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CO_2/CH_4 and CO_2/CO Selective Pebax-1657 Based Composite Hollow Fiber Membranes Prepared by a Novel Dip-Coating Technique

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Abstract: A novel and innovative method was developed to fabricate defect-free composite hollow fiber (HF) membranes using drop-casting under continuous flow. The synthesized Pebax-1657—based membranes were examined for gas separation processes, focusing on the separation of CO_2 from CH_4 and CO gases. The separation performance of the membranes was rigorously assessed under realistic binary gas mixture conditions to evaluate their selectivity and performance. The effect of pressure on separation performance was systematically investigated, with transmembrane pressures up to 10 bar being applied at a temperature of 298 K. Remarkable CO_2/CH_4 selectivities of up to 110 and CO_2/CO selectivities of up to 48 were achieved, demonstrating the robustness and effectiveness of these composite HF membranes, suggesting their suitability for high-performance gas separation processes under varying operational conditions. Overall, this study introduces a novel approach for scaling up the fabrication of HF membranes and provides valuable insights into their application in CO_2 separation technologies, offering the potential for advancements in areas such as natural gas processing and carbon capture from CO-containing streams.

Keywords: polymeric membranes; Pebax-1657; CO_2/CO selectivity; CO_2/CH_4 selectivity; novel dip-coating technique; ultra-thin gutter layer; mixed matrix membranes

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1. Introduction

Composite polymeric HF membranes are well-recognized for their excellent gas separation capabilities at relatively low cost [1]. They consist of a thin selective layer that minimizes resistance to gas diffusion, and a porous support that maintains the membrane's mechanical integrity even under high-pressure conditions. This combination allows for high fluxes and selectivities, making these membranes particularly effective candidates for applications such as CO_2 removal from natural gas and nitrogen separation from air [2]. The versatility and efficiency of composite HF membranes make them ideal for various industrial gas separation applications. Overall, research focused on enhancing the performance and durability of these membranes by developing novel materials and fabrication methods. The integration of advanced nanomaterials, such as graphene oxide and/or carbon nanotubes, into the selective layer is a promising approach to further increase selectivity and

permeability while ensuring robustness [3]. Additionally, there are ongoing efforts to scale up the production of composite HF membranes to address the growing demand for efficient gas separation technologies across various industries [4]. In the oil and gas industry, such membranes are used to purify natural gas by removing contaminants such as CO_2 and H_2S, while in the clean energy field, they play a vital role in hydrogen purification and recovery processes, where the separation of hydrogen from syngas mixtures is essential for fuel cell technologies. It is worth noting that the selection of a hollow fiber configuration is based on its distinct advantages to gas separation processes. HF membranes provide a significantly higher surface-area-to-volume ratio compared to spiral-wound configurations, resulting in more compact modules and enhanced gas transport efficiency. This feature is particularly beneficial for applications requiring high permeance and selectivity while maintaining a small footprint. Additionally, HFs can better accommodate high-pressure operations and are less susceptible to challenges such as concentration polarization and fouling, which can affect spiral-wound modules. While spiral-wound configurations are widely used and perform effectively in commercial gas separation systems, the hollow fiber design was chosen here to investigate its potential for improved performance and scalability, particularly for post-combustion carbon capture applications.

However, apart from the well-known natural gas sweetening process and capture from common flue gases, which basically are CO_2/CH_4 and CO_2/N_2 gas mixtures, CO_2 must also be captured from $CO_2/CO/N_2$ gas mixture byproduct gases of the steel industry [5]. These byproduct gases include blast furnace gas (BFG) and Linz Donawitz gas (LDG), which contain 15–49% N_2, 16–23% CO_2, and 23–67% CO [6,7]. Furthermore, CO is also present as a mixture with H_2 including some CO_2 in syngas from reforming or partial oxidation of hydrocarbons, where CO_2 has to be removed in order to obtain pure syngas [8,9].

High-purity CO also finds application in industries to produce valuable chemicals such as methanol, acetic acid, oxo-alcohols, higher hydrocarbons [10,11], and others [12,13]. More specifically, acetic acid (CH_3COOH) is primarily produced by means of the Cativa process [14], which is similar to the Monsanto process [15], where CO and methanol react in the presence of an iridium-containing catalyst [16]. CO is also used for methanol (CH_3OH) synthesis using the Fischer-Tropsch process [17], according to the reaction $CO + Cl_2 \rightarrow COCl_2$ and leading to the production of phosgene [18]. It is also involved in the production of formic acid (HCOOH) through a two-step process starting with the reaction of CO with methanol to produce acetic acid, which subsequently reacts with ammonia (NH_3) to yield HCOOH [19]. Moreover, carbon monoxide is also employed in the medical field [20], the food industry [21], and clinical trials [22].

Consequently, CO_2/CO separation is currently as relevant as CO_2/N_2 separation because the associated technology plays an important role in climate change mitigation and sustainability transformation by producing high-value-added chemicals from industrial side streams [23]. In this context and additionally to the CO_2/CH_4 separation, the current work also examines the typically used CO_2-philic Pebax-1657 membrane as a separation layer material for CO_2/CO gas separation, which is an almost unexplored area of research. In addition, Pebax-1657 exhibits the highest CO_2-philic selectivity among all PEBA grades, primarily due to its superior CO_2 solubility, a property particularly pronounced in the case of CO_2/N_2 separation. This makes it the most commonly chosen grade for post-combustion carbon capture applications.

2. Materials and Methods

2.1. Materials

Lenzing P84® co-polyimide (BTDA-TDI/MDI) from HP polymer GmbH (Lenzing, Austria), N-methyl-2-pyrrolidone (NMP), and γ-butyrolactone (GBL) by Sigma-Aldrich Chemie

GmbH (Taufkirchen, Germany) for the dope solutions. Graphene nanoplatelets (GNPs) were kindly provided by FutureCarbon GmbH (Bayreuth, Germany). PEBAX-1657 pellets from Arkema S.A. (Colombes, France) and 99.8% purity ethanol by Fisher Scientific UK Ltd. (Loughborough, UK) were used for selective layer solution, Sylgard^{TM} 184 silicone elastomer kit of Dow Chemical Company (Midland, TX, USA) and 98.5% purity n-hexane of CARLO ERBA Reagents GmbH (Emmendingen, Germany) for gutter layer solution. Araldite 2012 (Huntsman Corporation, The Woodlands, TX, USA) epoxy resin was used for HF potting in the membrane module.

2.2. Fabrication of Composite HF Membranes

Based on our previous work [24], and as depicted in Figure 1, we designed and constructed an upscaled HF coating device. This was used to simultaneously coat four 70 cm-long porous HFs made of porous polyimide/GNPs (prepared by dry jet-wet spinning with green GBL solvent-based P84/GNP dope, according to an earlier work [25]). The fibers were coated three times at a flow rate of 30 mL/min with 1% crosslinked PDMS (Sylgard 184) in n-hexane. Cross-linked PDMS is a well-known material for gutter layers in thin-film composite membranes. The primary function of the gutter layer is to facilitate the formation of uniform selective layers on its surface, while inhibiting pore intrusion. PDMS is particularly suitable for this application due to its high CO_2 permeability, which minimizes gas transport resistance. Subsequently, they were coated twice with a 5% Pebax-1657 solution using an eco-friendly ethanol/water solvent (70/30 wt.%). As a result, approximately 2 m of defect-free coated HFs (effective length of 0.5 m for each HF after coating) were prepared in about 2.5 h, including a 30-min interval between each coating cycle. The total amount of both coating solutions used was less than 100 mL, rendering this upscaled "drop-casting under flow" technique highly energy- and cost-efficient compared to other dip-coating methods.

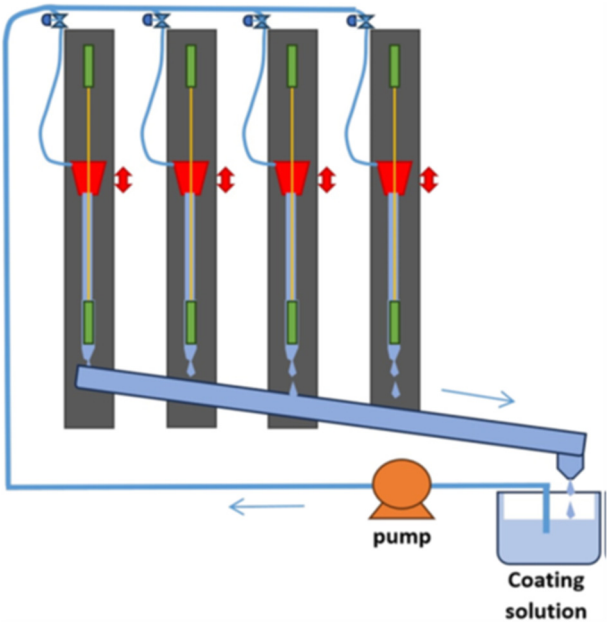


Figure 1. Upscaled, according to a previous work [24], HF coating device for underflow drop-casting.

2.3. Morphological Characterization

Scanning electron microscopy (SEM) was performed using a JEOL JSM-7401F field-emission gun (FEG) SEM (Tokyo, Japan) operated under standard conditions with an emission current of 10 mA and an operating voltage of 2 kV in Gentle Beam mode to examine the surface and cross-sectional morphology of the HF membrane samples. Before

imaging, the samples were sputtered with gold using an ion-sputtering device. For cross-sectional analysis, the samples were first immersed in liquid nitrogen and then fractured.

2.4. Gas Separation Experiments

Continuous gas flow rates were regulated by three Bronkhorst (Bronkorst, the Netherlands) mass flow controllers (two for mixture components and one for He sweep gas) and pressure drops across the membrane by one Bronkhorst back pressure regulator at the retentate (head-pressure) side, while permeate side remained at atmospheric pressure. The membrane feed stream concentration was regulated through proper adjustment of flow rates, giving a total of 100 ccSTP/min feed stream measured with a Supelco Optiflow 520 bubble flow meter (Sigma-Aldrich, St. Louis, MO, USA) at exit to atmosphere. The stage cut (ratio of permeate to feed flow rates) during the measurements was less than 2%. Gas concentrations were measured at permeate exit with an SRI 8610C gas chromatograph (SRI Instruments, Torrance, CA, USA) equipped with a 30 ft length, 1/8 in outer diameter, packed bed column, filled with porous polymer HayeSep DB 80-100 mesh adsorbent, operating at 180 °C, a TCD detector for CO_2, CO gas sensing and a FID detector for CH_4. The active surface area of the membrane module was approximately 19×10^{-4} m^2.

3. Results

3.1. Morphology

As illustrated in the SEM image in Figure 2a, the composite HF membrane exhibits a typical robust asymmetric structure, with an outer diameter of 900 μm and a wall thickness of about 160 μm. The lumen and bore surfaces have a finger-like structure, while between them is a highly porous "sponge" network with most pores ranging from 0.23 to 0.35 μm, suggesting a well-interconnected structure (Figure 2c). The irregular lumen contour (deformed shape) may stem from uneven stress or tension during the fabrication process. This deformation of the elastic cylindrical shell is influenced by the thermodynamic, kinetic, and rheological properties of the system [26]. Addressing this issue is beyond the scope of the current study and will be explored in future research. Figure 2b presents a close-up view of the outer surface layer, highlighting a uniform thin gutter layer with a thickness of approximately 300 nm.

The minimal thinness of this layer implies that it does not significantly impede permeability, thereby allowing efficient gas transport. Figure 2d displays the well-adhered separation layer on top of the gutter layer, with a measured thickness ranging between 4.5 and 5 μm. The smooth and uniform nature of this separation layer indicates effective separation capabilities. However, efforts are currently underway to further reduce the thickness of the separating layer by changing the conditions for dip-coating and tailoring them to match the thickness of the gutter layer.

3.2. CO_2/CH_4 Separation Performance of Composite HF Membrane

Gas separation experiments under continuous flow conditions were conducted to assess the effectiveness of the composite HF membranes in separating a real binary CO_2/CH_4 (10/90 vol.%) mixture under elevated pressure [27]. Additionally, pressurization-depressurization cycles were employed to examine the membrane's structural stability and to determine whether any structural changes that occurred during pressure application were reversible. This approach allowed for a comprehensive evaluation of both the separation performance and the long-term durability of the membranes under practical operating conditions.

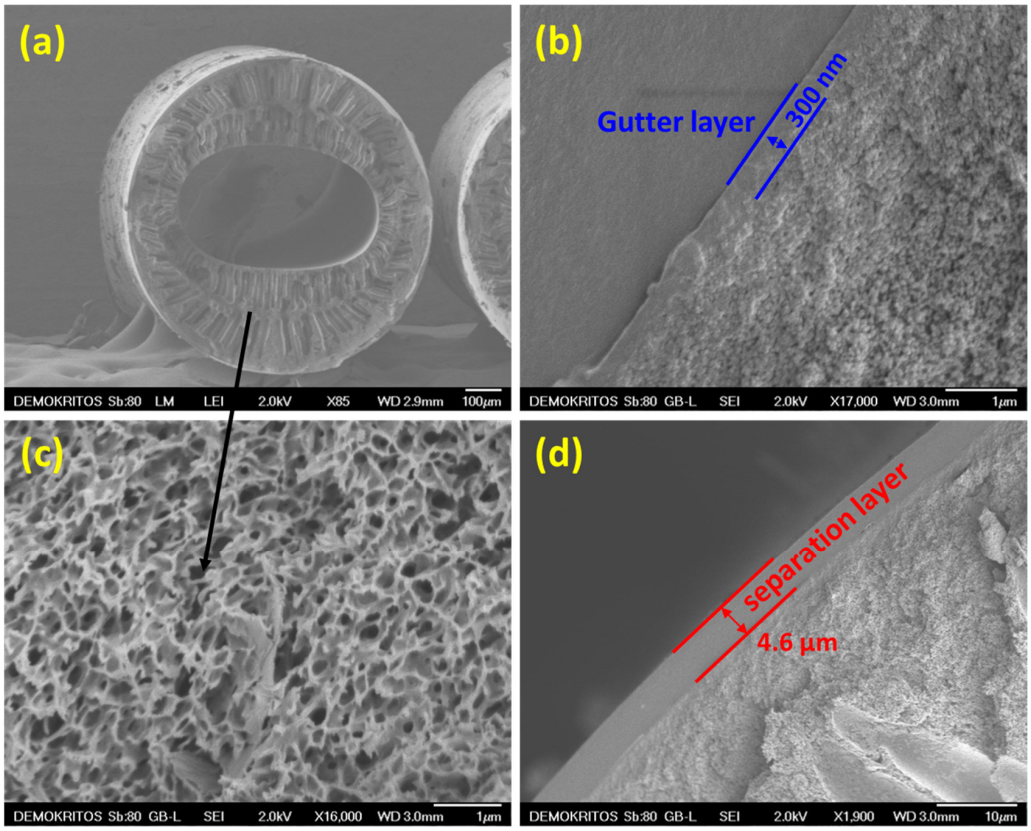


Figure 2. SEM micrographs of the composite HF membrane: (**a**) cross-sectional view showing overall morphology; higher magnification images illustrating (**b**) the gutter layer; (**c**) the wall region with a sponge-like structure region; and (**d**) the separation layer thickness.

Figure 3 presents the CO_2/CH_4 selectivity and CO_2 permeance of the composite HF membrane as a function of transmembrane pressure, ranging from 0 to 10 bar(a). The CO_2/CH_4 selectivity initially increases with pressure, reaching a peak selectivity at 3 bar(a), and then stabilizes around 100 to 110 as the pressure further increases up to 10 bar(a). This behavior indicates that the membrane exhibits strong selectivity towards CO_2 over CH_4 across the entire pressure range, particularly at moderate pressures.

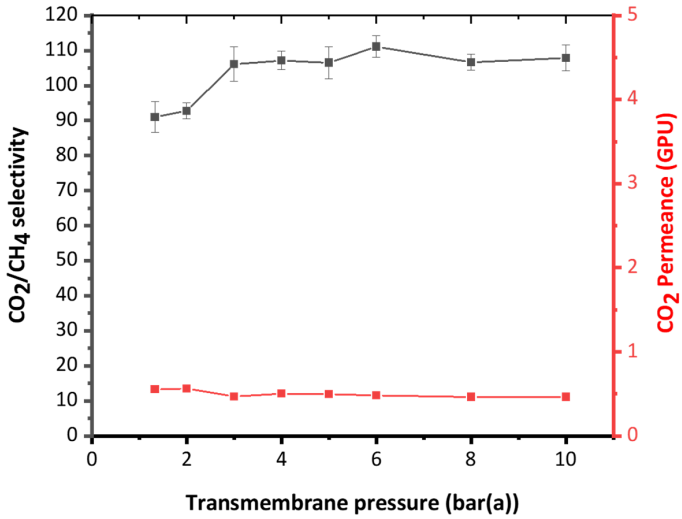


Figure 3. Separation factor (selectivity) and CO_2 permeance (GPU) as a function of pressure drop across the composite HF membrane for a gas mixture containing 10% v/v CO_2 in CH_4. The temperature was maintained at 298 K.

Regarding CO_2 permeance, the data show a relatively steady value of around 0.5 GPU throughout the entire pressure range. This consistency in CO_2 permeance suggests that the membrane's capacity to permit CO_2 passage remains highly unaffected by variations in transmembrane pressure. The stable permeance combined with high selectivity makes it suitable for applications requiring high CO_2 selectivity without compromising permeance, even with changes in operating pressure [28–32].

The overall impact of pressure on this composite HF membrane can be summarized as follows: initially, increasing pressure enhances CO_2/CH_4 selectivity, but this effect stabilizes at higher pressures. This behavior indicates that beyond a certain pressure threshold, the driving force for selectivity does not further enhance the separation performance. Conversely, the stable CO_2 permeance across the pressure range demonstrates the membrane's robustness, suggesting that it remains effective for CO_2 capture and separation processes under different pressure conditions. However, the relatively low CO_2 permeance observed in the composite HF membrane can primarily be attributed to the relatively thick separation layer. This thicker layer lengthens the diffusion path for gas molecules, slowing their transport and thus reducing permeance. In gas separation membranes, a thicker selective layer creates more resistance to gas flow, leading to a lower overall CO_2 flux through the membrane. This increased resistance impairs the efficient passage of CO_2 molecules, resulting in reduced permeance [33,34].

Another factor contributing to the low permeance could be the presence of the gutter layer in the composite membrane structure. This layer is designed to enhance mechanical stability, reduce defects in the separation layer, and improve its uniformity. However, it can also add extra resistance to gas flow, mainly by changing the flow path through a tortuous channel resulting in a high decrease in gas permeance. In this way and despite its thinness, the gutter layer introduces an additional barrier that gas molecules must overcome, further decreasing the overall permeance. Thus, while the combination of the gutter layer and Pebax-1657 separation layer enhances the overall membrane's selectivity and structural integrity, they also result in lower CO_2 permeance [35,36]. On the other hand, the combination of different materials for the support, gutter layer, and separating layer, and mainly the structural characteristics of the support (i.e., porosity and pore size) may lead to an increase in gas permeability and decrease in gas selectivity [37].

3.3. CO_2/CO Separation Performance of Composite HF Membrane

A binary CO_2/CO (33/67 vol.%) mixture, resembling an LDG byproduct gas stream of the steel industry, was chosen as the feed stream of the membrane under elevated pressure. Figure 4 presents the CO_2/CO selectivity and CO_2 permeance of the composite HF membrane across a range of transmembrane pressures from 0 to 8 bar(a). The CO_2/CO selectivity peaks at 4 bar(a), reaching a maximum value of approximately 50. This indicates that at this pressure, the membrane is most effective in differentiating between CO_2 and CO, likely due to the optimal balance between the pressure-driven force and the selective affinity of the Pebax-1657 layer for CO_2. At pressures beyond this point, the selectivity gradually decreases and stabilizes around 40 at higher pressures, up to 8 bar(a). This decline in selectivity at elevated pressures might be attributed to increased competitive sorption and diffusion of CO molecules, which start to compete with CO_2 for passage through the membrane as pressure increases [38].

Unlike the CO_2/CH_4 separation illustrated in Figure 3, the CO_2/CO selectivity exhibits a more pronounced dependence on pressure. This indicates that CO, being a smaller molecule than CH_4 with properties closer to CO_2, might be more susceptible to changes in transport dynamics within the membrane as pressure varies. The observed peak in selectivity followed by a decline also implies that the separation mechanism is more

pressure-sensitive to CO_2/CO than to CO_2/CH_4, likely due to the closer physicochemical properties of CO and CO_2 [39].

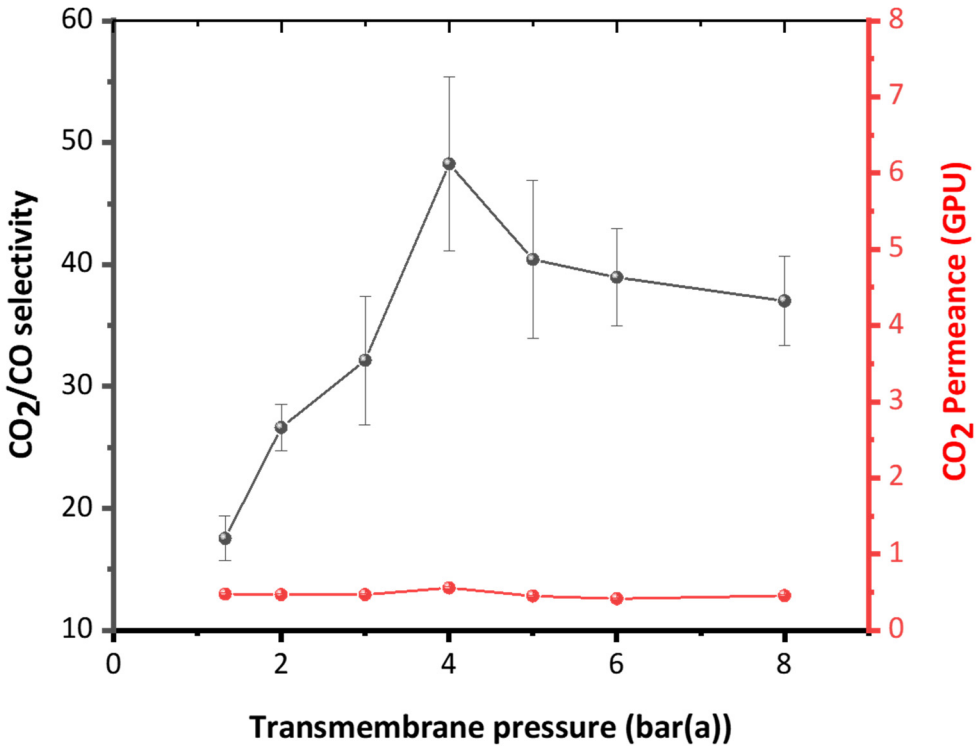


Figure 4. Separation factor (selectivity) and CO_2 permeance (GPU) as a function of pressure drop across the composite HF membrane for a gas mixture containing 33% v/v CO_2 in CO. The temperature was maintained at 298 K.

In the CO_2/CO separation, the CO_2 permeance remains low, similar to the CO_2/CH_4 separation, but it shows a slight increase at lower pressures up to 4 bar before stabilizing at higher pressures. Thus, pressure changes have a slightly greater impact on CO_2 throughput in CO_2/CO separation compared to CO_2/CH_4. Nevertheless, the permeance remains relatively low due to the thick separation layer. Indeed, as mentioned above, the 4.5–5 µm thickness of the Pebax-1657 layer imposes a substantial resistance to gas flow, keeping the permeance low regardless of pressure. While the thick separation layer improves selectivity by providing more material for CO_2 to preferentially interact with, it also lengthens the diffusion path for gases, thereby reducing permeance. This is a common trade-off in membrane design, where increased thickness can enhance selectivity for gases that interact strongly with the membrane material, but this improvement comes at the expense of reduced gas throughput.

Moreover, the stability of CO_2 permeance across varying pressures in both separation scenarios underscores the robustness of the Pebax-1657 membrane in maintaining consistent performance under different operating conditions. The gutter layer, with a thickness of 300 nm, is sufficiently thin not to notably impede gas flow, yet provides essential structural support to the separation layer. This combination effectively harnesses the benefits of both layers—the gutter layer offers structural reinforcement, while the thicker Pebax-1657 layer ensures selective separation.

In summary, comparing the selectivity trends for CO_2/CH_4 and CO_2/CO separations reveals distinct behaviors of the membrane for these gas pairs under varying pressures. The CO_2/CH_4 selectivity tends to be higher and more stable across a wider pressure range, whereas CO_2/CO selectivity peaks at intermediate pressures and then declines. This variation can be attributed to the differences in molecular size and interactions between

the gas pairs; CO_2 and CO have similar kinetic diameters and sorption characteristics, making their separation more sensitive to pressure changes compared to the larger and more distinct methane molecule.

These findings emphasize the need for a careful balance in membrane design for gas separation applications. For CO_2/CO separation, the pressure-sensitive nature of selectivity indicates that optimizing operating pressure is crucial for achieving optimal performance [40].

CO_2 and CO have a similar structure as small, linear molecules, and their sorption behaviors are relatively alike, making their separation more dependent on external factors like pressure [41]. Due to this similarity, at lower pressures, both gases are adsorbed in a comparable manner, resulting in lower selectivity. At intermediate pressures, slight differences in their interactions with the membrane material may lead to enhanced selectivity. However, as pressure increases, the available sorption sites in the membrane become saturated, causing both gases to compete for the same sorption sites. This competitive sorption reduces the difference in their adsorption characteristics, which in turn diminishes selectivity at higher pressures. This behavior is driven by the competitive dynamics of sorption and the specific interactions between CO_2 and CO with the membrane material [39,41,42]. In contrast, methane, with its more complex tetrahedral structure and slightly larger size, experiences less competition for sorption sites compared to CO_2. This size difference allows CO_2 to adsorb more effectively, maintaining higher and more stable CO_2/CH_4 selectivity across a broader range of pressures. The higher and more stable CO_2/CH_4 selectivity over a wider pressure range can be attributed to the significant difference in molecular size and interactions between the two gases. Methane is larger than CO_2, which leads to more pronounced size-sieving effects in membranes and adsorbents. This size difference makes the separation process less sensitive to pressure variations, as the larger methane molecules are more easily excluded. Additionally, the competitive sorption behavior in mixed-gas systems often tends to favor CO_2 over CH_4, because CO_2 has a stronger affinity for many membrane materials, resulting in higher and more stable selectivity over a range of pressures [43]. Another factor contributing to the selectivity variation could be the different interaction mechanisms between the gases and the membrane. CO_2, being a more polarizable molecule, can form stronger van der Waals forces or specific interactions, such as quadrupole interactions, with materials that preferentially adsorb polar species. In contrast, CO is less polarizable and interacts less strongly with the material at lower pressures. However, as the pressure rises, CO begins to compete for the same sorption sites, leading to a decrease in CO_2/CO selectivity at higher pressures. On the other hand, CH_4, a non-polar and more chemically inert gas, interacts weakly with most materials. This results in a more distinct separation behavior between CO_2 and CH_4, where CO_2 remains the dominant adsorbed species over a wider pressure range, ensuring higher and more stable selectivity for CO_2 over CH_4.

Conversely, for CO_2/CH_4 separation, the membrane's design is more tolerant to pressure variations, sustaining high selectivity over a wider pressure range. Therefore, selecting the appropriate membrane design and operating conditions should align with the specific requirements of the gas separation task and the desired trade-off between selectivity and permeance.

Finally, data on neat Pebax-1657 applied to HF supports for CO_2/CH_4 gas separation are rarely reported in the literature. Y. Zhang et al. [44] report an ideal selectivity of 22.46 and CO_2 permeance of 238.36 GPU with a separation layer thickness of approximately 1 micron. Our study will focus on enhancing the introduced coating method, aiming for thinner layers in the near future. Regarding CO_2/CO separations, the literature data

are even more scarce. A rare reference [23] reports a CO_2/CO selectivity of 30 and CO_2 permeability of 56 Barrer for neat Pebax-1657 dense membrane with flat sheet geometry.

4. Conclusions

In this study, the successful development of defect-free, composite hollow fiber (HF) membranes based on Pebax-1657, was accomplished using a novel drop-casting method under continuous flow. The membranes exhibited excellent performance in separating CO_2 from both CH_4 and CO, achieving selectivities of up to 110 for CO_2/CH_4 and 48 for CO_2/CO. The results highlight the effectiveness of the membranes for practical gas separation applications, especially for industries requiring CO_2 capture, such as natural gas processing and steel manufacturing. The scalability of the fabrication process, along with the robustness of the membranes under varying pressure conditions, make this method a promising solution for large-scale gas separation technologies.

The effect of pressure on separation performance was rigorously analyzed, revealing that while CO_2/CH_4 selectivity remains high and stable across a wide pressure range, CO_2/CO selectivity peaks at intermediate pressures before declining. This behavior is driven by the competitive sorption dynamics of CO_2 and CO at higher pressures, where both gases start to compete for the same sorption sites. In contrast, the distinct molecular structure of CH_4 allows for effective size exclusion, ensuring that CO_2 maintains high selectivity over CH_4, even under higher pressures. These findings underline the importance of molecular size and interaction mechanisms in the efficacy of membrane-based separations.

Finally, this study highlights important trade-offs between membrane selectivity and permeance. The relatively thick separation layer contributes to lower CO_2 permeance, suggesting that further optimization is needed to reduce membrane thickness and enhance gas throughput without compromising selectivity. Future research work should focus on optimizing membrane structure to balance these properties and expand the application of these HF membranes in other gas separation processes, such as CO_2/H_2 separation for hydrogen purification, further contributing to cleaner energy solutions.

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Data Availability Statement: Data are available on request from the authors.

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