Separation of CO_2/CH_4 through Carbon Tubular Membranes: Effect of Carbonization Temperature

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Abstract: Carbon membranes have received much attention as advance materials in the gas separation technology due to their superior gas permeation performance and thermal and chemical stability. In order to increase the mechanical strength of the membrane, supported carbon membrane were produced using ceramic tube as support layer. Carbon tubular membranes were produced by carbonizing polymeric tubular membrane under different process parameter. In this study, carbon tubular membranes originating from Matrimid were prepared and characterized in term of its gas permeation properties. The preparation method involved dip-coating of the ceramic tubes with a Matrimid-based solution. The carbon tubular membranes were obtained by carbonization of the resultant polymeric tubular membrane under Argon gas flow in the horizontal tube furnace. The effects of the carbonization temperature on the gas permeation performance were investigated. Pure gas permeation tests were performed using CO_2 and CH_4 at room temperature with pressure 8 bars. The permeance and selectivity data indicate that the highest CO_2/CH_4 selectivity of 87.30 was obtained for carbon tubular membrane prepared at carbonization temperature of 850 ºC.

Keywords: Polymeric membrane, carbonization, carbon tubular membrane, separation, carbon dioxide.

1. INTRODUCTION

Membrane separation technology has attracted increasing attention from the scientific community with research area involved in CO_2 capture due to its energy saving, simple process design, and ease of scale-up and module construction. Carbon membranes have shown to possess outstanding gas separation performance and superior thermal and chemical stability under corrosive and high temperature operation. During heat treatment process, the polymer membrane material will be transform to carbon membrane material. Typically there are two types of pores are created at this stage, namely micropores and ultramicropores. This structural property has made the gas transport properties of the membrane switch from solution-diffusion to a molecular sieving mechanism [1, 2]. Carbon membrane has been proven having better performance compared to polymeric membrane. Methods for the preparation of novel carbon membranes have been proposed and studied in recent years in order to improve the gas separation performance. Lots of efforts have been taken in the development of gas separation by carbon membranes [3-7].

In an attempt to attain excellent gas separation performance, there is several process parameters have been investigated in the literature such as preparation method, types of polymer precursor, carbonization temperature, heating rates, thermal soak time, and carbonization environment [8, 9]. Anderson and coworkers conclude that carbon membrane manufactured at 400, 600 and 800 ^{o}C have a pore size comparable to the molecular size of CO_2 and CH_4. An optimum carbon membrane performance is achieved by membranes made at a higher carbonization temperature [7].

Polyimides are known to exhibit high permselectivity for various gas pairs, especially for CO_2/CH_4 separation [1, 3]. Many researchers reported that Matrimid is one of the best materials for membrane based CO_2/CH_4 separation, due to its attractive combination of gas permselectivity and high glass transition temperature. Moreover, most of the aromatic polyimides offered rigid structures and high carbon yields during the carbon membrane preparation [10]. Therefore, in this study, Matrimid was used as a polymer precursor material. The effects of the carbonization temperature on the gas permeation properties were explored in order to provide the best combination of selectivity and permeability of the resultant carbon tubular membranes.

2. EXPERIMENTAL

2.1. Materials

Matrimid 5218 was selected as a polymer precursor. It was dried overnight at 80 ^{o}C to remove

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any moisture. The N-methyl-2-pyrrolidone (NMP) solvent was purchased from Merck (Germany) and was used without further purification. The polymer membrane was supported using a tube of porous α-alumina (porosity: 40-50 %) 13 mm in diameter and 3 mm in thickness, with a pore size of 0.2 μm and a length of 8 cm.

2.2. Carbon Membrane Preparations

The Matrimid-based carbon tubular membranes were fabricated using the simple dip-coating method. A 15 wt % Matrimid solution was prepared by dissolving it in NMP and continuously stirring using mechanical stirrer in the temperature of 80 °C for several hours until a homogeneous solution was obtained. The mixture was then degassed in sonication bath to remove the existence of gas bubbles. The prepared Matrimid-based polymer solution was coated on the surface of the ceramic tube using dip-coating technique. After 15 minutes of being coated, the membranes were aged at 80 °C for 24 hours. The membranes were then immersed in methanol for 2 hours, and then placed at 100 °C for 24 hours inside the oven to allow slow removal of the solvent. The prepared polymers tubular membranes were then placed in the centre of the Carbolite horizontal tubular furnace to undergo carbonization process. The carbonization process takes place in two steps. Firstly, the membranes were heated up to 300 °C with the heating rate of 2 °C/min under Ar gas flow (200 ml/min). The membranes were held at 300 °C for 30 min. Subsequently, the temperature was raised up to three different final carbonization temperatures of 600, 750, and 850 °C at the same heating rate and gas flow. The membranes were maintained at the final carbonization temperature for 30 min. After completing each carbonization cycle, the membranes were cooled naturally to room temperature. The detailed carbonization profile used in this study is as illustrated in Figure **1**. The nomenclature of the resultant carbon tubular membranes is given in the form of CM-Carbonization Temperature. In order to examine the morphological structure of the membrane, non-supported membrane/flat sheet membrane was fabricated follows the similar method as supported membrane.

2.3. Characterization Method

The structural morphology of carbon membrane was observed by a JEOL JSM-5610LV scanning electron microscopy (SEM). This approach can be used to observe the presence of several cracks or pinholes, and for estimating the obvious fluctuation in membranes dimensions as a consequence of the heat treatment process. The membrane samples were cut into small piece in liquid nitrogen and coated with gold prior the analysis.

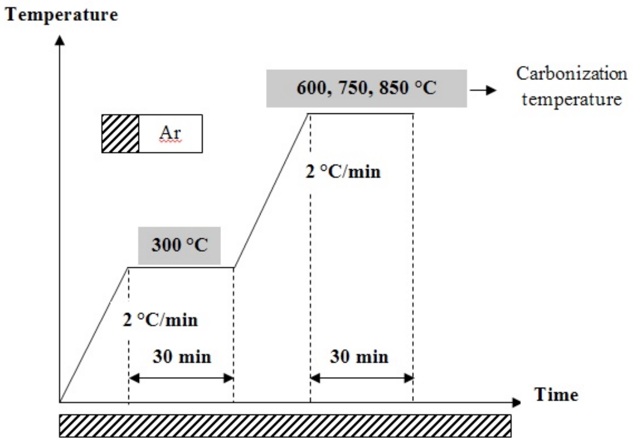

Figure 1: Carbonization profile.

2.4. Gas Permeation Measurement

The gas separation performance of the membrane can be evaluated based on two important parameters which are permeance and selectivity. The pure gas permeation tests were carried out following the sequence of CH_4 and CO_2. Each 8 cm carbon tubular membrane was placed inside the tubular stainless steel module. The membrane was then fitted with rubber O-rings to allow the membrane to be housed in the module without leakages. The gas was fed into the system at a trans-membrane pressure of 8 bars. The permeance, *P/l* (GPU) and selectivity, α, of the membranes were calculated using equations below:

Permeance, *P:*

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

Selectivity, α:

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

where *P/l* is the permeance of the membrane, *Qi* is the volumetric flow rate of gas *i* at standard temperature and pressure (cm^3 (STP/s), Δ*p* is the pressure difference between the feed side and the permeation side of the membrane (cmHg), *A* is the membrane surface area (cm^2), *n* is the number of fibers in the module, *D* is an outer diameter of the membrane (cm) and *l* is an effective length of the membrane (cm).

3. RESULT AND DISCUSSION

3.1. Morphological Structure Properties

Figure **2** shows the cross section of the Matrimid-based polymeric membrane and carbon membrane prepared at different carbonization temperatures. The SEM analyses of the membranes revealed that different structures can be obtained for polymeric and carbon membrane. The resulting polymeric membrane possesses an asymmetric structure that consists of a thin surface layer and supported porous structure. As observed in Figure **2**, the cross section images of the resulting carbon membrane prepared at 600, 750, and 850 °C showed a dense structure. In this case, the thickness of the dense structure was decreased as the carbonization temperature increased. After the heat treatment, the thickness of the polymeric membrane decrease approximately 12 % due to the weight loss of the membrane. The conversion of Matrimid polymer into carbon material was occurred during the heat treatment process at high temperature. During the decomposition stage, the cleavage of the pendant groups from the polymer backbones together with the cleavage of the polymer backbone itself was occurred. In addition, the removal of non-elementary carbon components and the arrangement of the carbon structure were significantly occurred at high temperature process [11].

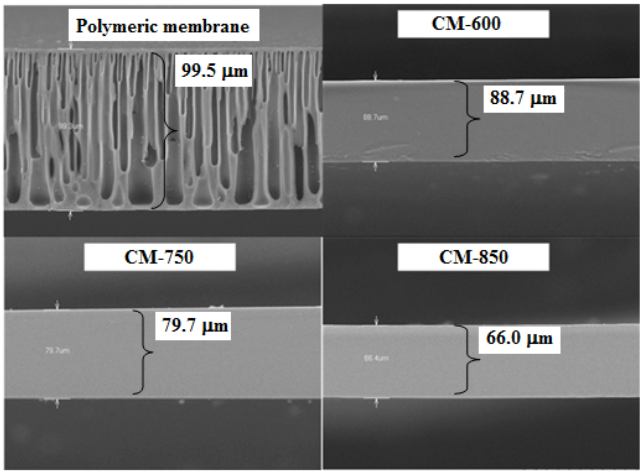

Figure 2: SEM images of Matrimid-based polymeric membrane and carbon membrane prepared at different carbonization temperatures.

3.2. Gas Permeation Properties

The carbonization process was carried out by heating the Matrimid-based polymeric membrane under Argon flow from room temperature to the final carbonization temperature. The permeance was examined using gas permeation test apparatus at 8 bars and room temperature. The results of the permeation performance of the prepared carbon membrane at different carbonization temperature are shown in Table **1**.

Table 1: Gas Permeation Properties of the Matrimid–Based Carbon Tubular Membrane

Carbon Membrane	Permeance (GPU)		Selectivity
	CO_2	CH_4	CO_2/CH_4
CM-600	34.70	1.11	31.36
CM-750	245.82	3.23	76.05
CM-850	287.36	3.30	87.30

Several researchers reported that carbon membranes prepared under the similar carbonization conditions do not exhibit similar separation performance [3, 12]. This can be related to the pore structure of the carbon membrane, which becomes rigid and compact thereafter, and some of the pores might change into closed pores during the carbonization process. As a result, highly selective carbon membranes with low permeance could be produced for the carbon membrane prepared at high temperature. In this study, when the carbonization temperature reached 850 °C, it was observed that the CO_2 permeance increased from 34.70 to 287.36, while for CH_4, the permeance increased from 1.11 to 3.30. The increase of prominent CO_2 permeance over that of CH_4 further suggests the formation of highly porous membrane with resulting effective molecular sieving properties. The results are in good agreement with the results in a research done by Itta and coworkers [13]. Hence, the increment of CO_2 permeance observed in this work suggests that similar phenomenon occurred. A continuous increase of selectivity from 31.36 to 87.30 was measured with the rise of the carbonization temperature from 600 until 850 °C. This indicates the availability of effective molecular sieving mechanism that was able to discriminate larger molecules, as the kinetic diameter of CO_2 was substantially smaller than CH_4 [14]. The result shows that Matrimid–based carbon tubular membrane with more selective behaviors can be obtained at carbonization temperature of 850 °C. As conclusion, the highest separation efficiency of carbon tubular membrane derived from Matrimid can be obtained at the ideal final carbonization temperature of 850 °C.

Table **2** shows the comparison between Matrimid-based carbon membranes prepared in this study with

Table 2: Comparison with Previous Studies (Matrimid-Based Carbon Membrane)

Heat treatment process (carbonization tempearature, heating rate, atmosphere)	Membrane configuration	CO_2/CH_4 selectvity	Ref
900 °C, 5 °C/min, N_2 saturated with water	Hollow fiber	22.5	[16]
700 °C, 0.5 °C/min, vacuum	Disk support	23	[17]
550 °C, 0.25 °C/min, vacuum	Hollow fiber	83	[15]
850 °C, 2 °C/min, Ar	Tubular support	87	This study

previous literatures. It is reported that an exceptionally high CO_2/CH_4 selectivity of 83 was obtained for carbon hollow fiber membrane prepared at 550 °C under vacuum environment. However, the data obtained from this study showed the highest value of the CO_2/CH_4 selectivity. The results indicated that the raising of the final carbonization temperature appears to reduce the effective pore sizes and decreased the gas permeation rate. The decreasing in the permeation rate will caused the selectivity to increase. Besides that, this is also can be due to the effect of the type of the gas flow and the configuration of the membrane. In summary, the gas permeation properties of the resultant carbon membrane can be tailored over a broad range of selectivity by manipulating the process parameter during the heat treatment process [15].

4. CONCLUSION

The result indicated that Matrimid is a good candidate for carbon membranes preparation. This study has shown that the gas separation properties of Matrimid-based carbon tubular membranes depend on the carbonization temperature. It is also found that excellent CO_2/CH_4 separation of 87.30 can be obtained for carbon membranes carbonized at 850 ^{o}C under Argon gas environment. This can be achieved as the high compactness of carbon membrane structure is produced at high temperature, which leads to the increase in selectivity.

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