Effect of Concentration of P84 co-polyimide thin film composite membrane on microfiltration membrane for Gas Separation

Tasya Faradilla Muara Zahra, Zeni Rahmawati, Hamzah Fansuri, Nurul Widiastuti, Suprapto Suprapto, Ratna Ediati, Triyanda Gunawana)

Department of Chemistry, Faculty of Science and Data Analytics, Institut Teknologi Sepuluh Nopember, Surabaya 60111, Indonesia

a) Corresponding author: triyanda@its.ac.id

**Abstract.** Gas separation is essential in various industrial and environmental applications, including biogas purification and carbon capture. Polymer-based membranes in recent years have been increasingly used widely due to their economical production costs, effectiveness in achieving the desired separation, and lower energy consumption compared to other separation technologies. In this study, P84 membranes were prepared with a polymer variation of 12-18% of the total mass of the membrane preparation solution in NMP solvent, which was prepared using the phase inversion method. The membrane with the best results was the 15% P84 membrane, with CO₂, N₂, and CH₄ gas permeabilities of 18,44 Barrer, 4,75 Barrer, and 13,88 Barrer. The CO₂/N₂ and CH₄/N₂ selectivities obtained were 3.89 and 2.93, respectively. The results of it showed that the optimum composition of the P84 membrane in this study is 15%.

# INTRODUCTION

Gas separation plays a crucial role in various industrial and environmental applications due to its ability to improve process efficiency, reduce costs, and reduce negative environmental impacts. One of the negative impacts of energy use in industry is the emission of huge amounts of greenhouse gases. In 2020, recorded CO2 levels in the atmosphere have reached 414 ppm and it is estimated that by 2035 it will increase to 450 ppm, causing an increase in global temperature by 2°C [1,2]. The utilization of natural gas as energy requires pre-treatment including the removal of contaminants to improve the quality and heating value of natural gas [3–5]. Gas separation has been practiced since decades ago. To date, the technologies used include cryogenic distillation, adsorption, and membranes [6]. Cryogenic distillation is notorious for requiring high cost and energy as well as a complex process that is less effective for certain types of gases being separated [7–9]. Adsorption itself has long been used in gas separation, but regeneration is required, which reduces efficiency and requires a lot of energy and cost [10]. Meanwhile, membranes have advantages such as lower energy requirements, ease of control and operation, simplicity, and compactness making membranes a widely used gas separation option today [6,11].

Polymer-based membranes in recent years have been increasingly used widely, including the oil and gas industry, because their production costs are economical, industrial conditions are suitable for using polymer-based membranes, they are effective for the desired separation, and they use less energy than other separation technologies [12–14]. Polymer membranes themselves are divided into two types, namely glassy and rubbery membranes. Glassy polymer membranes have superior selectivity than rubbery polymer membranes because the principle of separation is based on molecular diffusion, so it is often found in gas separation technology [3,15]. One example of a polymer for glassy membranes that has been commercialized is P84 co-polyimide which has high chemical resistance, good mechanical strength, high thermal stability, anti-plasticization, low hydrophilicity, and good solubility in most polar solvents [16–20] are proven effective for gas separation [21,22]. Based on previous research reports, the permeability of CH4 and CO2 on the P84 membrane was 0.88 and 0.67 Barrer with CO2/CH4 selectivity of 0.76 [4].

The composition of polymer in the casting solution plays an important role in membrane fabrication. If the polymer content is too low, the resulting membrane can be brittle and mechanically weak. On the other hand, if the concentration is too high, the structure becomes too dense, and gas transport is suppressed. Earlier studies on P84 membranes generally used relatively high polymer concentrations. For instance, at 20% P84 in NMP, an N₂ permeability of 1.73 Barrer with an O₂/N₂ selectivity of 4.11 was reported [23]. Another study with 21% P84 showed a CO₂ permeability of only 0.89 Barrer, but with a very high CO₂/N₂ selectivity of 20.23 [24]. These results highlight the potential of P84 for selective gas separations, although the low permeability remains a drawback. One limitation of P84 membranes prepared by non-solvent induced phase separation (NIPS) is their weak mechanical strength, which makes them difficult to handle and apply. Using a support layer to prepare thin-film composite (TFC) membranes is one way to address this issue. The support provides mechanical stability, while the thin selective P84 layer can still deliver good separation performance. In this study, P84 membranes were prepared at relatively low polymer concentrations (12–18% w/w) in NMP using the phase inversion method, with filter paper employed as a support layer. The membranes were then tested for CO₂, N₂, and CH₄ permeation to evaluate how polymer concentration influences gas transport properties, particularly permeability and selectivity. This approach also aimed to see how well supported P84 membranes can perform in gas separation applications.

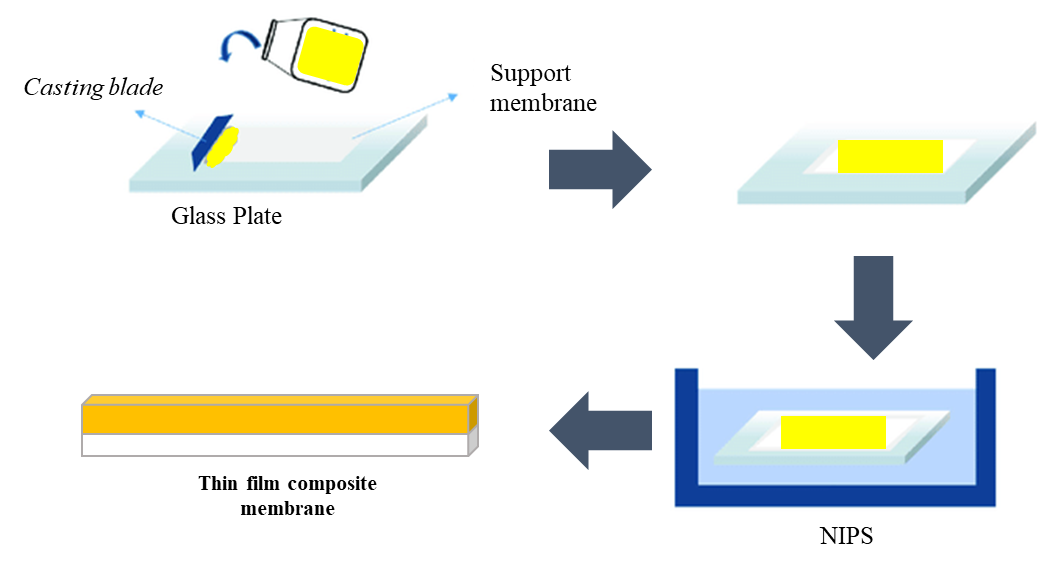
# Experimental

## Materials

The materials used for membrane fabrication were P84 (BTDA-TDI/MDI, Ensinger Sintimid GmbH) as membrane matrix, n-methyl-2-pyrrolidone (NMP, Merck) as solvent, filter paper as membrane support, technical ethanol (96%) for membrane post treatment after phase inversion process, aqua DM, and ultra-high purity gases CO2, N2, and CH4 (99.99%, PT. Samator Gas Industri) for membrane performance test.

## Fabrication of P84 Membranes

The fabrication of thin composite P84 membranes in the form of flat sheets using the phase inversion method (NIPS). P84 membrane solution was prepared with P84 powder (12, 15, 18%) put into NMP. Then, the mixture was sonicated for 60 minutes so that the powder was well dispersed, then stirred using a magnetic stirrer on a hot plate at 290 rpm and 80°C for 24 hours [21]. After sonicating for 30 minutes, the membrane solution was allowed to stand for 24 hours. The homogeneous solution was then sonicated to remove excess air bubbles so that the casted membrane did not experience defects. The membrane was cast on a filter paper as support layer using a 15 μm casting blade, then put into a coagulation bath filled with water and soaked for 4 hours. Then soaked in technical ethanol overnight before drying at room temperature until no liquid remains (FIGURE 1).



**FIGURE 1.** The schematic diagram of membrane fabrication method

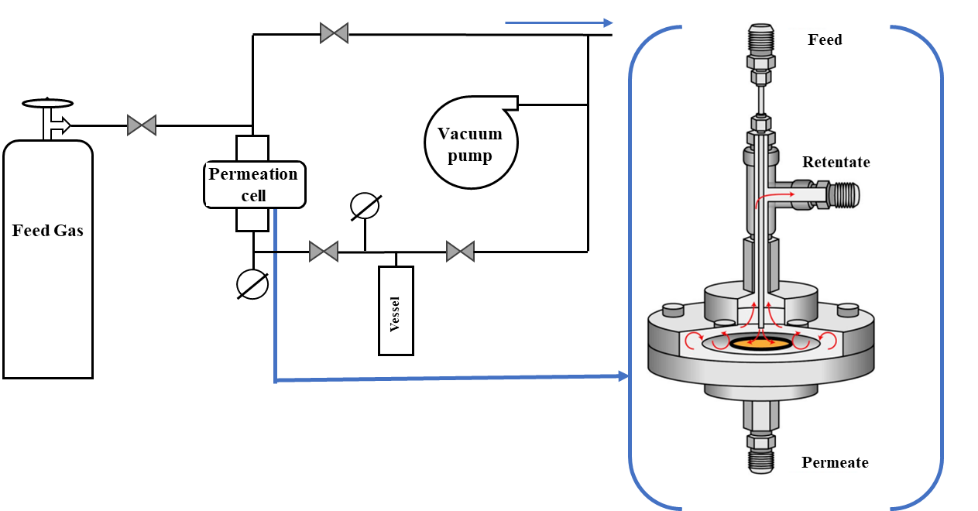
## Characterization of P84 Membranes

Scanning Electron Microscope(SEM, Hitachi H3000) characterization was performed to determine the surface morphology and cross section of the membrane. The SEM instrument was used at an electron accelerating voltage of 20 kV.

## Gas Permeation Measurements

Membrane performance tests, as shown in FIGURE 2, were conducted using CO2 (kinetic diameter: 0.33 nm), N2 (kinetic diameter: 0.36), and CH4 (kinetic diameter: 0.38 nm) gases at a pressure of 1 bar in room temperature, each tested four times. Membrane performance tests were Gas permeation was calculated using Equation i.

*Q* is the rate of pressure versus time at fixed volume and temperature (cmHg/s), ∆𝑃 is the change in pressure across the membrane (cmHg), *T* is the temperature (K), *l* is the dense layer of the membrane (cm), and A is the effective membrane surface area (cm2). Ideal selectivity is determined through the ratio between the permeation of fast gas i and slow gas j, as shown in Equation ii.

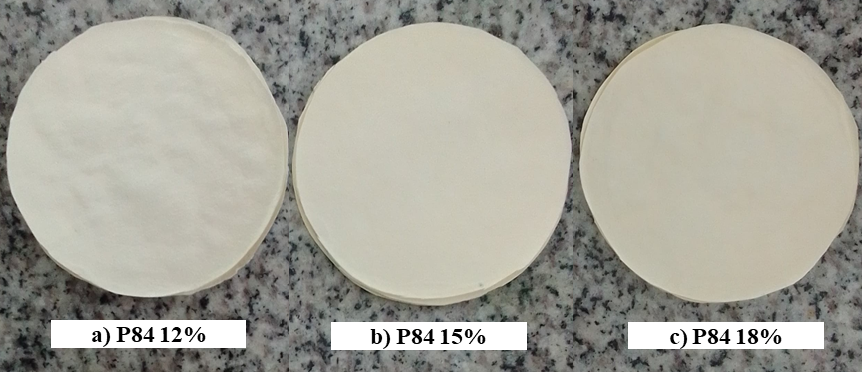


**FIGURE 2.** A set of membrane performance tests for gas separation.

# Results and discussion

## Fabrication of P84 Membrane

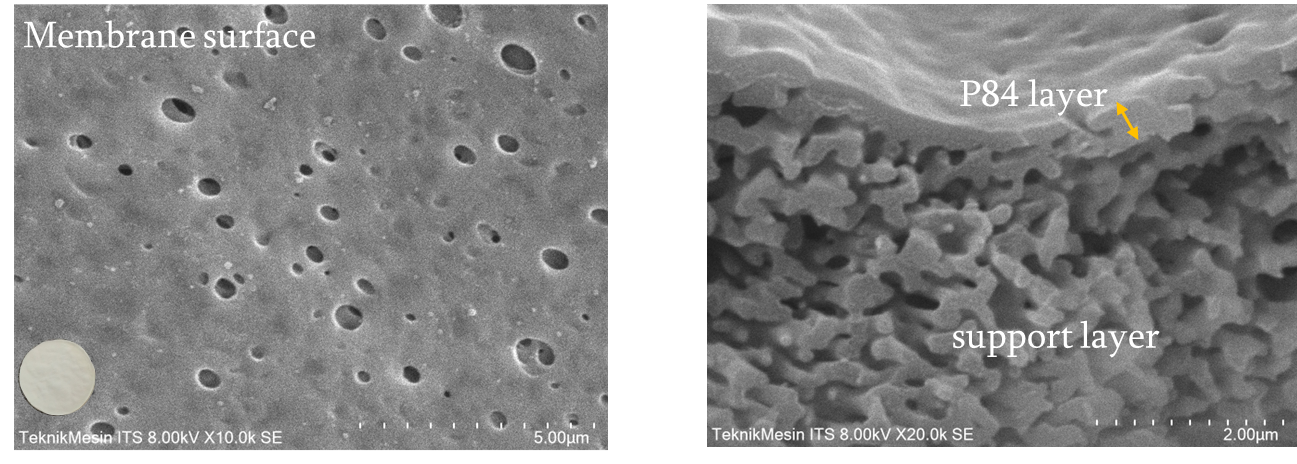
The P84 membranes obtained in this study are shown in FIGURE 3. The three membranes display very similar surface morphology from simple visual observation, and no significant variation appears between the different polymer concentrations. This result would not be expected, as the change in polymer content takes place over a comparatively narrow range. However, subtle variations which would not be visible at a macroscopic level may well exist at a microscopic level and could well affect both structure and functioning of the membranes. The average thickness of the membrane calculated from this study came out approximately 4.6 ± 0.12μm, while the selective dense layer required of the membrane ranging from 0.58 – 0.80 μm. This dense layer was used to calculate the permeability of the membranes.

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**FIGURE 3.** P84 co-polyimide membranes with variations of 12% (a), 15% (b), and 18% (c) after gas permeation tests.

## Morphology of P84 Membrane

The surface and cross-sectional structure of the P84 membranes were observed by SEM to see how the use of filter paper as a support affects the formation of the thin-film composite (TFC) structure. The SEM images of the 15% as the best performing P84 TFC membrane are shown in Figure 4. The surface of the membrane shows pores distributed evenly, with an average pore size of about 0.46 ± 0.02 μm. This indicates that the phase inversion process produced a porous structure that should support gas transport while keeping the membrane mechanically stable. The cross-sectional image clearly shows the typical TFC configuration: a thin, dense P84 selective layer formed on top of a porous support. The dense layer thickness is around 0.58 μm, while the overall membrane thickness is about 4.6 μm. This thin dense layer is the main barrier for gas diffusion and is therefore the part that determines the permeation performance. At the interface, no sign of delamination or chemical bonding between the P84 layer and the filter paper support can be seen. This suggests that the filter paper works only as a physical reinforcement and does not interfere with the separation function of the selective layer. The use of filter paper increases the mechanical strength of the membrane and makes it easier to handle, while still allowing the P84 layer to control the separation process. Overall, the SEM results confirm that the membranes produced here follow the expected structure of TFC membranes: a very thin selective film combined with a porous support layer. In this case, the filter paper support provides stability without reducing the performance of the selective P84 layer.

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**FIGURE 4*.***  SEM results of P84 15% membrane a) surface and b) cross section

## Gas Separation Performance

The gas separation performance of the membranes was evaluated by single gas permeation tests using CO₂, N₂, and CH₄ at 1 bar and room temperature. The results are summarized in **Table 1**. Across all membranes, the permeability follows the order **CO₂ > N₂ > CH₄**, which is consistent with the kinetic diameters of the gases (CO₂: 3.30 Å, N₂: 3.64 Å, CH₄: 3.80 Å). This shows that molecular size plays a key role in transport through the P84 dense layer, with smaller molecules diffusing more easily than larger ones. Similar trends have also been reported in earlier studies [4],[10]. Among the three membranes, the 15% P84 membrane shows the best performance. It has the highest CO₂ permeability (18.44 Barrer) and also higher CH₄ permeability compared to the 12% and 18% membranes. The improved performance at this concentration can be linked to the balance between selective layer thickness and pore structure. At lower concentration (12%), the selective layer is less dense, which allows higher gas flux but also reduces structural stability. This explains why the CO₂ permeability at 12% (11.15 Barrer) is lower than at 15%, as defects or micro voids may disturb selective diffusion. On the other hand, the 18% P84 membrane shows the lowest permeability for all gases. The denser morphology formed at higher polymer concentration makes the selective layer thicker and tighter, which increases resistance to gas transport. This is reflected in the CO₂ permeability dropping to only 6.18 Barrer. While such a dense structure may improve selectivity in some systems, in this case it mainly suppresses overall flux. The role of the filter paper support should also be noted. The SEM analysis confirmed that the P84 layer is well-formed on top of the support without visible defects or delamination. This means the differences in permeability observed here are dominated by changes in the P84 selective layer rather than the support. The filter paper mainly contributes to mechanical strength, allowing the thin dense layer to be cast and tested without breaking. Overall, the 15% P84 composition provides the most favourable balance, giving higher CO₂ permeability while still maintaining structural integrity. This indicates that optimization of polymer concentration is critical for preparing thin-film composite membranes with both good mechanical strength and competitive gas separation performance.

**TABLE 1.** Gas permeability test results.

|  |  |  |  |
| --- | --- | --- | --- |
| **P84 Membranes** | **Permeability (Barrer)** | | |
| **CO2** | **N2** | **CH4** |
| 12% | 11.15 ± 0.116 | 4.95 ± 0.024 | 7.38 ± 0.116 |
| 15% | 18.44 ± 0.313 | 4.75 ± 0.144 | 13.88 ± 0,159 |
| 18% | 6.18 ± 0.042 | 2.31 ± 0.008 | 5.68 ± 0.020 |

The separation performance of P84 membranes supported on filter paper was tested for CO₂, N₂, and CH₄. Figure 5 shows the effect of polymer concentration on permeability and selectivity. In general, CO₂ has the highest permeability compared to N₂ and CH₄, which is consistent with its smaller kinetic diameter (3.30 Å). Among the three variations, the 15% P84 membrane gives the best overall performance. At this concentration, the CO₂/N₂ and CH₄/N₂ selectivities reach 3.89 and 2.93, respectively. This suggests that the 15% membrane has a more favorable balance between chain packing and free volume, which allows good gas transport while still maintaining selectivity. The order of selectivity is clear: P84 15% > P84 18% > P84 12%. Interestingly, the highest CO₂/CH₄ selectivity (1.51) is obtained in the 12% membrane, even though its permeability values are lower. This could be due to looser packing of polymer chains at lower concentrations, which increases free volume but does not provide strong discrimination between gases with similar sizes. On the other hand, the 18% membrane shows a drop in performance for all selectivities (CO₂/CH₄: 1.09, CO₂/N₂: 2.68, CH₄/N₂: 2.46). One possible explanation is that at higher concentrations, the membrane layer becomes denser, and when combined with filter paper as support, defects or non-ideal transport pathways might appear. This needs to be examined further. From these results, polymer concentration strongly influences membrane performance. The use of filter paper as support may also have played a role in the inconsistent results, particularly for the 18% membrane. Future work should include more detailed characterization of the selective layer and reconsidering the support material. To further improve performance, composite approaches such as mixed-matrix membranes [25] or polymer blends [14] are promising options, as they can enhance both permeability and selectivity.

A diagram of a structure

AI-generated content may be incorrect.

**FIGURE 5.** Gas separation performance.

# CONCLUSION

P84 membranes were prepared by phase inversion at different polymer concentrations (12%, 15%, and 18%) on filter paper support. The results clearly show that polymer composition strongly affects gas transport behavior. As the polymer content increases, the membrane structure becomes denser, leading to lower permeability but a tendency toward higher selectivity. The best balance was obtained with the 15% membrane. At this composition, CO₂ permeability reached 18.44 ± 0.31 Barrer, with N₂ and CH₄ permeabilities of 4.75 ± 0.14 and 13.88 ± 0.16 Barrer, respectively. This gave the highest CO₂/N₂ (3.89) and CH₄/N₂ (2.93) selectivities. The 12% membrane, although less selective (CO₂/N₂ = 2.26; CH₄/N₂ = 1.49), provided the highest CO₂/CH₄ selectivity at 1.51, with CO₂ permeability of 11.15 ± 0.12 Barrer. In contrast, the 18% membrane showed the weakest performance, with CO₂, N₂, and CH₄ permeabilities of only 6.18 ± 0.04, 2.31 ± 0.01, and 5.68 ± 0.02 Barrer, resulting in lower selectivities (CO₂/N₂ = 2.68; CH₄/N₂ = 2.46; CO₂/CH₄ = 1.09). From these findings, it can be concluded that 15% P84 gives the most promising separation performance under the tested conditions. For a more complete understanding, further work should include detailed morphological characterization of the selective layer and consideration of the effect of the filter paper support. Looking ahead, improvements in separation could be pursued through composite membranes or polymer blends, which are known to enhance both permeability and selectivity.

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