 15% BEC |
| CCF (Capital charge factor) | 0.04 |
| TOC (Total overnight cost) | BEC + Container + transportation + assembly + contingency cost |
| Investment | TOC·CCF |
| **Operating cost (OPEX)** | |
| Labor cost | 0.3% TOC |
| Maintenance cost | 2% TOC |
| Insurance | 3% TOC |

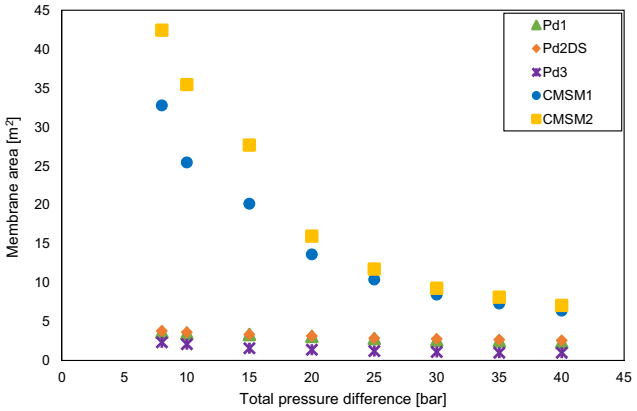


**Fig. 13 – Membrane area at different total pressure difference to separate 25 kg/day with Membrane Pd1, Pd2DS, PD3, CMSM1 and CMSM2 with a mixture of 90% $CH_4$ and 10% $H_2$.**

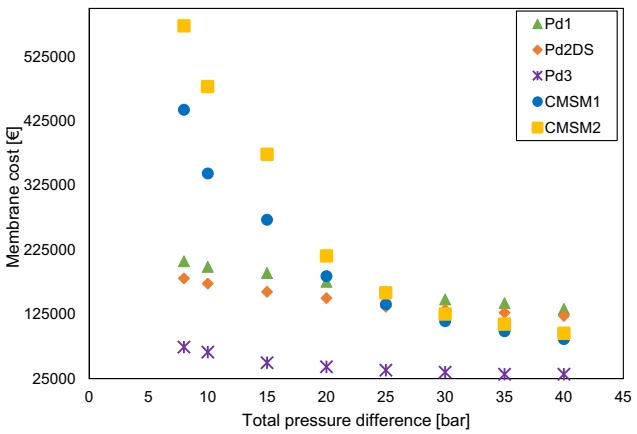


**Fig. 14 – Membrane costs at different total pressure difference with Membrane Pd1, Pd2DS, PD3, CMSM1 and CMSM2 with a mixture of 90% $CH_4$ and 10% $H_2$.**

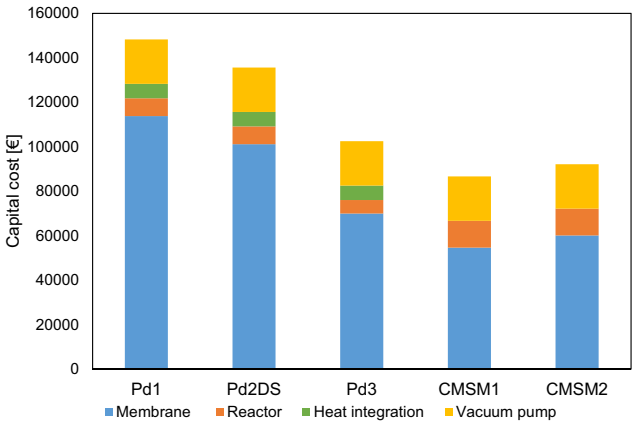


**Fig. 15 – Capital cost at 40 bar and 10% $H_2$ for hydrogen separation with Pd1, Pd2DS, Pd3, CMSM1 and CMSM2.**

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, CMSMs are less competitive than Pd–Ag membranes when the separation involves higher hydrogen content in the feed. Moreover, the hydrogen purity of Pd3 is lower than CMSM1 even if the $H_2$/$CH_4$ selectivity in pure gas, is higher for Pd3. A possible explanation has to be found in the different permeation mechanisms for the two membrane types, because for Pd–Ag membranes, the contaminant gas follows a linear trend with the pressure difference while the $H_2$ permeation has a linear trend with the pressure difference at the power of n, where n is lower than 1. In CMSMs, hydrogen follows the same linear trend with the pressure difference. Additionally, the influence of water adsorption on CMSMs, which blocks the surface pores, allowing only a smaller molecule to pass through, has to be considered. The purity of CMSM2 has a different trend with pressure in presence of 50% $H_2$ – 50% $CH_4$ mixture

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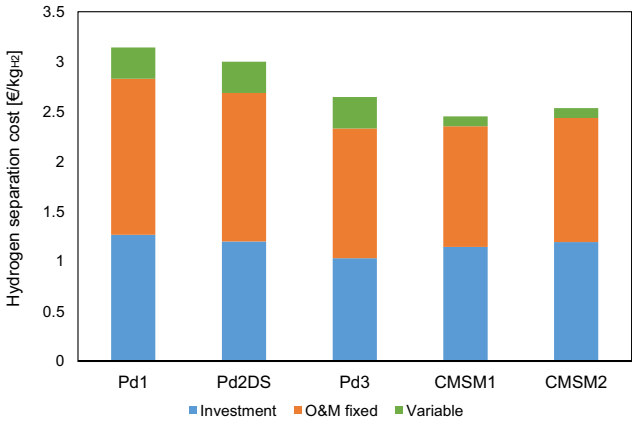


**Fig. 16 – Final hydrogen separation cost at 40 bar and 10% $H_2$ for hydrogen separation with Membrane Pd1, Pd2DS, PD3, CMSM1 and CMSM2.**

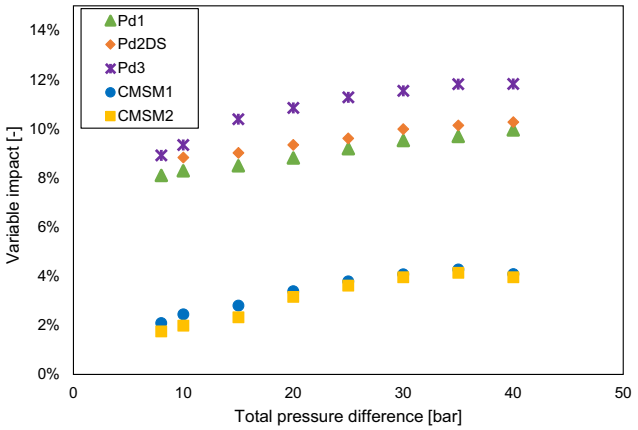


**Fig. 18 – Total hydrogen separation cost at different pressures and 10% $H_2$ for Membrane Pd1, Pd2DS, PD3, CMSM1 and CMSM2.**

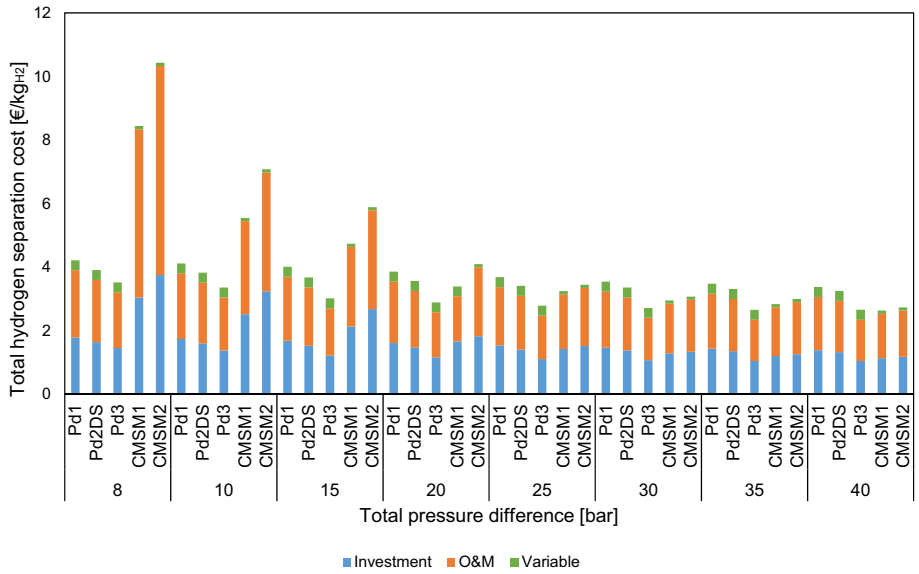


**Fig. 17 – Total hydrogen separation cost at different pressures and 10% $H_2$ for Membrane Pd1, Pd2DS, PD3, CMSM1 and CMSM2.**

compared to 10% $H_2$. A possible explanation is related to the higher hydrogen permeated flux which could partially desorbed the water, allowing higher methane flow rate to adsorb and permeate through.

The results confirm that CMSM become technically competitive with Pd–Ag membranes in specific conditions of purity and hydrogen content (lower temperature than Pd–Ag membranes). Moreover when comparing the proposed results of CMSM1 and CMSM2 to literature studies, the hydrogen purity in 10% $H_2$ and 50% $H_2$ is promising [41].

The next sections will assess whether supported CMSM are also competitive with Pd-based membranes from an economic point of view.

To further explain the focus of this work is to compare from an economic approach two types of membranes at different operating temperatures and showing the hydrogen purity is the key parameter of gas separation. Indeed, as expected, the hydrogen purity remarkably decreases with temperature as depicted in Fig. 10. On the other hand, as shown in Fig. 11, the membrane surface area, thanks to the permeance, is reduced at higher temperatures. In the following section, where an economic evaluation is proposed, CMSMs and Pd–Ag membranes, have been compared at two different working temperatures, to verify the final separation cost in case the hydrogen purity between the two different membrane types is similar. According to the results, at similar operating temperatures (400 °C), CMSM would be

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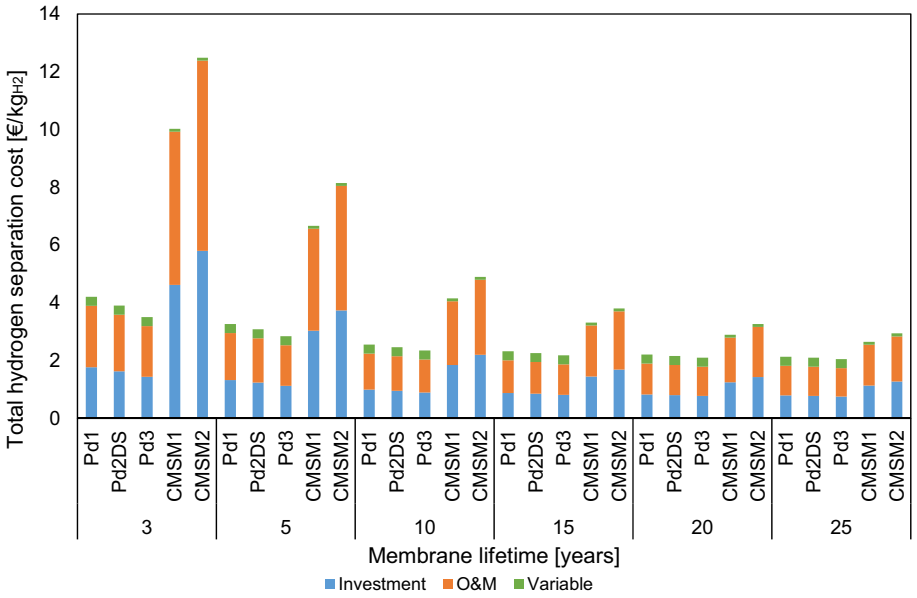


**Fig. 19 – Total hydrogen separation cost at 8 bar, 10% $H_2$ for Membrane Pd1, Pd2DS, Pd3, CMSM1 and CMSM2 and different membrane lifetimes.**

economically convenient but not relevant for the separation due to the extremely poor selectivity.

*Economic evaluation*

An economic evaluation, considering the membrane area needed for the CMSM and Pd–Ag membranes to separate the same hydrogen quantity, was performed to study more in detail the cost associated with the two membrane types tested.

The membrane area in the case of the Pd membranes has been estimated through the model which includes mass transfer limitations in the retentate side at 400 °C. A proper validation comparing experimental and simulation results has been performed with all the Pd–Ag membranes. For the case of CMSM, since no concentration polarization is observed, the hydrogen flux is calculated with a simplified model. The hydrogen partial pressure difference was calculated considering the average between inlet and outlet at the retentate side, while in the permeate the hydrogen partial pressure was calculated according to the obtained purity. The hydrogen separation capacity considered for the calculation of the membrane area is 25 kg/day (which is also the target for small-scale hydrogen separators).

At those temperatures, the membrane area needed with CMSMs is larger than with Pd–Ag membranes. Even if no concentration polarization is observed for CMSM, the hydrogen permeance in the mixture of Pd–Ag membrane is higher than the CMSM.

For the economic evaluation, the membrane production costs depending on the membrane type considered, was adopted based on the results listed in Fig. 12 [42]. The final capital cost of a double-skin membrane is lower than a ceramic supported Pd–Ag membrane due to thinner membrane layer. The reason has to be found in the higher selectivity when thinner membrane later is considered if there is an external ceramic layer to protect the Pd layer. It is interesting to perform an economic evaluation to calculate the membrane area costs needed for CMS and Pd–Ag membranes to separate 25 kg/day from 10% $H_2$ to 50% $H_2$ in the mixture, considering that the selective layer and production costs for CMSM are lower than for the Pd–Ag membrane.

For the calculation of the total hydrogen separation cost, CAPEX (capital expenses) and OPEX (operating expenses) costs have been included. In the capital costs, the product between TOC (total overnight cost) and CCF (capital charge factor) was considered. The TOC is equal to the sum of the BEC (bare erected cost) and transportation, assembly, contingency and container costs. The O&M costs include labor costs, maintenance and insurance costs, while variable costs include the electricity. In Table 3, the different assumptions are listed for the calculation of fixed and variable costs.

According to the results shown in Fig. 13, CMSM2 (CMSM) becomes economically competitive compared to Pd–Ag membrane mainly at high pressure. It is due to the linear proportionality of the hydrogen flux to the pressure difference for CMSM, while for the Pd–Ag membranes it is proportional to the pressure at the power of the exponent. Indeed, the membrane area required for the CMSMs decreases faster with pressure than for the Pd–Ag membranes.

The ultra-thin Pd–Ag membrane requires less membrane surface area due to the very high permeance related to the thickness of the Pd. The membrane area cost for CMSMs is lower than for Pd–Ag membranes for a pressure above 30 bar, while at lower pressures it is not economically beneficial to adopt CMSM (see Fig. 14). The capital cost, which includes the product between the TOC and CCF, is depicted in Fig. 15 and takes into account the membrane, reactor, heat integration and vacuum pump cost. The depicted result refers to the operating conditions at 40 bar and 10% $H_2$ - 90% $CH_4$.

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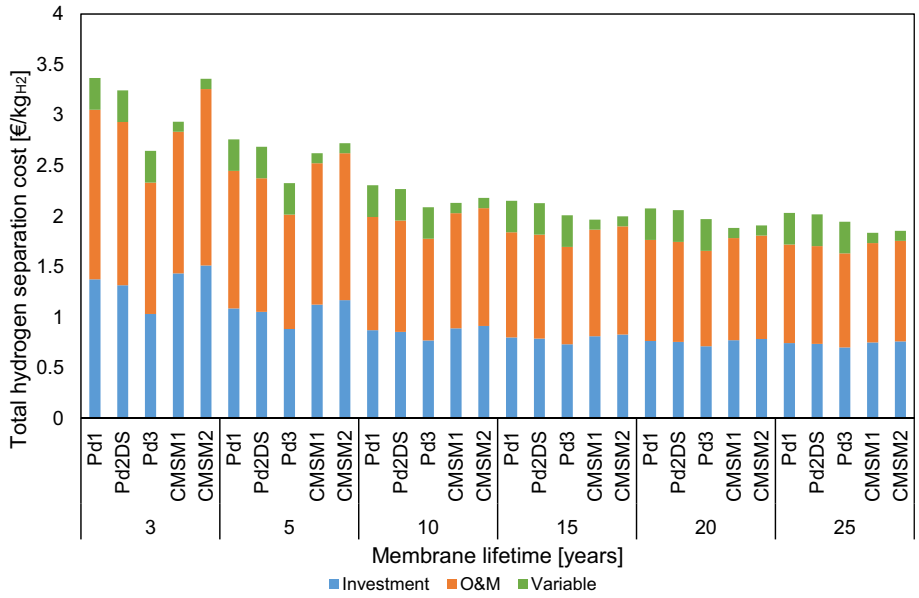


**Fig. 20 – Total hydrogen separation cost at 40 bar, 10% $H_2$ for Membrane Pd1, Pd2DS, Pd3, CMSM1 and CMSM2 and different Membrane lifetimes.**

According to the results, the lowest capital cost is found with the ultra-thin Pd–Ag membrane, due to the thinnest selective layer, which increases the hydrogen permeance and decreases the membrane area needed. The purity associated with this membrane, as mentioned previously, is not competitive compared to Pd1 and PdDS2, neither to CMSM2.

At the specified operating conditions, the investment required for CMSMs is lower than Pd–Ag membranes, except for Pd3, mainly due to the lower membrane area cost. It is worth noting, that the heat integration is a parameter that does not affect the capital cost of the CMSM, because the operating temperature is 20 °C. For all the cases, the cost of the membrane, is predominant, due to the cost of the support; if their production is scaled up and the cost is reduced, this will have a very significant impact on the capital cost, especially for CMSM.

Considering the final hydrogen separation cost, which includes investment, O&M and variable costs, it is more convenient to separate hydrogen with CMSMs than with Pd–Ag membranes at operating conditions of 40 bar and 10% $H_2$ content. In the variable costs the electricity needed for heaters and vacuum pumps is included. The results are shown in Fig. 16.

The total pressure difference is a key parameter to reduce the hydrogen separation cost. As explained before, it is especially valid for CMSM. Indeed, the total hydrogen separation cost is particularly convenient for CMSMs at high pressures. On the other hand the investment and O&M costs needed at lower pressure with CMSMs are not worthwhile, in comparison with Pd–Ag membranes, as shown in Fig. 17Figure.

The variable costs impact of CMSM1 and CMSM2, is extremely low compared to the Pd–Ag membranes, thanks to the saving of electricity. The result is depicted in Fig. 18.

In the described economic evaluation, membrane lifetime has been considered equal to 3 years for Pd–Ag and 5 years for CMSM, respectively, while the total plant lifetime is 25 years [44,45]. Every 3 years for Pd–Ag membranes and 5 years for CMSM, the membrane needs to be replaced and replacing costs have been included (recycling of materials have not been considered which could decrease the costs). Membrane lifetime is a relevant parameter which highly affects the

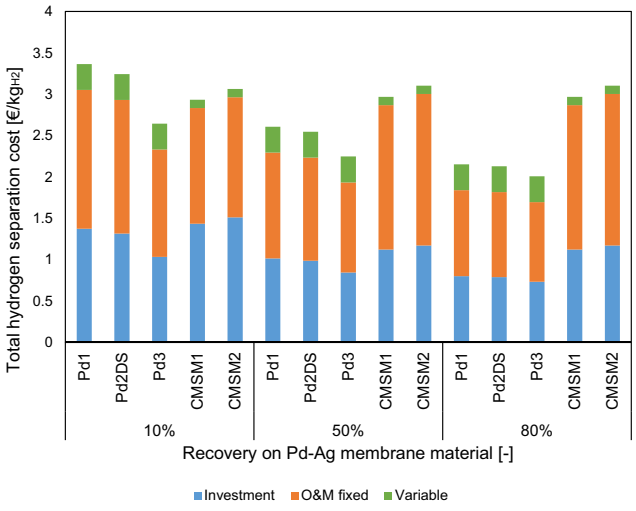


**Fig. 21 – Total hydrogen separation cost at 40 bar, 10% $H_2$ for Membrane Pd1, Pd2DS, PD3, CMSM1 and CMSM2 considering a saving the membrane cost re-using membrane layer and support.**

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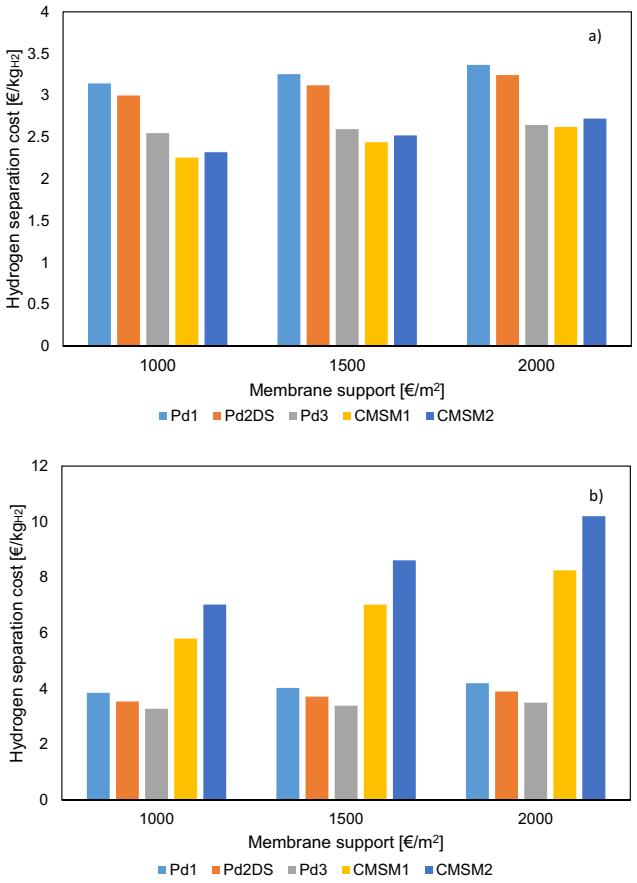


**Fig. 22 – Total hydrogen separation cost at different pressures, 10% $H_2$-90% $CH_4$ for Membrane Pd1, Pd2DS, PD3, CMSM1 and CMSM2 at 40 bar a) and 8 bar b).**

hydrogen final cost, as shown in Fig. 19 and Fig. 20, respectively for 8 and 40 bar of pressure difference.

At 8 bar, even in the optimum conditions of 25 years lifetime, it is not advantageous to separate hydrogen with CMSM. On the other hand, at 40 bar it is convenient above 5 years of lifetime.

In the previous considerations, the possibility to re-use the selective layer and support for each membranes lifetime was not taken into account, but in the following results, a cost saving of 10%, 50% and 80% was assumed in case the Pd–Ag and the support are re-used.

According to the results, depicted in Fig. 21, the recovery of membrane layer and support from a minimum saving of 50% of the membrane cost, guarantees a total hydrogen separation cost more convenient with Pd–Ag than with CMS membranes. In case the ceramic support is re-used for CMS membranes, similar results are obtained to Fig. 16Figure.

The comparison in terms of purity and costs between CMS and Pd–Ag membranes has been carried out for 50% $H_2$ - 50% $CH_4$ mixtures, which shows that in this case it is not interesting to consider CMSM because it is not competitive with more selective membranes (results reported in Appendix).

The porous support cost influence on the final separation cost has been analysed for the case of 40 and 8 bar for the five different membranes. Initially, the porous support cost was estimated at 2000 €/$m^2$, and it has been changed to 1500 and 1000 €/$m^2$ to investigate its influence. The porous support price has a major influence on the reduction of the hydrogen separation cost of CMSMs. Nevertheless, the final separation cost at 8 bar is more convenient with Pd–Ag membranes than CMSMs. Results at 40 and 8 bar are depicted in Fig. 22a) and b).

## 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 CMSM to compare the hydrogen permeance and purity. For the case of lower hydrogen content, very high purities are reached with the more selective CMSM, being the preferred strategy when working at high pressures (>30 bar).

An economic evaluation has been performed to calculate the final cost to separate 25 kg/day of hydrogen from a mixture of 10% $H_2$ - 90% $CH_4$ and 50% $H_2$ - 50% $CH_4$ with Pd–Ag and Al-CMSM membranes. In the case of 10% $H_2$, high pressure operation (>30 bar) with CMSM is economically the preferred selection. On the other hand, in the presence of 50% $H_2$, it is more advantageous to adopt Pd–Ag membranes to get very high purity. Furthermore, if the grid stays at low pressure (8 bar), for all the different scenarios investigated, the use of Pd–Ag is preferred over Al-CMSM.

A sensitivity analysis on the effect of membrane lifetime, the cost of the support, and the cost associated with Pd recovery from the membrane layer has also been done for a complete economic evaluation. In this regard, the membrane lifetime plays an important role to reduce the final separation cost and, in particular, for a membrane lifetime above 5 years, it is more advantageous to adopt Al-CMSM at high pressure and 10% $H_2$. If the selective layer (for Pd membranes) and the support are re-used, then at high pressure the use of Pd–Ag membranes is more convenient compared to CMSM.

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## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgments

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## Appendix

The same assumptions considered previously, are still valid in this condition. The membrane area needed to separate 25 kg/day of hydrogen for a mixture containing 50% $H_2$ was calculated with the model and results are shown in Fig. A1. Similar considerations are deduced considering the reduction in membrane area with pressure is more considerable in CMSM, compared to Pd membranes.

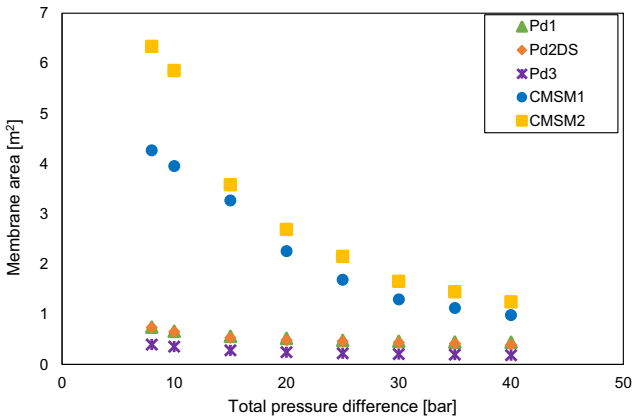


**Fig. A1 – Membrane area at different total pressure difference with Membrane Pd1, Pd2DS, PD3, CMSM1 and CMSM2 with a mixture of 50% $CH_4$ and 50% $H_2$.**

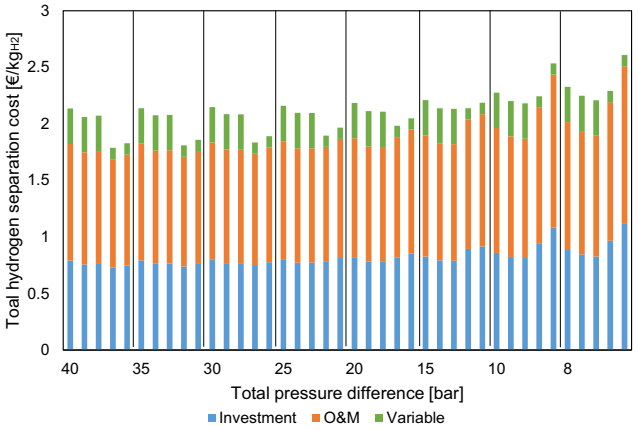


**Fig. A2 – Total hydrogen separation cost at different pressures, 50% $H_2$-50% $CH_4$ for Membrane Pd1, Pd2DS, PD3, CMSM1 and CMSM2.**

The total hydrogen separation cost, is economically convenient at higher pressure, above 20 bar for CMSMs. The results are depicted in Fig. A2.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ijhydene.2020.07.191.

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