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Matrimid-based carbon tubular membrane: Effect of carbonization environment

N. Sazali [a,b], W.N.W. Salleh [a,b,*], N.A.H.M. Nordin [a,b], A.F. Ismail [a,b]

[a] Advance Membrane Technology Research Centre (AMTEC), Universiti Teknologi Malaysia, 81310 Skudai, Johor Darul Takzim, Malaysia
[b] Faculty of Petroleum and Renewable Energy Engineering (FPREE), Universiti Teknologi Malaysia, 81310 Skudai, Johor Darul Takzim, Malaysia

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ABSTRACT

Among gas separation materials, carbon membrane exhibits the most interesting performance in terms of selectivity, stability, and gas permeance. By controlling and optimizing carbonization environment, excellent gas separation performances can be achieved. In this study, tubular supported carbon membrane was prepared using Matrimid as polymeric precursor. In order to produce high performance carbon membrane, the effect of carbonization conditions on the gas permeation properties was investigated. The polymer solution was coated on the surface of the tubular support by using dip-coating method. Carbon membranes were fabricated by heat treatment process under controlled carbonization environments; Ar or N_2. Pure gas permeation tests were performed using CO_2, CH_4, and N_2 at room temperature with pressure 8 bar. Based on the results, the highest CO_2/CH_4 and selectivity of 87.34 and CO_2/N_2 selectivity of 79.60 were obtained by carbon membrane carbonized under Ar gas. Despite the higher carbonization temperature, the carbonization under Ar created more permeable pores as compared to N_2 environment.

Introduction

Nowadays, membranes processes are very important in the industry; for example in medical applications, separation of petrochemicals, and water and waste water treatment. Conventional separation methods used for purification of chemical products, extraction, crystallization, and distillation are energy and cost intensive [1]. Over 50% of the energy costs in the chemical industry are used for the separation of gaseous and liquid mixtures. The costs for difficult separations can be reduced significantly with these membrane technologies [2,3]. It is well known that the membrane performance appears to be a trade-off between selectivity and permeability, for example a highly selective membrane tends to have a low permeability [4]. When permeability is higher, the cost of the system can be lowered and the membrane needed is also small. In order to surpass Robeson's upper bound, some methods can be applied to suitably prepare the membranes. Previous study mentioned that membranes which have the potential to exceed such upper bound are inorganic membranes [5].

In recent years, special attention has been concentrated on the relationship between the membrane polymer structure and gas separation performances [6]. Separation using polymeric membrane produces high performance separation method and provides lower operating cost compared to other separation techniques [7]. It is widely used for wastewater treatment, gas separation, seawater desalination, distillation, and dialysis [8]. Polymeric membrane is suitable to replace the conventional separation method due to modest energy and modular equipment requirement. Although polymeric membrane based gas separations offer low energy requirement and low capital cost, Robeson trade-off limit between permeability and selectivity is the main obstacle that hinders the polymeric membrane process application [9]. The limitations suffered by polymeric membranes have encouraged researchers to develop new class of membrane. Yet, in harsh environment, these membranes are not suitable to be used, for instance, those prone towards erosion besides high temperatures. Among various classes of membrane, carbon membrane produced from carbonization of polymeric precursor has superior gas separation properties [10].

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[*] Corresponding author at: Faculty of Petroleum and Renewable Energy Engineering (FPREE), Universiti Teknologi Malaysia, 81310 Skudai, Johor Darul Takzim, Malaysia. Tel.: +60 75535388; fax: +60 75535625.
E-mail address: hayati@petroleum.utm.my (W.N.W. Salleh).

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Carbon membrane separation development has become a great tool, and has undergone a rapid improvement since the past few years [11]. Because of their unique characteristics, carbon membranes are used in place of polymer membranes; owing to their high thermal and chemical resistance, long life, higher pore volume, and the simultaneous diffusion and chemical reaction [12]. It has been reported that the permeability obtained from carbon membranes is higher than those typically found in polymeric membranes, and these selectivity is achieved without sacrificing their productivity [13]. The carbonization environments are crucial to provide ideal carbonization conditions for Matrimid-based carbon membrane fabrication. Hence, the experiment was carried out by carbonizing Matrimid-based polymeric membrane under either N_2 or Ar atmosphere. The results support the potentiality of this simple and relatively fast procedure, which offers new ways of designing and directly characterizing supported carbon membranes for the gas separation.

Matrimid 5218 carbonized under vacuum was reported to produce less permeable but more selective carbon membranes compared to an inert gas carbonization system [14]. The carbonization using Argon gas produce better selectivity compared with other inert gas [15]. However, their potential use is often limited by the inability to economically manufacture large or complex-shaped components displaying reliable performance.

Furthermore, since carbon membrane is brittle, it requires a strong support or substrate to sustain its structure. When a supporting substrate is used for 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 [16]. While majority of the reported carbon membrane used flat substrate, tubular support hardly draws similar attraction even though it is mechanically stronger against a compressing pressure and higher membrane area per unit module volume. In this study, the carbon membrane fabrication was different to others study due to the supported used made from TiO_2 (4.5–5.5 mm) with a coating of ZrO_2 (2–3 nm) on the inner surface which can stand high temperature till 1200 °C. With that, it is important to focus the factors that make carbon membranes very attractive and useful as separation tools [17]. Since the development of the tubular supported carbon membrane is still in research stage, it is important to identify the most ideal carbonization environment that would result in high performance of carbon tubular membrane. Hence, this study aims to develop tubular supported carbon membrane for CO_2/CH_4 and CO_2/N_2 separations using different carbonization environments, which are Argon (Ar) and Nitrogen (N_2) atmosphere.

Experimental

Materials

Matrimid 5218 was purchased from Merck while N-methyl-2-pyrrolidone (NMP) was purchased from Sigma–Aldrich. In the fabrication of carbon tubular membrane, tubular support with 8 cm in length, 1.3 cm in diameter and 0.3 cm in thickness was used. The tubular support was purchased from Shanghai Gongtao Ceramics Co., Ltd with a nominal cut-off of 1 kDa (TAMI). The support are made from TiO_2 (4.5–5.5 mm) with a coating of ZrO_2 (2–3 nm) on the inner surface. The porosity of the support was 40–50% with an average pore size of 0.2 μm.

Carbon membrane preparation

In order to eliminate water vapour or moisture from the polymer and equipments, they were dried inside the oven for one day before the dope solution preparation. Polymer precursor solution was prepared by dissolving 15 wt%. of Matrimid with NMP for 7 h with mechanical stirring. The mixture was sonicated to remove all bubbles from the solution. Supported polymeric membranes were prepared by dip-coating the tubular support into the polymeric solution for 15 min. During the dip-coating process, the substrate was slowly dipped into and withdrawn from a tank containing the solution, with a uniform velocity, in order to obtain a uniform coating. The dip-coating cycle was repeated for three times to eliminate pinholes presences on the prepared carbon membrane.

The carbonization profile used in this study is adapted from the studies by Salleh and groups [18]. The supported polymeric membranes were undergone ageing at 80 °C for 24 h. The membranes were then immersed in methanol for 2 h before being placed at 100 °C for 24 h inside oven to allow slow removal of the solvent. Subsequently, the supported polymeric membranes were placed in the centre of the Carbolite (Model CTF 12/65/550) wire wound tube furnace to undergo heat treatment process. The length of the furnace tube is approximately 75 cm (heating zone 60 cm) and the diameter is 12 cm. The membranes were subjected to stabilization step at 300 °C at a heating rate of 2 °C/min. During this step, the membranes were held for 30 min at 300 °C. After that, the temperature was increased to the final carbonization temperature of 850 °C at a heating rate of 2 °C/min. During heat treatment process, the atmosphere in the furnace is controlled by flowing the gas using mass flow controller. The types of gas flow environments used throughout the heat treatment process were Ar and N_2 atmosphere with the flow rate of 200 ml/min. Finally, the membranes were cooled down naturally to room temperature. The detailed heat treatment profile used in this study is shown in Fig. 1.

Membrane characterization

The analysis on the existence of the functional group in the prepared membranes was analyzed using a Universal ATR (UATR, Single Reflection Diamond for the Spectrum Two) (PerkinElmer, L1600107). The cross section of the prepared carbon membrane was observed using Scanning Electron Microscopy (SEM).

Gas permeation measurement

A simple bubble flow metre was used to obtain the permeation properties of the prepared membranes. The apparatus used for this measurement can be found elsewhere [18,19]. The performance of

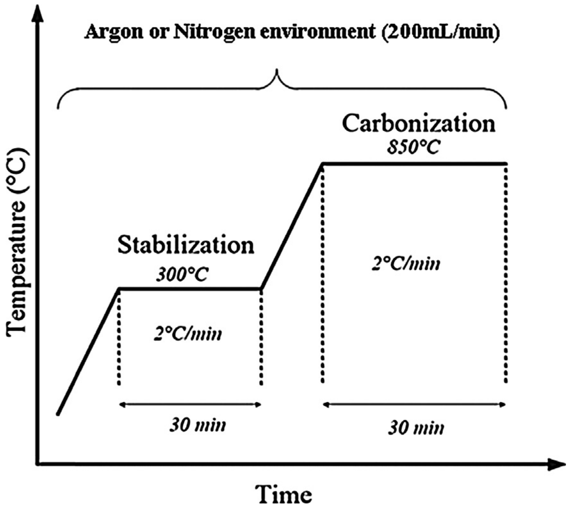

Fig. 1. Heat treatment profile.