Gas Separation Performance of CMS Membranes Derived from Phenolic Resin

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Abstract – The effect of pyrolysis temperature onto gas permeation performance of carbon molecular sieve (CMS) membranes derived from phenolic resin were presented. The membrane support was prepared first by blending fine particles of graphite with phenolic resin. The solution of phenolic resin diluted in N-methylpyrrolidone (NMP) was coated over the support using dip coating method. The resulting disk was pyrolyzed at temperature of 500-700°C. The performance of CMS membrane prepared was measured by CO₂, N₂ and CH₄ gases permeation as well as permselectivity of CO₂/N₂ and CO₂/CH₄. All samples prepared show molecular sieving behavior with high permselectivity. The average pore size and surface area of CMS membrane prepared at 700°C were found to be 0.35 nm and 623.1 m²/g, respectively. This sample exhibits the highest CO₂ permeance of 10.9x10⁻¹⁰ mol/m².s.Pa with CO₂/N₂ and CO₂/CH₄ permselectivity of 4.65 and 7.44, respectively.

Index Term - Carbon molecular sieve membranes, Permeation, Phenolic resin, Pyrolysis

I. INTRODUCTION
Carbon molecular sieve (CMS) membranes become more important in gas separation due to the grater thermal stability and chemical stability than zeolite membrane [1]. CMS membrane properties are greatly influenced by the polymeric precursor and pyrolysis variables. CMS membrane must exhibit molecular-sieving characteristic, which the pores sizes similar to those of the gas molecules to be separated. For example, CMS membrane with pore size less than 0.5 nm can separate nitrogen (N₂) from oxygen (O₂) and carbon dioxide (CO₂) from methane (CH₄) [2].

One of the methods to prepare CMS membrane is to deposit a suitable layer of organic polymeric precursor on support media, such as porous carbon followed by pyrolysis step. In order to pyrolyze a polymer layer without deforming the deposited layer, the polymer needs to have thermosetting properties. Such polymer does not fuse or melt when heated and thus retain structural shape during pyrolysis [3].

In this work, the phenolic resin was selected on the basis of its good thermosetting properties, high carbon yield and inexpensive polymer. More important, the phenolic resin contains some hexamethylene tetramine, which can lessen the large pores in the top layer of CMS membrane [4]. Furthermore the top layer of CMS membrane undergoes shrinkage at the same rate as the support during pyrolysis, which can avoid crack forming due to the different shrinkage of both parts [5]. In this way, defect-free CMS membrane can be fabricated readily and reproducibly.

II. MATERIALS AND METHODS

A. Materials
The phenolic resin, graphite particles and N-methylpyrrolidone (NMP) were purchased from Sigma Aldrich (M) Sdn. Bhd. Purified CO₂ (99.995%), N₂ (99.95% purity) and CH₄ gases (99.99% purity) were supplied by Air Product (M) Sdn Bhd.

B. Membrane support and casting solution
The carbon support was prepared by blending fine graphite particles with phenolic resin. This blend was pressed at 1200 bar in a static press resulting in disk-shaped supports of 35 mm in diameter and 2.5 mm in thickness. The support was cured in air at 100°C and subsequently pyrolyzed under nitrogen flow at a temperature of 850°C. Then it was polished until a mirror appearance was achieved. For coating solution, the phenolic resin was diluted in NMP to achieve a 35% phenolic resin solution with a viscosity around 30 cP. In order to produce homogeneous solution, overhead mechanical stirred was used at temperature of 85°C for 8 h. A small amount of the solution was deposited over the support using dip coating method. The sample was pyrolyzed to a final temperature of 500, 600 and 700°C (denoted as C500, C600 and C700, respectively) at a rate of 2°C/min for 1 h.

C. CMS membrane characterization and gas permeation
The surface area, total pore volume micropore volume and pore size distribution of the sample were characterized by N₂ adsorption (77K) using Micromeritics ASAP 2020 volumetric adsorption apparatus. The surface area was determined using Branauer-Emmett-Teller (BET) equation. Dubinin-Radushkevich (DR) equation was used to calculate the micropore volume over a range of relative pressure of 1.1x10⁻⁵ to 0.02. The total pore volume (Vₜ) was obtained at a relative pressure of 0.99. Pore size distribution (PSD) was obtained from Horvath-Kawazoe (HK) analysis. Prior to measurement, the samples were degassed at 120°C for 12 h in the degas pot of the adsorption analyser. Scanning electron microscopy
(SEM) was used to characterize the morphology of CMS membrane (JSM-6460 LV, model JEOL). SEM images were examined using an accelerating voltage of 15kV. Transmission electron microscope (TEM) images were obtained with a Philips CM12 TEM with Document Version 3.2 image analysis. This instrument operates up to an accelerating voltage of 120 kV.

Gas permeation measurement was performed using the variable volume-constant pressure rig set up which was developed for laboratory scale. Each sample was treated at temperature of 100°C for 10 min to ensure that all water vapor trapped on the membrane surface was completely vaporized. The system was maintained 2.5 bar at feed section and vacuum at the permeate section. Calibrated soap film flow meter was used to obtain the gas permeance penetrate traverse the membrane. The gas permeance of CMS membrane is defined by (1):

\[ P = S \cdot D \]  

where \( S \) and \( D \) are solubility coefficient and diffusion coefficient, respectively. The permselectivity or ideal selectivity factor \( \alpha \), is defined as:

\[ \alpha = \left( \frac{P_{\text{gas A}}}{P_{\text{gas B}}} \right) \]

III. RESULTS AND DISCUSSION

A. CMS membrane characterization

Table I shows the properties of CMS membranes. As the pyrolysis temperature increased, the surface area, pore volume and percentage of micropore volume increase. In addition the pore diameter becomes narrower. The pore size distribution (PSD) of CMS membranes is shown in Fig. 1. Sample C500 shows wide PSD at approximately 0.41 nm. The curve peak shifts to the left giving narrower PSD with pore size range of 0.35–0.37 nm at higher pyrolysis temperature. In addition, the differential pore volume \( (dW/dr) \) increases from 6.31 to 9.87 ml/g nm. This behavior seems to be related to the modification in micropore size as pyrolysis temperature changes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( S_{\text{BET}} ) (m(^2)/g)</th>
<th>( V_t ) (m(^3)/g)</th>
<th>( V_{\text{mic}} ) (m(^3)/g)</th>
<th>( V_{\text{mic}}/V_t ) (%)</th>
<th>( D_{\text{ave}} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C500</td>
<td>521.8</td>
<td>0.370</td>
<td>0.328</td>
<td>88.6</td>
<td>0.41</td>
</tr>
<tr>
<td>C600</td>
<td>573.4</td>
<td>0.386</td>
<td>0.355</td>
<td>91.9</td>
<td>0.37</td>
</tr>
<tr>
<td>C700</td>
<td>623.1</td>
<td>0.413</td>
<td>0.391</td>
<td>94.7</td>
<td>0.35</td>
</tr>
</tbody>
</table>

The surface morphology of sample C700 is shown in Fig. 2. Sample C700 gave a thinner pyrolytic layer on the first layer above the support of which the thickness was estimated to be less than 1 \( \mu \)m. In addition, fewer cracks with heterogeneous pore surface were observed as shown in Fig. 2 (b). From TEM micrograph shown in Fig. 3, the sample demonstrates a graphite-like structure appeared. The “black” region corresponds to carbon matrix. Carbon matrix was tight and arranged randomly indicate the amorphous characteristic of CMS membrane. Meanwhile the “white” region considered to be the microvoid of CMS membrane. The microvoid creates the ultramicroporosity of CMS membrane which was formed by channelling of evolved gas through phenolic resin matrices during pyrolysis. The pore size was found to be less than 1 nm, which suitable for gas permeation test.

![Fig. 1. Pore size distribution of CMS membranes.](image1)

![Fig. 2. SEM images of C700; (a) cross-sectional view; (b) top view.](image2)
TABLE II
PERMEANCE AND PERMSELECTIVITY OF PYROLYZED CMS MEMBRANES

<table>
<thead>
<tr>
<th>Sample</th>
<th>Permeance, x10^{-10} (mol/s.m^2.Pa)</th>
<th>Permselectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO_2</td>
<td>N_2</td>
</tr>
<tr>
<td>C500</td>
<td>6.61</td>
<td>1.89</td>
</tr>
<tr>
<td>C600</td>
<td>8.35</td>
<td>2.1</td>
</tr>
<tr>
<td>C700</td>
<td>10.94</td>
<td>2.35</td>
</tr>
</tbody>
</table>

All gases permeances were increase with increase in the pyrolysis temperature. Sample C500 possesses the lowest permeance of all gases due to the incomplete pore system [7]. Insufficient energy due to low pyrolysis temperature caused the phenolic resin molecular chains remain exist in the membrane. The resulting membrane might not be a complete carbon membrane [8]. Further pyrolysis at higher temperature induced CMS membrane to perform higher CO_2 permeance due to the well developed microporosity in CMS membrane structure. Meanwhile the N_2 and CH_4 permeation flux were almost constant, thus increased the CO_2/N_2 and CO_2/CH_4 permselectivities.

B. Gas permeation performance

High quality CMS membranes should have high gas permeation and high selectivity. The CMS membrane gases permselectivity and CO_2 permeation at different pyrolysis temperatures are represented in Table II and Fig. 4. The gas permeance was well correlated with the kinetic diameter of the gas molecule instead of molecular weight. CO_2 (kinetic diameter = 0.33nm) possesses higher permeance compared to N_2 (0.364 nm) and CH_4 (0.38 nm).

Sample C700 exhibits remarkable CO_2 permeance of 10.94x10^{-10} mol/m^2.s.Pa with CO_2/N_2 and CO_2/CH_4 permselectivities of 4.65 and 7.44, respectively. At this stage, ultramicropores and micropores were well developed throughout CMS membrane structure. Ultramicropore allow molecular sieving of the penetrating molecular while micropore may allow diffusion of the gas molecules into the CMS membrane [9]. The destruction of cross-links in phenolic resin at high temperature leads clustering of the aromatic units and subsequent rearrangement of stacking graphite planes. Centeno and Fuertes [10] stated that the alignment of graphitic structure, which leads to the narrower of existing micropores occurred at higher temperature. A similar trend was observed by Miura et al. [11], that found the textural development of a pyrolyzed phenolic resin appeared at approximately 500°C and narrowed to the size between 0.33 nm - 0.36 nm at higher temperature.

IV. CONCLUSIONS

CMS membrane was successfully prepared from phenolic resin for CO_2, N_2 and CH_4 permeation test. The CMS membrane prepared at 700°C exhibits CO_2 gas permeance of 10.94x10^{-10} mol/m^2.s.Pa with CO_2/N_2 and CO_2/CH_4 permselectivity of 4.65 and 7.44, respectively. This sample exhibit narrow pore size distribution with high surface area. It was proven in this study that the CMS membranes performance is controlled by pyrolysis temperature. Gas transport through the CMS membrane corresponds to molecular sieving mechanism.

REFERENCES


