Theoretical Performance Evaluation of Inorganic (Non Pd-Based) Membranes for Hydrogen Separation

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1. Introduction

In the last two decades, H₂ was extensively recognized as a clean fuel, predominantly in fuel cell supplying, where its reaction with O₂ produces an environmentally friendly emission as water steam, [1, 2]. In the field of the alternative technologies for the conventional process of low temperature PEM fuel cell supplying, the H₂ purity requirements are quite strict, mainly because CO (normally present in a conventional reformed stream) poisons the anodic catalyst of the fuel cell apparatus, with concentration higher than 10 ppm [3]. Therefore, a reformer or H₂ rich-stream needs an H₂ separation/purification stage before supplying a low temperature PEMFC. Consequently, the typology of the inorganic membrane to be housed in the H₂ separation/purification units has to be selected considering both the membrane cost and the H₂ purification performance. In particular, many research works have highlighted the utilization of both polymeric and inorganic membranes for H₂ separation [4, 5]. Among them, unsupported Pd-based membranes have been considered to a great extent because they are highly selective to H₂ permeation and useful for recovering the high purity H₂ stream [6]. Nevertheless, this kind of metallic membrane undergoes cracking problems during thermal cycling and readily evidenced surface contamination by CO or H₂S components. Moreover, Pd-based membranes are costly and their applications are restricted due to low H₂ permeance. In the last few years, composite membranes such as thin Pd and Pd/alloy layers deposited on...
years, composite membranes such as thin Pd and Pd/alloy layers deposited on porous substrates have attracted considerable attention due to their characteristics of higher mechanical resistance, reduced cost and higher H$_2$ permeance [7, 8]. Nevertheless, non-palladium based membranes such as silica, carbon and polymeric could represent an alternative and cheaper option for achieving an H$_2$-rich stream useful for supplying some typology of fuel cells (not requiring particular restrictions on H$_2$ purity such as PEMFCs), owing to their properties and lower preparation costs with respect to the palladium based membranes [9-13].

In the last three decades, the integration of both reaction and H$_2$ separation processes in a single device, the so-called membrane reactor (MR) technology, has been largely studied, highlighting the numerous advantages of these devices over the traditional reactors (TRs) [5, 14-20]. According to the Process Intensification Strategy, by compressing the process units, a MR could also attain higher efficiency than conventional multi stages processes. Nevertheless, as a general consideration, the H$_2$-selective membranes performance is greatly related to the design parameters of membrane modules and operating conditions, which play a noteworthy role in H$_2$ purification processes. In fact, it is well known that in most of the operating cases, a higher driving force positively affects the membrane process performance. Then, it can be considered that both operating conditions and membrane design (flow pattern) control the driving force magnitude and its distribution within the membrane module. Unfortunately, there are a few comprehensive studies about the H$_2$-selective membrane unit efficiency in H$_2$ separation from gaseous products [21].

To the best of our knowledge, there is no standpoint about the H$_2$ purification performance comparison among silica, carbon and polymeric membranes. Hence, to evaluate the effects of the operating parameters on various membrane performances, a modeling tool could play an interesting role, as in the case of silica membrane performance during the H$_2$ separation or production processes [11, 12, 22, 23]. However, recent modeling studies were carried out by using different approaches. For example, Cardoso et al. [28] simulated the gas permeation through silica-based membranes using a Maxwell-Stefan based model. Samei et al. [29] used a solution-diffusion based model for describing the permeation of gases through a silica based composite membrane, while Al-Rabiah et al. [30] simulated the carbon membranes permeation characteristics using a multi-component gas mixture model including the free-molecule or Knudsen flow.

The main target of this theoretical study is to use a black-box model for evaluating the performance of silica, polymeric and carbon membranes for purifying an H$_2$-rich stream coming from a methanol steam reforming (MSR) stage in a TR, by varying pressure gradient and stage cut.

2. Model theory

In this study, a typical black-box model [24] was presented based on a mathematical formulation for a multicomponent gas stream in a membrane module. Figure 1 illustrates the scheme of the simulated hybrid plant including a conventional methanol steam reformer in series with an H$_2$-selective membrane module. It should be noted that in the proposed model, three different membrane types, namely silica, polymeric and carbon membranes, are considered to be housed in the membrane separator.

The outlet stream coming out from the TR (composed by H$_2$, CO$_2$, CO, CH$_3$OH and H$_2$O) foresees a stage (ice bath) for removing the excess of unreacted methanol and water prior to entering the membrane separator module. The co-current flow pattern was assumed in the theoretical model and the derivation equations are cast in a suitable form of computer calculation, constituting an appropriate strategy for any multicomponent systems. On the other hand, the considered assumptions in the present modeling work are as follows:

- Fick’s law is considered for the calculation of permeation rates.
- In the permeation direction, the concentration gradient is considered negligible.
- Pressure drops of both the retentate and permeate sides are considered zero.
- Plug flow pattern in the retentate and permeate sides is assumed.

Moreover, the mass balance equation was considered for each type of membrane used in the separator. More details about the governing equations of this model can be found in Shindo et al. [24].

2.1. Governing equations

The co-current flow pattern is illustrated in Figure 2 and concerning the differential element (dA), the overall and partial material balances are as follows:

![Fig. 1. Scheme of a MSR reaction carried out in a traditional methanol reformer, followed by a membrane separator module.](image)

![Fig. 2. Scheme of a single permeation stage with co-current flow pattern.](image)
regarding the permeance values of the different gases of interest of this work. It should be noted that for the validation of the model used in this study, the details about our black box model have been already described in a previous work [23], showing good agreement with the experimental data.

3. Results and discussion

Initially, the effects of the most important design and operating parameters were evaluated on the $H_2$ selective membrane performance, in terms of $H_2$ purity and CO concentration in the permeate stream from a theoretical point of view. Hence, Table 3 summarizes the used conditions for implementing the $H_2$ separation performance in the different case study, depending on which of the three membrane materials was used, namely silica, polymeric and carbon membranes. Then, the simulation analyses can be subdivided into two sections, in which stage cut and feed (or retentate) pressure were changed.

It should be noted that for the validation of the model used in this study, the details about our black box model have been already described in a previous work [23], showing good agreement with the experimental data.

3.1. Investigation of stage cut effect

The stage cut influence on the performance of the three mentioned types of membranes in terms of permeate stream purity were evaluated for a co-current flow pattern. In this case, the simulation runs were carried out at a constant feed pressure of 2.0 bar.

Regarding the permeance values of the different gases of interest of this work, it should be noted that the membrane surface area cannot be attained constant values by varying the stage cut. Figure 3 displays the $H_2$ composition in the permeate and retentate sides versus the stage cut for the different membrane applications. For each case, the $H_2$ molar fraction decreased in both retentate and permeate sides at the higher stage cut value due to the increase of both the CO and CO$_2$ permeating flux. Furthermore, it is obvious that a higher performance is reached in the case of silica membrane utilization because it basically shows higher $H_2$/CO idéal selectivities and comparable $H_2$/CO values with respect to the polymeric and carbon ones (Table 2). Nevertheless, the higher the stage cut, the lower the $H_2$ concentration in the retentate side, particularly for silica membrane, whereas in the permeate side a consistent decrease of $H_2$ concentration is evident for the latter membrane at $\theta > 0.5$.

Figure 4 illustrates the molar fraction of CO in both permeate and retentate sides versus the stage cut for the three membranes considered in this work types. In all cases, the CO molar fraction increases on both sides by increasing the stage cut. However, in the permeate side the lowest CO molar fractions are achieved by using the silica membrane, and this is because the
membrane shows a high H2/CO selectivity and the highest H2 permeance among the different membrane materials studied here in this work (Table 2). In particular, at the low/medium stage cut (0.15 – 0.45), CO molar fraction is around 1%, while it is a bit lower than 2% for the carbon membrane and higher than 2% for the polymeric one. At higher stage cut, both silica and carbon membranes show an increase of CO molar fraction, reaching almost 2%, while for the polymeric one the trend is constant. A further qualitative comparison among the membranes performance is given in Table 4, where H2, CO and CO2 molar fractions in both permeate and retentate streams are summarized as a function of surface area. The modelling results show that the silica membrane presents noticeable performance to produce highly concentrated H2 (permeate stream) with a value around 90%, higher than the carbon membrane application, 86%, and the polymeric one, around 80%. Furthermore, the higher H2 permeance of the silica membrane (Table 2) with respect to the other studied membranes makes the required membrane surface area lower. Indeed, the simulations highlight that the lowest membrane surface area is required for the silica membrane (Table 4). Indeed, at stage cut of 0.65, a membrane surface area of 18 cm2 is attained for the silica membrane, while ~ 700 cm2 and ~ 13000 cm2 are needed for the polymeric and carbon ones, respectively, constituting a quite interesting result in terms of Process Intensification (lower plant volume) and reduced costs.

3.2. Evaluation of feed pressure effect

Feed (or retentate) pressure parameter was also considered because it can strongly affect the membrane performance. As presented in Figure 5, the hydrogen content in the permeate side (namely, H2 purity) is improved for all the considered membranes by increasing the feed pressure, particularly in the range of 2.0 – 4.0 bar.

Figure 5. H2 molar fraction in the permeate side versus retentate pressure for various membrane applications.

Afterwards, the trend is constant for all the considered membrane applications. Also in this simulation, the best performance was related to the silica membrane, which showed an H2 purity around 98% at 4.0 bar. At the same pressure, the carbon membrane reached a bit more than 90% of H2 purity and around 80% of the polymeric one. Furthermore, the simulations showed that higher pressures do not make any significant improvement for all the considered membranes. Meanwhile, in the range of 1.0 – 4.0 bar, the CO content in the permeate stream for the silica membrane is decreased from 1.5% to less than 0.5%, remaining constant around the latter value at higher feed pressures (Figure 6). Also in this case, both carbon and polymeric membrane applications show higher CO content in the permeate stream with respect to the silica membrane.

Furthermore, this theoretical study also evaluated the effect of feed pressure on the required membrane area for guaranteeing the maximum H2 permeate purity values of 90%, 86 and ~ 80% (Table 5). As summarized in this table, the total membrane area decreases with increasing the feed pressure owing to an enhancement of the H2 separation driving force.

As a further comment, the silica membrane showed better H2 permeate purity and quite low CO molar fraction in the permeate stream (Figure 5 and Figure 6). This globally constituting constitutes a much better solution than the polymeric and carbon membranes studied in this work, even considering the higher values of H2 permeance and H2/CO and H2/CO2 selectivities of the silica membrane, which are responsible for the better theoretical results shown in this work.

4. Conclusions

In this study, the purification of an H2–rich stream coming out from a MSR reaction stage carried out in a TR was theoretically evaluated using various non-palladium based membranes (silica, polymeric and carbon membranes). For this purpose, a theoretical black-box model was developed
for multicomponent gas mixture purification to evaluate the H₂ separation performance of the mentioned membranes in co-current flow pattern and by varying several designs and processing parameters such as stage cut and feed pressure.

For all cases, it was found that the H₂ purity in the permeate side decreased at a higher stage cut. However, this result was clearer than others for the silica membrane. In particular, it should be noted that, at a stage cut of 0.65, H₂ molar fractions of 90%, 86% and 78% were attained for silica, carbon and polymeric membranes, consequently requiring 18, 12933 and 713 cm² of surface membrane area, respectively. Furthermore, the effect of a pressure increase was positive in all cases, even though the silica membrane application showed more significant results than the other evaluated membranes. In particular, it is worth noting that 98% of H₂ purity and 0.3% of carbon monoxide in the permeate side can be obtained by using a single stage unit of silica membrane operating with a transmembrane pressure of 4.0 bar.

<table>
<thead>
<tr>
<th>Membrane type</th>
<th>Permeate Mole Fraction</th>
<th>Retentate Mole Fraction</th>
<th>Membrane Area(cm²)</th>
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<tbody>
<tr>
<td>Silica membrane</td>
<td>0.89</td>
<td>0.09</td>
<td>0.02</td>
</tr>
<tr>
<td>Polymeric membrane</td>
<td>0.78</td>
<td>0.19</td>
<td>0.03</td>
</tr>
<tr>
<td>Carbon membrane</td>
<td>0.86</td>
<td>0.12</td>
<td>0.02</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Retentate pressure side</th>
<th>Silica membrane</th>
<th>Polymeric membrane</th>
<th>Carbon membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
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<td>713</td>
<td>12934</td>
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<tr>
<td>10</td>
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<td>77</td>
<td>1041</td>
</tr>
</tbody>
</table>

Table 5 Effect of feed pressure on membrane area for silica, carbon and polymeric membranes.

Acronyms list

MR: Membrane reactor
MSR: Methanol steam reforming
PEMFC: Proton Exchange Membrane Fuel Cell
TR: Traditional reactor

Nomenclature list

A: Membrane Area (m²).
A₀: Total membrane area (m²).
J: permeating flux of component i through the membrane (mol/m².s).
L: Flow rate on feed side (mol/s).
Lᵣ: Retentate flow rate (mol/s).
Pₑ: permeance of component i (mol/m².s.Pa).
Pᵢ: Pressure on retentate side (Pa).
Pᵢᵢ: Pressure on permeate side (Pa).
Pᵢᵢᵢ: Partial pressure of component i in the retentate side (Pa).
Pᵢᵢᵢᵢ: Partial pressure of component i in the permeate side(Pa).
V: Flow rate on permeate side (mol/s).
Vᵢ: Permeate flow rate (mol/s).
𝑥ᵢ: Mole fraction of component i on feed side.
𝑥ᵢᵢ: Mole fraction of component i in feed.
𝑥ᵢᵢᵢ: Mole fraction of component i in retentate (outlet).
𝑥ᵢᵢᵢᵢ: Mole fraction of component i in permeate stream.
𝑥ᵢᵢᵢᵢᵢ: Mole fraction of component i in permeate at the outlet.

Greek letter list

θ₀: Stage cut
α: ideal selectivity

References
