POLYIMIDE HOLLOW FIBER MEMBRANES FOR CO₂ SEPARATION FROM WET GAS MIXTURES

F. Falbo, F. Tasselli[*], A. Brunetti, E. Drioli and G. Barbieri

National Research Council, Institute on Membrane Technology (ITM–CNR)
c/o The University of Calabria, cubo 17C, Via Pietro BUCCI, 87036 Rende CS, Italy.
www.itm.cnr.it, Phone: + 39 0984 492029, Fax: +39 0984 402103
E-mail: f.tasselli@itm.cnr.it

Abstract - Matrimid®5218 hollow fiber membranes were prepared using the dry-wet spinning process. The transport properties were measured with pure gases (H_2, CO_2, N_2, CH_4 and O_2) and with a mixture (30% CO_2 and 70% N_2) in dry and wet conditions at 25 °C, 50 °C, 60 °C and 75 °C and up to 600 kPa. Interesting values of single gas selectivity up to 60 °C (between 31 and 28 for CO_2/N_2 and between 33 and 30 for CO_2/CH_4) in dry condition were obtained. The separation factor measured for the mixture was 20% lower compared to the single gas selectivity, in the whole temperature range analyzed. In saturation conditions the data showed that water influences the performance of the membranes, inducing a reduction of the permeance of all gases. Moreover, the presence of water caused a decrease of single gas selectivity and separation factor, although not so significant, highlighting the very high water resistance of hollow fiber membrane modules.
Keywords: Matrimid 5218; CO_2 separation; Permeance; Gas mixtures.

INTRODUCTION

In recent years, membrane separation processes have been the subject of considerable research and have attracted the interest of industry, which is always looking for new technologies that are less invasive in terms of environmental impact and efficient from an economic point of view.

The control of the emissions of greenhouse gases such as CO_2 into the environment is one of the most challenging environmental issues related to global climate change. In the current carbon sequestration context, separation and capture are the greatest expense in the overall capture and storage processes. Improvements in capture and separation have the greatest potential to affect the cost of CO_2 mitigation, and membrane technology holds significant promise in this area.

Membrane technology plays an important role in various environmental and energy processes, such as

CO_2 capture (Zou and Ho, 2008; Hussain and Hägg, 2010; Brunetti *et al*., 2010; Yang *et al*., 2008), biogas upgrading (Deng and Hägg, 2010; Makaruk *et al*., 2010; Pakizeh *et al*., 2013; Momeni and Pakizeh, 2013), natural gas sweetening (Bernardo *et al*., 2009; Peters *et al*., 2011; Baker and Lokhandwala, 2008), and hydrogen production (Sà *et al*., 2009; Clem *et al*., 2006) and can potentially compete with some traditional separation methods in terms of energy requirements and economic costs (Xuezhong and Hägg, 2012).

CO_2 separation has attracted considerable attention in the last few decades owing to the new regulations of carbon dioxide emissions, which imply the development of specific CO_2 capture technologies that can be retrofitted to existing power plants as well as designed into new plants with the goal of achieving 90% of CO_2 capture while limiting the increase in cost of electricity to no more than 35% (Ciferno *et al*., 2009). Power and hydrogen production, heating

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*To whom correspondence should be addressed

systems (for example, in steel and cement industry), natural gas and biogas purification, etc. are examples where carbon dioxide is produced in huge (thousands of $Nm^3 h^{-1}$) amounts.

Membrane processes offer several advantages with respect to competing separation technologies, the most important of which are low capital and operating costs, low energy requirements and, generally, ease of operation. As a result, gas separation by membrane processes has gained great significance in the industrial scenario and represents today a valid solution for CO_2 capture from gaseous streams.

Various materials are currently under study and development for the preparation of membranes with suitable properties for CO_2 separation. Apart from the first requirement, which is proper separation properties, these membranes have to show other important characteristics such as durability under real conditions, thermal, mechanical and chemical resistance in the presence of harsh environments, reproducibility at a high scale level, easy handling, etc. to be suitable for industrial applications.

As demonstrated by Kraftschik *et al.* (2013), they offer, in fact, not only high efficiency and productivity, but also a superior resistance to penetrant-induced plasticization with respect to other materials like cellulose acetate, which is currently the industrial standard membrane material for acid gas separation.

Among the various types of polyimides, Matrimid®5218 is currently one of the most studied, particularly for hydrogen separation (Choi *et al.*, 2011; David *et al.*, 2011; David *et al.*, 2012; Peer *et al.*, 2007; Shishatskiy *et al.*, 2006) and most recently for CO_2/CH_4 separation (Kraftschik *et al.*, 2013; Dong *et al.*, 2010; Lee *et al.*, 2010). Many studies can be found in the open literature on the use of this material for the preparation of membranes to be used in gas separation applications. Most of the studies are also focalized on the improvement of the separation properties of these membranes by the addition of fillers (Askari and Chung, 2013; Nik *et al.*, 2012) or blends (Madaeni *et al.*, 2012) or by introducing new preparation techniques and post-treatments (Nisola *et al.*, 2011; Wang *et al.*, 2013) which also give improvements in terms of durability and resistance. In the meantime, there have been many patents developed up to now on the preparation of these membranes for various purposes in the field of gas separation and various aspects of their application have been investigated (Nagata, 1997; Liu *et al.*, 2012; Chung *et al.*, 2007). Among the various possible configurations of membranes in the modules, at an industrial level, asymmetric hollow fibers are pre-

ferred to others owing to their low production costs, high surface/volume ratios, reduced overall dimensions of the equipment (footprint) and excellent mechanical strength. Made up of a very thin dense layer, responsible for the separation, on a porous support made of the same material to increase the mechanical stability of the membranes against high pressure feed and with negligible mass transport resistance, this type of membrane configuration offers separation with high productivity.

This work reports the performance of asymmetric hollow fiber membranes of polyimide Matrimid®5218 prepared with the phase inversion dry-wet technique for CO_2 separation. The choice of this polymer was made on the basis of two main considerations; first, the very unusual and desirable properties of this material such as its high thermal stability, excellent mechanical stability and high glass transition temperature (Tin *et al.*, 2003); then the fact that the use of these membranes for CO_2 separation from flue gas streams has not yet been particularly investigated.

The key issue for the application of polymeric membranes in gas separation is to study their performance while considering gas mixtures of industrial interest (Spillman, 1989). In real applications, almost all the streams containing CO_2 to be separated are humidified and the mass transport properties exhibited by the membrane modules can be significantly affected by the relative humidity of the stream. This aspect is only partially investigated in the literature since generally the majority of studies refer to the transport properties measured in ideal conditions by using pure gases. In this work, the transport properties of the Matrimid®5218 hollow fiber membrane modules were measured by first feeding pure gases for evaluating the suitability of this material for CO_2 separation, then wet gases in saturation condition (100% relative humidity) and gaseous mixtures were fed to the modules at temperatures ranging from 25 °C to 75 °C and up to 600 kPa of feed pressure and keeping the permeate pressure at 1 bar, for evaluating the capability of the membrane to separate mixtures of industrial interest.

MATERIALS AND EXPERIMENTAL METHODS

Materials

Matrimid®5218 (Figure 1) was supplied by Huntsman Advanced Materials American, the Woodlands, TX. N-Methyl-2-pyrrolidone (NMP) was purchased from Carlo Erba (Italy).

A bi-component epoxy resin (Stycast 1266) used for potting fibers in the membranes preparation, was purchased from Emerson & Cuming (Belgium).

Tap water and distilled water were used as the external coagulant and as the bore fluid, respectively.

The mass transport properties of the hollow fiber membranes were evaluated using H_2, CO_2, O_2, N_2, and CH_4 (purity of 99.99%) and a binary mixture (70%N_2-30%CO_2).
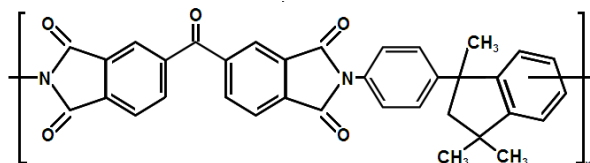
Figure 1: chemical structure of Matrimid® 5218. Glass transition temperature=338 °C (Chung *et al.*, 2003).

Hollow Fiber Preparation and Characterization

Hollow fiber membranes were prepared via the dry-wet spinning technique through the phase inversion process. The spinning setup, depicted in Figure 2, was previously described [Choi *et al.* (2010)]. The polymer solution (dope) was prepared by addition of the polymer to the solvent under mechanical stirring at 50 °C and stored in a thermostated vessel for the entire spinning run. Before starting, the dope was degassed under vacuum. The spinning tests were performed at room temperature. The operating conditions are reported in Table 1. At the end of the spinning test, the continuous bundle of the spun fibers was cut in pieces of ca. 30 cm and kept in distilled water for at least 24 hours in order to remove residual solvent. The fibers were then dried at room temperature for 48 hours. With the produced fibers, modules were prepared by assembling 10 fibers 20 cm long for a total membrane area of 50 cm^2 calculated taking into account the internal fiber diameter.
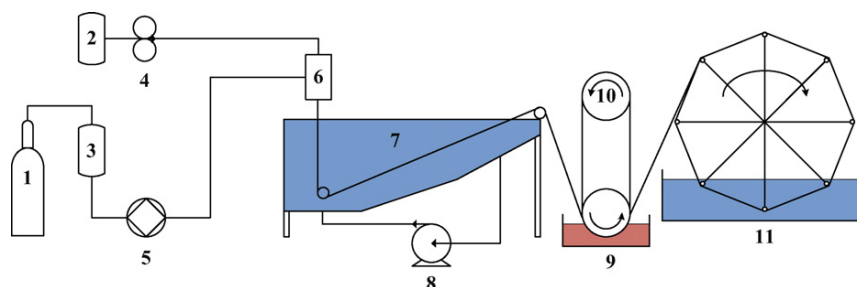
Figure 2: Schematic drawing of the spinning setup. 1: N$_2$ gas cylinder, 2: bore fluid tank, 3: dope tank, 4: bore fluid pump, 5: dope pump, 6: spinneret, 7: external coagulation bath, 8: circulation pump, 9: water pan, 10: take-up rollers, 11: reel collection.

Reprinted from "Separation Science and Technology", 46, Seung-Hak Choi, Adele Brunetti, Enrico Drioli et al. "H$_2$ Separation From H$_2$/N$_2$ and H$_2$/CO Mixtures with Co-Polyimide Hollow Fiber Module", 1-13, Copyright (2011) with permission from Taylor & Francis ".

Table 1: Spinning conditions for the preparation of Matrimid® 5218 hollow fibers.

Dope composition (wt%)	Matrimid® 5218: 25% NMP: 75%
Dope temperature	50 °C
Dope flow rate	8 g/min
Bore fluid	distilled water
Bore fluid flow rate	4 g/min
Spinneret orifice size (OD/ID)	2.0/1.0 mm
Air gap length	20 cm
Room temperature and	22 °C,
Relative humidity	52% RH
External coagulant	Tap water

Mass Transport Properties Evaluation

The mass transport properties of the hollow fibers packed in a module were measured with five different pure gases and with a mixture $CO_2:N_2=30:70$. All measurements were carried out at different temperatures, pressure differences and relative humidity as summarized in Table 2.

Table 2: Operating conditions used for gas separation measurements.

Temperature	25; 50; 60; 75 °C	
Pressure	Feed/Retentate: 400; 500; 600 kPa Permeate: 100 kPa	
Feed flow rate	400 dm³(STP) h⁻¹	
Relative Humidity	0 and 100%	
Feed composition	Pure gases: CO_2, H_2, CH_4, N_2, O_2	
	Mixture:	$CO_2:N_2=30:70$ molar%

STP: 0 °C and 100 kPa

The hollow fiber membrane module was placed in a furnace in order to carry out measurements at controlled temperature. The hollow fibers were fixed on a metal support by means of epoxy resin to give the module, which has two inputs and two outputs, feed and retentate on one side and permeate on the other side; no sweep was used. The mixture was obtained by mixing two pure gases of least 99.99% purity coming from different cylinders and was fed into the module by means of mass flow controllers.

In the experiments with saturated water vapor conditions, the feed stream, being pure gas or mixture, was first fed into a humidifier set at the same temperature and pressure as the membrane module and then, once saturated, into the module. The inlet of the feed stream was on the outside of the fibers and the permeate was collected from the bore side of the fibers to avoid any water condensation into the fibers. In addition, the module was placed in an oblique position inside the furnace also to avoid any liquid deposition on the external surface of the fibers. Any excess water remained in the module chamber without hindering the permeation.

The feed, the permeate and the retentate streams contained at least two species: the gas of interest (e.g., CO_2, H_2, CH_4, O_2 or N_2) and the water used for the humidification. Therefore, except for pure dry gas measurements that were carried out with the pressure drop method, the permeance evaluation of a specific single gas in saturated conditions was made by using the Concentration Gradient Method. A back-pressure regulator on the retentate line allowed the required trans-membrane pressures difference to

be operated in the module. The retentate and permeate flow rates were measured by means of two soap bubble flow meters, after the condensation of all the water contained in the two outlet streams. The composition of the dehydrated outlet streams was then analyzed by gas chromatography.

Figure 3 shows a scheme of the experimental apparatus utilized.

The performances of the membranes were evaluated in terms of permeating flux (Eq. (1)) and permeance (Eq. (2)). The permeation driving force is given by the difference of the species partial pressure (Eq. (3)).

$$Permeating\ flux = J_i = \frac{Permeate\ flow\ rate_i}{A\ Membrane},$$

$$mol\ m^{-2}s^{-1} \tag{1}$$

$$Permeance_i = \frac{Permeating\ flux_i}{Driving\ force_i},$$

$$mol\ m^{-2}s^{-1}Pa^{-1} \tag{2}$$

$$Driving\ force_i = \Delta P_i = P_i^{Feed} - P_i^{Permeate}, Pa \tag{3}$$

The single gas selectivity (Eq. (4)) and the separation factor (Eq. (5)) were calculated for evaluating the selective properties of the hollow fibers. The former is given by the ratio of the permeance of the pure feeding gases, which is a characteristic of the material and provides information on the behavior of the membrane in ideal conditions. The separation factor is given by the ratio of the mole fractions of the species measured in the permeate and in the feed and expresses the enrichment in the permeating flux with respect to the feed composition when a gas mixture is fed into the membrane system.

$$Single\ gas\ selectivity_{ij} = \frac{Permeance_i}{Permeance_j} \tag{4}$$

$$Separation\ factor_{ij} = \frac{\left(\dfrac{x_i^{Permeate}}{x_j^{Permeate}}\right)}{\left(\dfrac{x_i^{Feed}}{x_j^{Feed}}\right)} \tag{5}$$
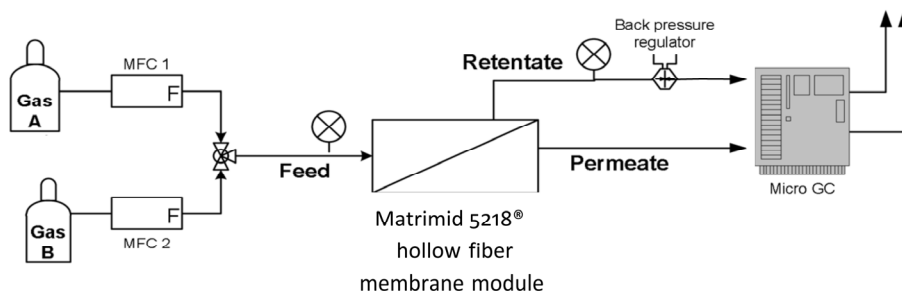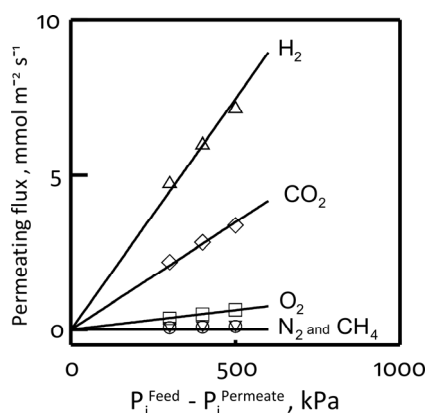
Figure 3: Scheme of the experimental setup used in the gas permeation measurements

RESULTS AND DISCUSSION

Gas Transport Through the Membranes

As first indication, to evaluate the transport properties of the hollow fibers, the measurements using five different pure gases H_2, CO_2, N_2, CH_4 and O_2 (Table 2) were carried out at 25 °C.

As shown in Figure 4, the permeating flux increases linearly with the driving force for all the gases indicating that the permeance is constant for all values of the driving force. Table 3 reports the values of permeance and single gas selectivity of hollow fibers for the five gases analyzed. Interesting single gas selectivities such as 31 for CO_2/N_2 and 33 for CO_2/CH_4 suggest that the gas permeation occurs according to the solution-diffusion model.

were carried out at 50 °C, 60 °C and 75 °C. Figure 5 shows the trend of the permeance as a function of the reciprocal temperature, which increases for all the analyzed gases, following an Arrhenius-type trend up 60 °C. At 75 °C, the permeance of CO_2 continued to follow this trend, whereas those of N_2 and CH_4 were considerably higher than expected. In particular, CO_2 permeance increases ca. 10% (from 60 °C to 75 °C), whereas for N_2 and CH_4 this increase is ca. 40%.

Table 3: Permeance of pure gases and single gas selectivity at 25 °C of Matrimid®5218 hollow fibers.

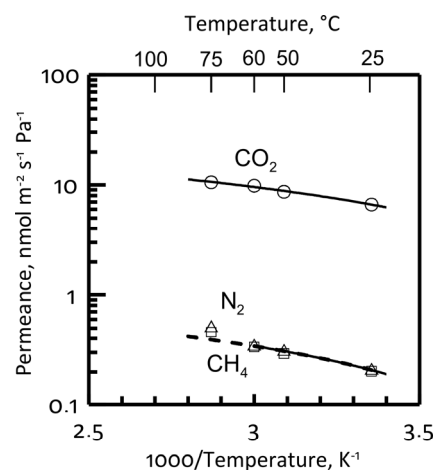| Gas	Permeance, nmol m^{-2} s^{-1} Pa^{-1}	Single gas selectivity,-				
		H$_2$	CO$_2$	O$_2$	N$_2$	CH$_4$
H$_2$	14.9	1	2	15	67	71
CO$_2$	6.9		1	7	31	33
O$_2$	0.97			1	4	5
N$_2$	0.22				1	1
CH$_4$	0.21					1

Figure 4: Permeating flux measured for pure gases as a function of the correspondent permeating driving force at 25 °C. Operating conditions: feed pressure range 400-600 kPa, permeate pressure 100 kPa. Symbols: experimental measures; solid lines: linear correlation of experimental data.

In order to evaluate the possibility of using these membranes at temperatures above 25 °C further tests

Figure 5: Permeance as a function of temperature. Operating conditions: feed pressure range 400-600 kPa, permeate pressure 100 kPa. Solid lines: Arrhenius correlation of experimental data. Experimental measures: (○) carbon dioxide; (Δ) nitrogen; (□) methane.

This behavior could be explained in terms of the dual-sorption model (Koros *et al.*, 1981), which describes the sorption as a combination of the Henry and Langmuir laws in a glassy polymer below its glass transition temperature. According to this model, the gas sorption in a glassy polymer occurs in both microvoids and free volume. Increasing the temperature, the number of available adsorption sites increases as well as their volume, but the amount of adsorbed species is lower. The sorption of less soluble species, such as N_2 and CH_4, is relatively favored with respect to that of CO_2 from this behavior. As a consequence, the permeance increases measured for N_2 and CH_4 are higher than that of CO_2; this also results in a reduction of selectivity (Figure 6).
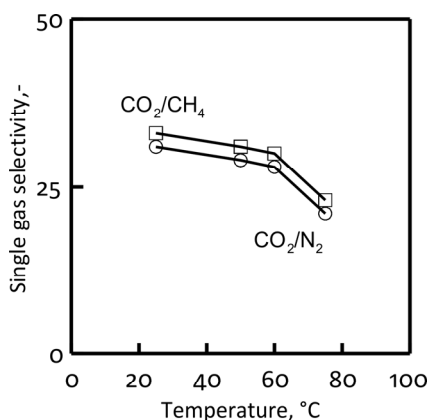
Figure 6: Single gas selectivity as a function of temperature. Operating conditions: feed pressure range 400-600 kPa, permeate pressure 100 kPa. Symbols: experimental measures; solid lines: correlation of experimental data.

Up to 60 °C, the membranes showed only a modest loss of selectivity with values of single gas selectivity that were between 31 and 28 for CO_2/N_2 and between 33 and 30 for CO_2/CH_4, suggesting that the membranes produced can also be utilized at temperature higher than 25 °C. A more evident single gas selectivity decrease from 60 °C up to 75 °C was observed, from 28 to 21 for CO_2/N_2 and from 30 to 23 for CO_2/CH_4.

The permeance shown by the Matrimid-fiber prepared in this work agrees well with that measured on the other Matrimid 5218 membranes. In addition, the CO_2/N_2 and CO_2/CH_4 single gas selectivities measured in this work are closer or, in such cases, higher than those of other literature works, except for the Matrimid 5218 membranes prepared by Syrtsova *et al.* (2004), which exhibited a significantly higher selectivity because the gas separation properties were improved by gas phase fluorination. It has to be highlighted that there are significant differences between the transport properties measured on a single fiber, as in most of the cases reported in Table 4, and that measured with a hollow fiber module, as in this work. The main difference in making the module is the capability of producing several meters of hollow fiber all exhibiting the same properties and, thus, without defects. Globally, comparing the permeance and selectivity measured on our module with respect to that reported in the literature (see Table 4) on a module prepared with a similar material, it can be said that the membrane modules prepared in this work show permeance values and ideal selectivities consistent with the literature and, in many cases, better.

Table 4: Comparison of the gas permeation properties of this study with those reported in the literature.

Material	T, °C	Permeance, nmol m^{-2} s^{-1} Pa^{-1} (GPU) 1 GPU= 0.335 nmol m^{-2} s^{-1} Pa^{-1}					Single gas selectivity, -			Ref.
		H$_2$	N$_2$	O$_2$	CH$_4$	CO$_2$	H$_2$/N$_2$	CO$_2$/N$_2$	CO$_2$/CH$_4$	
Matrimid 5218	25	14.9 (44.5)	0.22 (0.66)	0.97 (2.92)	0.21 (0.62)	6.92 (20.7)	67	31	33	This work
Matrimid 5218	25	59.5 (178)	14.1 (42)	-	-	-	4.2	-	-	Koros *et al.* (2001)
Matrimid 5218	20	-	0.53 (1.6)	2.8 (8.3)	0.12 (0.35)	3.9 (11.8)	-	7	34	Dong *et al.* (2010)
Matrimid 5218	35	-	-	-	0.08 (0.23)	2.84 (8.5)	-	-	37	Visser *et al.* (2007)
Matrimid 5218	25	-	-	0.21 (0.62)	0.19 (0.57)	9.5 (28.5)	-	45	50	Syrtosa *et al.* (2004)
Matrimid 5218	30	12.5 (37.7)	0,17 (0.51)	-	-	2.54 (7.59)	73	15	-	Peer *et al.* (2007)
6FDA-Durene (poly-hexafluoro dianhydride isopropylidene- Durene)	25	-	-	-	6.4 (19)	124 (373)	-	-	19	Chung *et al.* (2000)
P84 (Polyimide)	50	1.5 (4.44)	0.02 (0.06)	-	0,02 (0.06)	0.22 (0.65)	78	12	12	Choi *et al.* (2011)

Continuation Table 4

Continuation Table 4

Material	T, °C	Permeance, nmol m⁻² s⁻¹ Pa⁻¹ (GPU) 1 GPU= 0.335 nmol m⁻² s⁻¹ Pa⁻¹					Single gas selectivity, -			Ref.
		H_2	N_2	O_2	CH_4	CO_2	H_2/N_2	CO_2/N_2	CO_2/CH_4	
P84 (Polyimide)	25	0.34 (1.03)	0.02 (0.05)	0.03 (0.08)	0.02 (0.07)	0.06 (0.18)	20	4	3	Chatzidaki *et al.* (2007)
6FDA-IPDA (poly-hexafluoro dianhydride isopropylidene-dianiline)	35	-	-	2.51 (7.53)	0.23 (0.7)	10 (30)	-	-	42	Stern (1994)
6FDA-BAPHF (poly-hexafluoro dianhydride isopropylidene - 4,4′-Hexafluoroisopropylidee-bis-pphenyleneoxy-dianiline)	35	11.5 (34.3)	0.31 (0.94)	1.67 (5)	0.21 (0.64)	5.9 (17.6)	37	19	28	Stern (1994)
PI (Polyimide)	25	10.1 (30.1)	1.4 (4.2)	3.9 (11.9)	-	20.4 (60.9)	7	15	-	Marek *et al.* (1998)

Effect of the Relative Humidity on the Performance of Hollow Fibers

In most of the industrial streams containing CO_2 to be recovered, a certain fraction of water vapor corresponding to a specific degree of relative humidity can be found and can influence the separation performance. In order to evaluate the membrane module behavior in the presence of humidity, the transport properties of the hollow fibers were also measured in saturation conditions (relative humidity 100%). As can be seen in Table 5, the relative humidity considerably influenced the transport properties for all the gases investigated. In fact, the permeance decreased upon increasing the relative humidity.

Table 5: Single gas permeance and single gas selectivity as a function of the relative humidity at 25 °C. Operating conditions: feed pressure range 400-600 kPa; permeate pressure 100 kPa.

| Relative Humidity, %	Permeance, nmol m⁻² s⁻¹ Pa⁻¹			Single gas selectivity, -	
	CO_2	N_2	CH_4	CO_2/N_2	CO_2/CH_4
0	6.9	0.22	0.21	31	33
100	4.5	0.17	0.16	26	28

The solubility of water in the polymeric matrix is very high and the water molecules fill the microvoids (Scholes *et al.*, 2010). Also CO_2 has a good solubility in this polymer, occupying both microvoids and free volume, but its solubility is significantly lower than that of water. Water occupies most of the microvoids and CO_2 can fill only the free volume but not the microvoids when competitive sorption of both water and CO_2 occurs in the polymer. The reduced CO_2 sorption produces the lower (ca. 40%) permeation of this species (Table 5). The sorption reduction of N_2 and CH_4 in the presence of water is lower and, as a consequence, there is also a permeance reduction (ca. 25%). The effect on the selectivity reflects this

behavior. The selectivity decreased from 33 to 28 for CO_2/CH_4 and from 31 to 26 for CO_2/N_2. An analogous trend was observed at all the temperatures investigated (Figure 7). Nevertheless, as expected, the permeance of all the species increased with the temperature, but the CO_2/N_2 and CO_2/CH_4 selectivities did not show significant variations in the range of 25-60 °C (Figure 7 right side), whereas they decreased significantly from 60 to 75 °C owing to a significant increase of the N_2 and CH_4 permeances (Figure 7 left side), as discussed previously.

These results show the high water resistance of the membrane module prepared.

Permeation Measurements with Gas Mixture

To evaluate the hollow fiber membrane module application for CO_2 mixture separation, some experimental investigations were carried out using a CO_2/N_2 binary mixture of 30 and 70 molar%, respectively. The measurements were performed at a high feed flow rate (see Table 2) and, consequently, at a low stage-cut (ratio between the permeate flow rate and the feed flow rate). This assures the absence of concentration gradients on the feed side, allowing the membrane module to be considered as a lumped parameter system. Figure 8 shows the CO_2 and N_2 flux for the pure gases and the mixture, measured at 25 °C. A linear dependence of the flux on the corresponding driving force was observed for all the analyzed species. No change in CO_2 permeance was observed with respect to the pure gas tests, whereas the N_2 flux measured in the mixture differed from the flux measured with the pure gas. As a consequence, even though the CO_2 permeance measured by feeding the mixtures was unchanged with respect to that measured with pure gas, N_2 permeance significantly increased and a separation factor of 21 was measured for the CO_2:N_2 mixture against a single gas selectivity of 31.
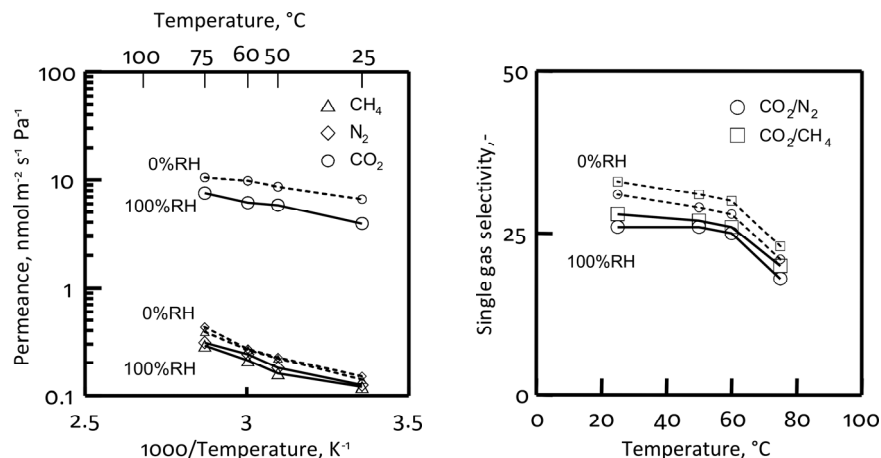
Figure 7: Permeance (left side) and single gas selectivity (right side) as a function of the temperature at RH=0% and RH=100%. Feed pressure 400-600 kPa, permeate pressure 100 kPa. Symbols: experimental measures; dashed and solid lines regression of experimental data measured at RH=0% and RH=100%, respectively.
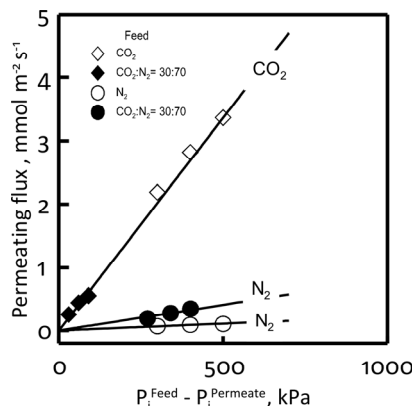
Figure 8: Permeating flux of pure CO_2 and N_2 and in the mixture as a function of the correspondent permeating driving force at 25 °C, RH=0%. Operating conditions: feed pressure range 400-600 kPa, permeate pressure 100 kPa. Symbols: experimental measures; solid lines: linear correlation of experimental data;

This behaviour could be attributed to the plasticization effect which occurs when a mixture containing CO_2 is fed, as in the present case, into a membrane module and its concentration in the polymer matrix is high and can cause some changes in its structure [Ismail and Lorna (2012)]. As a consequence of CO_2 plasticization, the permeation of N_2 increases and the membrane partially loses its selectivity [Bos *et al*. (1999)].

As for pure gases, the permeation measurements at different temperatures were also carried out for the mixture. Also in this case, an increase of the permeance of both gases was observed with temperature. However, similar to what was observed for pure gas measurements, this increase did not modify the selective properties of the fibers that remained almost constant up to 60 °C and then de-

cayed in the case of higher temperatures (Figure 9). In the whole temperature range analyzed, as with most glassy polymers, the values of the separation factor measured with the mixture were lower than the ideal selectivity measured in the same conditions.

The mass transport properties of the membrane module were also analyzed by feeding the same mixture in saturated conditions (Table 6). Similarly to the experiments carried out with pure gases (Table 5), the presence of water vapor depleted the permeance of both CO_2 and N_2, implying that the interaction of water vapor with the polymer matrix and the other gases did not change with the gases' fraction. Indeed, the separation factor also reduced, although not significantly. Analogous trends were observed at the other investigated temperatures.
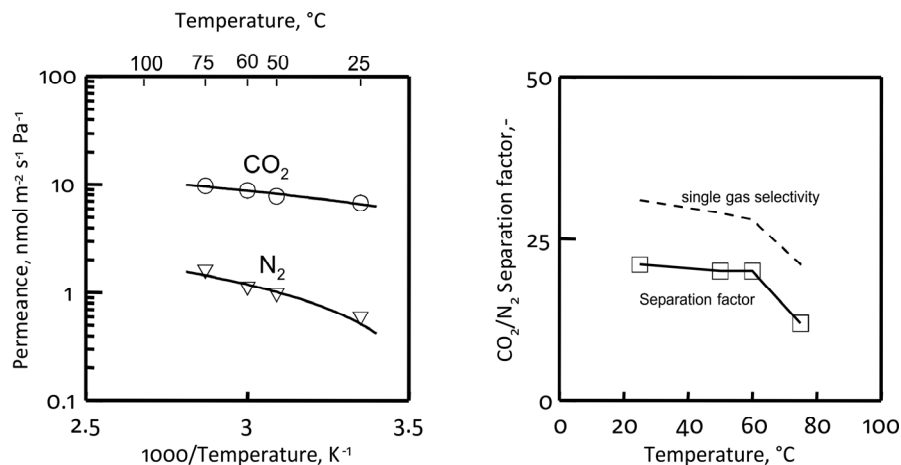
Figure 9: Permeance (left side) of CO_2 and N_2 and separation factor (right side) measured in the mixture as a function of temperature, RH=0%. Operating conditions: Feed pressure range 400-600 kPa, permeate pressure 100 kPa. Symbols: experimental measures; solid lines correlation of experimental data; dashed lines: correlation for single gas measurements.

Table 6: Permeance and separation factor of gases measured in the mixture as a function of the relative humidity at 25 °C. Operating conditions: feed pressure range 400-600 kPa; permeate pressure 100 kPa.

| Relative Humidity, %	Permeance, nmol m⁻² s⁻¹ Pa⁻¹		Separation factor -
	CO_2	N_2	CO_2/N_2
0	6.3	0.25	21
100	3.1	0.17	17

Figure 10 shows the trend of CO_2/N_2 single gas selectivity/separation factor as a function of CO_2 permeance. The measurements were carried out at different temperatures (25, 50, 60 and 75 °C).

Polymeric membranes, as well known, undergo a trade-off limitation between permeance and selectivity; when the selectivity increases, the permeance decreases, and vice versa.

This behavior could be due to the water, which occupies microvoids in the polymeric matrix, producing a reduction of CO_2 permeance (ca. 40%).

The experimental results obtained by feeding a dry mixture ($CO_2:N_2$=30:70) (full circles in Figure 10) show the same trend. A clear reduction of selectivity (ca. 35%) was evident by comparison between the dry mixture ($CO_2:N_2$=30:70) and single dry gas owing to the CO_2 plasticizing effect, which occurs when a mixture containing CO_2 is fed into the membrane module. On the contrary, it is important to observe that the CO_2 permeance does not undergo significant change but remains constant. This behavior

was not observed at 25 °C, comparing the humidified single gas value (full squares) with the humidified mixture value (open triangle); a reduction both of the permeance (ca. 30%) and of the separation factor (ca. 20%) was measured.
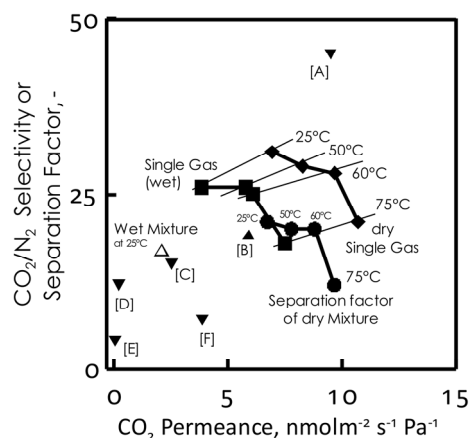
Figure 10: CO_2/N_2 single gas selectivity or separation factor of gases measured as a function of the CO_2 permeance. Experimental data: full diamond, full square, full circle and open triangle are for feed of single dry gas, single humidified gas, dry $CO_2:N_2$=30:70 mixture and humidified $CO_2:N_2$=30:70 mixture, respectively. Full triangles: data from open literature as referred to in square brackets. [A] Syrtsova *et al.* (2004); [B] Stern (1994); [C] David *et al.* (2012); [D] Choi *et al.* (2011); [E] Chatzidaki *et al.* (2007); [F] Dong *et al.* (2010).

In addition, Figure 10 shows a comparison between experimental data measured in this work, in the range between 25 and 75 °C, and the literature data obtained at room temperature (25-30 °C) feeding pure gases (Choi *et al.*, 2011; David *et al.*, 2012; Dong *et al.*, 2010; Syrtosa *et al.*, 2004; Chatzidaki *et al.*, 2007; Stern, 1994). It appears evident that the hollow fiber membrane modules developed in this work exhibit values of permeance and selectivity/ separation factor better than or consistent with most of the open literature data achieved using similar membranes. In addition, it has to be pointed out that the experimental results obtained in non-ideal conditions, feeding a gaseous mixture and humidified gas at temperatures higher than 25 °C, are very competitive. The hollow fiber membrane module maintains, in fact, a single gas selectivity of ca. 30 and a separation factor of ca. 20 up to 60 °C.

CONCLUSIONS

Matrimid®5218 hollow fiber membranes were prepared by dry-wet spinning and used for CO_2 separation in mixtures of industrial interest. In particular, membrane modules with reproducible properties were assembled with the hollow fibers that were prepared.

The modules were used to evaluate the mass transport properties in non-ideal conditions, showing the possibility of utilizing them in a temperature range between 25 °C and 60 °C. The measures obtained between 25 °C and 60 °C showed single gas selectivity values between 31 and 28 for CO_2/N_2, between 33 and 30 for CO_2/CH_4 and CO_2/N_2 separation factors between 21 and 20 up to 60 °C highlighting a very interesting resistance at temperature. A decrease of selectivity owing to an evident N_2 and CH_4 permeance increase at 75 °C was observed.

The measures carried out in wet condition (100% relative humidity) indicate that the membrane modules prepared in this work show high water resistance and little loss of selectivity with respect to measures obtained in the dry condition. Values of single gas selectivities between 28 and 26 for CO_2/CH_4 and between 26 and 25 for CO_2/N_2 up to 60 °C and a separation factor of 17 at room temperature were attained.

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