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RESEARCH ARTICLE

The performance of CO_2/N_2 separation on P84/NCC-based tubular carbon membrane under different carbonization conditions

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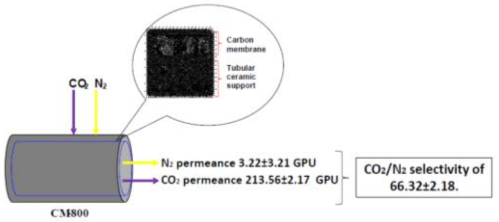
Graphical abstract



Abstract

In this study, the influence of carbonization environment on the performance of Tubular Carbon Membrane (TCMs) was explored. P84 co-polyimide/Nanocrystalline cellulose-based TCMs were synthesized by dip-coating technique. The permeation properties of TCMs were determined by employing pure gases of CO_2 and N_2. Heat treatment processes were carried out under the different environments (Argon, Nitrogen, and Helium) with the flow rate of 200 ml/min to boost the membrane's performance. The carbonization process was performed at a consistent carbonization temperature of 800ºC under a heating rate of 3ºC/min. Carbonization under Argon environment was found to be the best condition for PI/NCC-based TCMs preparation with the permeance of 3.22±3.21and 213.56±2.17 GPU for N_2, and CO_2 gases, respectively. This membrane exhibited the uppermost CO_2/N_2 selectivity of 66.32±2.18. TCMs prepared under Ar environment experienced less weight loss while showing highest CO_2/N_2 selectivity as compared to those prepared under He and N_2 environments.

***Keywords*:** Carbon membrane, carbonization environment, argon, tubular carbon membrane, nanocrystalline cellulose.

INTRODUCTION

In recent times, the widely held carbon membrane studies have been focusing on managing the incorporation of new carbon membrane materials by utilizing new polymeric antecedent materials, new thermal treatment systems and adjusting existing antecedents and carbon layers (Sreedhar *et al*., 2017). Unfortunately, researches on the impacts of carbonization condition particularly in the blending of carbon membrane are yet constrained. The adequacy of carbon membrane separation is relied upon the stream rate cleanse of inert gases, for example, argon, nitrogen, and helium amid carbonization process. This proclamation is bolstered by the outcomes attained in which the carbon layers delivered under 200 cm^3(STP)/min appeared more than 700 times higher flux when contrasting with tests created under lower inactive stream rate of 20 cm^3(STP)/min. Moreover, the inert gas stream contains prevalent warmth exchange that may quicken the carbonization procedure, resulting in the more open permeable structure in comparison to a vacuum condition (Song *et al*., 2008). Unfortunately, the nebulous membranes will begin to shrivel because of further response at an elevated temperature (Sun *et al*., 2016). To analyse the membrane separation for O_2, N_2, H_2, CH_4, and CO_2, these gas atoms should be tested in accordance with their sub-atomic sieving qualities. Likewise, the impacts of carbonization condition were studied in order to deliver high permeation separation by utilizing tubular carbon membrane. This research work was focused on PI/NCC carbon membrane with the control of carbonization condition. Given past examination, the improvement of carbon membrane-based gas detachment has generally been explored, contrasting with that permeation by polymeric layers (Sazali *et al*., 2015a).

Carbon membranes can offer the best platform for the improvement of new layer advancements as a result of their dependable qualities and sub-atomic sieving abilities. The most remarkable focal points of carbon membrane have been surveyed by Ismail and Li in contrast with those of polymeric layers (Ismail and Li, 2008). The prior studies reported that the polymer solutions containing γ-AlO(OH) and $AgNO_3$ is layered on α-Al_2O_3 tubes has been carbonized in a single step of dipping-drying-carbonization at 550°C (Teixeira *et al*., 2011). Meanwhile, Hosseini also reported the highest gas pair selectivity for O_2/N_2, CO_2/CH_4 and CO_2/N_2 can be obtained from PBI–Kapton carbonized at 800°C at 10−7 Torr. Thus, it is crucial to highlight the factors that rendered the carbon membranes to be very attractive and useful as separation tools (Hosseini *et al*., 2014). In addition, the commonly used commercial polymer for fabrication of carbon membrane is polyimide (Briceño *et al*., 2012). Briceno and co-workers have successfully carbonized Matrimid up to 800°C, ensuing in carbon membrane that comprised of ultra-micropores (<7 Å) and larger micropores. Commonly, P84 co-polyimide-based carbon membranes are found to have subdued permeability with selectivity improvement in the process of gas separation of CO_2/CH_4 and CO_2/N_2 (Tin *et a*l., 2004; Grosso *et al*., 2014).

As reported by the previous study, accelerated heat and mass transfer due to the inert gas involvement during the heat treatment process is thought to produce a more permeable and a less selective membrane structure (Geizler *et al.,* 1997). The permeate flux through the carbon membranes carbonized at 823 K under argon is helium or carbon dioxide that decreased by at least 2 orders of magnitude when the purge gas flow rate is increased from 20 to 200 cm^3/min, but the selectivity is not affected. Su and Lua (2007) prepared hollow fibre CMSMs from 6FDA/BPDA-DAM and Matrimid® 5218 polyimide for high pressure CO_2/CH_4 separation. The carbonization of Matrimid® polyimide at 823 K under helium instead of a vacuum resulted in a doubling of the CO_2 permeance, along with a loss of about 65% in CO_2/CH_4 selectivity. Hayashi *et al*., (1997) prepared carbon membranes from BPDA-pp'ODA polyimide by coating it on a porous alumina tube. The membranes carbonized at 973 K under nitrogen have micropore volumes of 0.25, 0.30, 0.19 and 0.14 cm^3/g while those membranes carbonized at 973 K under argon have micropore volumes of 0.36, 0.30, 0.19 and 0.14 cm^3/g, using CO_2, C_2H_6, n-C_4H_{10}, and i-C_4H_{10} adsorbates, respectively, in both cases. Centeno *et al.,* (2004) prepared CMSMs using phenolic resin as the precursor and porous ceramic tube as the support. The coated phenolic resin membranes are carbonised under both vacuum and nitrogen at 973 K with a heating rate of 1 K/min and a soak time of 1 h.

Carbonization environment is crucial process parameter need to be considered to fine tune the final properties of the carbon membrane. Therefore, in this study, attempts were made to investigate the effect of gas environments during the carbonization process on the physiochemical properties and gas permeation performance of the prepared coated membrane. By changing the gas environment conditions, the production of a higher order degree performance of carbon membrane can be achieved. In addition, a significant acceleration of the degradation reaction on carbon membranes can be obtained which leads to the formation of smaller pore size (Song *et al.*, 2010). Carbon membranes that are carbonized in inert gasses showed superior gas separation performance with more open porous structure compared with those membranes carbonized under vacuum environment. The ones under vacuum environment posses membranes with smaller pores, thus affecting the gas permeation and gas separation performance in general. There are different carbonization environments that can be applied during carbonization process, either under inert environment (He, N_2 and Ar), oxidative environment (CO_2) or vacuum state. Besides that, chemical damage and undesired burn off of the polymer membrane precursor during carbonization can be avoided by controlling the carbonization environment (Salleh *et al*., 2011).

EXPERIMENTAL

Materials and methods

P84 co-polyimide was acquired from Sigma Aldrich as the principal precursor while the solvent used was N-methyl-2-pyrrolidone (NMP) purchased from Merck (Germany). All chemicals were used without further purification. Nanocrystalline cellulose (NCC) was synthesized in-house, in accordance with methodologies as reported in the precede studies by (Sazali *et al*., 2018). Porous tubular ceramic support (TiO_2) with 8 cm in length, 3 mm in thickness and average pore size of 0.2µm (porosity of 40-50%) was purchased from Shanghai Gongtao Ceramics Co., Ltd and used as supplied.

Carbon membrane preparation

Polymer solution comprising 15% of P-84 (relative to the total wt.) and NMP was prepared and stirred under a constant stirring condition at 80 °C. About 7 wt% of NCC was added in stages into the solution and was constantly stirred to obtain a homogenous solution. Finally, all of the polymer solutions were sonicated for several hours to remove bubbles throughout the stirring process. The tubular support was then dip-coated into the polymer solution for 45 minutes. This method was used to ensure the formation of a thin top layer of the carbon membrane. Subsequently, the consequential membranes were immersed in methanol for 2 hours and then were placed inside an oven at 100 °C for 24 hours to completely remove the solvent. The TCMs were prepared through carbonization of the supported polymeric membrane. The supported polymeric membrane was heated at 800 °C under 3 different carbonization environments (Nitrogen, Argon, and Helium) with a gas flow rate of 200 ml/min in Carbolite horizontal tubular furnace at 3°C/min heating rate. The experimental techniques were performed according to our previous studies (Sazali *et al.,* 2017). An equavalent procedure was also employed to characterize the flat sheet carbon membrane (without substrate). The heating cycle was regulated by Eurotherm 2500 °C temperature control systems.

Pure gas permeation measurements

As explained in our prior studies, the gas permeation system was utilized to test the carbon tubular membranes (Sazali *et al.,* 2015a; Sazali *et al.,* 2015b). In the study, a 14 cm tubular stainless-steel module was utilized and the carbon tubular membrane was assembled into the module. The membrane was fitted with O-rings to prevent exudation in the module. 8 bars of trans-membrane pressure was employed while pure nitrogen (N_2) gas (0.364 nm) and carbon dioxide (CO_2) (0.330 nm) were introduced one at a time into the module. The permeance was calculated according to the equation denoted in our previous study (Sazali *et al*., 2017), at which P/I (GPU) and selectivity, α of the membranes were measured.

RESULTS AND DISCUSSION

Morphological structure analysis

The scanning electron microscopes (SEM, JEOL JSM-5610LV) was used to observe the cross-section morphology of polymeric and carbon-based PI/NCC membranes prepared under different carbonization environments. Figure 1 shows the cross-section microphotographs of carbon membranes prepared at various carbonization environments (He, Ar, and N_2). It can be clearly seen that all carbon membranes have a dense structure. Micrograph showed in Figure 1(a) indicated that polymeric membranes possessed lateral growth of the finger-like structures (Rhim *et al.,* 2010).

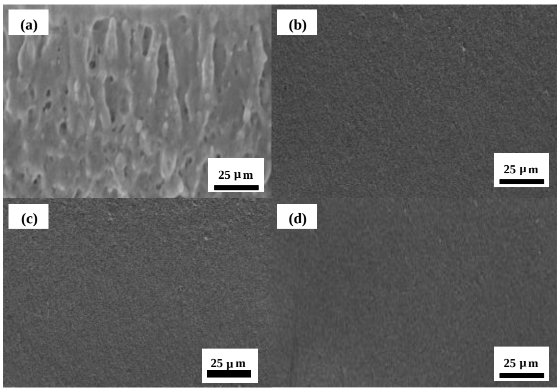


Figure 1 Cross-section microphotographs of (a) PI/NCC polymeric membrane and carbon membranes prepared under (b) He, (c) Ar and (d) N_2 environment.

The resultant pores begin to shrink as temperature increases which leads to the formation of a dense structure (Kiyono *et al*., 2010). Comparing experimental results from different studies is difficult due to slight variation in operational parameters (e.g., heating rates, polymer composition, coating cycles, and reaction times), as it can significantly influence the carbonization process. It is reported that a smooth and dense morphological structure can be detected when carbonizing the cellulose which indicated the formation of amorphous carbon (Chu and Li, 2006). He et al. analyzed the structure of carbonized cellulose and showed that the thickness of the cellulose-based carbon membranes is reduced and shrunk from 50 to 30 µm (He *et al.*, 2011). On the other hand, Kiyono et al. suggested that carbonization under an inert environment showed insignificant effects on micrograph structure (Kiyono *et al.,* 2010). These significant effects are due to complex morphology of asymmetric of the carbon membranes when comparing to a flat sheet or tubular membranes. In this study, the morphological structure of the carbon membrane is not significantly affected by the carbonization environments used. They reported that the carbonization environment under He and Ar gases will achieve a good and clear C distribution compared to the N_2 environment (Ismail *et al*., 2018). The inert gases (Ar and He) have a lighter molecular weight which helped them to have better C distribution on the carbon membrane.

The effect of different inert gases on the in-plane size of the graphitic clusters is not too obvious at a lower temperature of 600°C because the carbon structure is just started to form as the amorphousness is high at this temperature. When the carbonization temperature is increased to 800°C, the carbon pore structure is shrank, and the effect of the three inert atmospheres becomes significant. Carbonization at the higher temperature for the inert gas environment resulted in a higher degree of graphitization, and therefore the largest graphitic clusters. The smallest graphitic clusters resulted from vacuum carbonization is another indication of a lower reaction rate under a vacuum environment.

Gas permeation measurements

The conducted experiments showed that the carbonization environment has a significant correlation with transport properties. During the heat treatment process, the formation of amorphous carbon consisting of irregularly packed sheets of sp^2 hybridized carbon is believed to generate slit-like pore structures. Large pores provide adsorption sites and ultramicropores act as molecular sieve sites, are both believed to co-exist. The ultramicropores are speculated to be created at “kinks” in the carbon sheet or from the edge of a carbon sheet. These sites have more reactive unpaired sigma electrons prone to oxidation than other sites in the membrane. While carbonization process during the formation of carbon membranes is complex, the results presented here indicate that performance of carbon membrane can be controlled by carefully tuning the carbonization environment. There are several inert gases such as helium, argon, nitrogen, neon, xenon, krypton, and radon. However, three different gases which are Ar, He and N_2 have been chosen rather than other inert gases in order to investigate the control separation performance of carbon membranes based on fundamental principles. In comparison to the membranes carbonized under other inert gases, it proves that the ultra-micropores predominantly control the transport properties of the membranes, owing to the effects from Ar, He and N_2 gases (Su and Lua, 2007).

The high selectivity of TCMs can be obtained by manipulating the carbonization environment. The gas permeability of two pure gases through the resultant TCMs from different carbonization conditions was analyzed regarding their structures as well as the performance of gas separation as shown in Table 1. The gas permeation rate and molecular sieving properties are possibly due to the changes in porous membrane structure variation due to the employment of unique inert environment amid carbonization. This variation is owing to the pores which created by the evolution of gaseous products generated during the decomposition stage. For example, CO_2 gas shows higher permeance in contrast to He gas even though He is much smaller in molecular size which denoted that there is a different transport mechanism for CO_2 in the process. The CO_2 gas has the possibility to be adsorbed onto the pore surface, and subsequently, the adsorbed CO_2 molecules will diffuse on the surface and across the pore. Carbonization under an inert condition such as He gas flow has the probability to result in the acceleration of the decomposition which caused in higher gas permeation rate in contrast to membranes synthesized under Ar and N_2. The mass and heat transfer during the carbonization will add on to the occurrence of the more porous structure. The transport properties of TCMs are interrelated with the environment of carbonization. All through the carbonization, the reaction between inert gases and the TCM reactive site will occur which leads to the binding of the gases, hence creating the ultra-micropores. The slit-like pore structures are the results from the formation of amorphous carbon consisting of irregularly packed sheets of sp^2 hybridized carbon produced. The gas permeance of the prepared TCMs follows the order of $CO_2 > N_2$, which in agreement with the molecular sieving mechanism (Shao and Huang, 2007, Mahdyarfar *et al*., 2013). In this mechanism, ultra-micropores and large pores that providing adsorption sites are co-existing, denoting that as the selectivity increases, the permeability reduces.

Table 1 The comparison of gas separation performance of TCMs with different carbonization environments

Sample	Gas permeance (GPU)		Selectivity
	N_2	CO_2	CO_2/N_2
TCMs -Ar	3.22±3.21	213.56 ±2.17	66.32±2.18
TCMs -He	2.99±1.76	177.16 ±3.62	59.25 ±1.83
TCMs -N_2	2.59 ±2.59	143.14 ±1.85	55.27 ±3.42

Previous research conducted by Favvas et al. demonstrated that the pore volume of the TCMs prepared under He environment is more porous than those made under Ar or N_2 at a similar temperature (Favvas *et al*., 2015). The TCMs attained from N_2, and Ar gas environment only vary in terms of gas permeance results due to the inconsequential difference between both molecular sizes; Ar: 3.40Å, N_2 3. 64Å. It is also found that carbonization under He gas environment displayed the highest permeance owing to the lesser shrinkage of the membrane pore and smallest kinetic diameter (2.60Å). In addition, by monitoring the molecular sieving capacity, the increase of the gas molecular size, will ensue in the gas permeance reduction. CM-Ar exhibited higher gas selectivity as compared to CM-He and CM-N_2. This is due to the carbonization under Ar environment showed lesser weight loss while carbonization under N_2 environment has the tendency to speed up carbonization in increased temperature. The membranes carbonized under Ar environment showed the highest selectivity of 66.32±2.18 for CO_2/N_2 at 800°C. Taking the gas separation performance and its physicochemical properties into consideration, the carbonization process under Ar environment will bring about better gas separation separation in contrast to others.

CONCLUSION

Argon environment was found to be the most preferred carbonization condition for preparation of PI/NCC-based tubular TCMs at which the TCMs prepared under Argon environment underwent less weight loss although it exhibited highest CO_2/N_2 selectivity in comparison to those fabricated under He and N_2 environment. A highly permeable membrane was obtained from the carbonization under He environment in which it has slightly lower selectivity than TCMs fabricated under Ar due to high weight loss. Membrane fabricated under N_2 environment exhibited the least anticipated separation performance amongst the TCMs fabricated in this study.

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