



Research Paper

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

Kamran Ghasemzadeh ¹, Abbas Aghaeinejad-Meybodi ², Adolfo Iulianelli ^{3,*}, Angelo Basile ^{3,*}¹ Faculty of Chemical Engineering, Urmia University of Technology, Urmia, Iran.² Department of Chemical Engineering, Urmia University, Urmia, Iran.³ Institute on Membrane Technology of the Italian National Research Council (CNR-ITM), Via P. Bucci Cubo 17/C c/o University of Calabria, Rende (CS) – 87046, Italy.

Article info

Received 2017-10-26

Revised 2018-02-12

Accepted 2018-02-16

Available online 2018-02-16

Keywords

H₂ separation

Modelling

Silica membrane

Polymeric membrane

Carbon membrane

Highlights

- The silica based membrane module theoretically allows 98% of H₂ purity at $\Delta p = 4.0$ bar
- H₂ purity of 90%, 86% and 78% are reached with silica, carbon and polymeric membranes at a stage cut of 0.65
- 90% of H₂ purity is reached using 18 cm² of silica membrane surface at stage cut of 0.65

Abstract

The aim of this work theoretical study is to theoretically investigate a inorganic membrane assisted purification process of an H₂-rich stream derived from a conventional methanol steam reforming stage. In particular, a black-box model for multicomponent gas mixture purification is developed to evaluate the H₂ separation performance of such non-palladium based membranes such as silica, polymeric and carbon membranes, by varying design and processing variables such as stage cut and feed pressure. The most significant modeling result is achieved by using a silica membrane based separation module in which 98% of H₂ purity and 0.3% of carbon monoxide in the permeate side are reached, operating with a transmembrane pressure of 4.0 bar.

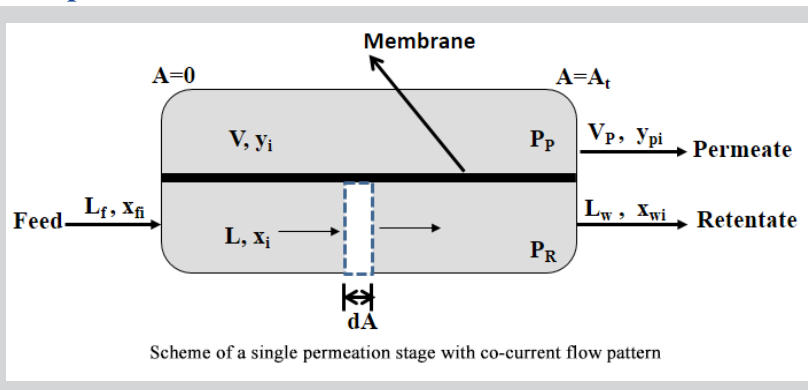
© 2018 MPRL. All rights reserved.

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 reformed 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

Graphical abstract



* Corresponding author at: Phone: +39 0984 492011; fax: +39 0984 402103 (A. Iulianelli); Phone: +39 0984 492013; fax: +39 0984 402103 (A. Basile)
E-mail address: a.iulianelli@itm.cnr.it (A. Iulianelli); a.basile@itm.cnr.it (A. Basile)

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 H₂ permeance [7, 8]. Nevertheless, non-palladium based membranes such as silica, carbon and polymeric could represent an alternative and cheaper option for achieving an H₂-rich stream useful for supplying some typology of fuel cells (not requiring particular restrictions on H₂ 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 H₂ 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 H₂-selective membranes performance is greatly related to the design parameters of membrane modules and operating conditions, which play a noteworthy role in H₂ 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 H₂-selective membrane unit efficiency in H₂ separation from gaseous products [21].

To the best of our knowledge, there is no standpoint about the H₂ 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 H₂ 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 H₂-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 H₂-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 H₂, CO₂, CO, CH₃OH and H₂O) 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:

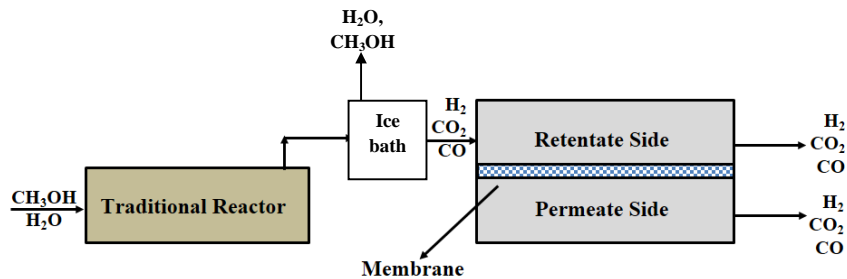


Fig. 1. Scheme of a MSR reaction process carried out in a traditional methanol reformer, followed by a membrane separator module.

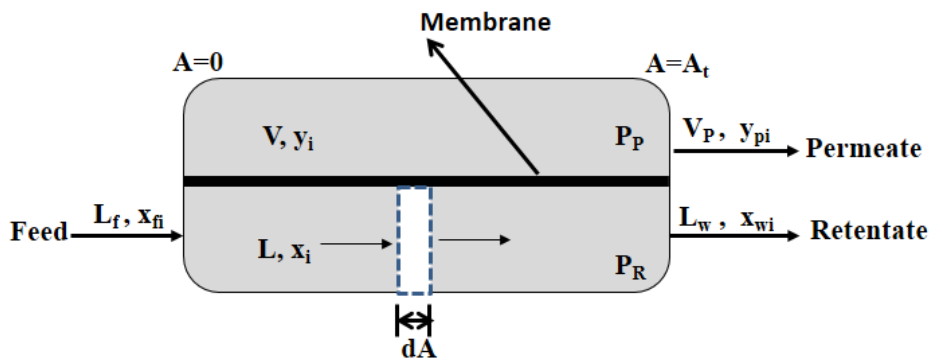


Fig. 2. Scheme of a single permeation stage with co-current flow pattern.

Table 1

The feed compositions of a reformed stream coming out from a TR in which MSR reaction is carried out at at 250 °C and 2 bar.

Components	Mole fraction
H ₂	0.7420
CO	0.0433
CO ₂	0.2137
Total flow rate (mL/min)	51.40

Table 2

Permeance and ideal selectivities (α) values used in the simulations.

Membrane type	Permeance coefficient of H ₂ (mol/ s·m ² ·Pa)	α (H ₂ /CO ₂)	α (H ₂ /CO)	Ref.
Silica membrane	2.8×10 ⁻⁶	44	56	[25]
Polymeric membrane	1.48×10 ⁻⁹	7	60	[26]
Carbon membrane	3.45×10 ⁻¹¹	16	45	[27]

Table 3

The investigated conditions during the utilization of the different type of membranes (silica, polymeric and carbon membrane).

Parameters	Stage cut Effect	Pressure Effect [bar]
Stage cut (-)	Various Silica Membrane: 5	0.65
Feed side pressure (bar)	Carbon membrane: 5 Polymeric membrane: 7	Various

$$-dL = dV = dA \sum_{i=1}^n P_{e_i} (p_R x_i - p_P y_i) \quad (1)$$

$$-dx_i L_i = dy_i V = dA P_{e_i} (p_R x_i - p_P y_i) \quad (2)$$

where P_{e_i} is permeability coefficient, p_R and p_P the total pressure of the retentate and permeate sides, respectively, L the retentate molar flow rate, V the permeate molar flow rate, A membrane surface area, y_i and x_i the molar fractions of the permeate and retentate sides, respectively.

The following equations can be achieved by integrating Eqs. 1 and 2:

$$dx_i = \frac{-dA}{L} \left[P_{e_i} (p_R x_i - p_P y_i) - \sum_{i=1}^n P_{e_i} (p_R x_i - p_P y_i) \right] \quad (3)$$

$$y_i = \frac{x_{F_i} L_F - x_i L}{L_F - L} \quad V \neq 0 \quad (i = 1, \dots, n-1) \quad (4)$$

$$y_i = \frac{P_{e_i} (p_R x_i - p_P y_i)}{\sum_{i=1}^n P_{e_i} (p_R x_i - p_P y_i)} \quad \text{at } V = 0 \quad (5)$$

where x_{F_i} is the feed composition and L_F the feed flow rate.

In this model formulation, the calculation for a multicomponent separation in a membrane separator with co-current flow pattern can be performed by the use of Eqs. (1, 3-5). Regarding the modeling problems, an initial guess should be used to start the calculation loop as reported below:

$$L = L_F x_i = x_{F_i} (i = 1, 2, \dots, n-1) \quad \text{at } A = 0 \quad (6)$$

It should be noted that each flux of a component permeating through the membrane, as in Eq. (7), is described by its local driving force and its permeance value at such an operating temperature, also taking into account that all components show permeation through the membrane.

$$J_i = P_{e_i} (p_{i,retentate} - p_{i,permeate}) \quad (7)$$

J_i represents the permeating flux of the i -compound, P_{e_i} the permeance of component i , $p_{i,retentate}$ and $p_{i,permeate}$ are the partial pressure for component i in the retentate and permeate sides, respectively. The exponent of the partial pressures of Eq. (7) (n -value) was chosen equal to 1 because silica and carbon membranes cannot obey the Sieverts-Fick law (n -value = 0.5, typical of dense palladium layers with a thickness > 5 μm and without the presence of defects or surface modifications) to represent, for example, the permeation of hydrogen through these membranes. Indeed, they are not dense, but porous and the mechanism controlling the permeation process can be Hagen-Poiseuille or Knudsen. For polymeric membranes, even though they are dense, the solution-diffusion mechanism describes the hydrogen permeation process, but not following Sieverts-Fick law. Indeed, hydrogen passes through the polymeric layer in molecular form and is not dissociated in atomic form as in the case of permeation through dense inorganic layers (as for example through the palladium). Therefore, also in this case, n -value cannot be equal to 0.5.

2.2. Procedure of numerical solution

With the aim of modeling the H₂ separation in the presented membrane process, it is essential to solve the governing equations in view of the corresponding boundary conditions. Consequently, a fourth order Runge-Kutta method was used to solve them. In particular, the simulations concerning generic silica, polymeric and carbon membranes were considered for purifying a typical syngas stream coming out from a TR, in which the MSR reaction was carried out at 250 °C and 2.0 bar of reaction pressure (Table 1).

The perm-selectivity characteristics and hydrogen permeance of the considered silica, polymeric and carbon membranes are summarized in Table 2 and their values were the used parameters for the simulations reported in this work.

3. Results and discussion

Initially, the effects of the most important design and operating parameters were evaluated on the H₂-selective membrane performance, in terms of H₂ purity and CO concentration in the permeate stream from a theoretical point of view. Hence, Table 3 summarizes the used conditions for implementing the H₂ 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 H₂ composition in the permeate and retentate sides versus the stage cut for the different membrane applications. For each case, the H₂ molar fraction decreased in both retentate and permeate sides at the higher stage cut value due to the increase of both the CO and CO₂ permeating flux. Furthermore, it is obvious that a higher performance is reached in the case of silica membrane utilization because it basically shows higher H₂/CO₂ ideal selectivities and comparable H₂/CO values with respect to the polymeric and carbon ones (Table 2). Nevertheless, the higher the stage cut, the lower the H₂ concentration in the retentate side, particularly for silica membrane, whereas in the permeate side a consistent decrease of H₂ 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.

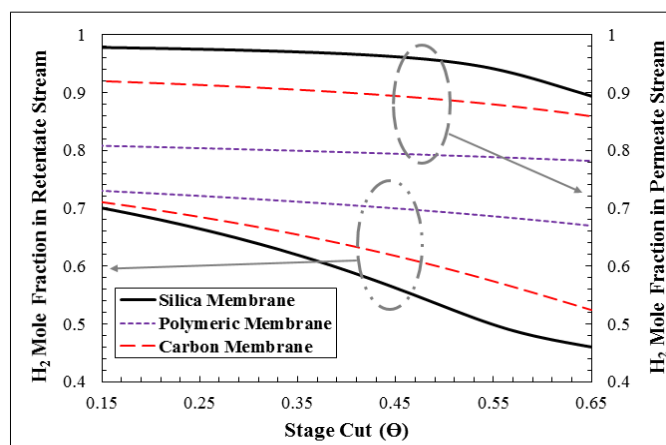


Fig. 3. The H₂ molar fraction in the permeate and retentate sides versus stage cut for various membranes (at T = 250 °C for silica and carbon membranes; at T = 50 °C for the polymeric membrane).

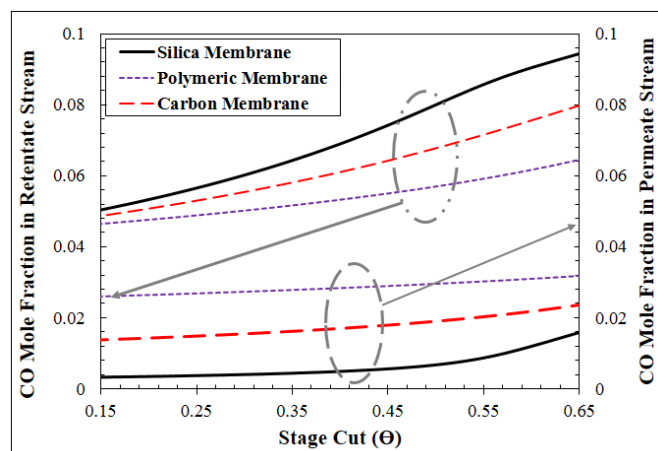


Fig. 4. CO molar fraction in the permeate and retentate sides versus stage cut for various membranes.

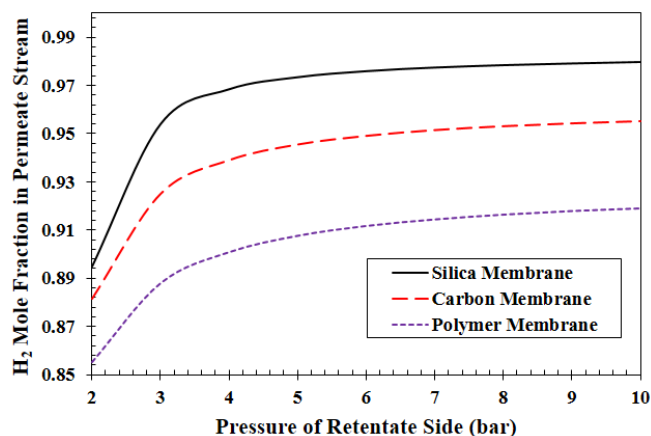


Fig. 5. H₂ molar fraction in the permeate side versus retentate pressure for various membrane applications.

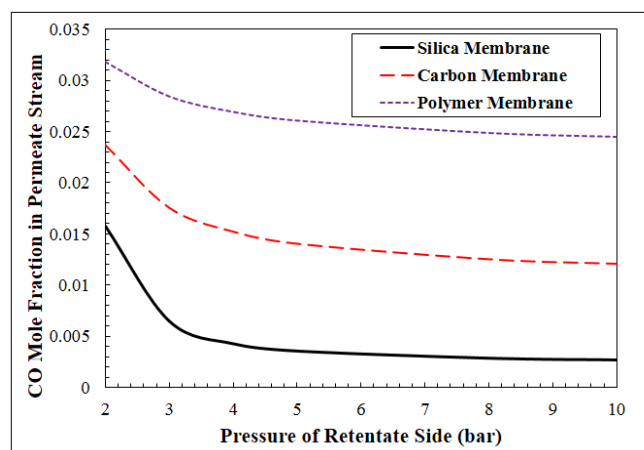


Fig. 6. CO molar fraction in the permeate side versus feed (or retentate) pressure: qualitative comparison among silica, carbon and polymeric membranes.

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 4

H₂, CO and CO₂ molar fractions in the permeate and retentate streams as a function of membrane surface area at stage cut = 0.65: qualitative comparison among silica, polymeric and carbon membranes.

Membrane type	Permeate Mole Fraction			Retentate Mole Fraction			Membrane Area(cm ²)
	H ₂	CO ₂	CO	H ₂	CO ₂	CO	
Silica membrane	0.89	0.09	0.02	0.46	0.45	0.09	18
Polymeric membrane	0.78	0.19	0.03	0.67	0.26	0.07	713
Carbon membrane	0.86	0.12	0.02	0.53	0.39	0.08	12934

Table 5

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

Retentate pressure side	Membrane area (cm ²)		
	Silica membrane	Polymeric membrane	Carbon membrane
2	18	713	12934
3	4.6	351	5524
4	2.4	233	3444
5	1.6	174	2492
8	0.8	99	1358
10	0.6	77	1041

Acronyms list

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

Nomenclature list

A: Membrane Area (m²).
 A_t: Total membran area (m²).
 J_i: permeating flux of component i through the membrane (mol/m².s).
 L: Flow rate on feed side (mol/s).
 L_F: Feed flow rate (mol/s).
 L_w: Retentate flow rate (mol/s).
 Pe_i: permeance of component i (mol/m².s.Pa).
 p_R: Pressure on retentate side (Pa).
 p_P: Pressure on permeate side (Pa).
 p_{i,retentate}: Partial pressure of component i in the retentate side (Pa).
 p_{i,permeate}: Partial pressure of component i in the permeate side(Pa).
 V: Flow rate on permeate side (mol/s).
 V_p: Permeate flow rate (mol/s).
 x_i: Mole fraction of component i on feed side.
 x_{Fi}: Mole fraction of component i in feed.
 x_{wi}: Mole fraction of component i in retentate (outlet).
 y_i: Mole fraction of component i in permeate stream.
 y_{pi}: Mole fraction of component i in permeate at the outlet.

Greek letter list

θ: Stage cut
 α: ideal selectivity

References

[1] A. Basile, A. Iulianelli, G. Bagnato, F. Dalena, Hydrogen production for PEM fuel

- cells, in: Z. Fang, R.L. Smith, X. Qi (Eds.) Production of hydrogen from renewable resources, Springer, Netherlands, pp. 339-356, 2015.
- [2] B. McLellan, E. Shoko, A. Dicks, J. D. Da Costa, Hydrogen production and utilisation opportunities for Australia, Int. J. Hydrogen Energy, 30 (2005) 669-679.
- [3] A. Iulianelli, A. Gugliuzza, G. Clarizia, D. Ebrasu, A. Bevilacqua, F. Trotta, A. Basile, Sulfonation of PEEK-WC polymer via chloro-sulfonic acid for potential PEM fuel cell applications, Int. J. Hydrogen Energy, 25 (2010) 12688-12695.
- [4] G.F. Tereschenko, M.M. Ermilova, V.P. Mordovin, N.V. Orekhova, V.M. Gryaznov, A. Iulianelli, F. Gallucci, A. Basile, New Ti-Ni dense membranes with low palladium content, Int. J. Hydrogen Energy, 32 (2007) 4016-4022.
- [5] F. Gallucci, E. Fernandez, P. Corengia, M. van Sint Annaland, Recent advances on membranes and membrane reactors for hydrogen production, Chem. Eng. Sci. 92 (2013) 40-66.
- [6] A. Iulianelli, T. Longo, S. Liguori, A. Basile, Production of hydrogen via glycerol steam reforming in a Pd-Ag membrane reactor over Co-Al₂O₃ catalyst, Asia-Pac. J. Chem. Eng., 5 (2010) 138-145.
- [7] C. Mateos-Pedrero, H. Silva, D.A. Pacheco Tanaka, S. Liguori, A. Iulianelli, A. Basile, A. Mendes, CuO/ZnO catalysts for methanol steam reforming: the role of the support polarity ratio and surface area, Appl. Catal. B Environ., 174 (2015) 67-76.
- [8] A. Iulianelli, M. Alavi, G. Bagnato, S. Liguori, J. Wilcox, M.R. Rahimpour, R. Eslamlouyan, B. Anzelmo, A. Basile, Supported Pd-Au membrane reactor for hydrogen production: membrane preparation, characterization and testing, Molecules, 21 (2016) 581-594.
- [9] K. Briceño, D. Montané, R. Garcia-Valls, A. Iulianelli, A. Basile, Fabrication variables affecting the structure and properties of supported carbon molecular sieve membranes for hydrogen separation, J. Membrane Sci., 415-416 (2012) 288-297.
- [10] A. Iulianelli, C. Algieri, L. Donato, A. Garofalo, F. Galiano, G. Bagnato, A. Basile, A. Figoli, New PEEK-WC and PLA membranes for H₂ separation, Int. J. Hydrogen Energy, 42 (2017) 22138-22148.
- [11] K. Ghasemzadeh, P. Morrone, A. Iulianelli, S. Liguori, A. Babaluo, A. Basile, H₂ production in silica membrane reactor via methanol steam reforming: Modeling and HAZOP analysis, Int. J. Hydrogen Energy, 38 (2013) 10315-10326.
- [12] K. Ghasemzadeh, P. Morrone, S. Liguori, A. Babaluo, A. Basile, Evaluation of silica membrane reactor performance for hydrogen production via methanol steam reforming: modeling study, Int. J. Hydrogen Energy, 38 (2013) 16698-16709.
- [13] A. Arratibel, U. Astobieta, D.A. Pacheco Tanaka, M. van Sint Annaland, F. Gallucci, N₂, He and CO₂ diffusion mechanism through nanoporous YSZ/γ-Al₂O₃ layers and their use in a pore-filled membrane for hydrogen membrane reactors, Int. J. Hydrogen Energy, 41 (2013) 8732-8744.
- [14] B.K.R. Nair, M.P. Harold, Hydrogen generation in a Pd membrane fuel processor: productivity effects during methanol steam reforming, Chem. Eng. Sci., 61 (2006)

- 6616-6636.
- [15] S. Wieland, T. Melin, A. Lamm, Membrane reactors for hydrogen production, *Chem. Eng. Sci.*, 57 (2002) 1571-1576.
 - [16] K. Ghasemzadeh, S. Liguori, P. Morrone, A. Iulianelli, V. Piemonte, A. Babaluo, A. Basile, H₂ production by low pressure methanol steam reforming in a dense Pd–Ag membrane reactor in co-current flow configuration: Experimental and modeling analysis, *Int. J. Hydrogen Energy*, 38 (2013) 16685-16697.
 - [17] K. Ghasemzadeh, R. Zeynali, A. Basile, Theoretical study of hydrogen production using inorganic membrane reactors during WGS reaction, *Int. J. Hydrogen Energy*, 41 (2016) 8696-8705.
 - [18] A. Iulianelli, S. Liguori, J. Wilcox, A. Basile, Advances on methane steam reforming to produce hydrogen through membrane reactors technology: a review, *Catal. Rev. Sci. Eng.*, 58 (2016) 1-35.
 - [19] A. Brunetti, G. Barbieri, E. Drioli, Pd-based membrane reactor for syngas upgrading, *Energy Fuel.*, 23 (2009) 5073-5076.
 - [20] A. Brunetti, E. Drioli, G. Barbieri, Medium/high temperature water gas shift reaction in a Pd-Ag membrane reactor: An experimental investigation, *RSC Adv.*, 2 (2012) 226-233.
 - [21] A. Brunetti, Y. Sun, A. Caravella, E. Drioli, G. Barbieri, Process intensification for greenhouse gas separation from biogas: More efficient process schemes based on membrane-integrated systems, *Int. J. Greenh. Gas Con.*, 35 (2015) 18-29.
 - [22] M. Abdel-Jawad, S. Gopalakrishnan, M. Duke, M. Macrossan, P.S. Schneider, J.D. da Costa, Flowfields on feed and permeate sides of tubular molecular sieving silica (MSS) membranes, *J. Membr. Sci.*, 299 (2007) 229-235.
 - [23] A. Aghaeinejad-Meybodi, K. Ghasemzadeh, A. Babaluo, A. Basile, Theoretical analysis of butane isomers separation using various membrane process configurations, *Int. J. Membr. Sci. Technol.*, 2 (2015) 45-54.
 - [24] Y. Shindo, T. Hakuta, H. Yoshitome, H. Inoue, Calculation methods for multicomponent gas separation by permeation, *Sep. Sci. Technol.*, 20 (1985) 445-459.
 - [25] K. Ghasemzadeh, Preparation of nanostructure silica membranes and their performance in membrane reactors for hydrogen production via methanol steam reforming process, PhD thesis, Sahand University of Technology, Tabriz, Iran, 2013.
 - [26] S.-H. Choi, A. Brunetti, E. Drioli, G. Barbieri, H₂ separation from H₂/N₂ and H₂/CO mixtures with Co-Polyimide hollow fiber module, *Sep. Sci. Technol.*, 46 (2011) 1-13.
 - [27] A. Harale, H. Hwang, P. Liu, M. Sahimi, T. Tsotsis, Experimental studies of a hybrid adsorbent-membrane reactor (HAMR) system for hydrogen production, *Chem. Eng. Sci.*, 62 (2007) 4126-4137.
 - [28] P. Simão Cardoso, Z. Lin, I. Portugal, A.E. Rodrigues, C.M. Silva, Synthesis, dynamic characterization, and modeling studies of an AM-3 membrane for light gases separation, *Microp. Mesop. Mater.*, 261 (2018) 170-180.
 - [29] M. Samei, M. Iravaninia, T. Mohammadi, A.A. Asadi, Solution diffusion modeling of a composite PVA/fumed silica ceramic supported membrane, *Chem. Eng. Proc. Proc. Intens.*, 109 (2016) 11-19.
 - [30] A.A. Al-Rabiah, A.M. Ajbar, M.A. Soliman, F.A. Almalki, O.Y. Abdelaziz, Modeling of nitrogen separation from natural gas through nanoporous carbon membranes, *J. Nat. Gas Sci. Eng.*, 26 (2015) 1278-1284.