



Disk supported carbon membrane via spray coating method: Effect of carbonization temperature and atmosphere



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ABSTRACT

This paper presents a method for the separation of CO₂/CH₄ and CO₂/N₂ by the use of disk supported carbon membranes derived from polyimide. The supported polyimide membranes were carbonized under controlled gas flow (three different atmospheres: N₂, Ar and He) at different carbonization temperatures from 600 to 900 °C. The carbon membrane fabricated at various carbonization temperatures and atmospheres, showed improvement in gas permeation performance. The gas permeability increased with the increase of carbonization temperature due to densification of the micropores in the carbon membranes, leading to enhanced gas permselectivity. All carbon membrane samples carbonized under three different atmospheres at 800 °C surpassed the polymeric CO₂/CH₄ upper bound. Pure-gas permselectivity reached 98 for the carbon membrane carbonized at 800 °C under He gas flow, with CO₂ permeability of about 120 Barrer, becoming the most selective carbon membrane for CO₂/CH₄ separation.

1. Introduction

Natural gas commonly consists of methane gases with several impurities such as carbon dioxide, hydrogen sulphide, water, heavy hydrocarbons, and inert gases. Among these impurities, the most abundant with almost above 50% content is carbon dioxide [1]. United States utilizes around 22 trillion standard cubic feet of natural gas per year, while global usage reaches almost 95 trillion standard cubic feet per year. Recently, membrane technology has been applied in natural gas separation as it simplifies the process while reduces energy and costs [2]. These phenomena are significant with membrane advance technology and energy efficiency potential. Membranes have gained increasing attention for gas separation as they are highly potential in several applications including hydrogen separation or recovery, carbon separation or capture, as well natural gas upgrading. Use of membranes is also favorable for mixing gases in industrial scale due to their high efficiency with simple operation and low operating cost [3]. Membrane is also highly potential alternative for gas separation as it is more economical, as well as having low environmental impact. For gas separation, pre-treatment processes for polymeric precursor are needed to predict the microstructure of derived carbon membrane beforehand. The processes are also vital to ensure proper permeation properties and prevent any problems related to pore structural rearrangement for gas separation.

Carbon membranes prepared from several materials have been widely adopted by numerous researchers since past decades [4]. Carbon membrane production is inclusive of removal of all non-carbon compounds, precursor thermal decomposition, and pore structure rearrangement with solely or carbon atoms. Carbon membrane is generally prepared by heat treatment process of available precursor, normally involving several modifications in order to enhance gas separation performance. Heat treatment process, also known as carbonization process, takes into account several conditions such as final and stabilization temperature, heating rate, thermal soak time, as well as carbonization environment; depending on the membranes properties required. During carbonization process, precursor membrane will undergo pre-treatment to rearrange its chain packing, as well as chain segmental mobility of the polymeric precursor. The main objective of pre-treatment is to stabilize or rearrange the polymeric precursor structure during or before undergoing high temperature carbonization. Some studies reported that pre-treatment will enhance the uniformity of pore formation [5]. In some cases, carbon membrane with high selective and promising separation performance can be achieved by specific pre-treatment [5,6]. Carbon membrane pre-treatment may either be by oxidation, physical or chemical treatments. The pore dimensions and microstructure distribution also depend on the carbonization conditions. This is because carbon matrix population is formed by the chemical composition, depending on the thermal history of

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carbon precursor itself.

Fu et al. [7] formed 6FDA/DETDA:DABA (3:2) CMS dense films from carbonization of precursor films under UHP Argon at three final carbonization temperatures of 550 °C, 675 °C, and 800 °C. As per result, both gas permeability and permselectivity of resultant membranes were significantly higher than those of the precursor membranes, and surpassed the polymeric upper bound. As the carbonization temperature was increased, the gas permeability dropped dramatically, while the corresponding permselectivity increased. Briceño et al. [8] reported that the carbon membrane carbonized at 550 °C indicated Knudsen diffusion mechanism, while carbon membrane carbonized at 650 °C showed molecular sieving mechanism behaviour based on the decline of gas permeability, in line with the analyzed kinetic diameter of gas molecules. This transport mechanism difference proved that the final carbonization temperature will affect the pore size distribution (meso and micropores) in carbon membrane fabrication.

Barsema et al. [9] reported thermal decomposition of Matrimid PI precursor below 425 °C, in which the precursor had undergone annealing process (underwent physical aging) and formed weak charge transfer complexes (CTC). Unfortunately, carbonization up to 475 °C had increased the gas permeability due to thermal decomposition, as well as polymer transition to carbon form. Meanwhile, carbonization process below T_g would lead to polymer densification; in contrary with carbonization process above T_g which would form dense membrane, rearrange chain packing, reduce gas permeability, as well as high composition of CTCs [9].

Suda and Haraya reviewed the effect of carbonization atmosphere on carbon membrane derived from Kapton co-polyimide at 1000 °C [10]. The results demonstrated that the use of Ar gas or vacuum environment only gave minor difference to the resultant carbon membrane. Su and Lua [11] reported that carbonization atmosphere played an important role in carbon membrane performance. They utilized common atmosphere consisting of vacuum, inert gases (helium (He), argon (Ar) and nitrogen (N₂)) and oxidative atmosphere (O₂/N₂ or CO₂). As stated in [12] that carbon membrane prepared under vacuum atmosphere obtained higher result in permselectivity of O₂/N₂ and H₂/N₂ compared to membrane prepared under inert atmosphere. This was due to the chemical reaction involved during the carbonization process. Meanwhile, Kiyono et al. [13] stated that the essential part in fabricating the carbon membrane is by controlling the amount of oxygen present during the carbonization process. Oxygen will induce the formation of pore size and pore distribution of the carbon membrane. However, there are also studies which claimed that the carbonization atmosphere effect can be negligible [14]. Thus, this study was conducted with the objectives to investigate the effect of the carbonization temperature and atmosphere, towards the morphological structure, thermal analysis and gas separation performance of carbon membrane.

2. Experimental

2.1. Materials

Commercial co-polyimide BTDA-TDI/MDI (P84) powder purchased from Sigma Aldrich (CAS#: 58,698-66-1) was used as polymer precursor. N-Methyl-2-pyrrolidone (NMP) procured from Merck (Germany) was chosen as the solvent. Commercial supporting material of porous alumina disk with diameter of 47.0 mm, thickness of 1.0 ± 0.05 mm, and mean pore size of 0.14 μm was bought from Shanghai Gongtao Ceramics Co., Ltd.

2.2. Carbon membrane preparation

P84 polyimide powder was dried in oven at 60 °C for one day to remove water vapour. Polymeric solution was prepared by mixing 12 wt% of P84 in NMP. The polymeric solution was then stirred and heated at 70 °C until it formed a homogenous solution. It was later

sonicated for 4 h to eliminate bubbles formed during stirring process. Polymeric supported membrane was then prepared by coating the prepared polymeric solution onto the top surface of the supporting material by spray coating technique. The polymeric solution was sprayed directly onto the supporting material using air spray, at distance of 20 cm between spray nozzle and the alumina supporting material, and at 1 bar pressure at room temperature. Detailed explanation on the spray coating method can be found in the previous work [15]. The prepared polymeric supported membrane was later dried in oven at 60 °C overnight. The supported carbon membrane was then put into a ceramic tube set of a three-zone Carbolite horizontal furnace. The supported precursor was placed at the central zone of the furnace, with uniform temperature profile. The carbonization of the supported precursor was conducted in a two-stage procedure. Firstly, the temperature was raised from ambient to 350 °C at a rate of 3 °C/min, and then maintained at 350 °C for 30 min. Secondly, the temperature was increased from 350 °C to four different carbonization temperatures of 600, 700, 800 and 900 °C at the same heating rate and then maintained for 30 min. Three different gas atmospheres (N₂, Ar and He) were applied throughout the experiments at 800 °C. After completing the heating cycle, the furnace was let to cool down to room temperature. The details of experimental procedure can be found in previous study [16]. Three different samples were tested, and three readings were taken for each of the samples. The result of present for the gas permeability and permselectivity are the average value of three samples. To avoid aging effects induced by oxygen chemisorption, the supported carbon membranes were kept in a desiccator and characterized immediately. The notations of supported carbon membranes were given in the form of CM-carbonization temperature (CM-600, CM-700, CM-800, CM-900) and CM-carbonization atmosphere (CM-N₂, CM-Ar, CM-He).

2.3. Membrane characterization

The functional groups present in the sample were evaluated using Fourier transform infrared spectroscopy (FTIR), using single reflection diamond for Spectrum Two spectrometer (PerkinElmer, L1600107). Elemental analysis was carried out using Vario Micro Cube elemental analyser to determine the percentage of the carbon (C), oxygen (O), nitrogen (N) and hydrogen (H) in the membrane sample. Raman spectroscopy analysis was conducted using Jasco RMP-510 Versatile Laser Raman Spectrometer. X'Pert PRO X-ray diffractometer (XRD) from PANalytical with 2θ diffraction angle of 10–90° was used to conduct Cu Kα radiation with 1.54 Å wavelength. Bragg's Law ($n\lambda = 2d \sin \theta$) was adopted to determine the inter planar distance (*d*-spacing) between the individual layers of the carbon. Nitrogen (N₂) adsorption (BET) method was used to measure the surface area and pore volume of the carbon membrane by utilizing Micromeritics 3 Flex Surface Characterization Analyzer. The value for BET was determined based on the Isotherm Linear plot. The surface, cross sectional morphologies and EDXS mapping of the carbon membrane were recorded by using scanning electron microscopy (SEM) model OL JSM-5610LV. The prepared samples had been coated with gold by sputter coating, under vacuum to create neutral charge during SEM characterization.

2.4. Gas permeation study

Pure gas permeation properties were manipulated in this study to obtain the most ideal separation performance of the membrane materials. CO₂ (3.30 Å), N₂ (3.64 Å) and CH₄ (3.80 Å) gases were utilized for gas permeation measurement. The gas permeation properties of the prepared membrane were tested at room temperature, with feed pressure of 4 bar using bubble soap flow meter. The gases had been tested following the sequence of N₂ > CH₄ > CO₂. Although CO₂ had the smallest kinetic diameter among the gases, it was noted as the last gas to be tested, because its acidic characteristic would change the morphological structure of the membrane hence, thus a high tendency for a

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