

Tubular Carbon Membrane Prepared from PI/NCC: Effects of Pyrolysis Atmosphere

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The performance of Tubular Carbon Membrane (TCMs) due to pyrolysis conditions was studied. Dip-coating technique was used to synthesize the P84 co-polyimide/Nanocrystalline cellulose-based TCM, and pure gas O₂ and N₂ were used to determine the permeation properties of the TCMs. Different atmosphere i.e Argon, Nitrogen and Helium were introduced during the heat treatment processes at a flow rate of 200 mL/min to enhance the membrane's performance. The pyrolysis temperature and heating rate were set at 800 °C and 3°C/min. It was found that the best pyrolysis condition for the preparation of PI/NCC-based TCMs was conducted in Argon atmosphere with the permeance of 3.22 ± 3.21 and 29.90 ± 2.98 GPU for N₂, and O₂ gas. The membrane also demonstrated that the highest O₂/N₂ selectivity of 9.29 ± 2.54. In comparisons to all other carbonization atmosphere, preparation of TCMs in Ar atmosphere showed the lowest weight loss and revealed the highest N₂ selectivity in this study.

1. Introduction

In membrane fabrication, polymers are known as the predominant materials utilized because of the simplicity in processing with sufficient permselectivity capability for some set of gases. Transport properties of polymer membranes can be custom fitted by presenting pressing repressing massive gatherings and naturally unbending linkages in the polymer spines (Yang et al., 2017). An "upper bound" threshold restricts the separation performance of the unmodified polymeric material. One or the other must be sacrificed in order to surpass this limit barrier. As the development of membranes progressing, early findings reported of carbon membranes having capabilities to perform well beyond this upper bound limit. Carbon membranes are made via carbonization of polymers. And in this paper, the impact of pyrolysis condition is explored to control and enhanced the separation performance of carbon membranes.

Apart from polymeric membranes, inorganic-based membranes have now received a great interest among researchers because of their outstanding gas separation capabilities. Fabricated via the pyrolysis of polymer precursors, carbon membranes are perceived to have potential to be on par with inorganic membranes, particularly for gas separation application. They are known to have an excellent capability to purify and separate O₂/N₂, CO₂/CH₄, and hydrocarbons gas blends (Kiyono et al., 2010). Polymers such as phenolic resin (Abd Jalil et al., 2017), polyimide (Sazali et al., 2018), poly(vinylidene chloride) (Garnier et al., 2012), poly(furfuryl) alcohol (Hu et al., 2015) and polyetherimide (Hamm et al., 2017) are often being used to prepare a carbon membrane by various techniques including plunge coating, turn coating, shower coating or stage reversal. The focus of this study is to introduce a carbon membrane (the 'next generation' of membrane materials) derived from polymer blends of nanocrystalline cellulose (NCC) and BTDA-TDI/MDI polyimide. The NCC was synthesized and used as an additive to tune the overall characteristics of the final carbon membranes. The gas permeation data

demonstrated that polyimide/NCC-based carbon membrane can be considered as a new candidate for O₂ separation.

Carbon membranes provide the advantage in term of operation atmosphere such as in the presence of organic vapor or solvent and non-oxidizing acids or bases environments which is prohibitive to polymeric membrane. Furthermore, it is more resistant towards radiation, chemicals and microbiological attack. Carbon membrane can be used for a prolonged period under an environment that contains low levels of oxidants in air. This is to make sure that this type of membranes possessed longer life time compared to polymeric membranes. The membranes become more attractive as its pores characteristic can be controlled based on the preferable separation applications. In fabrication of carbon membrane, the same material can be used to develop carbon membrane with different permeation properties for different gas mixtures (Centeno et al., 2004). This is completed by conducting simple thermos-chemical treatment to meet different separation requirements and objectives. Due to those features, it attracts more researches in carbon membrane in order to tailor its separation performance in different applications.

Pyrolysis conditions become among the factors that influence the performance of carbon membranes (Ismail et al., 2018a). Different atmospheres i.e. vacuum, inert atmosphere (helium, nitrogen, or argon) and oxidative air (O₂/N₂ or CO₂) had been employed for fabrication of carbon membranes (Ismail et al., 2018b). Vu et al. (2002) have successfully arranged empty fibers of CMSMs from 6FDA/BPDA-DAM and Matrimid® 5218 polyimide, intended for excellent CO₂/CH₄ separation (Vu et al., 2002). The pyrolysis of Matrimid® polyimide at 823 K under helium rather than vacuum resulted in multiple CO₂ permeance which has also cost the loss of CO₂/CH₄ selectivity around 65 %. On the other hand, Hayashi and colleagues have fabricated BPDA-pp'ODA polyimide carbon membranes, layered on top of an alumina support (Hayashi et al., 1997). The membranes carbonized at 973 K under nitrogen gas had micropore volumes of 0.25, 0.30, 0.19 and 0.14 cm³/g while those carbonized at the same temperature using argon gas possessed micropore volumes of 0.36, 0.30, 0.19 and 0.14 cm³/g, applying CO₂, C₂H₆, n-C₄H₁₀, and i-C₄H₁₀ adsorbates, separately. In a study by Geiszler and Koros (1996), it was noticed that the carbon membrane arranged under vacuum air exhibited better H₂/N₂ and O₂/N₂ selectivity compared to the membrane arranged in the still atmosphere at a similar temperature. The faster heating rate and quicker mass exchange as the results of using inactive gas prior to pyrolysis procedure were believed to induce the formation of more porous membrane with less defined structure. The pervade motion across the carbon membranes carbonized at the temperature of 823 K, exposed under helium, argon or CO₂ was reduced after the rate of the cleanse gas stream was expanded from 20 to 200 cm³/min. This phenomenon however did not influence the selectivity of the membrane (Salleh and Ismail, 2011).

According to previous investigations, carbon membrane carbonized at 550 °C displayed Knudsen dispersion mechanism, while carbon membrane carbonized at 650 °C showed sub-atomic sieving mechanism (Briceño et al., 2012b). This mechanic component difference proved that the final pyrolysis temperature can influence the formation of pores (meso and micropores) in carbon membrane preparation (Briceño et al., 2012a). In other study, Fu et al. (2016) have shaped 6FDA/DETDA:DABA (3:2) CMS thick layer from the pyrolysis of precursor membranes under UHP Argon at three pyrolysis temperatures: 550 °C, 675 °C, and 800 °C. Based on the study, the fabricated membranes showed a substantial increment of two-gas permselectivity and porosity compared to those of the precursor membranes and outclassed the polymeric upper bound. As the pyrolysis temperature increased, the membrane porosity decreased drastically with expended permselectivity performance. Centeno and collaborators prepared carbon membranes, in which phenolic pitch became the main polymer, supported by a porous ceramic tube (Centeno et al., 2004). The covered phenolic pitch membranes were carbonized in both nitrogen gas and vacuum environments at 973 K, heated at the rate of 1 K/min for 60 min. Fundamentally, exposure towards nitrogen gas during pyrolysis would enhance the porosity of membrane. It turned out that membranes carbonized in nitrogen gas condition produced greater hydrocarbon/N₂ selectivity. Besides, permeation rates of nitrogen gas and hydrocarbon gas increased up to five times the membranes carbonized under vacuum condition. These series of investigations have set a clear goal to investigate the effect of the pyrolysis atmosphere towards the structural morphology and gas separation performance of carbon membrane.

2. Experimental

2.1 Materials

Principal precursor used in this study was the P84 co-polyamide which obtained from Sigma Aldrich. The P84 co-polyimide type polyimide is a thermally stable co-polyimide of 3,3',4,4'-benzophenone tetracarboxylic dianhydride with 80 % methylphenylene-diamine and 20 % methylene diamine. N-methyl-2-pyrrolidone (NMP) was used as the solvent was purchased from Merck (Germany). NMP possessed a high chemical and thermal stability and is completely miscible with water at all temperatures. Besides that, it is also miscible with most common solvents such as ketone, ethyl acetate, benzene, and chloroform. All chemicals were used directly without further purification. Nanocrystalline cellulose (NCC) was produced in-house, in accordance to the

techniques reported in preceding conducted by (Sazali et al., 2018). A Porous tubular ceramic support (TiO₂) (length - 8cm, thickness – 3 mm, average pore size – 0.2 μm, porosity – 40-50 %) was obtained from Shanghai Gongtao Ceramics Co., Ltd as tabulated in Figure 1. All the tubular alumina ceramic supported were polished utilizing SiC paper and cleaned with distilled water in a sonication bath for 30 min and then dried in air to remove any dust and unnecessary particles that can influence the final results.

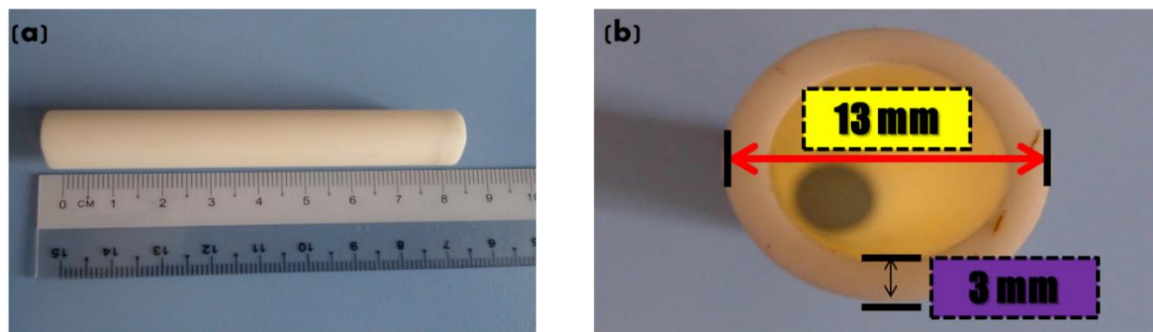


Figure 1: Porous tubular ceramic support measurements (a) length; (b) thickness.

2.2 Fabrication of carbon tubular membrane

15 wt% of P-84 was dissolved in NMP. Stirring temperature was maintained below the NMP boiling point to avoid the solvent from vaporize. The dope comprised of P84 co-polyimide and NMP was heated at 80 °C and stirred for 24 h. Then 7 wt% of NCC were added in stages into the polymer dope and continuously stirred until homogeneous solution was formed. The dope solution was degassed in ultrasonic bath for bubbles removal. The solutions were used to dip-coated the hollow tube support by immersing the tube in the solution for 45 min. Dip-coated technique was chosen as a preferable method for supported carbon membrane fabrication as this technique could produce a carbon membrane with a thin layer on the top. Following the immersion was the total removal solvent step where the samples were immersed in methanol solution for 2 h followed by an overnight drying in the oven at 100 °C. To produce the TCMs, the tubular coated membrane samples were introduced into three different carbonization atmospheres (helium, argon and nitrogen) at a gas flow rate of 200 mL/min. Samples were heated in Carbolite horizontal tubular furnace up to 800 °C at a heating rate of 3 °C /min. The same methods were applied according to our earlier studies (Sazali et al., 2018). The same technique was used to characterize the flat sheet unsupported carbon membranes. Eurotherm 2,500 °C temperature control systems was used to regulate the heating cycle.

2.3 Pure gas permeation measurements

Two parameters were explored for membrane performance measurements: permeance and selectivity. The carbon tubular membranes were tested by utilizing an in-house gas permeation rig setup (Sazali et al., 2015). The rig comprised of flexible hose, separation cell, valve, weight controller and bubble flow meter as shown in Figure 2a. The 8 cm carbon tubular membrane was assembled inside a tubular stainless-steel module of 14 cm long as pictured in Figure 2b. The membrane was fitted with elastic O-rings to enable the membrane to be housed in the module without any leakage. Pure O₂ (0.346 nm), and N₂ (0.364 nm) gases were introduced into the system during the experiments at a trans-membrane pressure of 8 bars.

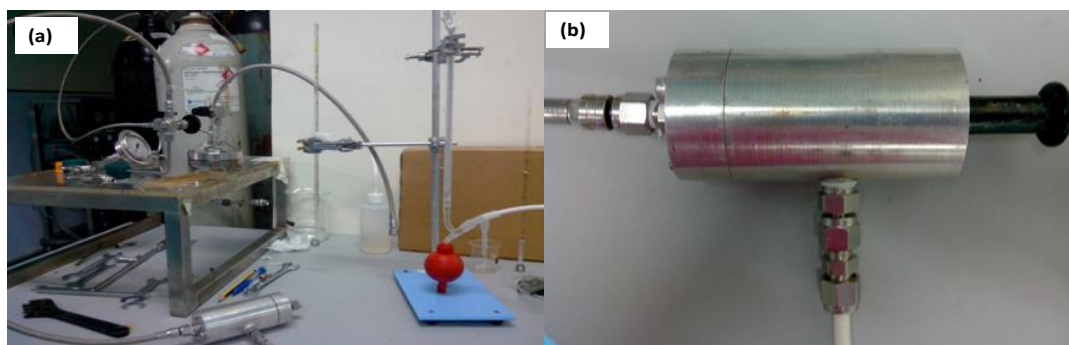


Figure 2: (a) Gas permeation apparatus; (b) Tubular membrane module.

The selectivity, α , and permeance, P/l (GPU, of the membranes) were calculated with the accompanying conditions:

Permeance, $(P/l)_i$:

$$(P/l)_i = \frac{Q_i}{A \cdot \Delta p} = \frac{Q_i}{\pi D L \Delta p} \quad (1)$$

1 GPU = $1 \times 10^{-6} \text{ cm}^3 \text{ (STP) cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$.

where P/l is the permeance of the membrane (GPU), Q_i is the volumetric flow rate of gas i at standard temperature and pressure ($\text{cm}^3 \text{ (STP/s)}$), p is the pressure difference between the feed side and the permeation side of the membrane (cmHg), A is the membrane surface area (cm^2), D an outer diameter of the membrane (cm) and L is the effective length of the membrane (cm).

Selectivity, α :

$$\alpha_{i/j} = \frac{(P/l)_i}{(P/l)_j} \quad (2)$$

Volumetric flow rate of the permeate was measured by the soap bubble flow meter reading of 1.0 mL. Different membrane samples were used to repeat the permeation test. The gas permeation test was conducted at ambient temperatures with similar setup as used in previous studies (Sazali et al., 2015).

3. Results and discussion

In this examination, the impact of pyrolysis climate was analyzed by looking at the differences in the arrangement of carbon membranes under an inactive condition at a warming rate of $3 \text{ }^\circ\text{C /min}$ up to $800 \text{ }^\circ\text{C}$. Based on the gas permeation study, it was discovered that the expansion of NCC to the basic polymer as an added substance created better gas permeation properties when contrasted with unmodified PI. Table 1 shows gas permeation properties of PI/NCC polymeric membrane. The present finding shows that PI/NCC polymeric membrane has the best gas permeance and selectivity. The gas permeance of the chosen gases were in the sequence of $\text{O}_2 > \text{N}_2$ for every membrane what was tasted.

Table 1: Gas permeation performance of PI/NCC polymeric membrane

Sample	Permeance (GPU)		Selectivity
	O_2	N_2	O_2/N_2
PI	0.77 ± 3.22	0.77 ± 3.22	1.10 ± 5.12
PI/NCC	0.77 ± 3.22	0.94 ± 3.54	1.41 ± 1.92

As reported in Table 2, the pure PI and PI/NCC carbon membrane under Ar gas condition demonstrated the selectivity of 9.29 ± 2.54 for O_2/N_2 separations, which is the highest among others. As discussed in the published works before, the existence of pore former materials could offer different pores growth during the development of the permeable structure. This phenomenon was ascribed to the presence of additives, would alter and bring down the pyrolysis temperature. Therefore, manipulating the pyrolysis condition could potentially enhance the pore distribution, pore volume and creating a unique diffusional pathway in the membrane wall (De Almeida Filho and Zarbin, 2006).

Table 2: Gas permeation performance of PI and PI/NCC carbon membrane under different pyrolysis atmosphere

Sample	PI carbon membrane			PI/NCC carbon membrane		
	Permeance (GPU)		Selectivity	Permeance (GPU)		Selectivity
	N_2	O_2	O_2/N_2	N_2	O_2	O_2/N_2
CM-Ar	2.78 ± 1.28	20.24 ± 4.51	7.28 ± 3.82	3.22 ± 3.21	29.90 ± 2.98	9.29 ± 2.54
CM-He	3.21 ± 2.39	22.77 ± 3.14	7.09 ± 1.77	3.84 ± 4.85	32.61 ± 1.00	8.49 ± 1.92
CM- N_2	2.69 ± 1.22	17.88 ± 1.65	6.64 ± 1.81	3.14 ± 3.42	24.29 ± 2.91	7.74 ± 3.39

As compared to carbon membranes formed from pyrolysis under N_2 and He, the one made with Ar were found to have better partition properties. The porosity of carbon membrane under Ar was evidently enhanced as well as the pure gas permeation rates. The presence of the carbon membrane in the membrane caused the carbon-based membrane to have a superior performance than the polymeric membrane. It could be caused by the

restriction of the passageway in the polymeric membranes due to the small channels. As it is known that the separation properties are controlled by the atomic sieving effects, the transport flow is limited by the physical characteristics of the ultra-micropores. With an increase in the pyrolysis temperature, the gas permeation profiles show a variation of the gas permeance results. Thus, the effects of changing the pyrolysis atmosphere were more significant at a higher temperature. Membranes carbonized under helium gas at 800 °C represented the top separation performance as compared to the one carbonized under Ar and N₂ at a similar temperature most likely due to the porous pores, and it contained more permeable membranes. Additional reason for this performance might be because of a few pores inside He gases are dead and, in this way, not amiable for the gas to penetrate through.

In spite of the higher temperatures, the pyrolysis under Ar condition created more beneficial pores than with N₂ and He gas. Membranes which were carbonized under the pyrolysis temperature of 800 °C show considerable increment in their selectivity as compared to the polymeric membranes. At this high temperature, the membranes had contracted to show diminished surface territory and aggregated pores volume of the resultant membrane. A few pores have contracted to such a degree, to the point that there are not any more specific to the gas atoms. The membranes acquired from various pyrolysis condition deliver indistinguishable gas permeances for all gases except He. He conditioned pyrolysis membranes presents a better permeation performance might be due to a lesser degree of pore shrinkage. While for both Ar and N₂ conditions, the pore structure refinement resulted in smaller pathways which reduces the permeation value for the membranes. Interestingly, all carbon membranes showed higher selectivity values for O₂/N₂ than those for polymeric membranes. This was due to the membrane shrinking phenomenon at higher temperature, bringing about smaller pores and subsequently, an enhanced selectivity (Kim et al., 2018). View from this study shows that pyrolysis under inert gases is suitable for the arrangement of consistent dispersed tight pores due to the merging of pores under high-temperature heat treatment. The selectivity however depends on the sub-atomic size differences between the gases. But since the distinction sizes between O₂ (2.80 Å) and N₂ (3.64 Å) is small, it would not cause much impacts. The membranes carbonized under Ar condition create the best selectivity of 9.29 ± 2.54 for O₂/N₂ with a permeance of 3.22 ± 3.21 and 29.90 ± 2.98 GPU for N₂, and O₂ gases.

4. Conclusions

This work focused on the fabrication of polyimide-based tubular supported carbon membrane, by two stages of the pyrolysis cycle. The different pyrolysis conditions chosen were investigated to enhance the gas penetrability and permselectivity for O₂/N₂ separation. It was found that gas permeation increases with the addition of temperature during the carbonization process. The carbon membrane arranged at 800 °C under Ar gas stream exhibited great pure gas separation for CO₂/N₂, with the best selectivity of 29.90 ± 2.98 GPU for O₂ and 3.22 ± 3.21 GPU for N₂. From all conditions tested, carbon membrane prepared under Argon atmosphere showed the least weight loss with the highest O₂/N₂ selectivity. In sequence, He induced carbonization atmosphere performed lower than in Ar conditioned for their selectivity which is believe to be caused by the increase in weight loss. The least favourable performance was for membranes made under N₂ pyrolysis condition.

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