

Gas Permeation Properties of the Matrimid based Carbon Tubular Membrane: The Effect of Carbonization temperature

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Abstract— Carbon membranes produced from the carbonization of polymeric materials is a promising candidate for gas separation, as it offers good permeability-selectivity combination exceeding polymeric membranes. Carbon membranes are particularly useful in gas separation, and excellent separation could be achieved even between gases with almost similar molecular size. In this study, tubular supported carbon membrane was prepared using Matrimid 5218 as polymeric precursor. The polymer solution was coated on the surface of tubular support by using dip-coating method. In order to produce a high quality carbon membrane, the effect of carbonization temperature on the gas permeation properties was studied. The polymer tubular membrane was carbonized under Argon atmosphere at different carbonization temperature of 600, 750, and 850 °C. Pure gas permeation tests were performed using CO₂ and N₂ at room temperature with pressure 8 bars. Based on the results, the highest CO₂/ N₂ selectivity of 79.69 was obtained for carbon membrane prepared at 850 °C. High carbonization temperature is necessary to break down the functional group of polymeric precursor into carbon material. An ideal carbon membrane carbonized at optimum temperature would possess high separation properties with high crystalline, density and compactness.

Keywords- Carbonization, polymeric membrane, carbon membrane, Carbon dioxide, Nitrogen, Argon.

I. INTRODUCTION

Progress in membrane gas separation technology has become prominently potential to compete with conventional separation process to be implemented for industrial applications. Emerging concern regarding membrane for gas separations is to develop defect-free with high permeability and selectivity with good mechanical and thermal stability while economically feasible(1). Membrane-based separations processes are becoming increasingly important in various industrial processes, for instance gas separation process. Recently, the membrane gas separation technology has become prominently progressive and can be marked as a competing industrial gas separation technique (2). Membranes processes have also emerged as important media for wide range of industrial applications, namely medical applications

(hemodialysis and drug delivery), gas separation (acid gas removal, air purification, nitrogen enrichment), and water treatment (desalination, reverse osmosis, wastewater treatment). The continuity in development of membrane for gas separation process has been reviewed by Baker (3). Besides, the advantages contributed by membrane gas separation include its simplicity in operation that can be fitted easily onto the power plant without requiring complicated integration, and it does not require any addition of chemical or regenerating an absorbent or adsorbent(4).

Recently, polymeric membranes as Matrimid 5218 are widely used in membrane separation process due to their process ability, and flexibility (5). Over the years, polyimide-based polymeric membranes have shown encouraging performances in both gas permeability and gas pair selectivity. The aromatic polyimide type polymer appears are one of the promising materials to yield polymeric membranes with excellent separation properties. Superior membrane stability and durability, high permeation flux, and selectivity and low production cost are always the most important criteria when developing a membrane for a specific separation (6). However, some limitations like thermal and mechanical stability need to be considered when selecting the existing commercial polymers. It has been reported that the permeability obtained from carbon membranes is much higher than those typically found with polymeric membranes, and this selectivity is achieved without sacrificing productivity (7).

Among various classes of membrane, carbon membranes have been identified as promising candidates for gas separation (8). Carbon membranes are the product from carbonization of polymeric membrane. At elevated process temperature, the breakage of benzene ring and other functional groups within the polymeric precursor can lead to formation of mesopores and/or micropores within the carbonized product. The unique pores characteristic grant the attractive gas separation properties by providing highly permeable and selective membrane. To date, numerous numbers of reports have proven and indicated that carbon membranes can indeed serve as an ideal candidate for gas separation (9-11). For example, carbon membranes have been refined for variation of

industrialized operation involving gas separation performance (12). Moreover, carbon membranes also have attracted significant attention as they can offer great performance without increasing energy and processing cost, as the cooling step can be eliminated(13). Previous researchers stated that the distribution and pore dimensions in a carbon membrane can be deftly accommodated by a simple thermochemical treatment to reach various separation requirements and objectives(14).

Carbon membranes are very brittle and fragile. Without any support, it will not easily operate in the system. The most common substrate used by the previous researchers are α -Al₂O₃ (15), TiO₂-ZrO₂ macroporous tubes(16), and porous graphite(17). When a supporting substrate is used for the development of carbon membrane, the substrate must be chemically and physically stable and possess a diffusion resistance, which is lower than that of the carbon membrane. Tubular substrates are mechanically stronger against compressing pressure than flat substrates. In this study, TiO₂-ZrO₂ tubular support was used as a substrate to overcome the brittleness of the carbon membranes due to high thermal resistance, which is necessary to sustain high carbonization temperature and chemically stable against various solvent.

II. EXPERIMENTAL

A. Materials

Matrimid 5218 was selected as a polymer precursor. It was dried overnight at 80 °C to remove any moisture. N-methyl-2-pyrrolidone (NMP) purchased from Merck (Germany) was used as a solvent. The high performance tubular support purchased from Shanghai Gongtao Ceramics Co., Ltd., China, was made from TiO₂ (4.5-5.5 mm), and coated with ZrO₂ (2-3 nm) on inner surface. The outer diameter of the tubular support was 13mm and the diameter was 11mm inner.

B. Carbon Membrane Preparation

Polymer precursor solution was prepared by dissolving 15 wt % of Matrimid 5218 in NMP for 7 hours with mechanical stirring. The mixture was sonicated to remove all bubbles from the solution. Supported polymer membranes were prepared by dip-coating the tubular ceramic support (8cm in length, 13mm outer radii) into the polymeric solution for 15 minutes. The supported membranes then underwent aging at 80 °C for 24 hours. The membranes were then immersed in methanol for 2 hours before being placed at 100 °C for 24 hours inside an oven to allow slow removal of the solvent. The supported membranes were placed in the centre of the Carbolite horizontal tubular furnace to undergo heat treatment process. Firstly, the membrane was heated up to 300 °C for stabilization purpose. The membrane was maintained at this temperature for 30 min. After that, carbonization process was performed at temperature of 600, 750, and 850 °C. The heating rate of 2 °C /min under Argon gas flow (200ml/min) was applied throughout the process. Finally, the membranes were cooled naturally to room temperature. 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 was characterized into two important parameters which were permeance and selectivity. The carbon tubular membranes were tested in pure gas permeation system. An 8 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 membrane. The membrane was then fitted with rubber O-rings to allow the membrane to be housed in the module without leakages. Pure gas CO₂ and N₂ 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 :

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

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 (GPU), Q_i is the volumetric flow rate of gas i at standard temperature and pressure (cm³ (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 (cm²), n is the number of fibers in the module, D is the outer diameter of the membrane (cm) and l is the effective length of the membrane (cm).

III. RESULTS 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 permeances of the resultant membranes were measured using gas permeation test apparatus at 8 bars and room temperature. Table 1 shows the gas permeation properties as a function of carbonization temperature for CO₂/N₂ separation.

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

Carbon Membrane	Permeance (GPU)		Selectivity (CO ₂ /N ₂)
	CO ₂	N ₂	
CM-600	34.7	1.12	31.00
CM-750	245.82	3.32	74.00
CM-850	287.36	3.61	79.69

In order to break down the functional group of polymeric precursor into carbon material, it is necessary to carry out the carbonization process at high temperature. Generally, the gas permeance would decrease with the increase of final carbonization temperature, due to the selective layer compaction and some of the pores might change into closed pores during the carbonization process (18). However, in this study the gas permeance for both gases (CO₂, N₂) was slightly increased as the carbonization temperature increase from 600 to 850 °C. This might be attributed to better structural packing induced at high temperature which could provide more channel for gas transport even when compaction of selective layer occurred. In addition, significant increase in smaller molecule permeance were more prominent compared to larger molecules, leading to higher gas pair selectivity as the carbonization temperature increased. The permeance and gas pair selectivity increased concurrently, indicating the absence of unselective cracks even at high carbonization temperature. In related study, Tin and Coworkers prepared P84-based carbon membrane to determine the effect of carbonization temperature on gas permeation performance (19). The results showed that the carbon membrane derived from commercially available P84 exhibited the highest separation efficient for gas separation. On the other hand, Rungta's Group (2012) had successfully fabricated carbon membrane from Matrimid and investigated the effect of carbonization temperature (20). The results showed that the pure gas CO₂ permeance was consistently higher than that of N₂.

As can be seen in Table 2, CM-850 showed excellent separation properties compared to CM-750 and CM-600. This indicates that, as the carbonization temperature increased, the size of pores of carbon membranes became smaller. This pattern is in agreement with the fact that carbonized membranes possess a micropore structure that is capable to recognize the different kinetic diameter of gases and increase the selectivity (21). For all gases, there was an increase in the pure gas permeance with increasing carbonization temperature. The increase in permeance could be directly related to the increase in porosity with increasing carbonization temperature(22).

IV. CONCLUSIONS

The results revealed that an excellent CO₂/N₂ separation of 79.69 was obtained for carbon membranes carbonized at 850 °C under Argon gas environment. It was attributed to better structural packing induced at high temperature which could provide more channel for gas transport even when compaction of selective layer occurred. In addition, significant increase in smaller molecule permeance was more prominent compared to larger molecules, leading to higher gas pair selectivity as the carbonization temperature increased. Also, the use of tubular support made the carbon membrane become more chemically and physically stable, plus possessing a diffusion resistance, which was lower than that of the carbon membrane itself.

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