

The Effect of Polymer Composition on CO₂/CH₄ Separation of Supported Carbon Membrane

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Recently, membrane technology has attracted vast attention from many scientists and engineers, particularly from the industrial area. The membrane for gas separation is favoured due to its economically feasibility and high separation performance with respect to gas permeability and selectivity. In this study, the effect of different polymer concentrations (5, 10, 13, 15 and 18 wt%) on the gas permeation properties of CO₂/CH₄ separation was investigated. Matrimid 5218 was chosen as the based polymer for tubular carbon membrane preparation owing to its excellent membrane properties (i.e. high mechanical and thermal stability) in order to fulfil the membrane requirement for high gas separation performance. The commercialised tubular membrane was dip-coated into Matrimid/NMP solution and then proceed with carbonisation process at the optimum condition with a heating rate of 2 K/min and under Argon gas flow rate at 200 mL/min at temperature of 1,123.15 K by using argon gas. The pure gas permeation tested for both CO₂ and CH₄ was carried out under room temperature at pressure controlled at 800 kPa.. From the experimental results, the tubular membrane made of 15 wt % Matrimid performed the highest CO₂/CH₄ selectivity (87.34 %) as compared to the other membranes. The excellent performance obtained from the membrane could be attributed by the micropores formation, where the chain of the polymer had increased its packing density. Thus, membrane porosity can be increased by increasing the polymer concentration in the solution.

1. Introduction

Nowadays, membrane technologies are playing an important role in the development of the fluid separation system, such as membrane distillation (Etoumi et al. 2014), membrane contractor and membrane gas separation. With the high potential of adaptability, low energy consumption and low capital cost inviting more research and development to invest for this attractive alternative membrane separation application. Furthermore, these technologies can be widely used in various fields, including, environment, health and daily lifestyle. Before this, most of the gas separation applications rely on the conventional system that has several weaknesses as compared to the membrane technology. For instance, tray column and distillation column are examples of the conventional systems that may render flooding, dumping, weeping and entrainment in tray columns. Recently, there has been a growing interest in the development of gas separation by using carbon membrane as it may give high separation performance (Wey et al., 2014). This results to a force to conduct to a better selectivity, thermal stability and chemical stability as opposed to the existing polymeric membrane. Carbon membrane is produced by the carbonisation process and it has high potential to attain high selectivity without deteriorating its permeability (Barsema et al., 2004). This study will report the different composition of polymer that will affect the performance of carbon membrane. The main objective of this study is to find the optimum composition of precursor polymer and its effect towards the gas permeation performance of carbon membrane.

In the fabrication of carbon membrane, it is crucial to choose the right precursor polymer as the chemical and physical properties must be considered in order to get the best performance of carbon membrane (He and Hägg, 2011). In this report, Matrimid 5218 has been chosen as the precursor polymer, in which the

gas separation performance for CO₂/CH₄ is expected to improve by using this polyimide polymer (Li et al., 2015), agreed by most researchers. For instance, Matrimid was supported by tubular ceramic via dip-coating in Matrimid/ N-methyl-2-pyrrolidone solution. Thus, the carbon membrane fabricated will have asymmetric morphology that obtain from the carbonised polymer and the tubular support (Paymoonii et al. 2014). The dip-coating process is quite a challenging task, as it requires several repetitions to fabricate the defect-free carbon membrane. There is also a study, stating that one-time coating-carbonisation process should be enough to prevent the defect (Mahdyarfar et al., 2013). However, it seems that repetition is required in this study and the fabricated carbon membrane thickness must be considered in order to produce high performance gas separation membrane (Nagy et al., 2015) . Moreover, the effect from the carbonisation process forms a brittleness of carbon membrane structure that influences it to create cracks. Besides that, micro-cracks or macro cracks might be formed with width more than 2 µm (Mahdyarfar et al., 2013), allowing larger molecule to permeate and that will prevent from obtaining good result.

2. Experiment

2.1 Materials

Matrimid 5218 in the form of powder was selected as precursor membrane. N-methyl-2-pyrrolidone (NMP, 99.55) from Meck (Germany) was selected as solvent. The commercialize tubular support was purchased from Shanghai Gongtao Ceramics Co., Ltd, China. Tubular support was fabricated from TiO₂ (4.5-5.5 mm) and the inner surface was coated by ZrO₂ (2-3 nm).

2.2 Carbon Membrane Preparation

Matrimid 5218 was first dried in a vacuum oven at temperature 353.15 ± 275.15 K overnight in order to remove any possible moisture on the polymer surface. Afterwards, the dope solutions were prepared by dissolving different composition of 5 wt%, 10 wt%, 13 wt%, 15 wt% and 18 wt% polymer precursors. Matrimid was dissolved in NMP for 7 h under a stirring rate around 400 rpm at 353.15 K. Next, the homogenous dope solution was sonicated to remove bubbles in the solution. A commercialised 8 cm length and 13 mm outer radius of tubular support was dip-coated into the polymer solution for 15 min. Then, the tubular supported polymer membranes undergo aging at 353.15 K for 24 h. After that, it was immersed for two hours in methanol before it was placed inside the oven at 373.15 K for 24 h to allow slow removal of the solvent. During the carbonisation process, supported membranes were placed in the centre of the Carbolite horizontal tubular furnace at 1,123.15 K under Argon. The heating rates of 2 K/min and 200 mL/min of gas flow rate were applied during the process. After completing the heating cycle, the furnace was allowed to cool gradually to room temperature.

Figure 1 below shows the summary of heat treatment protocol along side the carbonisation process. The nomenclature of resultant carbon membranes is given in the form of CM-polymer composition.

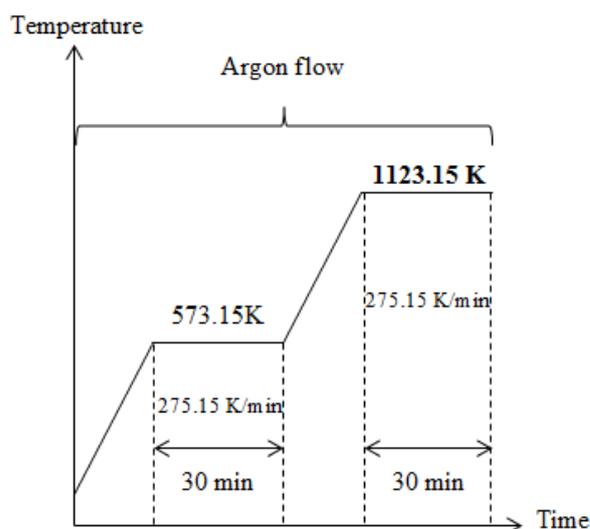


Figure 1: Heat treatment protocol

2.3 Gas Permeation Measurement

A gas permeation system was used to measure the permeance of pure CO₂ and CH₄ gas through the supported tubular carbon membrane. For instance, a 14-cm length tubular stainless steel module was used to place an 8-cm tubular supported carbon membrane. The membrane was fitted with O-rings rubber to enable the membrane to be housed in the module without any leakage. Furthermore, the pure gas was fed into the module at eight bars. Besides that, the permeance was determined in the sequence of CH₄ and CO₂ at room temperature. Based on the common gas permeation method, the gas permeance for carbon membrane can be expressed as:

Permeance, P:

$$(P/l)_i = \frac{Q_i}{\Delta p A} = \frac{Q}{\eta \pi D l \Delta P} \quad (1)$$

$$1 \text{ GPU} = 1 \times 10 \frac{\text{cm}^3 \text{ (STP)}}{\text{cm}^2 \text{ s cm Hg}}$$

Selectivity, α :

$$\alpha_{A/B} = \frac{P_B}{P_A} = \frac{(P/l)_A}{(P/l)_B} \quad (2)$$

where P/l is the permeance of the membrane (GPU), Q_i is the volumetric flow rate of gas i at standard temperature and pressure (cm³ (STP)/s), Δp is the pressure difference between the feed side and the permeation side of the membrane (cmHg), A is the membrane surface area (cm²), while n is the number of the membrane and l is an effective length of the membrane (cm).

3. Result and Discussion

The Matrimid 5218 that was chosen as precursor polymer had undergone the carbonisation process at temperature of 1,123.15 K by using Argon gas as the atmosphere. Five different compositions of precursor polymer weight percentage were prepared, in order to prove if its concentration in the dope solution affect the carbon membrane performance. The thickness of each sample is uniform as difference thickness will affect the performance of the membrane (Nagy and Hegedüs 2014). The gas permeance and selectivity result of the membrane were taken from the gas permeation measurement, where the test was conducted at 800 kPa pressure at room temperature. Table 1 below shows the result obtained from the prepared carbon membrane.

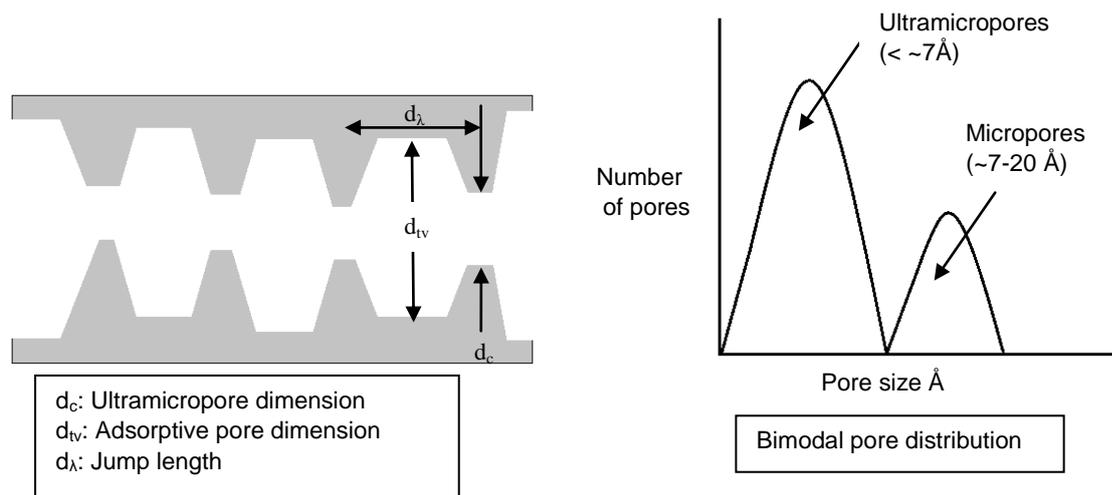
Table 1: Gas Permeation Properties of the Matrimid/NMP-Based Carbon Tubular Membrane

Carbon Membrane	Permeance (GPU)		Selectivity (CO ₂ /CH ₄)
	CO ₂	CH ₄	
CM-5wt%	145.73	2.50	58.29
CM-10wt%	174.40	2.66	65.56
CM-13wt%	212.50	2.86	74.30
CM-15wt%	287.36	3.29	87.34
CM-18wt%	219.40	2.85	76.98

Result from Table 1, have proved that Matrimid 5218 is one of the promising polymer precursors owing to its high performance in gas permeation test permeance and selectivity. Ning and Koros (2014) fabricated carbon membrane from Matrimid 5218, under an inert argon atmosphere at 800°C while Favvas and coworkers (2007) prepared carbon membrane by carbonization process up to 900 °C using Matrimid 5218 and result in high performance of carbon membranes. Although small amount of Matrimid (5 wt%) was used, the membrane still obtained high CO₂/CH₄ selectivity. It is believed that the main contribution for the high performance is due to the micropores formation within the carbon membrane. As CO₂ (3.3 Å) has smaller molecular size as compared to CH₄ (3.8 Å), thus CO₂ permeance was reported higher than CH₄ permeance and resulted in higher CO₂/CH₄ selectivity (Youn et al., 2004). This is because the micropores only allow certain size of molecules to pass through it. The mechanism behind this phenomena is known as

molecular sieving action, the effect arising from the breakage of benzene ring and other functional groups that create a bimodal rigid pore distribution during the carbonisation process.

Figure 2 shows the idealised pore and idealized bimodal pore size distribution of carbon membrane after the carbonisation process. The carbon membrane structures were mostly disorganised, with turbostatic structure after undergo the carbonisation process. Figure 2 (a), is known as “slit-like” pore structure, or the formation of it, because of the packing imperfections between ordered regions (Ning and Koros, 2014). The disordered sp^2 and hybridised condensed hexagonal sheets formed the amorphous structure. On the other hand, Figure 2 (b) describes a bimodal pore distribution of the carbon membrane structures, that have certain size of ultramicropores and micropores, where most of the carbon membrane surface were conquered by the ultramicropores size $< \sim 7\text{\AA}$.



a) Idealized pore structure of carbon membrane (Bhuwania et al. 2014)

b) Idealized bimodal pore size distribution of carbon membrane (Ning and Koros, 2014)

Figure 2: Structure of carbon molecular sieve

This study shows that, the precursor concentration is also important as it affects the membrane's performance. The selectivity of the membrane increased when the concentration of the precursor went up until 15 wt%. However, its performance decreased when the concentration of precursor were marked at 18 wt%. This happened due to the formation of micropores and the carbon structure during the carbonisation process that resulted in the carbon structure becoming rigid and compact. As a result, it reduced the permeability of both penetrants for CO_2 and CH_4 (Ning and Koros, 2014). Besides, reduction in selectivity was observed when the amount of the precursor polymer exceed its optimum value.

Table 2: Comparison of membrane performance from other type of membrane

Types of Membranes	Polymer	Permeance (GPU)		Selectivity (CO_2/CH_4)	Reference
		CO_2	CH_4		
Mixed Matrix Membrane	Polysulfone (PSF)	4.40	1.20	3.67	Kiadehi et al., 2015
Polymeric Membrane	Polyethersulfone (PES)	6.75	0.37	18.10	Saedi et al., 2012
Polymeric Membrane	Cardo-type Polyimide (PI)	37.00	1.75	21.14	Chenar et al., 2006
Carbon Membrane	Matrimid 5218	287.36	3.29	87.34	Author's study

Although most of researchers had admitted that polyimide-based carbon membrane could give a good performance for gas separation (Hosseini and Chung, 2009), the optimum amount of polymer composition must be applied so that it will not interfere the final performance of the membrane. Moreover, the polymer solution that has high polymer concentration will not give a good performance as the pores may close or

shrink during carbonisation process. Besides that, the external mass transfer resistance will exist since these dead-end pores appear (He and Hägg, 2012). Poor structural arrangement of carbon membrane will reduce the gas separation performance for all tested gases.

A previous study of physical aging of polymeric membrane was conducted for gas separation and the result showed that the membrane are able to stand for almost eighteen months (Fu et al., 2008). Inorganic membrane is well-known for its excellent thermal resistance and higher chemical stability compared to the other polymeric membranes (Ismail and David, 2001). Therefore, it is predicted that the carbon membrane has higher membrane life-span compared to the other polymeric membrane, as long as the membrane is operate under moderate conditions. For example in this study, the optimum pressure to apply is 8 bar, so it is expected that the membrane may sustain for a longer period if operate below than 8 bar.

4. Conclusions

Carbon tubular membrane deriving from Matrimid 5218 with different composition were fabricated using the commercialised tubular support via dip-coating method. Based on the results, it was shown that the performance of the carbon membrane depended on the precursor polymer composition. Furthermore, the carbon membrane selectivity increased gradually when the precursor polymer rose from 5 wt% to 15 wt%. However, when exceeding the polymer composition at 18 wt% precursor polymer, the performance dropped. The optimum polymer composition for Matrimid 5218-based carbon tubular membrane preparation is at 15 wt% of polymer. The highest CO₂/CH₄ selectivity of 87.34 (CO₂ permeance = 287 GPU) was obtained when an optimum polymer composition was used. This study concludes that, the carbon membrane performance is very much linked to its precursor polymer composition.

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