

## Influence of Carbonisation Temperature on Gas Permeation Properties of Matrimid-based Carbon Membrane

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The utilisation of tubular support for carbon membrane preparation is beneficial for gas separation by providing high membrane area per unit volume and mechanically stronger than conventional flat substrate. In this study, tubular carbon membrane derived from Matrimid was fabricated via dip-coating method and three different carbonisation temperatures were used in order to produce high performance carbon membrane (600 °C,

750 °C and 850 °C). The physicochemical property of the carbon membrane is highly dependent on the final carbonisation temperature. By increasing carbonisation temperature, it will result in higher micropores and increasing gas pair selectivity. Whereas, low carbonisation temperature constricts pore formation and resulting in lower gas separation properties. The carbon membrane carbonised at 850 °C showed the highest gas separation properties of CO<sub>2</sub>/CH<sub>4</sub> selectivity of 87.30 with CO<sub>2</sub> permeance of 287.36 GPU. The resulted membrane is compared with literatures and has highlighted the potential of carbon tubular membrane for future membrane development.

### 1. Introduction

In the process industries, the gas separation by employing membranes has become progressively vital. Membrane has the concept to act as a semi permeable wall and separation occurs by the membrane controlling the rate of movement of various molecules between two liquid phases, two gas phases, or a liquid and a gas phase (Ismail and David, 2001). An emerging technology in membrane gas separation is facilitated by the demand in membrane with desirable mechanical properties and most importantly, improved separation performances. Due to some advantages over traditional methods such as pressure swing adsorption, cryogenic distillation and amine absorption, the membrane separation technology is rapidly developing (Buonomenna and Bae, 2015). Membranes separation processes are not a recent invention, which have experienced a fast development amid the previous couple of decades. Membranes and membrane processes were initially presented as an analytical tool in chemical and biomedical laboratories: they formed quickly into industrial products and techniques with huge specialised in technical and commercial value. Currently most of the commercialised membranes are polymeric membrane. Polymeric membranes are constricted by poor mechanical, thermal and chemical stability hinders their applications especially in harsh environment. Membrane for gas separation is bounded by the trade-off limit between gas permeability and gas pair selectivity; where highly permeable membranes possess low selectivity and vice versa. The trade-off limit was first highlighted by Robeson (2008) and since then, research has been focused on surpassing the limitation. Carbon membranes have been identified as a promising candidate for gas separation application. Carbon membrane has demonstrated to perform well above the trade-off limit. Carbon membrane is amorphous carbonaceous product that formed from the breakage of functional groups presence in the polymeric precursor

membrane. Carbon membrane consists of wide range of pore size distribution, ranges from micropore (7 - 20 Å) and ultramicropore (< 7 Å), that provide excellent gas permeability and gas pair selectivity by Briceño et al. (2012) superior than polymeric membranes. Previous study by Salleh and groups mention that, carbonisation conditions impose strong effect on the gas permeation properties of carbon membranes (Salleh et al., 2011). The final carbonisation temperature controls the evolution rate of volatile components from polymeric membranes to carbon membranes during carbonisation process. Carbonisation temperature, one of the carbonisation conditions that give strong effect on the separation performances, membrane structures as well as transport mechanism of the carbon membranes itself. The brittleness of carbon membrane makes researcher focusing on the preparation of the supported carbon membrane. The most common substrate used by the previous researchers are  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (Yin et al., 2013), TiO<sub>2</sub>-ZrO<sub>2</sub> macroporous tubes (Briceño et al., 2012), and porous graphite (Mahdyarfar et al., 2013). When a supporting substrate is used for the development of carbon membrane, the substrate must be chemically and physically stable and possess negligible diffusion resistance, which is lower than that of the carbon membrane. Tubular substrates are mechanically stronger against a compressing pressure than flat substrates (Simon et al., 2015). In this study, a ceramic tube is used as a support to overcome the brittleness of the carbon membranes. It is due to high thermal resistance; which necessary to sustain high carbonisation temperature and chemically stable against various solvent. This study aims to fabricate tubular supported carbon membrane for CO<sub>2</sub>/CH<sub>4</sub> separation. Matrimid was selected as the polymer precursor since it has been widely investigated and considered as preferable precursor due to its tremendous thermal, chemical, and mechanical stabilities (Kiyono et al., 2010). The fabrication parameter such as carbonisation temperature was investigated to produce high performance carbon tubular membrane.

## 2. Experimental

### 2.1 Materials

The polymer precursor, Matrimid 5218, was purchased from Merck while the solvent, N-methyl-2-pyrrolidone (NMP), was purchased from Sigma-Aldrich and were used without further purification. The tubular support with diameter of 13 mm and 3 mm thickness used in this study was purchased from Shanghai Gongtao Ceramics Co., Ltd. It was made from TiO<sub>2</sub> (4.5 - 5.5 mm) and coating of ZrO<sub>2</sub> (2 - 3 nm) on inner surface with an average pore size of 0.2 µm and a porosity of 40 - 50 %.

### 2.2 Fabrication of Carbon Tubular membrane

Matrimid powder was dried in oven overnight to remove absorbed water prior sample preparation. Polymer solution was prepared by dissolving the Matrimid powder in NMP with vigorous mixing at 80 °C until homogenous solution was obtained. The polymer solution was sonicated to remove trapped bubble formed during the mixing. Prior to dip-coating, both ends of the tubular support were covered with solefon tape to avoid coating on inner surface of the tubular support. The support was dipped into the polymer solution and left undisturbed for 15 min before being pulled out. The supported polymer membrane was dried at 80 °C for 24 h to induce slow solvent evaporation. Then, the membrane was immersed in methanol for 2 h and further dried at 100 °C for 24 h. The carbonisation process was done by placing the supported polymer membrane at the centre of Carbolite (Model CTF 12/65/550) wire wound tube furnace and heating cycle was controlled by Eurotherm 2,500 °C temperature control systems. The heat treatment process was performed under argon (Ar) environment using two steps of heating. The polymer tubular membrane was heated up to 250 °C with heating rate of 2 °C/min for stabilisation and held for 30 min. The temperature was then increased to final carbonisation temperature (600, 700 and 850 °C) at heating rate of 2 °C/min and soaked for 30 min before cooled down naturally to room temperatures. The dip-coating cycles was repeated for three times to eliminate possible pinholes presences on the surface of the prepared carbon tubular membranes. The carbon membrane prepared at temperature 600, 750, and 850 °C are denoted as CM-600, CM-750, and CM-850.

### 2.3 Membrane Characterisation

Free-standing carbon membrane without tubular support was prepared for characterisation purposes. Prior to characterisations, the samples were heated at 130 °C for 1 h to remove any trapped moisture. Fourier Transform Infrared Spectroscopy (FTIR), Single Reflection Diamond for the Spectrum Two (PerkinElmer, L1600107) is used to distinguish the actuality of the functional groups in a membrane. The FTIR sequences show the variation of the functional groups in the membranes once they stayed heated from room temperature to carbonisation temperature. Scanning Electron Microscopy (SEM) (TM3000, Hitachi) was used to determine the morphology of the prepared samples. The sample was first fractured and placed on carbon-taped holder before undergoes analysis. The morphology of the samples under various magnifications was taken to determine the thickness of the selective layer, the presence of cracks or pinholes, and for estimating the

obvious fluctuation in membranes dimensions as a consequence of the heat treatment process. Ni-filtered CuK $\alpha$  radiation with a wavelength of  $\lambda = 1.54 \text{ \AA}$  was applied in the experiments. The interplanar distance (d-spacing) of the carbon membranes were calculated by the Bragg equation, as in Eq(1):

$$n\lambda = 2d \sin \theta \quad (1)$$

Where, d is the dimension spacing ( $\text{\AA}$ ),  $\theta$  is the diffraction angle,  $\lambda$  is the X-ray wavelength ( $\text{\AA}$ ), and n is an integral number (1,2,3,...).

## 2.4 Pure Gas Permeation Measurements

The gas permeation a property of the prepared carbon membrane was measured via in-house built permeation modules as described elsewhere (Sazali et al., 2015). The permeation of CH $_4$  (3.80  $\text{\AA}$ ) and CO $_2$  (3.30  $\text{\AA}$ ) was taken at room temperature under feed pressure of 8 bar. During the gas permeation test, the gas flow rate was taken by the time taken for the gas to permeate at a constant volume of 1.0 mL. Permeate side exit from bore side of the tubular membrane were flowed straightforward to the bubble flow meter (burette) (Khezli et al., 2016). The gas permeance, P/l, (GPU) and gas pair selectivity,  $\alpha$ , of the membranes were calculated using Eq(2) and Eq(3):

$$(P/l)_i = \frac{Q_i}{A\Delta p} = \frac{Q_i}{\pi D l \Delta p} \quad (2)$$

$$1 \text{ GPU} = 1 \times 10^{-6} \text{ cm}^3 (\text{STP}) \text{ cm}^{-2} \text{ s}^{-1} \text{ cm Hg}^{-1}.$$

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 ( $\text{cm}^3 (\text{STP/s})$ ),  $\Delta p$  is the pressure difference between the feed side and the permeation side of the membrane (cm Hg), A is the membrane surface area ( $\text{cm}^2$ ), D the an outer diameter of the membrane (cm) and l is the effective length of the membrane (cm).

$$\alpha_{i/j} = \frac{(P/l)_i}{(P/l)_j} \quad (3)$$

where,  $\alpha_{i/j}$  is the selectivity of gas penetrant i over gas penetrant j,  $(P/l)_i$  and  $(P/l)_j$  are the permeance of gas penetrant i and j.

## 3. Results and Discussion

### 3.1 Characterisation of polymer and carbon tubular membrane

The prepared membranes were characterised using different characterisation techniques to understand the influence of final carbonisation temperature on the carbon tubular membrane properties.

#### 3.1.1 FTIR Analysis

The molecular orientation analysis of Matrimid-based carbon membrane under different carbonisation temperature was performed using FTIR and illustrated in Figure 1. The result shows that the intensity of the peaks for the carbon membrane was decreased as compared to the polymeric membrane (Sazali et al., 2015). The chemical structure changes taking place through the transformation from polymer to carbon can be observed by FTIR. For all membranes, the band in the range of 1,400 - 1,900  $\text{cm}^{-1}$  indicates the presence of C-H aromatic monosubstituted benzene. Unfortunately, at the 1,600  $\text{cm}^{-1}$  reading for polymeric Matrimid and CM-300 - 600  $^\circ\text{C}$ , one single clear peak can be seen. Compared to CM-300 - 750  $^\circ\text{C}$  and CM-300 - 850  $^\circ\text{C}$  its counterpart, two peaks were observed in the FTIR ranges 1,600  $\text{cm}^{-1}$ . It can be seen that the decomposition and breakage of the chemical structure and bonding as the carbonisation temperature increase. Ismail have characterised the transformation of other polymers structure according to thermal history. A significant reduction of the peaks was observed for all the carbon membranes It was observed since the structure compaction and become closer to the ATR crystal interface hence decreased transmission intensity.

#### 3.1.2 Morphological structure properties (SEM)

Figure 2 shows the cross-sectional morphology of the Matrimid-based polymeric and carbon membranes prepared under different carbonisation temperature. Figure 2(a) shows the polymeric precursor has asymmetric structure with average thickness of  $\sim 99.5 \mu\text{m}$  with dense skin layer supported on a finger-like structure. As the polymeric membrane underwent carbonisation, it was observed that the resulted carbon membrane possessed symmetric dense structure independent on different carbonisation temperature. As discussed earlier, the breakage of functional group (see Figure 1) has caused the membrane structure to

collapse and densified its reorientation and densification of carbon membrane microstructure has occurred and leads to thinner and denser membrane.

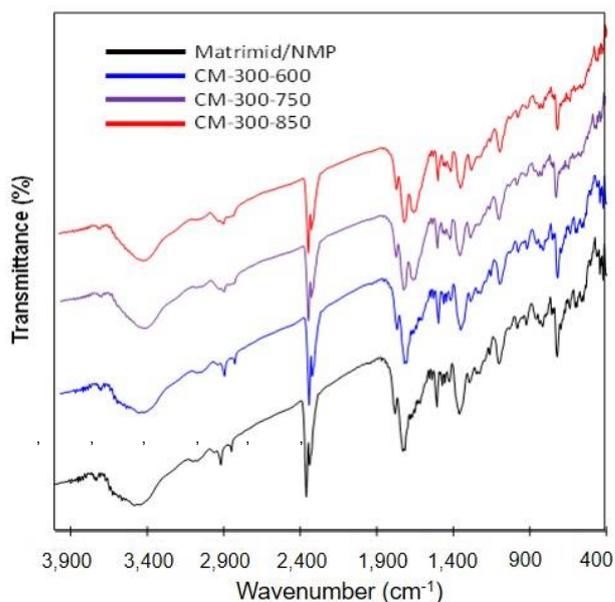


Figure 1: FTIR analysis of Matrimid-based carbon membranes prepared at different carbonisation temperature

This structure was generated during the dip-coating process as the result of the phase inversion between polymer solution and ceramic supported. The same micrograph was also observed for carbon membrane derived from Matrimid (Briceño et al., 2012). The results support the potentiality of this simple and relatively fast procedure, which offers new ways of designing and directly characterising supported carbon membranes for the gas separation. Although similar morphological structure was observed using different carbonisation temperature, the thickness of the membranes was suppressed as higher carbonisation temperature was applied. For example, CM-600 having thickness of 88.7  $\mu\text{m}$  (Figure 2(b)), while CM-750 thickness is 72.6  $\mu\text{m}$  (Figure 2(c)), and CM-850 having thickness of 66.4  $\mu\text{m}$  (Figure 2(d)). Increasing carbonisation temperature has prompt microstructure rearrangement to pack closely in molecular level and cause membrane densification to occur.

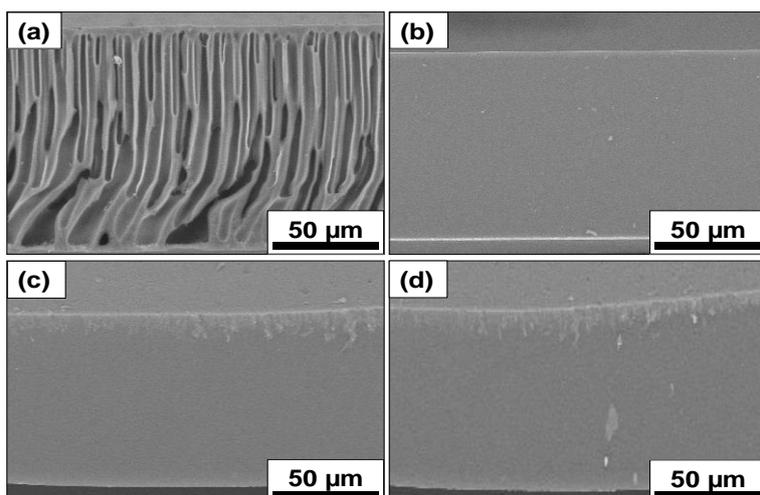


Figure 2: SEM images of the cross-sections for Matrimid/NMP-based (a) Polymeric membrane, (b) CM-600, (c) CM-750 and (d) CM-850

### 3.2 Gas permeation properties

The pure gas permeance test was measured at 8 bar and room temperature. The gas permeation performance of the carbon membranes prepared under different final carbonisation temperatures is summarised in Table 1. High carbonisation temperature would have attributed to better structural packing induced at high temperature provide more channel for gas transport even compaction of selective layer occurred. It is reported that the gas permeance would decrease with the increase of final carbonisation temperature due to the selective layer compaction and some of the pores might change into closed pores during the carbonisation process (Song et al., 2010). In contrast, increasing carbonisation temperature from 600 °C to 850 °C has resulted in increased the permeance of CO<sub>2</sub> from 27.57 to 287.36 GPU, while CH<sub>4</sub> permeance increased from 1.05 to 3.29 GPU even after structural compaction was observed at higher carbonisation temperature (Figure 2). This phenomenon was directly related to the increase in porosity as carbonisation temperature. Tin and groups have been used P84 to determine the effect of carbonisation temperature on the gas permeation performance of the carbon membranes (Blyss Tin et al., 2004). They suggested that, high carbonisation temperature is requiring to produce high separation performance carbon membrane. The permeance and gas pair selectivity increase concurrently, indicates the absence of unselective cracks even at high carbonisation temperature. Similar study has been reported by Rungta who also used Matrimid to investigate the effect of carbonisation temperature at 500 - 800 °C (Rungta et al., 2012). These results show that the pure gas CO<sub>2</sub> permeance is consistently higher than that of N<sub>2</sub> and CH<sub>4</sub>.

*Table 1: Gas permeation properties of the Matrimid-based Carbon Tubular Membrane prepared at different carbonisation temperature under argon environment*

CM	Permeance (GPU)		Selectivity
	CO <sub>2</sub>	CH <sub>4</sub>	
CM-600	27.57 ± 6.6 %	1.05 ± 3.0 %	26.18 ± 5.0 %
CM-750	107.38 ± 6.4 %	1.58 ± 4.0 %	67.95 ± 4.1 %
CM-850	287.36 ± 7.3 %	3.29 ± 6.0 %	7.0 %

Significant increase in smaller molecule permeance (kinetic diameter of CO<sub>2</sub> is 3.3 Å) is more prominent compared to larger molecules (kinetic diameter of CH<sub>4</sub> is 3.8 Å), resultant higher gas pair selectivity as carbonisation temperature increase (Table 1). Increasing carbonisation temperature from 600 to 850 °C has significantly increased the CO<sub>2</sub>/CH<sub>4</sub> selectivity from 26.18 ± 5.0 % to 87.30 ± 7.0 %. This restriction has improved the ability of the carbon membrane to separate the gases based on their kinetic diameter, hence, increased the CO<sub>2</sub>/CH<sub>4</sub> selectivity. Although decreased in permeance was expected since the restriction would increase the transport resistance for both gases, the superior surface area as carbonisation temperature increased are more dominant to increase their permeance.

### 4. Conclusions

An excellent performance of carbon membrane has been obtained by carbonising Matrimid-based membrane at 850 °C under Argon atmosphere. It is found that, the morphological structures of the carbon membranes were dense and the thickness of the skin layer decreased as the carbonisation temperature increased with the highest CO<sub>2</sub>/CH<sub>4</sub> selectivity of 87.30 ± 7.0 % was obtained. The results show that the CO<sub>2</sub>/CH<sub>4</sub> selectivity increased when the carbonisation temperature increased. This indicates that the pores and carbon structure of the carbon membrane become rigid, compact and some of the pores might change into closed pores during the carbonisation.

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