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THE EFFECT OF CARBONIZATION TEMPERATURE ON THE GAS PERMEATION PROPERTIES

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***Abstract*- Carbon membranes have been studied in the last few years as a promising candidate for energy-efficient gas separation processes in replacing the traditional membranes such as polymeric membranes. Carbon tubular membrane can be achieved by carbonizing polymeric tubular membrane under different process parameter. Carbonization is the most important step in the fabrication of carbon membrane and can be recognized as the heart of the carbon membrane production. The preparation and characterization of carbon membranes originated from Matrimid were studied. Matrimid-based carbon tubular membrane will be fabricates and characterize in terms of its gas permeation properties. The carbonization temperature during the carbon membrane fabrication was studied. The polymer solution was coated on the surface of tubular ceramic tubes by using dip-coating method. The polymer tubular membrane was then carbonized under Argon atmosphere at different carbonization temperature; 600, 750, and 850 ◦C. Pure gas permeation tests were performed using CH_4 and CO_2 at room temperature with pressure 8 bars. Based on the results, the highest CO_2/CH_4 selectivity of 87.30 was obtained for carbon membrane prepared at 850 ºC.**

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

I. INTRODUCTION

Nowadays, to enhance the growing global demand for greener energy and pursuit of higher energy efficient processes, extensive research studies have been developed to produce new membrane materials with potentials to reduce cost and complexity in process operation and control. Carbon membranes have emerged as a promising class of material for the separation of gas molecules with comparable kinetic sizes (Burns R.L. *et al* (2003); Centeno, T. A. *et.al* (2001)). The preparations of novel carbon membranes have been study in past recent years in order to improve the gas separation performance. Nowadays, there are a lots of efforts have been taken on the investigation or the other important aspects on the development of gas separation performance by carbon membranes.

Carbons membranes are novel materials derived from the carbonization of the polymeric precursors and have been well-developed ultramicropore network that can separate small gas pairs with minor difference in diameter, thus exhibit higher gas permeability and selectivity compared to polymeric membranes (Lin L. *et.al* (2012)). Carbon membranes have been receiving considerable attention because they exhibit higher thermal and chemical stabilities and better gas separation performance than polymeric membranes (Li H.C. *et.al* (2014)). These key advantages have encouraged many researchers since the 1980s to investigate and develop carbon membranes for gas separation.Polyimides are known to exhibit high permselectivity for various gas pairs, especially for CO_2 /CH_4 (Lin L. *et.al* (2012)) and mechanical strength (Pugazhenthi G. *et.al* (2005)). Many researchers reported that Matrimid 5218 as one of the best material choices for membrane based CO_2 /CH_4 separation, due to its attractive combination of gas permselectivity and high glass transition temperature (Robeson L.M. *et.al* (2008)).

The preparation of a high performance carbon membrane is a difficult task, since it involves many steps that must be well controlled and optimized. The fabrication process for carbon membranes normally consists of six important steps, which are material selection, material characterization, precursor membrane preparation, pre-treatment, carbonization, and post-treatment. Each step includes many parameters which need to be optimized in order to obtain a high performance membrane. Among these steps, the carbonization process is the most important and can be regarded as the heart of the carbon membrane fabrication process. Therefore, in this study the effect of the carbonization temperature on the gas permeation properties are explored in order to provide the best selectivity and permeability of carbon membranes, Matrimid with polymer concentration of 15wt% that carbonized under 850 ºC of carbonization temperature and under Argon environment have prove it.

II. EXPERIMENTAL

A. Materials

Matrimid 5218 was selected as a main polymer precursor. It was dried overnight at 80 ºC to remove any moisture. N-methyl-2-pyrrolidone (NMP) that purchased from Merck (Germany) is used as a solvent.

B. Carbon Membrane preparation

Polymer solution was prepared by dissolving 15 wt % of Matrimid 5218 in N-methyl-2-pyrrolidone (NMP) for 7 hours with mechanical stirring. The mixture was maintained under

room temperature to remove all bubbles from the solution. Polymer supported membranes were prepared by dip-coating a uniform layer of the polymeric solution over the external surface of a tubular ceramic supported (6cm in length, 13mm outer radii). After 15 minutes coated, the membranes were then aged at 80 ^{o}C for 24 hours. The membranes were then immersed with methanol for 2 hours and then placed at 100 ^{o}C for 24 hours inside oven to allow slow removal of the solvent. The prepared polymers tubular membranes were placed in the centre of the Carbolite horizontal tubular furnace undergo carbonization process. The carbonization process was performed at temperature of 600, 750, and 850 ^{0}C under Argon gas (200ml/min). The heating rate of 2 ^{o}C /min was applied throughout the process. After completing each heating cycle, membranes were cooled naturally to room temperature. The detailed carbonization protocol is illustrated in Fig 1. The nomenclature of the resultant carbon tubular membranes is given in the form of CM-Carbonization Temperature.

C. Gas Permeation Measurement

The performance of the membrane can be characterized into two important parameters which are permeance and selectivity.

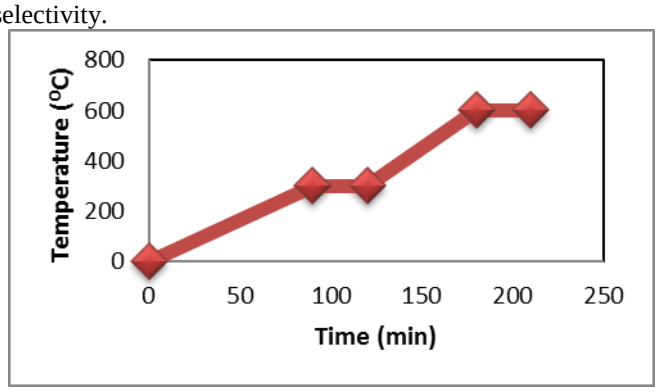

Figure 1: Carbonization protocol

The carbon tubular membranes were tested in pure gas permeation system. The 6 cm carbon tubular membrane was placed inside the membrane module. A tubular stainless steel module of 14 cm in length was used to contain the carbon tubular ceramic membrane. The membrane was fitted with rubber O-rings that allowed the membrane to be housed in the module without leakages. Pure gas CO_2 and CH_4 were fed into the module 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:*

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

Selectivity, α :

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

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), 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). The permeance, P (GPU) and selectivity, α of the membranes were calculated by using the equations (1) and (2). This is in good agreement with the research done by Salleh and Ismail (2012).

III. RESULT AND DISCUSSION

The carbonization process was performed by heating the Matrimid-based polymeric membrane under Argon flow from room temperature to the final carbonization temperature. The permeance was measured 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/NMP – 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 have reported that carbon membranes prepared under the similar carbonization conditions do not exhibit the similar separation performance, especially selectivity (Williams P J, Koros W.J. 2008). This can be related to the pore structure of the carbon membrane become rigid, compact and some of the pores might change into closed pores during the carbonization process. As a result, highly selective carbon membranes with low permeance would be produced. However, the increasing trend of permeance and selectivity behave differently than expected. In contrast, when the carbonization temperature reach 850 ^{o}C, the result shows that the CO_2 permeance was increase from 34.70 to 287.36 while for CH_4, permeance increase from 1.11 to 3.30. At the higher temperature, highly porous carbon membranes with effective molecular sieving enhance both CO_2 permeance and selectivity. Itta *et.* al (2011) suggested that higher carbonization temperature would induce more porous structure. Hence, the incremental of CO_2 permeance observed in this work suggest similar phenomenon occurred. A continuous increase of selectivity is calculated with the rise of the carbonization temperature from 600 until 850 ^{o}C was 31.36 to 87.30. It indicates effective molecular sieving mechanism that able to discriminate larger molecules, as the kinetic diameter of CO_2 is substantially smaller than CH_4.The result shows that Matrimid–based carbon tubular membrane with more selective behaviors' can be obtained at carbonization temperature of 850 ^{o}C. Figure 2 shows comparison between CO_2 permeance with CH_4 readings. As conclusion, to gain the highest separation efficiency of carbon tubular membrane derived from Matrimid, the ideal final carbonization temperature for polymer concentration of 15wt% is at 850 ^{o}C and under Argon gas environment for CO_2/CH_4 separation at room temperature. Prominent CO_2 permeance increase over CH_4 permeance

further suggest the formation of highly porous membrane with resulted effective molecular sieving.

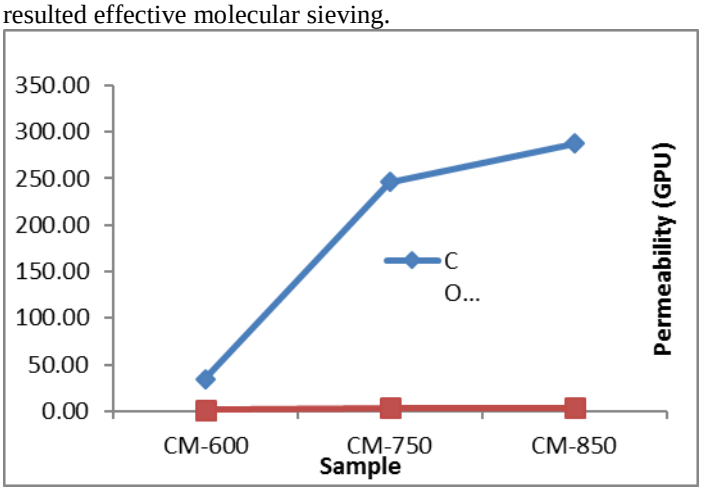

Figure 2: Comparison between CO_2 permeance readings with CH_4 permeance readings

IV. CONCLUSION

The result shows that Matrimid 5218 is a good candidate for carbon membranes preparation. It is indicated that the gas separation properties of Matrimid-based carbon tubular membranes are depends on the carbonization temperature. The results reveal that an excellent CO_2/CH_4 separation of 87.30 was obtained for carbon membranes carbonized at 850°C under Argon gas environment. It is because a high compactness of carbon membrane structure was produced at high temperature and it leads to the increase in selectivity.

V. ACKNOWLWDGMENT

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