P84 Co-Polyimide Based-Tubular Carbon Membrane: Effect of Heating Rates on Helium Separations

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Abstract:
Helium is one of the most valuable gases with unique features and properties as well as widely used in various applications. Helium sources was extracted from natural gas and it is very crucial to develop efficient technology for helium recovery from natural gas sources, in order to overcome the deficit of the helium supply. Up to now, there are various available traditional separation methods for helium recovery, however these methods possessed several disadvantages such as expensive in cost and energy intensive. Recently, gas separation by using membranes have been utilized and showed potential in recovering and purifying helium from natural gas. This method directly separating the helium from the methane through natural gas liquefaction process where in this process the helium is recovered from the nitrogen rejection unit (NRU) exit gas. Due to the potential benefits that can be obtained from this membrane-based separation method, this current study is aiming to provide more comprehensive scientific reports on the effects of preparation parameters on the performance of tubular carbon membranes (TCMs) for helium separation. In this study, the carbonization heating rate was varied from 1 to 7°C/min by controlling the final temperature at 800°C under Argon environment for all polymeric tubular membranes. The permeation performance of the resultant TCMs have been determined by using a single permeation apparatus. It is necessary to fine-tuning the carbonization conditions in order to obtain the desired permeation properties. From the results, it can be concluded that the most optimum heating rate was found to be at 3°C/min with 463.86±3.12 selectivity of He/N2 separation.
Introduction

These past few decades, membrane separation method has appeared as desirable gas separation technology and its fast development could be attributed by its outstanding and unique characteristics including smaller area, higher efficiency, and environmentally friendly as compared to the available conventional separation technologies such as amine adsorption and cryogenic distillation [1]. However, in these past few years, due to the urge by colossal interest in refining various of gas sources especially natural gas, the improvement on the membrane structure has been taken into deep consideration. Through a study conducted by Rungta and co-workers (2017), they have discovered that membranes are conceivable to be utilized in various kinds of medium in order to separate the gas mixtures [2]. Helium is a remarkable noble gas that possesses broad application in enhanced technologies including arc welding, cryogenics, silicon-wafer manufacture, and space rockets [3]. This gas is high in value product because of its lighter than air property, chemical inertness, and ability to achieve cryogenic temperatures near absolute zero.

Anyhow, the limitation of the helium resources on the Earth has became the main concern and up to now, the most accessible and the richest sources of helium could be extracted from natural gas. Due to that, purification of helium from natural gas mixtures has attracted many studies in order the helium can be safely stored and utilized [4, 5]. Amongst available technologies for helium separation, the most stand out technology is the membrane separation due to its simplicity in operation, high efficiency, ease of scale up, environmental friendly, and small footprint [3, 6]. Moreover, membrane is an important material in this technology as it represents a selective barrier for gas molecules. It is believed that an ideal membrane should possessed very thin structure to maximize flux, mechanically sturdy to hinder rupture, and have well-defined pore size to improve the selectivity [7]. Despite of that, the type of the material used as a membrane is another factor that affecting the success of a membrane-based separation process for the purification of helium. Membrane with high selectivity and permeability of helium are required for an efficient separation performance. Membranes with high selectivity but low permeability are useless as these membranes required high capital cost and large surface area. In contra, membranes with high permeability but low selectivity are also become undesirable as it would not achieve the separation with high purity. It is noteworthy to mention that membranes with both high gas selectivity and permeability are required in obtaining membranes with efficient performance. Therefore, many studies have been conducted in
designing and developing of new membrane materials that can efficiently purifying helium from natural gas.

In the past few years, carbon membranes have shown their credibility in the gas separation processes. The utilization of membrane in separation technology have gained major interests due to their outstanding features including good stability, environment capability, flexibility, efficiency, high selectivity and permeability. Therefore, the preparation of carbon membranes is not a simple step as the great quality membranes will guarantee good quality carbon membranes. Due to that, several ideal specifications need to be considered. Accordingly, it is necessary to fabricate defect-free carbon membranes to lessen the issues that might happened during the fabrication process [8]. Thus, this current work aiming to investigate the preparation and characterization of TCMs derived-P84 co-polyimide. This precursor was selected due to the fact of its feasibility such as low in cost, availability, and easy to process. The properties of the membrane also can be influenced by process parameter such as carbonization heating rate in the range of 1-13°C [9, 10]. Salleh and co-workers have found that the most effective heating rate to be in the range of 1-5°C in the preparation of the polymer-based carbon membrane. The PEI/PVP-based CHFMs prepared at low heating rate showed decreases in gas permeance for all examined gases such as N₂, CH₄ and CO₂, and increases of CO₂/CH₄ and CO₂/N₂ selectivity. From the experimental results, the best heating rate in the preparation of PEI/PVP-derived CHFMs for CO₂/CH₄ and CO₂/N₂ separation is 3°C/min [9].

**Experimental Section**

**Materials**

The main precursor of P84 co-polyimide was purchased from Sigma Aldrich, the solvent of N-methyl-2-pyrrolidone (NMP) was procured from Merck (Germany) and all chemicals were directly used without any further purification. The nanocrystalline cellulose (NCC) used in this study was self-synthesized based on the experimental procedures as reported in previous research conducted by previous study [11]. TiO₂- supported tubular ceramic membranes with average pore size of 0.2 μm, 8cm in length and 3mm of thickness were purchased from Shanghai Gongtao Ceramics Co. Ltd.
Carbon Membrane Preparation

P84 co-polyimide (15% relative to total wt.) and NMP have been used to prepare the polymer solution and the solution was stirred at 80°C. Subsequently, NCC (7 wt%) was added gradually into the solution and was continuously stirred to obtain homogenous solution. Finally, in order to remove the air bubbles produced during the stirring process, all the polymer solutions were sonicated for a few hours. The ceramic tubes were immersed in the dope solution for 45 minutes in order to produce tubular membranes. Thereafter, the resultant membranes were soaked in methanol for 2 hours and were placed inside the oven for 24 hours at 100°C to remove the solvent. Then, the supported polymeric membrane was heated at 800°C in tubular furnace under 200 ml/min of Argon gas flow with four different heating rates which is 1, 3, 5, and 7°C/min. All the procedures were conducted based on our preceding studies [12]. The characterization of a flat sheet carbon membrane (without substrate) was also used the same procedure.

Pure Gas Permeation Measurements

The carbon tubular membranes were tested by using the gas permeation system as detailed in our previous study [11, 12]. The resultant TCMs was put inside the tubular stainless-steel module of 14 cm in length and an O-ring was fitted in order to prevent any leakage on the module. Subsequently, 8 bars of trans-membrane pressure was applied and pure helium (He) (0.380 nm) and nitrogen (N2) (0.364 nm) gases were fed separately into the module. The calculation of the permeance, P/I (GPU) and the selectivity, α of the membranes were calculated by using the equation as described in previous study [11].

Results and Discussion

Gas Permeation Measurements

In literature, the rate of evolution of the volatile compounds can be determined by carbonization heating rate as it is believed could affect the microstructure of the carbon membranes [9]. The variation in carbonization heating rates have showed different gas separation results on the PI/NCC carbon membranes as represented in Table 1. The data obtained showed an average value from at least three different PI/NCC carbon membranes with small error analysis of ±10% for both selectivity and permeance value.
Table 1: Gas separation results for PI/NCC carbon membranes carbonized at different heating rate

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carbon membrane</th>
<th>Permeance (GPU)</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>N₂</td>
<td>He</td>
</tr>
<tr>
<td>PI/NCC 1°C/min</td>
<td></td>
<td>3.11±1.43</td>
<td>1271.55±3.21</td>
</tr>
<tr>
<td>PI/NCC 3°C/min</td>
<td></td>
<td>3.22±3.21</td>
<td>1493.62±1.88</td>
</tr>
<tr>
<td>PI/NCC 5°C/min</td>
<td></td>
<td>3.08±2.87</td>
<td>1057.29±3.14</td>
</tr>
<tr>
<td>PI/NCC 7°C/min</td>
<td></td>
<td>3.01±1.44</td>
<td>1018.32±2.33</td>
</tr>
</tbody>
</table>

Previously, numerous studies have reported that increases in carbonization heating rate can affect the pore size distribution by producing pores with smaller size and this is believed to cause another limitation in the degree of gases rotation freedom [13, 14]. According to Centeno et al. (2004), they found that random smaller pore size distribution polymer-based carbon membranes can be affected by the higher carbonization heating rate [10]. This is might due to the loss of most of the volatile compounds during the increases in the heating rate and subsequently, the partial carbon vapor deposition occurred in the pores that were formed previously. Moreover, it is believed any further increment to the heating rate might cause pinholes creation and microscopic crack on the membrane surface. During the heat treatment, the membrane are expected to deform.

The implement of low heating rate to the carbon membrane have resulting reduction in the values of gas permeance. In comparison to the other tested membranes, these membranes possessed lower separation value, however the value obtained is acceptable as its value is still comparable with previous hydrogen separation studies [4]. Furthermore, the highest He/N₂ separation was obtained by carbon membrane carbonized at heating rate of 3°C/min as compared to 5 and 9°C/min. This was caused by long contact of membrane with the inert gas that consequently, narrow down the pore size distribution. The increment of carbonization heating rate from 5 to 7°C/min will decreasing the selectivity of the CO₂/N₂. Sazali and co-workers (2017) have also stated that the pore size distribution was also attributed by selection.
of types of the polymer precursors such as the chemical composition of the polymer precursor [12].

Conclusions
Carbonization parameters such as rate of heating have affected the performance of the PI/NCC carbon membrane. In this study, the properties and performance of tubular carbon membranes (TCMs) that were fabricated by blending of PI/NCC has been studied. It was found that stabilization conditions can affect the morphologies of the membrane and also their separation capabilities. The results suggest that the membrane selectivity can be improved by applying optimum heating rate of 3°C/min during carbonization process, however in this case, it will reduce the permeability of the membrane. In He/N₂ separation, it was found that carbon membrane prepared at 3 °C/min exhibited the selectivity of 463.86±3.12 From this study, it can be concluded that PI/NCC carbon membrane have potential characteristics in various gas separation applications including H₂ recovery, O₂ enrichment and also CO₂ capture.

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References


