



ELSEVIER

Contents lists available at SciVerse ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Hydrogen separation from multicomponent gas mixtures containing CO, N₂ and CO₂ using Matrimid[®] asymmetric hollow fiber membranes

Oana C. David^{a,1}, Daniel Gorri^{a,2}, Kitty Nijmeijer^{b,3}, Inmaculada Ortiz^{a,4}, Ane Urtiaga^{a,*}

^a Department of Chemical Engineering, University of Cantabria, Avda. Los Castros s/n, 39005 Santander, Spain

^b Membrane Science & Technology, University of Twente, PO Box 217, 7500 AE, Enschede, The Netherlands

ARTICLE INFO

Article history:

Received 10 April 2012

Received in revised form

20 June 2012

Accepted 23 June 2012

Available online 3 July 2012

Keywords:

Hydrogen recovery

Mixed gas separation

Polyimide hollow fiber

Plasticization

Competitive sorption

Carbon monoxide

ABSTRACT

The application of hollow fiber membranes for the separation of industrial gas mixtures relies on the correct characterization of the permeation of the involved gaseous components through the hollow fiber membranes. Thus, this study is focused on the characterization of the permeation through Matrimid[®] hollow fiber membranes of four gas mixtures containing H₂ (H₂/N₂, H₂/CO, H₂/CO₂), and the quaternary gas mixture H₂/N₂/CO/CO₂, working at a constant temperature of 303 K and pressures up to 10 bar. The main differences and similarities in the gas permeation properties of hollow fibers with respect to flat membranes, as well as in the permeation of gas mixtures with respect to pure gases, are discussed. Our results suggest that for mixtures containing H₂ and CO₂ hollow fiber membranes perform better than flat membranes given that a lower depression in the permeability of H₂ has been observed. At 2.3 bar feed pressure, ideal selectivity values obtained for H₂/N₂, H₂/CO and H₂/CO₂ gas pairs were 74.4, 42.6 and 5 respectively, with a H₂ permeance of $50.2 \times 10^{-8} \text{ m}^3(\text{STP}) \text{ m}^{-2} \text{ s}^{-1} \text{ kPa}^{-1}$. The specific behavior observed in the permeation through hollow fiber has been explained by a combination of different phenomena such as hollow fiber membrane substructure resistance, CO₂ induced plasticization and competitive sorption effects between the components of the gaseous mixtures.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Hydrogen can become an affordable, clean and reliable energy supply to be used in fuel cell vehicles, stationary power generation using fuel cells, or in more conventional engines to achieve a sustainable energy system. Nowadays, the most widely used method (80%) for H₂ production is the steam reforming of light hydrocarbons [1]. The production of H₂ from the gasification of coal is expected to present a significant increase in the future due to the important research efforts dedicated to the technological improvement to make the process more economic [2]. Besides, other sources of H₂ are the electrolysis of water and coke oven gas, with typical H₂ compositions above 50% [3]. Membrane technology, considered the ideal choice for hydrogen purification due to its lower power usage and cost, its simplicity in operation,

as well as its compactness and portability [4], today gains increasing importance in the separation of H₂/CO₂ mixtures coming from shifted or un-shifted syngas. There are numerous literature studies dedicated to H₂/CO₂ membrane-based separation, but they are generally limited to flat membranes. To the best of our knowledge, the few studies that use hollow fiber membranes for the separation of H₂/CO₂ do not report results with complex gas mixtures [5–9].

Polymeric membranes are capable of producing H₂ product streams with a maximum purity of 99.5% which can be used in several industrial applications with moderate purity requirements; hydrodesulfurization (90% purity), hydrocracking (70–80% purity) and also as fuel gas (54–60% purity) [3]. This work deals with the recovery of hydrogen from the combustion gaseous stream obtained in the production of carbon black, a commodity powdered product with widespread applications obtained by the combustion of a fuel under reducing conditions. The tail gas which is formed contains 60.5% N₂, 17.9% CO, 16.4% H₂ and 5.3% CO₂ (vol.%, dry basis). At the moment, the exhaust flue gases generated in the reactor are further used for power generation, where they are converted to carbon dioxide, water and heat. A global approach which considered a first step dedicated to the reactive absorption of carbon monoxide using ionic liquid media was studied in a previous work [10]. The remaining mixture

* Corresponding author. Tel.: +34 942 201587; fax: +34 942 201591.

E-mail addresses: oanacristina.david@unican.es (O.C. David), daniel.gorri@unican.es (D. Gorri), d.c.nijmeijer@utwente.nl (K. Nijmeijer), inmaculada.ortiz@unican.es (I. Ortiz), ana.urtiaga@unican.es (A. Urtiaga).

¹ Tel.: +34 942 206778; fax: +34 942 201591.

² Tel.: +34 942 201586; fax: +34 942 201591.

³ Tel.: +31 53 489 4185; fax: +31 53 489 4611.

⁴ Tel.: +34 942 201585; fax: +34 942 201591.

would contain a low concentration of valuable H_2 , the major component being the low permeating N_2 . Then, the recovery of H_2 by means of membrane technology needs an H_2 selective membrane which allows for high permeabilities and good selectivities towards H_2 . Since H_2 permeation rate is strongly affected by the presence of CO_2 even at low concentrations, a detailed study of the binary H_2/CO_2 mixtures is reported here. The H_2 enriched stream could be further used in the industrial synthesis routes of a variety of valuable added products, such as fuel gas or as the first stage in a multi-stage separation process, designed to obtain a high purity (>99.9 vol%) H_2 stream which is required in fuel cell applications [11].

In a previous work [12], we reported on the specific phenomena that occur in the permeation of gas mixtures containing H_2 through flat dense Matrimid[®] membranes and we determined a different transport behavior of the gaseous mixtures with respect to pure gas components. Phenomena like concentration polarization and competitive transport were thoroughly studied and modeled in dense films. In this work we assess the same application using asymmetric Matrimid[®] hollow fibers membranes, because large-scale gas separation applications demand highly productive membranes with elevated membrane surface/volume ratios, and membranes with hollow fiber geometry have a distinctive advantage over flat sheet membranes. The hollow fiber membranes used in the gas separation technology are high flux membranes that have an asymmetric structure with a thin selective skin on a much thicker, but highly porous supporting layer. In contrast with dense films, the complex morphology of asymmetric hollow fibers distinctively influences behavior towards the transport of gases [13,14]. First of all, a microporous transition layer (substructure) found between the dense skin and the highly porous sub-layer provides an important contribution to the overall resistance when the gas transport through the substructure is by Knudsen or/and a surface flow mechanism. Secondly, due to a much thinner dense skin of the asymmetric hollow fiber layer, compared to the thickness of a flat dense film (0.1–0.5 μm compared to 30 μm), accelerated plasticization with CO_2 is induced [15]. Finally, in the case of the permeation of H_2/CO_2 gas mixtures, competitive sorption effects may take place and are partially balanced by plasticization. Therefore, it is clear that the use of thick film data to design or select membrane materials only gives a rough approximation of the performance that might be achieved in practice. To the best of our knowledge, little or no available information can be found in the open literature on the separation of gas mixtures containing H_2 and CO_2 with Matrimid[®] asymmetric hollow fiber membranes and more specifically, quaternary gas mixture $N_2/H_2/CO/CO_2$. Therefore, this work is focused on the characterization of the permeation through Matrimid[®] hollow fiber membranes of pure H_2 , N_2 , CO and CO_2 and of four H_2 -containing gas mixtures: H_2/N_2 , H_2/CO , H_2/CO_2 and the quaternary gas $H_2/N_2/CO/CO_2$.

2. Experimental

2.1. Preparation of asymmetric hollow fiber membranes

The fabrication of Matrimid[®] hollow fibers was based on a dry wet spinning process. The commercial polymer, Matrimid[®] 9725 (polyimide of 3,3',4,4'-benzophenone tetracarboxylic dianhydride and diamino-phenylidane), was kindly provided by Huntsman Advanced Polymers. Matrimid[®] 9725, a micro-pulverized version of Matrimid[®] 5218, is a hydrophobic polymer soluble in several solvents and has excellent mechanical and thermal properties with a glass transition temperature above 315 °C [16]. The formation conditions for the fibers are summarized in Table 1 and are based

Table 1
Formation conditions for Matrimid[®] asymmetric hollow fiber membranes.

<i>Dope composition</i>	
Matrimid [®]	26.2 wt%
NMP [*]	58.9 wt%
EtOH	14.9 wt%
<i>Bore composition</i>	
NMP	96 wt%
H_2O	4 wt%
<i>Spinning conditions</i>	
Tube in orifice spinneret	
OD	0.5 mm
ID	0.2 mm
Spinneret temperature	50 °C
Dope flow rate	122.4 mL h ⁻¹
Bore flow rate	360 mL h ⁻¹
Air gap height	12 cm
Room temperature	22 °C
Room humidity	32%
Quench temperature	20 °C, water
Take-up rate	13.4 m min ⁻¹
<i>Sequential dehydration procedure</i>	
(1) Water baths	continuous flow 24 h
(2) MeOH baths	3 (20 min each)
(3) Hexane baths	3 (20 min each)
(4) Ambient dry	

* NMP: *n*-methyl pyrrolidone.

on optimized procedures reported in literature [17–20]. The polymer powder was dried in a vacuum oven at 100 °C for at least 12 h prior to use. The dope solution was prepared at 50 °C in a Pyrex[®] vessel with mechanical stirring (Heidolph RZR 2041) and a coiled condenser was used to prevent ethanol loss. After mixing for at least 8 h, the dope solution was filtered with a 15 μm sintered metallic filter (Bekipor STAL3 Bekaert) and poured into a sealed spinning dope tank where it was left to degas at 50 °C for 24 h before spinning. The bore solution and the water quench bath were also left to degas 24 h before spinning. The polymer solution and the bore fluid were simultaneously pumped through a tube-in-orifice spinneret using gear pumps. The spinneret dimensions are listed in Table 1. The hollow fibers were manufactured using a spinning line with features such as those described in literature [21]. During the spinning process we were able to obtain the hollow fiber structure at a minimum bore flow rate of 360 mL h⁻¹, which is three times higher than the dope flow rate. The fiber was not hollow at lower values of the bore flow rate and this might be a consequence of the low concentration of non solvent in the bore liquid.

After spinning, the hollow fibers were rinsed for 24 h in a water bath, continually being renewed with tap water. Next, the solvent exchange procedure using methanol and hexane listed in Table 1 was applied. In the gas separation experiments, well-aged fibers (12 months of storage) were used, since the impact of physical aging over the permeation properties of Matrimid[®] hollow fiber membranes has been shown to determine a decrease in the permeation of N_2 in time, even after 250 days of storage prior to permeation experiments [19]. The physical aging is a process in which the non-equilibrium polymer chains slowly relax towards the equilibrium state [22] and it is detectable in reasonable timescales in the samples approximately 0.1 μm thick or less [23].

2.2. Permeation set-up

Membrane permeation properties were determined using the experimental set-up and procedure described in a previous work

[12]. Hollow fiber membrane modules were built by insertion of a fiber of ~ 10 cm length within a tubular stainless steel container in a counter-flow configuration. The hollow fiber modules were pressurized with the feed gas mixture at the bore side and an argon sweep gas was passed through the fiber shell to remove and transport the permeate stream to a gas chromatograph (Agilent Micro GC 3000). The feed gas flowed counter currently with the argon sweep gas flow. This configuration allowed side effects like concentration polarization to be removed and thus achieve ideal fluid-dynamics conditions needed for the specific purpose of our study. The feed gas pressure was measured at both the inlet and outlet ports of the membrane module. At the inlet port of the membrane module a pressure gauge (Swagelok PGI-40M-BC9-LANX) was inserted, and at the outlet port the pressure was indicated by a back pressure regulator (Brooks 5866) which controls the pressure at the feed side of the membrane. In order to calculate the gas permeability through the membrane, the logarithmical mean between the pressures at the entrance and exit of the module (feed and retentate stream pressures) was used as total feed pressure.

Pure and mixed gas permeation studies were carried out at feed pressures ranging from 2 to 10 bar with H_2 , CO_2 , CO and N_2 using the Matrimid[®] hollow fiber membranes, prepared according to the methodology described in Section 2. All the other operational parameters were kept constant: the temperature at 30 °C, the feed flow rate at $100 \text{ cm}^3(\text{STP}) \text{ min}^{-1}$ and the sweep gas flow rate at $10 \text{ cm}^3(\text{STP}) \text{ min}^{-1}$.

Permeation experiments with mixed gases were performed with binary mixtures (H_2/CO_2 , H_2/N_2 and H_2/CO) and with a quaternary mixture ($H_2/CO_2/N_2/CO$) at compositions listed in Table 2, using the Matrimid[®] hollow fiber membrane developed as described in Section 2.

Each experimental run was conducted at specific conditions until constant steady-state values of permeate flux and composition were reached. Normally, the time needed to reach the steady state level was 1 h. Once the steady state was reached, the concentration of each component was analyzed at least five times at 3 min intervals. All the gas permeation data reported in the results and discussion section are average values obtained from at least two experimental runs performed at different moments, usually after performing other experimental runs at different

operation conditions. In all of the cases, the standard deviation was 2% lower than the average value.

3. Results and discussion

3.1. Morphological and structural characterization

The morphological and structural characteristics of the asymmetric hollow fibers were investigated using SEM analysis (Fig. 1). The hollow fiber membranes displayed satisfactory cross-sectional circularity and concentricity. The values of the outer and inner diameters of the fibers were evaluated using at least four cross-sectional SEM images on average taken from sample cuts at different lengths of the same fiber (Table 3).

The fibers have a microporous sponge-like structure with isolated macrovoids and have an external dense skin layer whose thickness (l) values were calculated from pure gas permeation data obtained at a feed pressure of 2 bar using

$$l(\text{nm}) = \frac{\text{Permeability} (\text{m}^3(\text{STP}) \text{ m m}^{-2} \text{ s}^{-1} \text{ kPa}^{-1})}{\text{Permeance} (\text{m}^3(\text{STP}) \text{ m}^{-2} \text{ s}^{-1} \text{ kPa}^{-1})} 10^9 \quad (1)$$

where the permeability ($\text{m}^3(\text{STP}) \text{ mm}^{-2} \text{ s}^{-1} \text{ kPa}^{-1}$) represents the intrinsic permeation property of the polymeric material obtained from pure gas permeation experiments with a dense Matrimid[®] film of known thickness. The permeance ($\text{m}^3(\text{STP}) \text{ m}^{-2} \text{ s}^{-1} \text{ kPa}^{-1}$) is the transport flux per unit transmembrane driving force through the asymmetric hollow fiber.

The pure gas permeability of the Matrimid[®] dense film and the hollow fiber permeance used to calculate the dense layer thickness in the asymmetric hollow fibers developed in this study are listed in Table 4 and the results depend on the tested gas. In literature [17,24], the thickness of the dense layer is usually calculated from the data obtained with one gas; usually O_2 . Another method consists of fitting the permeability versus permeance data for a number of different pure gases in the same plot and obtaining the fiber thickness from the slope [25]. In our case, the latter procedure gives an average value of 354 nm when pure gas (H_2 , CO_2 , CO and N_2) permeability versus permeance data obtained in the feed pressure ranging between 2 and 10 bar are plotted together (see Fig. 2). This result is close to the thickness

Table 2
Mixed gas compositions used for gas permeation experiments.

Gas mixture	Compositions (vol.%)
H_2/CO_2	20/80, 40/60, 60/40, 80/20
H_2/N_2	20/80, 50/50, 80/20
H_2/CO	20/80, 50/50, 80/20
$H_2/CO_2/N_2/CO$	16.4/5.36/60.3/17.9

Table 3
Structural dimensions of Matrimid[®] asymmetric hollow fiber membranes. Skin layer thicknesses were calculated according to Eq. (1) from pure gas permeation data.

OD (μm)	ID (μm)	Skin layer thickness (nm)			
		H_2	CO_2	N_2	CO
500 ± 10	291 ± 31	358	540	239	274

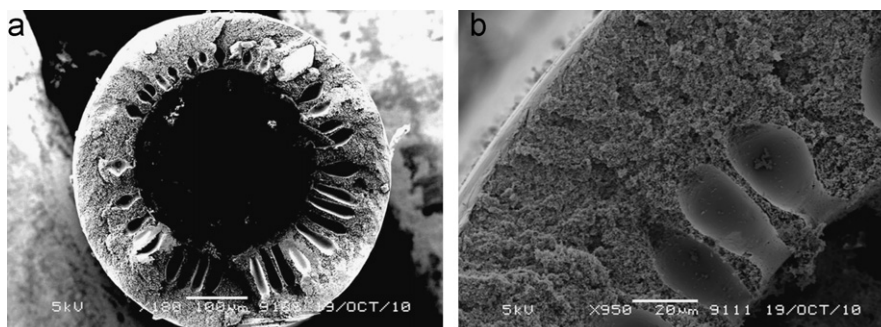


Fig. 1. SEM images of Matrimid[®] hollow fibers: (a) cross section and (b) detail of the dense skin layer.

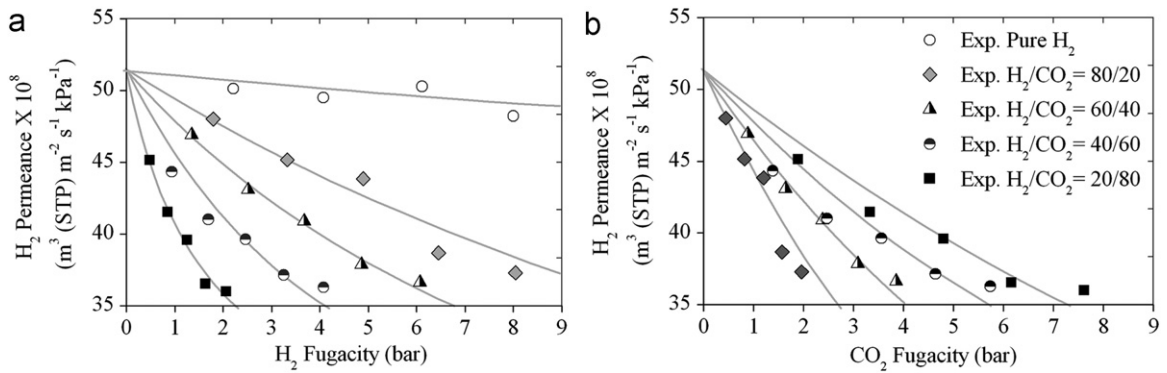


Fig. 3. H₂ permeance variation as function of the fugacity of H₂ (a) and of CO₂ (b) for H₂/CO₂ mixtures and pure H₂ in asymmetric Matrimid[®] hollow fiber membranes. The lines are drawn for a better visualization of the gas permeation tendency.

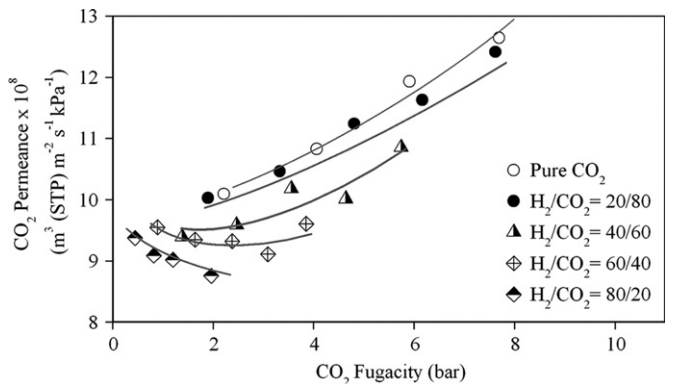


Fig. 4. CO₂ permeance variation with its fugacity for H₂/CO₂ mixtures and pure CO₂ in asymmetric Matrimid[®] hollow fiber membrane. The lines are drawn for a better visualization of the gas permeation tendency.

prepared and characterized in this work which were calculated from the values reported in Table 4 are 34% for H₂ and of 61% for CO₂ at 2 bar.

Another remarkable aspect is that in the studied pressure range, from 2 to 10 bar, H₂, CO and N₂ pure gas permeance data through the hollow fiber remained almost constant. In contrast, the permeance of CO₂ rose strongly and increased by 42% when the pressure increased from 2 to 10 bar. This tendency in the permeation of condensable gases like CO₂ has already been well-documented in literature for asymmetric hollow fibers, thin and thick flat membranes and has been attributed to plasticization phenomena [32,33]. In dense thick Matrimid[®] films (thickness around 30 μm), the permeability of CO₂ first decreases with pressure until it reaches a minimum from where it then begins to increase. This minimum was reported to be 15 bar at 308 K [34] and 12 bar at 295 K [35]. The decrease in gas permeability is related to the decrease in gas solubility coefficient with pressure, since the polymer sorption sites found in the polymer matrix become saturated with gas molecules at increasing values of pressure. At plasticization pressure, the polymeric chain-packing is disrupted by the penetrant molecules due to the increase in the segmental mobility that expands both the frequency and the average size of transient gaps that enable diffusion, thereby increasing the permeability. It was reported in literature that in Matrimid[®] thin films (thickness below 5.2 μm) [15] or for even thinner films such as those obtained in asymmetric hollow fibers, the minimum observed in permeability versus pressure plot may even disappear and permeability increases immediately, even at low feed pressures. It is assumed that accelerated plasticization occurs because of the steep swelling-induced stress gradients

related to the thinner membrane [36]. Comparative results for the variation with pressure of CO₂ permeance in Matrimid[®] hollow fibers were previously reported in other studies [37]. In our work, the different trend in the transport rate of H₂ and CO₂ determines a decrease in the H₂/CO₂ ideal selectivity, with increasing pressure from a value of 4.9 at 2 bar to 3.4 at 10 bar as shown in Table 4.

3.2.2. Mixed gas permeation

Fig. 3 shows permeation results for H₂ transport from the binary H₂/CO₂ feed mixtures plotted against the fugacity of H₂ (Fig. 3a) and plotted against the fugacity of CO₂ (Fig. 3b) at different total feed pressures. In comparison with pure gas permeation results, the permeance of H₂ from mixtures is lower and for a constant gas composition it decreases at increasing total feed pressure, i.e., when the fugacity of both H₂ and CO₂ increases. This phenomenon is related to the competitive sorption between H₂ and CO₂, for the sorption sites which are associated to the excess (non-equilibrium) free volume fraction of the polymer [38]. Working with gas mixtures, the availability of the sorption sites for one component is lowered due to the presence of the other components and thus its transport rate is also lowered when it is compared with pure gas transport rate. While H₂ is a relatively inert and fast permeating gas whose transport rate is diffusion-based, CO₂ is a more condensable gas and possesses higher solubility in membranes. Therefore, the polymer sorption sites are preferentially occupied with CO₂ than with H₂ leading to a higher decay in the permeability of H₂ than in the permeability of CO₂, for H₂/CO₂ gas mixtures with respect to pure gases, in both hollow fiber and flat membranes. In flat membranes, the mixed gas permeation of H₂ was only dependent on the fugacity of CO₂; i.e. equal values for the H₂ mixed gas permeability data were obtained for H₂/CO₂ mixtures when the fugacity of CO₂ was kept constant and the fugacity of H₂ was increased [12]. In contrast, this behavior is not repeatable in hollow fiber membranes and lower H₂ permeance values were obtained at higher fugacity of H₂ for the same fugacity of CO₂ (see Fig. 3b). The explanation of such behavior will be discussed later, after analysis of the CO₂ permeation data.

Fig. 4 shows the permeation results for CO₂ transport in binary H₂/CO₂ mixtures plotted against the fugacity of CO₂ for different feed compositions in the range H₂/CO₂=20/80 to H₂/CO₂=80/20. The maximum operating pressure was 10 bar and therefore the maximum attainable fugacity of CO₂ in the mixture H₂/CO₂=80/20 was 2 bar. The permeance of CO₂ decreased with its fugacity for the H₂/CO₂ mixture of 80/20 (vol.%). It practically remained constant for the mixture H₂/CO₂=60/40 (vol.%) and for the rest of

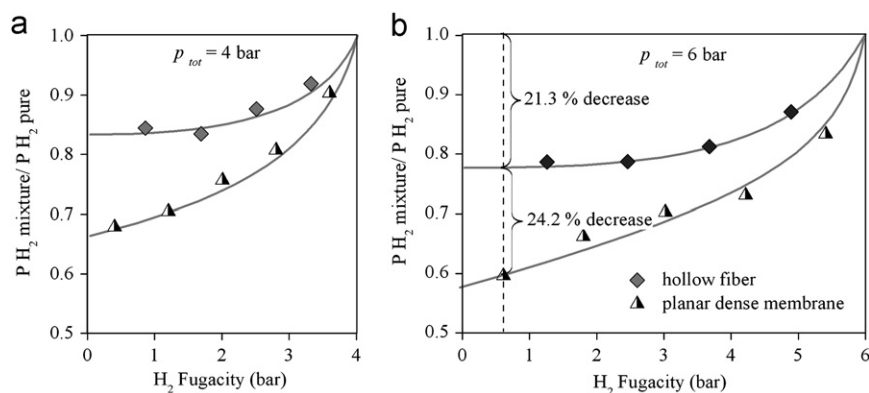


Fig. 5. Hollow fiber versus flat dense membrane comparative study for the depression in the permeation of H₂ for H₂/CO₂ mixtures with respect to pure gas, at total feed pressure of 4 bar (a) and 6 bar (b).

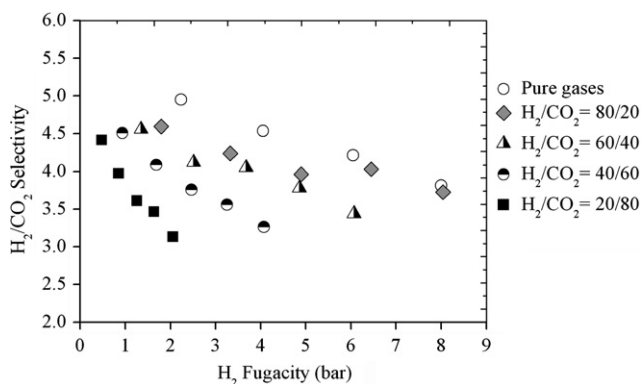


Fig. 6. H₂/CO₂ selectivity variation with the fugacity of H₂ for binary H₂/CO₂ mixtures in asymmetric Matrimid[®] hollow fiber membranes.

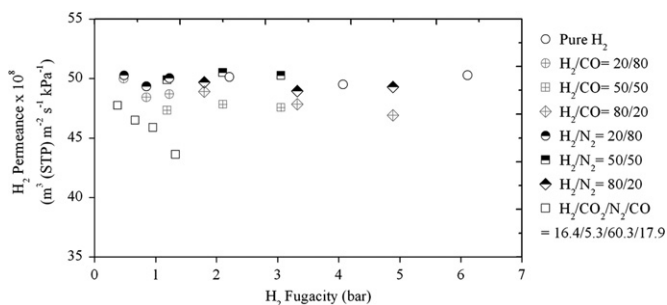


Fig. 7. H₂ permeance variation with its fugacity for H₂/N₂, H₂/CO and H₂/CO₂/N₂/CO mixtures and pure H₂ in asymmetric Matrimid[®] hollow fiber membranes.

the mixtures (with CO₂ concentration > 40%), the CO₂ permeance increased with the concentration of CO₂ in the mixtures, reaching values close to permeance data of pure CO₂. This tendency corresponds to a balance between two opposite effects that affect CO₂ transport through a thin Matrimid[®] layer: competitive sorption and plasticization phenomena for H₂/CO₂ mixtures in hollow fibers. While plasticization increases the permeation of CO₂ with pressure, competitive sorption between H₂ and CO₂ determines a decrease in the permeation of CO₂. In the previous study, using thick flat Matrimid[®] films where plasticization was not found, the permeability of CO₂ was slightly lower than pure gas permeability and presented a similar behavior of decreasing permeability with increasing CO₂ fugacity [12] at any composition of the feed gas mixture. In Matrimid[®] hollow fibers, at a high concentration of H₂ in the H₂/CO₂ mixture, competitive sorption

prevails and the permeance of CO₂ decreases with its fugacity. As the concentration of CO₂ increases, plasticization counteracts competitive sorption, and equilibrium between the two phenomena is reached when the permeance of CO₂ remains constant with its fugacity. At a high concentration of CO₂ in the H₂/CO₂ mixture, plasticization dominates the transport rate of CO₂ and the permeance of CO₂ increases with its fugacity. Similar results were reported in literature for CO₂/CH₄ mixtures in Matrimid[®] asymmetric hollow fiber membranes. In some studies [15,20,36], plasticization was dominant at high CO₂ feed gas concentrations (80 vol% CO₂), while competitive sorption effects were dominant at low CO₂ feed gas concentrations (20 vol%). In a different study [19], working with a 10/90 (vol%) CO₂/CH₄ feed mixture, competitive sorption was also dominant and the permeance of CO₂ decreased with CO₂ partial pressure.

Plasticization of the membrane by CO₂ can also affect the transport rate of H₂. Fig. 5 presents the ratio between H₂ permeation values obtained when working with pure gas and binary H₂/CO₂ feed mixtures for dense films and hollow fibers. The effect of using thin asymmetric layers in hollow fiber structure versus flat thick Matrimid[®] films appears. The pure and mixed gas H₂ permeability values for flat films were reported in our previous study [12]. At a total feed pressure of 6 bar, decay in the permeation values of H₂ with respect to pure gas values is higher for Matrimid[®] films than for hollow fibers. In Matrimid[®] flat films the decay was 45%, whereas the decay in the hollow fibers was only 21%. Following previous operating conditions with pressures up to 6 bar, CO₂ plasticization phenomena in dense Matrimid[®] films were not found, and only competitive sorption was observed. We can conclude that CO₂ plasticization found for the permeation of H₂/CO₂ mixtures through Matrimid[®] hollow fibers leads to higher permeation values for H₂. This behavior is better explained in terms of the so-called “transport plasticization” which can occur in the presence of highly sorbing penetrants which are capable of swelling the polymer matrix and introduce additional free volume that enables higher values for penetrant diffusion [39]. Therefore, as shown in Fig. 3, at a constant fugacity of CO₂, the decay in the permeation of H₂ was higher for mixtures with a higher concentration in H₂, due to a lower plasticization with CO₂ and an increased competitive sorption between H₂ and CO₂.

Hollow fiber mixed gas selectivity values, calculated as described in our previous work have been plotted in Fig. 6 for H₂/CO₂ mixtures. The lower permeation of H₂ in binary H₂/CO₂ mixtures determines a considerably lower selectivity for the gas pair H₂/CO₂ than the ideal selectivity. The mixed gas selectivity strongly varies with gas composition and pressure with values of $\alpha=3.1$ for the 20/80 H₂/CO₂ mixture at a total pressure of 10 bar

and H₂ fugacity of 2 bar compared to 4.6 for the 80/20 H₂/CO₂ mixture at total pressure of 2 bar. The selectivity values are lower for gas mixtures than for pure gases but are higher than the average mixed gas selectivities obtained with flat membranes with a value of 2.7. Two factors might contribute to this difference; (i) a lower depression in the transport rate of H₂ in H₂/CO₂ mixtures for hollow fiber membranes than for dense films and (ii) a higher substructure resistance towards the transport of CO₂.

In the case of H₂ mixtures with relatively more inert gases such as N₂ and CO, the permeance values for H₂ are close to pure gas values and are slightly lower when the co-partner for H₂ was CO (Fig. 7). This demonstrates that between H₂ and N₂ or CO, only slight competitive sorption effects are found which are relatively stronger for H₂/CO mixtures than for H₂/N₂ mixtures. Contrary to other reports [26], plasticization does not occur in H₂/CO mixtures or for pure CO, whose permeance is constant within the pressure range 1–10 bar (see Table 4). These results are consistent with published literature data for pure H₂ and CO and for H₂/CO mixtures in another polyimide membrane [40]. Fig. 7 also shows H₂ permeance values for the quaternary H₂/CO₂/N₂/CO mixture. With respect to pure gas permeability a small percentage of CO₂ (5.36 vol%), such as that found in the tail gas from carbon black manufacturing, determines a 12% decrease in the permeance values for H₂, working at a total feed pressure of 8 bar.

The concentration of H₂ in the permeate stream leaving the hollow fiber membrane module was between 87 vol% and 89 vol%, calculated on Ar-free basis. We assume that under industrial operating conditions the concentration of H₂ in the permeate stream is expected to be somehow lower, since our experimental values were obtained by working close to ideal operation conditions, that is to say counter current plug flow and very low stage cuts.

4. Conclusions

The pure and mixed gas permeation behavior of a Matrimid[®] asymmetric hollow fiber membrane has been investigated over a broad range of concentrations for the separation of H₂ from N₂, CO and CO₂. Distinct gas separation performances were found for asymmetric hollow fibers in relation to thick flat dense Matrimid[®] films. In the case of pure gas permeation, a higher membrane substructure resistance for CO₂ than for H₂ determines higher H₂/CO₂ selectivity and a higher membrane substructure resistance for H₂ than for N₂ and CO determines a lower H₂/N₂ and H₂/CO ideal separation factors compared to flat membranes. As in flat dense membranes, the permeance of H₂, N₂ and CO remained almost constant with pressure (up to 10 bar), with average values of $49.5 \times 10^{-8} \text{ m}^3(\text{STP}) \text{ m}^{-2} \text{ s}^{-1} \text{ kPa}^{-1}$ for H₂, $0.7 \times 10^{-8} \text{ m}^3(\text{STP}) \text{ m}^{-2} \text{ s}^{-1} \text{ kPa}^{-1}$ for N₂ and $1.2 \times 10^{-8} \text{ m}^3(\text{STP}) \text{ m}^{-2} \text{ s}^{-1} \text{ kPa}^{-1}$ for CO. In contrast, the permeance of CO₂ strongly increased with pressure, with values of $10.1 \times 10^{-8} \text{ m}^3(\text{STP}) \text{ m}^{-2} \text{ s}^{-1} \text{ kPa}^{-1}$ at 2 bar and $14.4 \times 10^{-8} \text{ m}^3(\text{STP}) \text{ m}^{-2} \text{ s}^{-1} \text{ kPa}^{-1}$ at 10 bar. The presence of CO₂ shows the opposite behavior compared to that observed in flat membranes, where it decreased. This is related to an induced plasticization phenomenon when in asymmetric membranes: the segmental mobility of the polymer chains under the transport of highly sorbing penetrants like CO₂ is increased, the polymer matrix swells and an additional free volume is introduced increasing the permeability of the material. In the case of the permeation of gas mixtures, as in flat membranes, competitive sorption effects determine a decrease in the permeation of H₂ with respect to pure gases. This depression is higher for H₂/CO₂ binary mixtures than for H₂/N₂ or H₂/CO mixtures, where it is almost null. Due to plasticization-induced

higher transport rates of H₂ in H₂/CO₂ mixtures, the decay in the permeation of H₂ is not as high as in flat membranes. A maximum decay in the permeation of H₂ of 21.3% was reached for H₂ fugacities below 1 bar and 6 bar total feed pressure, whereas in the flat membranes the decay was 45.5% at the same conditions. These results determine the variation of mixed gas H₂/CO₂ selectivity with composition and pressure, with values ranging from 4.6 to 3.1. These values are higher than in flat membranes; the minimum reached for the composition H₂/CO₂=20/80 at 10 bar total pressure of 3.1 approaches the average value of 2.9 obtained with flat membranes. Our results suggest that for H₂ mixtures containing CO₂ the hollow fiber membrane performance is better than that of flat membranes, and therefore using thick film data to design or select membrane materials only gives a rough approximation of the performance that might be reached in practice.

Acknowledgments

Financial support from the Spanish Ministry of Science under the projects: ENE 2010–15585 and CTQ 2008–00690/PPQ is gratefully acknowledged. Oana C. David also thanks the Ministry of Education for a FPU postgraduate research grant.

References

- [1] N.W. Ockwig, T.M. Nenoff, Membranes for hydrogen separation, *Chem. Rev.* 107 (2007) 4078–4110.
- [2] <http://www.netl.doe.gov/technologies/hydrogen_clean_fuels/central.html>.
- [3] J.D. Perry, K. Nagai, W.J. Koros, Polymer membranes for hydrogen separations, *MRS Bull.* 31 (2006) 745–749.
- [4] L. Shao, B.T. Low, T.-Chung, A.R. Greenberg, Polymeric membranes for the hydrogen economy: contemporary approaches and prospects for the future, *J. Membr. Sci.* 327 (2009) 18–31.
- [5] E.P. Favvas, E.P. Kouvelos, G.E. Romanos, G.I. Pilatos, A.C. Mitropoulos, N.K. Kanellopoulos, Characterization of highly selective microporous carbon hollow fiber membranes prepared from a commercial co-polyimide precursor, *J. Porous Mater.* 15 (2008) 625–633.
- [6] E.P. Favvas, G.C. Kapantaidakis, J.W. Nolan, A.C. Mitropoulos, N.K. Kanellopoulos, Preparation, characterization and gas permeation properties of carbon hollow fiber membranes based on Matrimid[®] 5218 precursor, *J. Mater. Process. Technol.* 186 (2007) 102–110.
- [7] S.S. Hosseini, N. Peng, T.S. Chung, Gas separation membranes developed through integration of polymer blending and dual-layer hollow fiber spinning process for hydrogen and natural gas enrichments, *J. Membr. Sci.* 349 (2010) 156–166.
- [8] S.C. Kumbharkar, Y. Liu, K. Li, High performance polybenzimidazole based asymmetric hollow fibre membranes for H₂/CO₂ separation, *J. Membr. Sci.* 375 (2011) 231–240.
- [9] X. Jie, Y. Cao, B. Lin, Q. Yuan, Gas permeation performance of cellulose hollow fiber membranes made from the cellulose/N-methylmorpholine-N-oxide/H₂O system, *J. Appl. Polym. Sci.* 91 (2004) 1873–1880.
- [10] O.C. David, G. Zarca, D. Gorri, A. Urtiaga, I. Ortiz, On the improved absorption of carbon monoxide in the ionic liquid 1-hexyl-3-methylimidazolium chlorocuprate, *Sep. Purif. Technol.*, in press, <http://dx.doi.org/10.1016/j.seppur.2012.02.015>.
- [11] J.A. Turner, Sustainable hydrogen production, *Science* 305 (2004) 972–974.
- [12] O.C. David, D. Gorri, A. Urtiaga, I. Ortiz, Mixed gas separation study for the hydrogen recovery from H₂/CO/N₂/CO₂ post combustion mixtures using a Matrimid[®] membrane, *J. Membr. Sci.* 378 (2011) 359–368.
- [13] M. Mulder, *Basic Principles of Membrane Technology*, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1996.
- [14] R.W. Baker, *Membrane Technology and Applications*, 2nd edition, John Wiley & Sons, New York, 2004.
- [15] M. Wessling, M. Lidon Lopez, H. Strathmann, Accelerated plasticization of thin-film composite membranes used in gas separation, *Sep. Purif. Technol.* 24 (2001) 223–233.
- [16] B. Zornoza, C. Téllez, J. Coronas, Mixed matrix membranes comprising glassy polymers and dispersed mesoporous silica spheres for gas separation, *J. Membr. Sci.* 368 (2011) 100–109.
- [17] D.T. Clausi, W.J. Koros, Formation of defect-free polyimide hollow fiber membranes for gas separations, *J. Membr. Sci.* 167 (2000) 79–89.
- [18] G. Dong, H. Li, V. Chen, Factors affect defect-free Matrimid[®] hollow fiber gas separation performance in natural gas purification, *J. Membr. Sci.* 353 (2010) 17–27.

- [19] J.S. Lee, W. Madden, W.J. Koros, Antiplasticization and plasticization of Matrimid[®] asymmetric hollow fiber membranes—Part A. Experimental, *J. Membr. Sci.* 350 (2010) 232–241.
- [20] T. Visser, N. Masetto, M. Wessling, Materials dependence of mixed gas plasticization behavior in asymmetric membranes, *J. Membr. Sci.* 306 (2007) 16–28.
- [21] G.C. Kapantaidakis, G.H. Koops, High flux polyethersulfone–polyimide blend hollow fiber membranes for gas separation, *J. Membr. Sci.* 204 (2002) 153–171.
- [22] M.B. Moe, W.J. Koros, D.R. Paul, Effects of molecular structure and thermal annealing on gas transport in two tetramethyl bisphenol-A polymers, *J. Polym. Sci. B* 26 (1988) 1931–1945.
- [23] D. Punsalan, W.J. Koros, Thickness-dependent sorption and effects of physical aging in a polyimide sample, *J. Appl. Polym. Sci.* 96 (2005) 1115–1121.
- [24] S.B. Carruthers, G.L. Ramos, W.J. Koros, Morphology of integral-skin layers in hollow-fiber gas-separation membranes, *J. Appl. Polym. Sci.* 90 (2003) 399–411.
- [25] J.C. Jansen, M. Macchione, E. Drioli, On the unusual solvent retention and the effect on the gas transport in perfluorinated Hyflon AD[®] membranes, *J. Membr. Sci.* 287 (2007) 132–137.
- [26] M. Peer, S.M. Kamali, M. Mahdeyfar, T. Mohammadi, Separation of hydrogen from carbon monoxide using a hollow fiber polyimide membrane: experimental and simulation, *Chem. Eng. Technol.* 30 (2007) 1418–1425.
- [27] D.T. Clausi, S.A. McKelvey, W.J. Koros, Characterization of substructure resistance in asymmetric gas separation membranes, *J. Membr. Sci.* 160 (1999) 51–64.
- [28] I. Pinnau, W.J. Koros, Relationship between substructure resistance and gas separation properties of defect-free integrally skinned asymmetric membranes, *Ind. Eng. Chem. Res.* 30 (1991) 1837–1840.
- [29] T. Matsuura, *Synthetic Membranes and Membrane Separation Processes*, 1st ed., CRC Press, Inc., Florida, 1993.
- [30] J.O. Hirschfelder, C.F. Curtiss, R.B. Bird, *The Molecular Theory of Gases and Liquids*, John Wiley & Sons, Inc., New York, 1954.
- [31] J.M.S. Henis, M.K. Tripodi, Composite hollow fiber membranes for gas separation: the resistance model approach, *J. Membr. Sci.* 8 (1981) 233–246.
- [32] S. Matteucci, Y. Yampolskii, B.D. Freeman, I. Pinnau, Transport of gases and vapors in glassy and rubbery polymers, in: *Materials Science of Membranes for Gas and Vapor Separation*, John Wiley & Sons, Ltd, 2006, pp. 1–47.
- [33] K. Simons, K. Nijmeijer, J.G. Sala, H. van der Werf, N.E. Benes, T.J. Dingemans, M. Wessling, CO₂ sorption and transport behavior of ODPa-based polyetherimide polymer films, *Polymer* 51 (2010) 3907–3917.
- [34] A. Bos, I.G.M. Pünt, M. Wessling, H. Strathmann, Plasticization-resistant glassy polyimide membranes for CO₂/CO₄ separations, *Sep. Purif. Technol.* 14 (1998) 27–39.
- [35] A. Bos, I.G.M. Pünt, M. Wessling, H. Strathmann, CO₂-induced plasticization phenomena in glassy polymers, *J. Membr. Sci.* 155 (1999) 67–78.
- [36] T. Visser, M. Wessling, Auto and mutual plasticization in single and mixed gas C₃ transport through Matrimid[®]-based hollow fiber membranes, *J. Membr. Sci.* 312 (2008) 84–96.
- [37] T. Visser, G.H. Koops, M. Wessling, On the subtle balance between competitive sorption and plasticization effects in asymmetric hollow fiber gas separation membranes, *J. Membr. Sci.* 252 (2005) 265–277.
- [38] W.J. Koros, R.T. Chern, V. Stannett, H.B. Hopfenberg, Model for permeation of mixed gases and vapors in glassy polymers, *J. Polym. Sci., Part A-2: Polym. Phys* 19 (1981) 1513–1530.
- [39] J.S. Lee, W. Madden, W.J. Koros, Antiplasticization and plasticization of Matrimid[®] asymmetric hollow fiber membranes, Part B. Modeling, *J. Membr. Sci.* 350 (2010) 242–251.
- [40] K. Haraya, K. Obata, N. Itoh, Y. Shndo, T. Hakuta, H. Yoshitome, Gas permeation and separation by an asymmetric polyimide hollow fiber membrane, *J. Membr. Sci.* 41 (1989) 23–35.
- [41] H.-. Zhao, Y.-. Cao, X.-. Ding, M.-. Zhou, Q. Yuan, Effects of cross-linkers with different molecular weights in cross-linked Matrimid[®] 5218 and test temperature on gas transport properties, *J. Membr. Sci.* 323 (2008) 176–184.
- [42] S. Shishatskiy, C. Nistor, M. Popa, S.P. Nunes, K.V. Peinemann, Polyimide asymmetric membranes for hydrogen separation: influence of formation conditions on gas transport properties, *Adv. Eng. Mater.* 8 (2006) 390–397.
- [43] H.-W. Röslér, *Membrantechnologie in der prozessindustrie — polymere membranwerkstoffe*, *Chem. Ing. Tech* 77 (2005) 485–503.
- [44] S.S. Hosseini, M.M. Teoh, T.S. Chung, Hydrogen separation and purification in membranes of miscible polymer blends with interpenetration networks, *Polymer* 49 (2008) 1594–1603.
- [45] Y. Zhang, I.H. Musselman, J.P. Ferraris, K.J. Balkus Jr., Gas permeability properties of Matrimid[®] membranes containing the metal-organic framework Cu-BPY-HFS, *J. Membr. Sci.* 313 (2008) 170–181.