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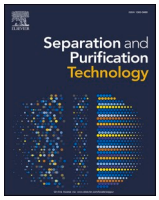

Matrimid®/ZIF-8 hollow fiber mixed matrix membranes for hydrogen recovery from industrial waste streams

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ABSTRACT

The development of efficient separation technologies to recover hydrogen from industrial waste streams plays an important role to satisfy the increasing demand for hydrogen. In this work, mixed matrix hollow fiber membranes were synthesized by incorporating an inorganic filler (ZIF-8) with molecular sieve properties, into a Matrimid® polymer matrix. The membranes were tested under conditions that reproduce real industrial processes, focusing on H_2/CO_2 separation. Addition of 5 wt% ZIF-8, whose well distribution along the fiber was confirmed by SEM and EDX analysis, resulted in a significant improvement in H_2 permeance (30.5 GPU) compared to pristine Matrimid® (16 GPU) at 30 °C. Moreover, selectivity was improved by 67 % reaching values of 3.3 and 41 for H_2/CO_2 and H_2/bulk compounds at 30 °C. The increase in the separation performance is attributed to the molecular sieve effect of ZIF-8 together with the increase of the free volume due to the inclusion of the filler in the polymer matrix, enhancing H_2 flux over the other gases. Moreover, the hollow fiber membranes were tested under varying conditions of pressure, temperature and feed composition, including multicomponent streams that represent real process conditions, confirming promising results helping to scale up mixed matrix hollow fiber membranes.

1. Introduction

The global energy transition, driven by political agreements and technological advancements, aims to combat climate change and environmental degradation [1,2]. In this context, green hydrogen has emerged as a key energy vector that can be coupled with renewable energy sources to balance the mismatch between supply and demand [3,4]. As hydrogen demand grows, its recovery from industrial waste streams presents a valuable opportunity to meet this demand. Up to 0.5 Mt of H_2, with concentrations exceeding 60 vol%, is currently flared or underutilized for heat and power generation from streams such as ammonia (APG) and methanol purge gas (MPG) streams and the coke oven gas. While H_2 recovery from industrial waste streams shows great potential, the economic feasibility is hindered by high costs of separation, which can represent up to 70 % of production costs [5]. Therefore, developing efficient, low-footprint technologies is critical to reduce the overall cost. In this sense, membranes offer a lower energy consumption and more flexible operation than state-of-the-art gas separation technologies [6,7]. Among the different types of membranes, Pd membranes are widely employed at industrial scale for producing high purity hydrogen (> 99.9 vol%), with module production ranging from 40 to 70 Nm^3/h [8]. However, their high cost has driven interest in polymeric hollow fiber (HF) membranes, which are more cost-effective and offer reduced energy consumption [9,10]. Despite the advantages of polymeric HF membranes, commercially available modules typically achieve only 98 vol% hydrogen purity mainly due to their moderate H_2/CO_2 separation performance [11]. This is a critical challenge, as the high sorption coefficient of CO_2 in polyimides, which is the most used material in commercial modules, limits the effectiveness of the separation [12,13]. As a result, research has increasingly focused on developing polymeric-based HF membranes with improved performance. Matrimid®, a polyimide with high thermal and chemical resistance and moderate separation capability, has gained attention in recent years. Although, Koros et al. [14] initially reported Matrimid® HF membranes for O_2/N_2 separation, Favvas et al. [15] were the first to report their use for H_2 purification, producing carbon HF membranes. These membranes achieved high H_2 permeance (342 GPU) but their low selectivity towards bulk compounds (N_2, CH_4 and CO) indicated the presence of minor defects in the dense selective layer. Subsequent advancements, such as those reported by David et al. [16] have improved the

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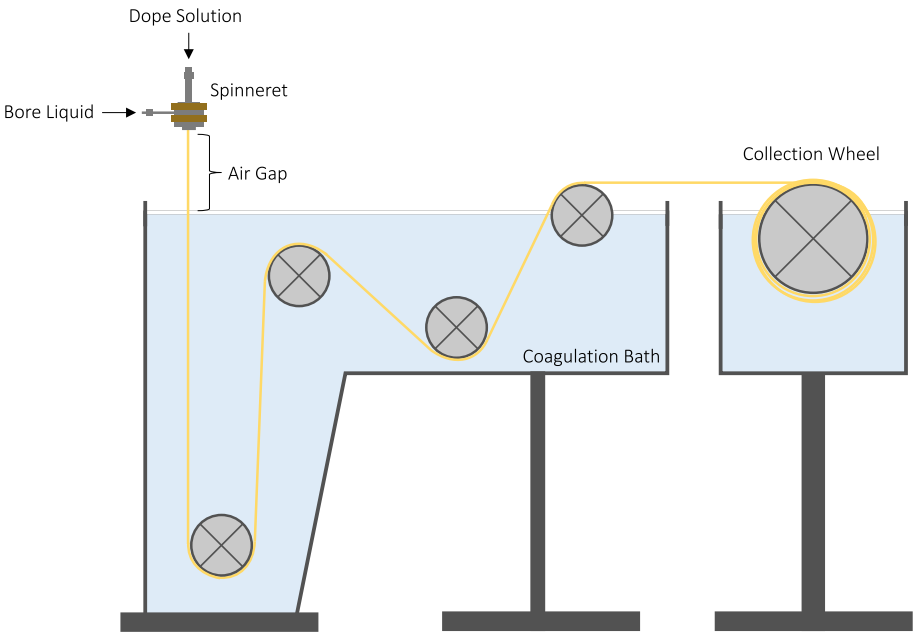

Fig. 1. Illustration of the spinning process.

manufacturing process of Matrimid® HF, resulting in membranes with separation performance comparable to flat-sheet configuration. The H_2/CO_2 selectivity achieved by HF ranges from 3 to 3.5 in binary mixtures at 30 °C, with a decrease in selectivity observed as the CO_2 content increases. Since the spinning conditions significantly influence the separation performance of HF, the effects of various dry-wet spinning conditions have been extensively studied [17,18]. For example, the combination of solvent/non solvent in the bore liquid and moderate air gap (distance between the outlet of the spinneret and the water bath) can lead to the formation of asymmetric HF membranes with a thin selective layer, enhancing H_2 flux. Although the promising results, polymeric HF membranes still require further improvements in separation performance to become more competitive and facilitate their penetration in the market. In this regard, the development of mixed matrix hollow fiber membranes (MMHFMs), which are still in development, will play a major role in the scale up of polymeric-based membranes. The synthesis of MMHFMs using poly(styrene-co-butadiene) copolymers (SBC) and ZIF-8 as fillers in a polyetherimide matrix was done by Lai et al. [19], achieving 6.85 GPU of H_2 permeance and a H_2/CH_4 selectivity of 152 with a loading of 50 wt%. Although, the use of a small proportion (4 %) of SBC increased the flexibility of the fibers, improving the processing, the MMHFMs were obtained by the dip-coating method, and thus, the scalability of the manufacturing method remains a challenge. In this sense, Etxeberria-Benavides et al. [20] were able to synthesise polybenzimidazole (PBI)/ZIF-8 MMHFMs by the dry-wet spinning method. The MMHMs deliver a H_2 permeance of 65 GPU with H_2/CO_2 selectivity of 18. However, the high operating temperature required by PBI membranes (>150 °C) increases energy costs. Based on the increasing interest in MMHFMs studies and the growing demand for H_2, this work aims to advance the scale-up of MMHFMs by the synthesis and testing of Matrimid®/ZIF-8 membranes for the recovery of hydrogen from industrial waste streams with multicomponent gases. The incorporation of metallic-organic frameworks (MOFs) as additives has demonstrated significant improvements in both permeability and selectivity in flat-sheet membranes, attributed to their high specific surface area and narrow pore size. In particular, ZIF-8, a commercially available MOF, features a pore aperture closely to the CO_2 kinetic diameter (3.3 Å), resulting in a high H_2/CO_2 selectivity (≈ 3.5) [21]. These characteristic addresses one of the most critical challenges in hydrogen purification with polymeric membranes. Despite the incorporation of high filler loadings (>10 wt%) has been explored in flat-sheet membranes, demonstrating improved gas separation performance, its application in hollow fiber configuration poses challenges, as it may generate minor defects in the selective layer. In this regard, hollow fiber membranes studies with a loading exceeding 5 wt%, usually necessitate a post-treatment step to seal minor pores caused by the accommodation of large amounts of inorganic particles within polymer chains with polydimethylsiloxane (PDMS) [22,23]. The need of a post-treatment step significantly complicates the manufacturing process, limiting the scalability and reliability of producing larger lengths of MMHFMs. Thus, this study aims to evaluate the scalability of these membranes with a loading of 5 wt% that improves the separation performance; to check the stability during the synthesis process, the membrane performance under various operating conditions and the comparison with the results obtained from flat-sheet configuration to ensure the production of a thin dense selective layer has been carried out.

2. Experimental

2.1. Chemicals

ZIF-8 was purchased from ACSYNAM and used as received. Matrimid® 5218 was kindly provided by Huntsman Advanced Materials. N-Methly-2-pyrrolidone (NMP), > 99.8 % was purchased from Merck. Gases for permeation experiments such as hydrogen (H_2), nitrogen (N_2), methane (CH_4), carbon dioxide (CO_2), carbon monoxide (CO) and helium (He) with purities > 99.50 % were obtained from Air Liquide.

2.2. Synthesis of the membranes

The flat-sheet membranes with a 5 wt% of ZIF-8 loading were synthesized following the method reported in a previous work [24]. The membranes had a thickness of 70.5 ± 3.2 μm. On the other hand, the Matrimid® HF and Matrimid®/ZIF-8 MMHFMs were manufactured by the dry-wet spinning method (Fig. 1).

The dope and bore liquid solution were stored in a stainless-steel syringe of 20 mL and 100 mL respectively. The solutions were extruded with a syringe pumps Fusion 6000-X (dope solution) and KDS 410 Legacy syringe from KD Scientific (bore liquid) to a double orifice

Table 1
Spinning condition for the synthesis of hollow fibers.

Spinning Conditions	Matrimid®	Matrimid®/ZIF-8
Polymer content in dope solution (wt.%)	26	25
Filler load (wt.%)	0	5
Dope solution flow rate (mL min^{-1})	3	
Dope solution extrusion temperature (°C)	50	
Bore liquid composition (wt.%)	20 % NMP / 80 % Water	
Bore liquid flow rate (mL min^{-1})	1.5	
Bore liquid extrusion temperature (°C)	Room	
Air gap (cm)	16	
Coagulation bath temperature (°C)	Room	
Take up rate (m min^{-1})	12	

Table 2
Operational conditions of gas permeation experiments.

Parameters	Value
Feed Flowrate (mL min^{-1})[1]	100
Sweep Gas (mL min^{-1})	100
Feed Composition	Pure gases, H_2-binary mixtures, APG, COG, MPG
Temperature (°C)	30 / 50 / 80
Feed Pressure (bar)	1.25–6
Permeate Pressure (bar)	1

[1] The chosen feed flowrate was used to ensure a low stage cut (< 5 %), which is defined as the ratio of transmembrane gas flow to feed flowrate.

spinneret. Then, the fibers contacted the air prior to entering the coagulation bath. Finally, the fibers were collected in a collection wheel. The spinning conditions are shown in Table 1 and were selected based on previous works [14,16]. The dope solution was prepared by combining mechanical stirring and temperature (60 °C). Once the polymer was dissolved in NMP, it was left overnight to degas. Finally, the collected fibers were kept in a water bath for 72 h to complete coagulation. Then, they were washed in 3 baths of methanol (20 min) and dried at room temperature for 48 h.

2.3. Analysis of the morphology of the hollow fiber membranes

The cross section of the Matrimid® and Matrimid®/ZIF-8 HF membranes was characterized by scanning electron microscopy (SEM) on a Zeiss EVO MA 15 scanning electron microscope. The samples were prepared by freeze-fracture after immersion in liquid nitrogen and coating with a thin layer of gold. Moreover, elemental maps were performed by energy disperse X-ray analysis (EDX) 10 mm^2 Silicon Drift detector from Oxford Ins (model X-act), operated by INCA software.

2.4. Gas permeation experiments

The separation performance of the HF membranes was tested with a continuous permeation setup at lab scale. The membrane modules were constructed with a shell of stainless steel of 15 cm and 5 fibers that were introduced and sealed with epoxy resin. The modules were placed in a thermostatic chamber (Memmert Excel) to ensure isothermal operation. The feed flowrate was controlled using Bronkhorst digital mass flow controllers' series F − 201CV (0–0.1 L_N min^{-1}) for all gases, except for H_2 that was F − 201CV (0–0.2 L_N min^{-1}). The permeate stream is removed by a sweep gas (He) to prevent the accumulation of the components, maximizing the driving force. The feed pressure was controlled by needle valves and pressure transducers (Ashcroft GC − 35, 0–8 bar). The composition of the streams was analyzed in real time with a gas chromatograph (Shimadzu Tracera GC − 2010) that is provided with a Barrier Ionization Discharge (BID) detector of ppb level. The GC contains two columns depending on the component to be analyzed, 1) molecular sieve capillary column (SH/Rt®/Molecular sieve 5A) for H_2 and N_2, CH_4 and CO and 2) fused silica capillary column (Carboxen® 1010 Plot) for CO_2. The gas experiments were carried out with pure gases, binary mixtures of 50 vol% H_2 and the synthetic multicomponent mixtures with similar composition to the industrial waste streams. The summary of the operating conditions of gas permeation experiments and the composition of the industrial waste streams is shown in Tables 2 and 3 respectively.

Table 3
Composition of industrial waste streams [25].

Industrial waste stream	Composition (vol.%)				
	H_2	N_2	CO_2	CO	CH_4
Ammonia Purge Gas (APG)	58.6	25.7	–	–	15.7
Coke Oven Gas (COG)	60.2	4.7	2.1	6.8	26.2
Methanol Purge Gas (MPG)	63.1	11.3	11.1	3.4	11.2

The experimental effective permeance was calculated normalizing the experimental flux with the partial pressure gradient, and the selectivity by the ratio of permeances:

$$P_i = J_i \bullet \frac{1}{p_i^{Feed} - p_i^{Permeate}} \quad (1)$$

$$\alpha_{H_2/i} = \frac{P_{H_2}}{P_i} \quad (2)$$

where subscript i refers to H_2, N_2, CO_2, CH_4 and CO.

3. Results and Discussion

3.1. Analysis of the morphology of the hollow fiber membranes

The morphological and structural analysis of the asymmetric hollow fibers was studied using SEM images that are shown in Fig. 2.

As can be shown in Fig. 2, the hollow fibers displayed good circularity and concentricity. Average values of 10 measurements taken from the SEM images using imageJ software were used to determine the outer and inner diameters of the fibers (Table 4). The slightly higher outer diameter of Matrimid®/ZIF-8 could be attributed to the increase of the viscosity of the MMHFM due to addition of the inorganic filler, which can affect the extrusion process [26]. Moreover, the hollow fibers present asymmetric structure where the inner finger-like pores transition to a sponge-like pores and finally, to the outer dense layer. Since the operating conditions of the dry-wet spinning process determine the structure of the hollow fiber, their selection was based on previous studies on Matrimid® hollow fibers [14,27]. The chosen air gap ensures sufficient residence time for the evaporation of a small fraction of the solvent at the outer surface of the hollow fiber, leading to a concentration gradient in the dope composition, facilitating the formation of a dense selective layer without minor defects. Furthermore, the dope-to-bore liquid flowrate ratio delivers the fiber circularity while the extrusion temperature promotes the formation of macrovoids in the fiber and thus, an asymmetric structure is obtained [28]. In addition, the distribution of the ZIF-8 is shown by the EDX analysis of Fig. 2.b.3 where Zn is equally found along the filler avoiding its accumulation in certain regions in the case of Matrimid®/ZIF-8 MMHFM. The good distribution and interfacial contact between the ZIF filler and polymer was observed and confirmed by gas permeation experiments. Since the thickness of the dense selective layer is a critical factor in hollow fiber membranes, it has been theoretically estimated from the values of permeability and permeance:

$$l = \frac{Permeability}{Permeance} \quad (3)$$

where the permeability (Barrer, $1\ Barrer = 3.35{\cdot}10^{-16} mol\ m\ m^{-2}s^{-1}Pa^{-1}$) was measured from pure gas experiments at 30 °C with flat-sheet membranes and the permeance (GPU, $1\ GPU = 3.35{\cdot}10^{-10} mol\ m\ m^{-2}s^{-1}Pa^{-1}$) from the results obtained with HF membranes

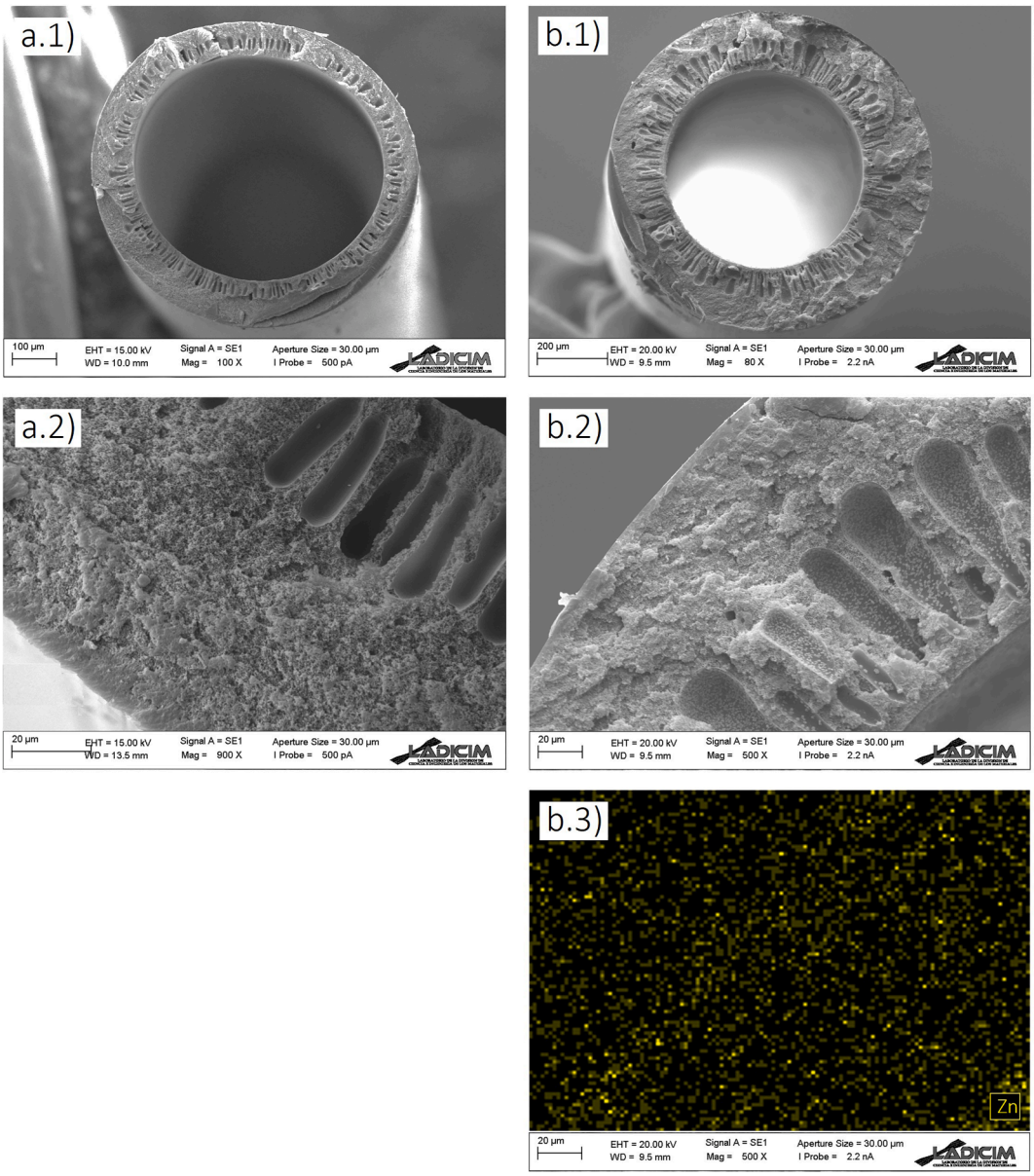

Fig. 2. SEM images of a.1) Matrimid® cross section, a.2) zoom of Matrimid® cross section, b.1) Matrimid®/ZIF-8 cross section, b.2) zoom of Matrimid®/ZIF-8 cross section and b.3) Matrimid®/ZIF-8 EDX of the cross section showed in b.2).

Table 4
Structural dimensions of the HF membranes.

Membrane	OD (μm)	ID (μm)	Selective layer thickness (μm) calculated with Eq. (3)				
			H_2	CO_2	N_2	CH_4	CO
Matrimid®	753 ± 12	527 ± 21	1.43 ± 0.03	1.40 ± 0.05	1.52 ± 0.08	1.51 ± 0.06	1.45 ± 0.07
Matrimid®/ ZIF-8	915 ± 10	570 ± 17	1.15 ± 0.03	1.13 ± 0.03	1.32 ± 0.07	1.25 ± 0.03	1.18 ± 0.08

at the same operational conditions. The comparison of the values is shown in Fig. 3.

As it can be seen there is an increase in both permeability and permeance due to the influence of the filler. The addition of ZIF-8 leads to an increase in the free volume which enhances the flux of the compounds through the membrane [29]. Moreover, the spinning conditions allow for a thin and dense layer (1.46 ± 0.05 μm for Matrimid® and 1.21 ± 0.08 μm for Matrimid®/ZIF-8) in both membranes as it can be seen in Table 4; it is worth noting that these values were in accordance with estimated values for all gases, which validates the accuracy of the estimation. The slight reduction in the dense selective layer of MMHFM is related to the residence time of nascent fiber in the air gap distance. The higher viscosity of MMHFM lead to an increase in the elongation which reduces the outer diameter in comparison with the inner diameter and thus, decreasing the dense layer thickness [23]. Once the morphology of the hollow fiber membrane was characterized, the separation performance was studied by gas permeation under different operating conditions.

3.2. Gas permeation experiments

The separation performance of Matrimid® and Matrimid®/ZIF-8 hollow fiber membranes was evaluated by permeation experiments of hydrogen mixtures. First, pure gas experiments were performed to establish the benchmark for the multicomponent gas mixtures and also,

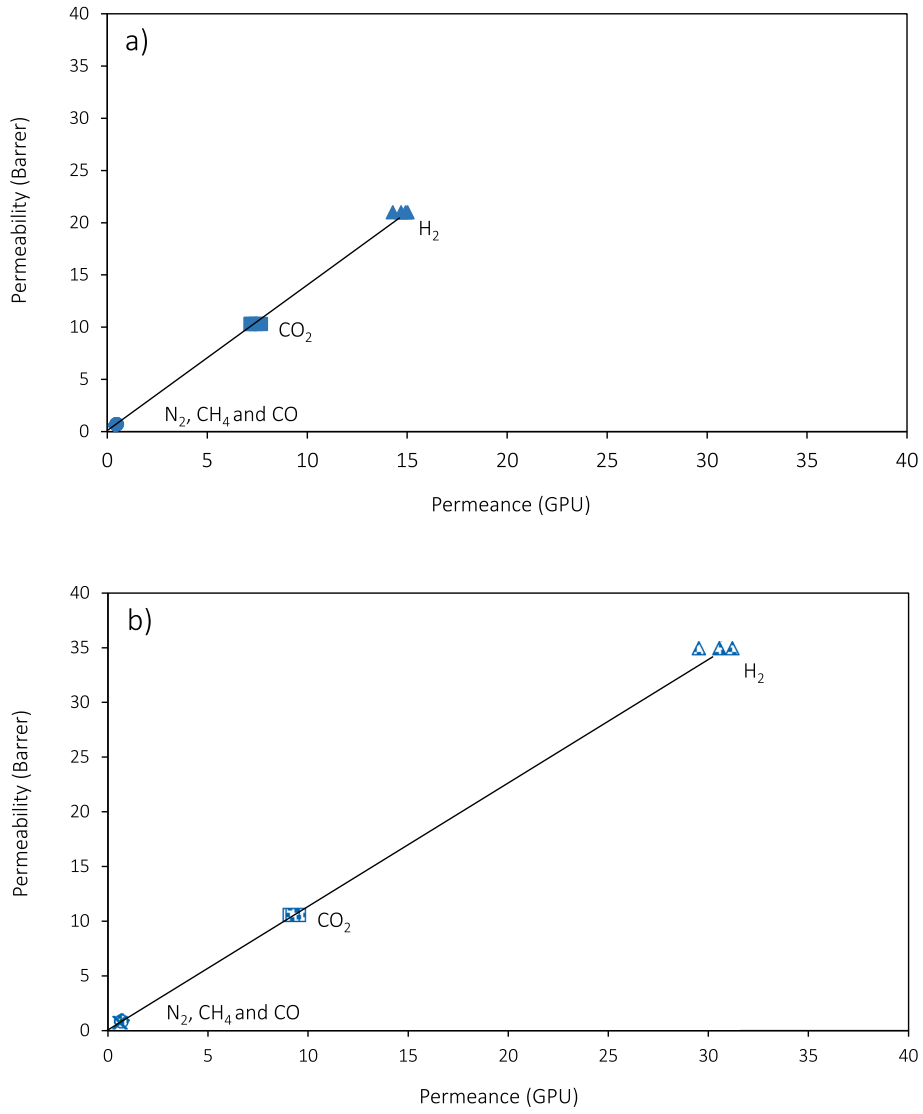

Fig. 3. Permeability vs permeance for determination of the dense layer in; a) Matrimid® and b) Matrimid®/ZIF-8 hollow fibers. The permeability of pristine Matrimid® flat-sheet membrane was taken from Moral et al. [24].

Table 5
Ideal selectivity data for Matrimid® and Matrimid®/ZIF-8 HF for pure gas permeation at 30 °C and partial pressure gradient of 2 bar.

Configuration	Membrane	H_2/CO_2	H_2/N_2	H_2/CH_4	H_2/CO
Hollow fiber	Matrimid®	2.1	38.3	32.8	36.5
	Matrimid®/ZIF-8	3.3	41.1	42.5	45.0
Flat-sheet	Matrimid®	2.0	35.0	30.0	35.0
	Matrimid®/ZIF-8	3.3	35.7	38.8	44.7

to compare with data from flat-sheet membranes (Table 5). Pure gas measurements were carried out at different feed pressures whereas the influence of temperature and feed composition was evaluated with binary and multicomponent mixtures. The experiments were repeated twice to ensure reproducibility, and the results showed a deviation lower than 5 %.

3.2.1. *Pure gas permeation*

The ideal selectivity values, determined from permeation with pure gases, measured at 30 °C and a partial pressure gradient of 2 bar are shown in Table 5 while the influence of feed pressure is shown in Fig. 4.

As shown in Table 5, addition of ZIF-8 to the polymer matrix results in an increase in selectivity, worth noting the increase from 2 to 3.3 with a 5 wt% of loading in the separation of H_2/CO_2, which is the most concerning separation in polymeric membranes.

The increase in selectivity is attributed to the molecular sieve effect deliver by the ZIF-8. Gas permeation in a polymeric membrane is typically described by the solution-diffusion model, wherein gas molecules are absorbed at the polymer surface, diffuse throughout the free volume between the polymer chains, and desorbs on the opposite side of the membrane. Nevertheless, the incorporation of an inorganic filler requires consideration of the relation between the pore size of the particles and the kinetic diameter of the gas molecules. In this regards, ZIFs particles are tetrahedral networks formed by linking transition metals with imidazolate ligands, that confer high stability, polymer compatibility and tunability as well as a with a narrow pore size [30]. Specifically, the relation between the pore size of ZIF-8 (3.4 Å) and the kinetic diameter of the compounds enables the discrimination of H_2 molecules (2.89 Å) during the diffusion step, effectively separating them from CO_2 (3.3 Å) and achieving high separation from bulk compounds (N_2, CH_4 and CO > 3.6 Å) [31,32]. The comparison of the ideal selectivity of flat-sheet and hollow fiber membranes is used to determine the presence of minor defects on the dense selective layer which could reduce the selectivity compared to the flat-sheet configuration [6]. The similar

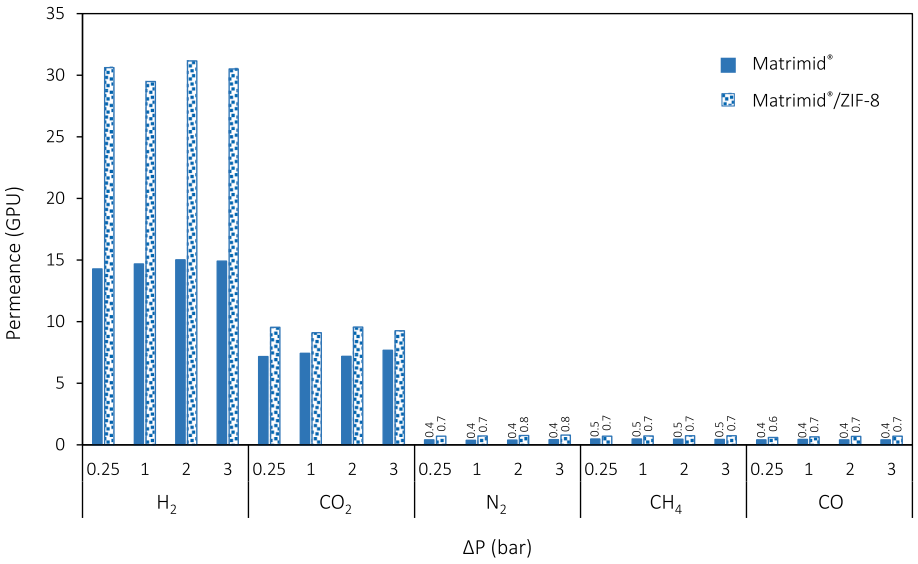

Fig. 4. Pure gas permeation data for Matrimid® and Matrimid®/ZIF-8 HF at 30 °C and different partial pressures gradients.

Table 6
Permeance and selectivity data in the separation of binary mixtures working with Matrimid® and Matrimid®/ZIF-8 hollow fibers.

Feed (50:50 vol%)	Temperature (°C)	Permeance (GPU)				Selectivity (—)	
		Matrimid®	Matrimid®/ZIF-8	Matrimid®	Matrimid®/ZIF-8	Matrimid®	Matrimid®/ZIF-8
		H_2		CO_2		H_2/CO_2	
H_2/CO_2	30	17.3	26.1	7.4	7.9	2.3	3.3
	50	19.7	33.7	10.9	11.3	1.8	3.0
	80	26.0	41.9	13.3	15.4	2.0	2.7
		H_2		N_2		H_2/N_2	
H_2/N_2	30	16.7	26.4	0.6	0.7	28.3	38.8
	50	19.4	33.1	0.7	1.0	26.9	32.3
	80	25.3	42.9	1.0	1.6	25.0	26.6
		H_2		CH_4		H_2/CH_4	
H_2/CH_4	30	17.2	26.8	0.6	0.7	27.0	40.2
	50	19.2	33.3	0.8	0.9	24.1	35.3
	80	25.8	42.6	1.2	1.5	22.3	28.0
		H_2		CO		H_2/CO	
H_2/CO	30	17.0	27.3	0.5	0.6	31.9	44.6
	50	19.3	33.8	0.8	0.8	24.8	40.0
	80	25.0	41.3	1.1	1.4	23.8	28.8

values obtained in this study prove that the separation performance of the hollow fiber membranes is comparable to flat-sheet configuration and thus, it evidences that there are no defects in the dense selective layer. The HF membrane was tested under different operating conditions; the influence of the partial pressure gradient is depicted in Fig. 4.

Higher H_2 permeance values are observed with MMHMs (30 GPU) compared to pristine Matrimid® HF (15 GPU) at 30 °C. This is due to the combination of the effect of Matrimid®, that is a glassy polymer that allows higher H_2 flux, with the addition of ZIF-8 in the case of the MMHMs, which increases the free volume and enhances permeation through the membrane [33]. Moreover, the high solubility of CO_2 leads to values of 7 and 9.6 GPU for Matrimid® and Matrimid®/ZIF-8 respectively, whereas for the rest of bulk compounds permeance values ranges from 0.4 to 8 for Matrimid® and from 0.7 to 8 for Matrimid®/ZIF-8. The experiments were conducted at four feed pressures from 1.25 to 4 bar. The results evidence that there is no influence of pressure on the permeance in the studied range and thus, it can be concluded that depends mainly on the material of the hollow fiber. This finding can be described by the solution-diffusion model that for membranes with filler only accounts for a molecular sieve mechanism in the case of H_2 and neglects the potential influence of facilitated transport [34]. Since there is no influence of pressure, the permeance was calculated from the slope of permeation flux data vs different partial pressures and is considered constant for each temperature in the next sections.

3.2.2. *Gas permeation in binary mixtures*

Pressure, temperature and feed composition are the main operating conditions in the process, thus, once the partial pressure effect on hollow fiber membranes has been assessed, the influence of temperature and feed composition is analyzed by gas permeation experiments with binary mixtures with 50 vol% of H_2 and the rest of the components. The main results are shown in Table 6.

Table 6 presents a comprehensive comparison of the performance of Matrimid® and Matrimid®/ZIF-8 membranes, in terms of permeance and selectivity. The data show consistently a significant improvement in both permeance and selectivity due to the addition of ZIF-8, a metal–organic framework (MOF) that has high surface area and molecular sieving properties for this pair of gases [35]. Focusing on permeance, the Matrimid®/ZIF-8 membrane outperforms pure Matrimid® for all gas pairs and temperatures. For example, for H_2/CO_2 separation at 50 °C, H_2 permeance for Matrimid® membrane is 19.7 GPU, whereas for the composite Matrimid®/ZIF-8 membrane the permeance increases to 33.7

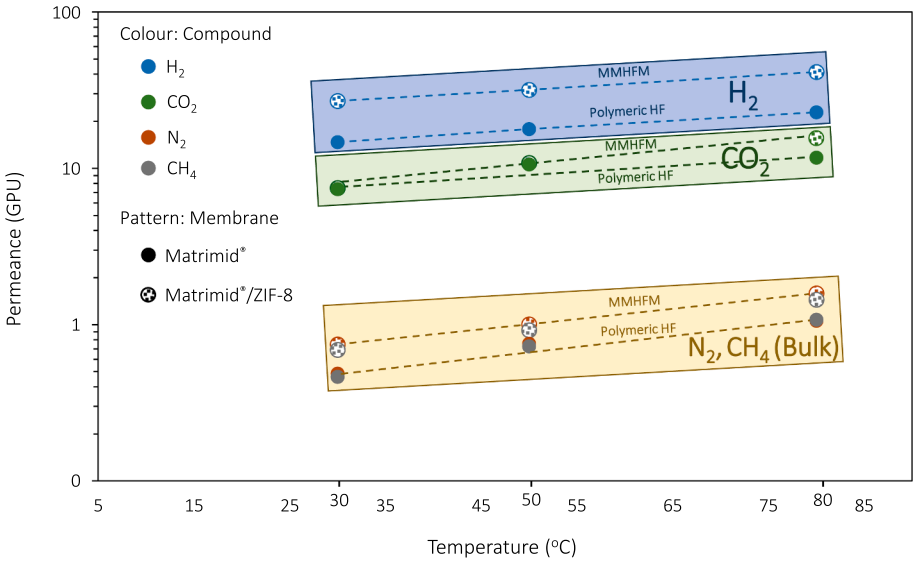

Fig. 5. Permeance values for Matrimid® and Matrimid®/ZIF-8 HF at 30, 50 and 80 °C in multicomponent mixtures.

GPU, representing a 71 % enhancement. Similar improvement is observed for other gas pairs. In the case of H_2/CH_4 at 50 °C, the H_2 permeance increases from 19.2 GPU for Matrimid® to 33.3 GPU for Matrimid®/ZIF-8, an improvement of approximately 73 %. The increase in permeance indicates that addition of ZIF-8 improves the rate of hydrogen transport through the membrane, likely due to the improved diffusion pathways provided by the porous structure of the ZIF-8 framework. Moreover, the comparison of the permeance values for different binary mixtures with pure gas permeation data reveal that there is a slight decrease when working with binary mixtures compared to pure gas permeation at 30 °C which could be related to the competitive effect in multicomponent mixtures. Regarding selectivity, the Matrimid®/ZIF-8 membrane shows substantial improvement compared to pure Matrimid® membrane. H_2/CO_2 selectivity is particularly important for hydrogen purification from multicomponent mixtures containing CO_2 due to its high permeance values, compromising H_2 purification performance. For instance, H_2/CO_2 selectivity for Matrimid® is 1.8 at 50 °C, while for Matrimid®/ZIF-8, it increases to 3.0, representing a 67 % increase in selectivity. This trend is consistent with other gas pairs, i.e., for H_2/CH_4 at 50 °C, the selectivity rises from 24.1 for Matrimid® to 35.3 for Matrimid®/ZIF-8 due to the molecular sieving properties of ZIF-8. The effect of temperature was found to be the same as in other works on polymer-based membranes [24,25]. As temperature increases, permeance values increase for both membranes, while selectivity decreases. As example, in the H_2/CO_2 binary mixture the H_2 permeance for Matrimid® and Matrimid®/ZIF-8 increases by 50.3 % and 60.5 % from 30 to 80 °C respectively. In terms of selectivity, the Matrimid® membrane shows a value of 1.6 at 80 °C, while Matrimid®/ZIF-8 achieves a selectivity of 2.7 compared to 2.3 and 3.3 respectively at 30 °C. This trend is due to the increase in the mobility of the polymer chains with temperature, which enhances the permeation flux of the bulk compounds compared to hydrogen. Moreover, the comparison of permeance values between the binary and pure gas permeation experiments (Fig. 4) reveals that there is no significant influence of feed composition on the experimental permeance values. Once the effect of temperature and feed composition has been assessed, the hollow fiber membranes were tested with multicomponent feed composition simulating the industrial waste gas streams to reproduce real process conditions.

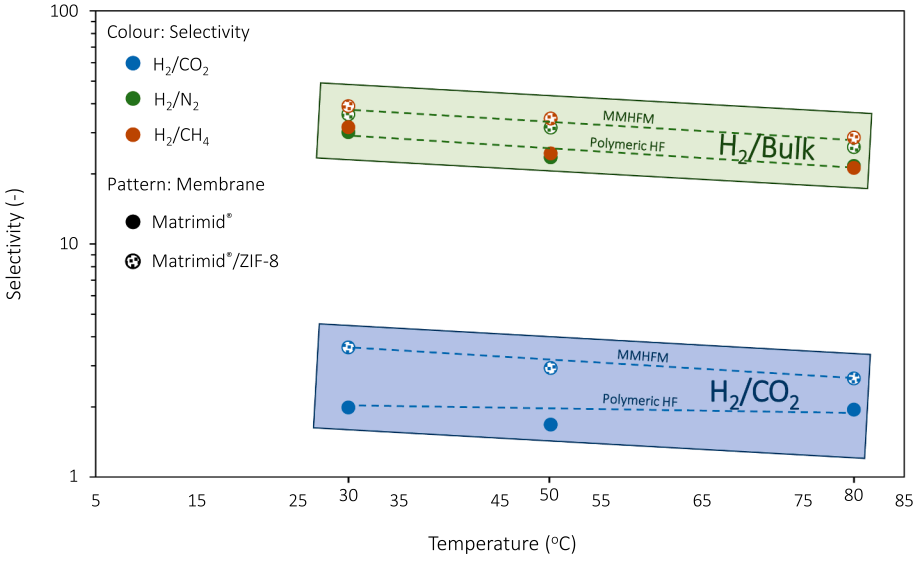

Fig. 6. Selectivity values for Matrimid® and Matrimid®/ZIF-8 HF at 30, 50 and 80 °C in multicomponent mixtures.

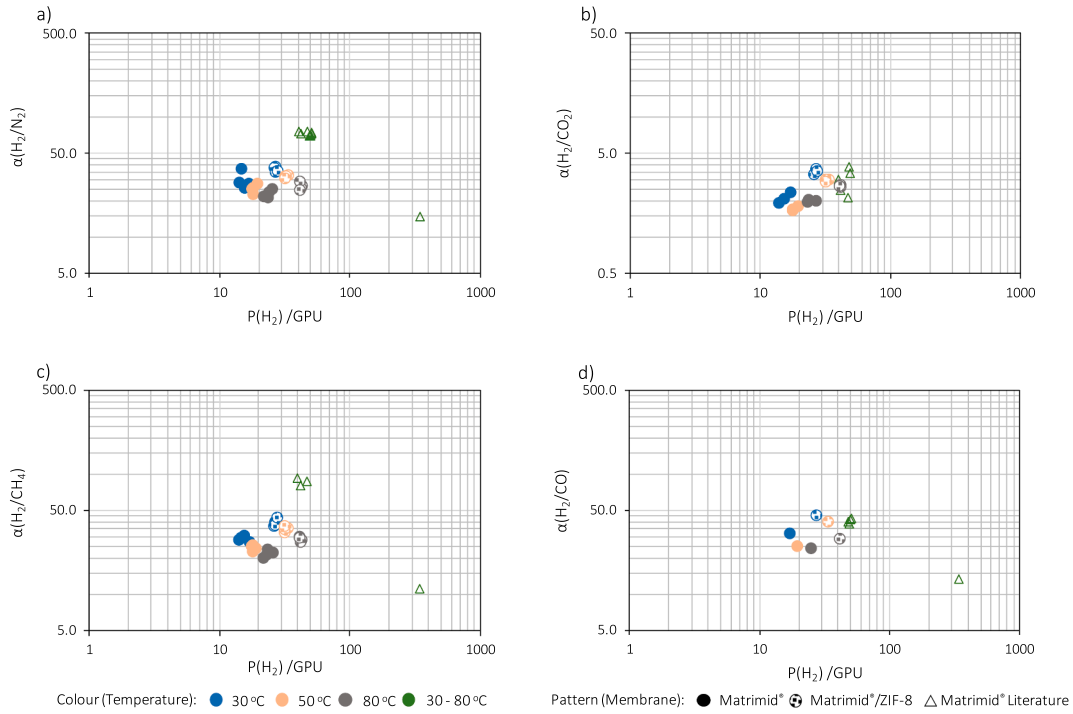

Fig. 7. Robeson plot for the permeability and selectivity data obtained with industrial waste streams. Literature values for pristine Matrimid® hollow fibers were taken from [15,16,18,36].

3.2.3. *Industrial waste streams gas permeation*

The hollow fiber membranes were evaluated with multicomponent mixtures with composition similar to industrial waste streams with the aim of testing their performance under real process conditions. The data in Figs. 5 and 6 correspond to average values of permeance and selectivity since no major difference was observed between the multicomponent mixtures. In addition, the values of permeance and selectivity for each multicomponent stream can be found in Tables S1 and S2 in the supplementary material.

The permeance and selectivity data shown in Figs. 5 and 6 indicate trends consistent with previous observations from binary mixtures and pure gas permeation data. In this sense, the increase in H_2 permeance is accompanied by higher selectivity coefficients, highlighting the separation H_2/CO_2 where it is observed an increment of 70 % with 5 wt% ZIF-8 loading. Nevertheless, the presence of multiple components affects the transport properties of each individual gas due to competitive sorption effects, which lead to deviations compared to the results in binary mixtures and pure gas permeation. While the difference in the permeance values ranges from 1.0 to 5.5 % and from 0.9 to 8 % for Matrimid®/ZIF-8 and Matrimid® HF respectively, a greater deviation is observed compared to the pure gas data where it ranges from 3 to 20 % for both HF membranes. Although the hollow fiber membranes exhibit similar permeance and selectivity coefficients for the multicomponent mixtures, slight differences can be observed in Tables S1 and S2 of the supplementary material. In this context, the higher permeance values observed for the COG and MPG streams could be attributed to the elevated CO_2 content, which induces minor plasticization phenomenon. For instance, the H_2 permeance reaches values of 27.7 and 26.8 GPU for the MMHFM at 30 °C for COG and MPG respectively, compared to 26.4 GPU for the APG stream. A similar trend is observed in selectivity, where the increase in permeance coefficients due to the plasticization effect, a phenomenon related to the opening of polymer chains caused by CO_2 absorption, leads to a reduction in selectivity. For example, an H_2/N_2 selectivity of 37.8 is achieved for the Matrimid/ZIF-8 hollow fiber membrane with the APG stream, compared to 34.9 for the MPG stream at 30 °C. Despite a trend related to the CO_2 concentration in the feed stream, can be identified, the MMHFM consistently delivers comparable permeance and selectivity coefficients, regardless of the feed stream composition. Regarding temperature, Figs. 5 and 6 depict an increase in permeance and a corresponding decrease in selectivity as temperature rises for binary and multicomponent gas permeation tests which is in agreement with previous research studies on polymer-based mixed matrix membranes as it was explained in the previous section for binary mixtures. As example, the selectivity towards bulk compounds decreases from 27 and 30 % for Matrimid®/ZIF-8 and Matrimid® HF respectively when the temperature changes from 30 to 80 °C. Thus, the polymer-based MMHFMs deliver higher selectivity at low temperatures which could lead to lower operating costs compared to Pd membranes. Moreover, this study provides valuable original data, particularly for Matrimid®/ZIF-8 MMHFM at different temperatures (30–80 °C) and feed compositions, which cannot be found in the open literature to our knowledge. Finally, the results of multicomponent mixtures are shown in a Robeson-type graph to compare with previous studies on Matrimid® hollow fibers in Fig. 7.

Fig. 7 shows the comparison of the performance of Matrimid® and Matrimid®/ZIF-8 hollow fiber membranes synthetized in this work with the previous studies on Matrimid® hollow fibers. MMHFMs improve the separation performance compared to the pristine polymer for all hydrogen gas pairs. For example, at 50 °C, hydrogen permeance for Matrimid®/ZIF-8 is increased by approximately 71 % compared to pure Matrimid® membrane, highlighting the benefits of incorporating a filler with a high surface area and narrow pore size. The slight difference in selectivity values that is observed compared to the results reported in literature (green markers), especially for H_2/N_2 and H_2/CH_4 separations, could be attributed to the experimental methods of each study. While the permeance and selectivity values are obtained from continuous gas permeation experiments using multicomponent mixtures simulating real industrial conditions in this study, literature values were mainly obtained from pure gas permeation experiments with the time-lag method except in the case of David et al. [16] where continuous gas permeation tests were carried out. In multicomponent mixtures, competitive solubility and permeation effects can reduce the observed

Table 7
H_2 purity of the permeate gas in multicomponent mixtures simulating industrial conditions.

Temperature (°C)	COG		APG		MPG	
	Matrimid®	Matrimid®/ZIF-8	Matrimid®	Matrimid®/ZIF-8	Matrimid®	Matrimid®/ZIF-8
30	96.94	97.85	98.07	98.24	90.95	94.66
50	95.54	97.41	97.23	98.02	89.53	93.69
80	95.25	96.71	96.80	97.42	88.92	92.63

selectivity, which more accurately reflects the behaviour of membranes under real operating conditions. Thus, the testing conditions under multicomponent feeds provides a more robust assessment of the membranes' performance and scalability, confirming their potential for industrial applications of hydrogen recovery. In terms of temperature dependence, both Matrimid® and Matrimid®/ZIF-8 membranes follow typical polymeric membrane behaviour, with increased permeance and reduced selectivity at higher temperatures. Finally, since the main objective of this work was the evaluation of hollow fibers membranes for hydrogen recovery, the purity of the permeate gas has been calculated (Table 7) with the aim of analyzing the viability of using a purified hydrogen for end-use applications. Nevertheless, purity depends on the operating conditions, the geometry of the membrane module and area and thickness of the membrane, thus, it should be deeply analyzed in future works based on the design and scale up of the separation process.

As observed in Table 7, the feed composition notably impacts the purity of the hydrogen collected in the permeate side. Specifically, multicomponent mixtures, representative of industrial waste streams with approximately 60 vol% H_2, displayed a variety of permeate compositions. Matrimid®/ZIF-8 achieved higher purity compared to pristine Matrimid® hollow fibers. At 30 °C, the maximum H_2 purity is reached for all mixtures: 98.24, 97.85 and 94.66 vol% for APG, COG and MPG. Therefore, the purity trend follows the sequence APG > COG and MPG, which is attributed to the different compositions of the gas mixtures, particularly the presence of CO_2, which was defined as the most concerning separation. As a result, hydrogen purity decreased with increasing CO_2 concentration in the feed gas, with APG containing 0 vol %, 2.1 vol% in COG and 11.1 vol% in MPG [25]. In this sense, the addition of ZIF-8 to the polymer matrix increases H_2 purity by 4.3 %. Beyond achieving high hydrogen purity, membrane systems need to operate with high recovery rates.

4. Conclusions

This work presents a detailed analysis of the separation performance of Matrimid®/ZIF-8 hollow fibers as an essential step towards the scale-up of mixed matrix hollow fiber membranes. First, SEM and EDX analyses revealed an asymmetric structure with a thin, dense outer layer, where the filler was uniformly distributed along the fiber. Gas permeation experiments were conducted under varying conditions and thoroughly investigated the influence of operating parameters on the separation performance. The theoretical thickness of the dense layer was calculated from the ratio of the permeance to permeability coefficients for both hollow fibers and flat-sheet membranes. A thin selective layer of 1.46 μm for Matrimid® and 1.21 μm and Matrimid®/ZIF-8 was achieved using the dry-jet spinning method, with the absence of defects confirmed by the similar values of selectivity between hollow fibers and flat-sheet membranes. Gas permeation experiments with pure gases at 30 °C demonstrated that permeance values were not influenced by feed pressure in the range studied, consistent with the solution-diffusion transport phenomena inherent to these polymer-based hollow fiber membranes. Then, the experiments with binary gas mixtures for varying temperatures revealed that Matrimid®/ZIF-8 delivered 65.5 % higher H_2 permeances (42.2 GPU) than pristine Matrimid® hollow fibers (25.5 GPU) at 80 °C. The addition of ZIF-8 also improved selectivity, particularly for the H_2/CO_2 gas pair, with selectivity increasing to 3.3 compared to 2.3 at 30 °C. Thus, the inclusion of inorganic particles, which combine high surface area and narrow pore size, enhanced both permeance and selectivity compared to pristine polymeric hollow fiber membranes. It was observed an increase of permeance with rising temperature, while selectivity decreased, due to the greater mobility of polymer chains, which enhances the flux of bulk compounds over hydrogen. Finally, the mixed matrix membranes were tested under conditions simulating real industrial waste streams, providing a practical assessment of their performance. The multicomponent gas mixtures used in this study demonstrated no significant influence of feed composition on the separation performance (permeance and selectivity), and thus, Matrimid®/ZIF-8 hollow fiber membranes, offer significant advantages in hydrogen recovery applications compared to pristine polymer hollow fibers. Additionally, hydrogen purity in the permeate stream reached high values up to 98.2 % for the simulated ammonia purge gas stream, demonstrating the potential of these mixed matrix hollow fiber membranes for for hydrogen recovery from industrial waste streams.

This work confirms the feasibility of Matrimid®/ZIF-8 hollow fiber membranes as a promising solution for hydrogen recovery, facilitating the scalability of gas separation to real-world conditions.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2025.131890.

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