

Journal of Advanced Research in Materials Science

Advanced Research in Materials Science

Journal homepage: www.akademiabaru.com/arms.html ISSN: 2289-7992

The Effect of Different Pyrolysis Environment towards Carbon Membrane Performances



Norazlianie Sazali^{1,2,*}

¹ Structural Performance Material Engineering (SUPREME), Faculty of Mechanical & Automotive Technology Engineering, Universiti Malaysia Pahang, 26600 Pekan, Pahang, Malaysia

² Centre of Excellence for Advanced Research in Fluid Flow (CARIFF), Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia

ABSTRACT

This work investigates the effect of pyrolysis setting on the performance of Tubular Carbon Membrane (TCMs). In order to determine the properties of TCMs permeation, the synthetisation of P84 co-polyimide/Nanocrystalline cellulose-based TCM was done using the dip-coating method with pure nitrogen and hydrogen. The performance of the membrane was enhanced by implementing different environment such as helium, nitrogen and argon in the heat treatment processes where the gas flow rate was fixed at 200 ml/min. The rate of heating applied was 3°C/min, whereas the temperature of pyrolysis was set at 800°C. The performance results revealed that argon was the best pyrolysis environment for the preparation of PI/NCC-based TCMs, with 3.22±3.21 and 1399.66±5.22 GPU of nitrogen and hydrogen permeance, respectively, meanwhile the highest selectivity obtained was 434.68±1.39. As compared with the membranes prepared in nitrogen and helium environment, the resultant TCMs from argon environment exhibited the lowest loss of weight as well as the highest selectivity of nitrogen.

Keywords:

Pyrolysis; Tubular carbon membrane (TCMs); PI/NCC-based membrane; gas selectivity

Copyright © 2019 PENERBIT AKADEMIA BARU - All rights reserved

1. Introduction

A few researchers have recently come out with their new discovery that aims to develop membranes with high efficiency through the blending of new precursors and membrane preparation manipulation. The recognition of membrane technology is highly influenced by the attractive properties of chemicals as well as the excellent performance in separation. The membrane separation processes are no longer a new term considering their fast and growing development over the past decades [1, 2]. Polymeric membranes normally can be found in the forms of hollow fibres or flat sheets, in which these membranes have the ability to achieve moderate selectivity and permeability under low cost through the utilisation of scalable manufacturing processes [3, 4]. Despite the vast interest from the gas separation industries, these membranes encountered slow commercialisation growth due to some restrictions, for instance the performance trade-off, also identified as the Robeson upper-bound relationship [5, 6].

* Corresponding author.

E-mail address: azlianie@ump.edu.my (Norazlianie Sazali)



Additionally, as compared to polymer membrane, both high in selectivity and permeability along with excellent productivity can be achieved by using carbon membrane, as a result of the distinct and disarray structures of carbon material which differ from zeolites. Carbon material offers ideal distribution of pore size when being implementing in gas separation, thus proposing homogenously defect free membranes. While significant findings have been reported since the inception of carbon membrane, it is important to enhance the properties of gas separation so that the membrane is feasible for real application [7]. In particular, the pyrolysis conditions affect both the properties of gas permeation and the gas structure. Regarding this matter, the researchers concentrate primarily on investigating the effect of the pyrolysis environment on the carbon membrane. Geiszler and coworkers reported that the pyrolysis of asymmetric hollow fibres carbon membranes in various gases conditions (argon, helium as well as carbon dioxide) with 6FDA/BPDA-DAM displayed insignificant findings for H_2/N_2 and O_2/N_2 separations [8]. Nonetheless, it was discovered that the efficiency of the carbon membrane was affected by the inert gas flow rate at 200 cm3/min with 700 times higher flux compared to the samples purged at 20cm3/min. Furthermore, the flow of inert gas consists of a superlative heat transfer, which fastens the process of pyrolysis. Hence, more open and porous structures would be produced compared to under the vacuum environment. However, the amorphous membranes could shrink by additional reaction at higher temperature[9]. Numerous attentions are given to carbon membrane enhancement with broad selection of gas separation precursors, focusing primarily on the effect of implementation of the pyrolysis environment via the heat treatment process. Due to its ability to withstand high temperatures while the pyrolysis process is going on, PI-copolyimide was used as the primary precursor in this work.

BTDA-TDI/MDI (P-84) does not lose its shape during the melting phase transition by controlling the temperature of pyrolysis, rate of heating and pyrolysis environment, thus making it to be preferred as a precursor in carbon membrane production. In addition, this material exhibited high polymeric membrane gas selectivity suggesting it as a good option for gas separation, thus suitable as the main selection in carbon membrane manufacturing due to its physical properties and compound [10-12]. Membranes with a polymeric base show the best properties as well as high permeability qualities, high selectivity and high chemical and thermal stabilities. Growing interest in the benefits of gas separation induces the capability of membrane technology as a more promising approach to replace the conventional method. Due to its microstructure-dependent nature, the efficiency of membrane carbonisation is affected by the molecular structure of the polymer precursor. In contrast with the other polymers used in polymeric membranes preparation, polyimide attracts numerous attentions due to molecular sieving characteristic and its superior penetrant diffusivity. For this current work, commercial polyimide known as P84 co-polyimide was selected as the starting material in the fabrication of carbon membrane. The blend technique that uses pure polymer as its precursor and blends it with other inorganic substances or materials, has gained significant interest in carbon membrane production from various researchers. This technique is advantageous in changing the properties of polymer material, leading to the discovery of novel material that exhibits high potential in various areas. [13, 14]. Our research group recently successfully conducted synthetization of nanocrystalline cellulose (NCC) from recycled newspaper [15].

Previously, a few studies had been conducted on the effect of carbonisation environment on the carbon membranes produced. Nevertheless, investigation regarding the impact of stabilisation environment on the process of heat treatment is scarce. Some inert gases for example radon, helium, krypton, argon, xenon, nitrogen, and neon can be used to manipulate the carbonisation environment. In this work, argon, helium and nitrogen were selected in finding the separation efficiency of carbon membranes according to the fundamental principles. This paper aims to discuss the method of



fabricating tubular-supported carbon membrane for separation or purification of hydrogen. The dipcoating technique is utilised via deposition of PI/NCC carbon membrane as carbon precursor. In particular, the effect of different manufacturing parameters on PI/NCC carbon membrane structure was explored in this work. The results produced agree on the prospective of this method, which is deemed as fast and simple, offering novel ways of characterising as well as designing the supported carbon membranes for hydrogen separation purpose.

2. Experimental section

2.1 Materials

The performance of the pyrolysed membranes is influenced by the molecular structure of polymer precursors. Polyimide is a polymer precursor with greater penetrant diffusivity and excellent molecular sieving properties. Polyimide (PI) (P84, Merck) was used in pellet form as the primary material for membrane fabrication; meanwhile N-methyl-2-pyrrolidone (NMP, Sigma Aldrich) was used without further purification, as a solvent to dissolve the polymer. Preparation of nanocrystalline cellulose (NCC) was previously conducted because it was commercially unavailable [15]. The commercial grade of tubular ceramic having pore size with an average of 0.2 μ m, an inner diameter of 11 mm, an external diameter of 13 mm and 40-50% porosity was obtained from Shanghai Gongtao. The 8 cm long membrane support of Ceramics Ltd. consisted of titanium dioxide (TiO2) with an average particle size of 4.5-5.5 mm and zirconium dioxide (ZrO2) with an average particle size of 2-3 mm which covers the inner surface of the support.

2.2 TCM preparation

TCM was prepared using 15 wt% BTDA-TDI/MDI (P84) dope solution dissolved in NMP which acts as a solvent, followed by drying in an oven for 24 hours at 50°C. In order to obtain a homogeneous solution, gradual addition of NCC into the solution was performed before stirring. P84 polymer powder was added into the solution prior to continuous stirring at 600 rpm until complete dissolution of all polymers was achieved. Before the dip-coating process, ultrasonication was applied on the dope to eliminate air bubbles from the solution. Subsequently, the ceramic tube support was immersed in the dope for 15 minutes before 24 hours of room temperature drying. The dope coating was applied on the external surface of ceramic tube support. Both ends of the ceramic tube support were tightly sealed as to prevent any solution from flowing into the support. The cycle of dip-coating process was repeated twice in order to eliminate pinholes in the membrane structure. The aging process of the prepared polymeric membrane was then conducted at 80°C for 24 hours, and subsequently dipped in methanol for 2 hours prior to another 24 hours of room temperature drying. Repetition of these steps was performed twice before starting the process of heat treatment. Next, the polymeric membranes were inserted into the carbolite wire wound tube furnace (Model: CTF 12/65/550) for the process of heat treatment. The furnace tube is 75 cm long with 60 cm zone of heating and diameter of 12 cm. The heat treatment process was conducted under stabilisation temperature of 300°C and final pyrolysis temperature of 800°C. The rate of heating was kept constant at 3°C/min for the entire process. The membrane was introduced to the stabilisation phase through membrane heating up to 300°C, prior to carbonisation at 800°C, where the rate of heating was fixed at 3°C/min. Variation of pyrolysis environment was applied through the furnace tube saturation using different gases such as nitrogen, helium and argon, whereas the thermal soak time was kept constant at 120 minutes. The resultant membranes were naturally cooled down to room temperature at the end of each heating cycle.



2.3 Gas separation measurement

The in-house gas permeation system was employed to evaluate the performance of TCM's, in which the performance was determined in terms of two crucial parameters namely selectivity and permeance. The system comprises soap bubble meter flexible hose, valve, permeation cell, and pressure regulator. The 8 cm carbon tubular membrane was inserted into the 14 cm tubular stainless steel module. The membrane was fitted with rubber O-rings to restrain leakages during the evaluation test. Hydrogen and nitrogen were separately inserted into the module at 8 bars of transmembrane pressure. Afterwards, the membrane selectivity and permeance were calculated by referring to the equations from the previous work [15]. Specifically, selectivity is a term that refers to the relationship between the rapid gas permeation ratio to slow gas permeation ratio. The permeate gas volumetric flow rate was obtained using soap bubble flow meter with 1.0 ml reading at room temperature. Production of TCM's with high selectivity was done by manipulating the pyrolysis environment. The permeance of two pure gases with different molecular sizes namely hydrogen and nitrogen; were measured at 8 bars of feed pressure through the TCM's produced, at different pyrolysis conditions.

3. Results and Discussion

3.1 Effect of pyrolysis environment on gas permeation properties

The pyrolysis environment effect on the gas separation efficiency of the fabricated TCM's is shown in Table 1. The disparity in the gas permeation rate as well as the molecular sieving properties indicates the alteration in the structure of porous membrane as a result of the implementation of different inert environment of pyrolysis. This is because pores are formed by the evolution of gaseous products generated during decomposition stage [16]. As an example, carbon dioxide gas showed higher permeance compared to helium gas even though helium has a smaller molecular size than carbon dioxide, indicating the presence of an additional mechanism of transport for carbon dioxide. Carbon dioxide gas possibly is adsorbed onto the surface of the pore prior to surface diffusion through the pore [16].

TCM's gas permeation performance			
Membrane	Permeance (GPU)		Selectivity
	H ₂	N ₂	H_2/N_2
PI/NCC polymeric membrane	24.52±1.34	0.94±3.54	26.09±2.49
PI/NCC TCM's (Nitrogen)	1221.25±2.61	3.02±1.44	404.39±1.26
PI/NCC TCM's (Argon)	1399.66±5.22	3.22±3.21	434.68±1.39
PI/NCC TCM's (Helium)	1306.78±2.04	3.12±3.11	418.84±2.73

Table 1

Inert environment pyrolysis, for example under helium gas flow would speed up the decomposition reaction resulting in elevated rate of gas permeation, in contrast to TCM's prepared under argon and nitrogen environment. Increased mass and heat transfer can be observed throughout the pyrolysis process, creating more porous structure. The transport features of TCM's are associated with the pyrolysis environment. During the pyrolysis process, inert gases are likely to react as well as bind to the reactive sites of TCM's and thereby producing ultra-micropores [17]. The configuration of amorphous carbon which consists of erratically packed sp² hybridized carbon sheets



resulting in a slit-like pore structure [18]. The gas permeance of the resultant TCM's follows the order of $H_2 > N_2$, which are in line with the mechanism of molecular sieving [19] In the mechanism of molecular sieving, ultra-micropores as well as large pores which provide the adsorption sites are coexist, resulting in increased selectivity and reduced permeability. Favvas et. al. reported that the pore volume of carbon membrane produced under helium environment pyrolysis was more porous compared to the carbon membrane fabricated under argon and nitrogen environment pyrolysis at similar temperature [20]. Due to slight difference in the molecular size of argon (3.40Å) and nitrogen (3.64Å), TCM's produced under argon and nitrogen environment show different gas permeance ability. Unfortunately, due to less membrane pore shrinkage and the smallest kinetic diameter of helium (2.60Å), the pyrolysis under helium environment exhibited higher permeance. Furthermore, according to the capacity of molecular sieving, the increment in gas molecular size led to the lower gas permeance. TCM-N2 and TCM-He have lower gas selectivity as compared to TCM-Ar. This is because the pyrolysis under argon environment has less weight loss, whereas the pyrolysis under nitrogen environment tends to accelerate as the temperature increases [21-23]. Pyrolysis of membrane in argon environment resulted in the highest selectivity of 434.68 ± 1.39 for H_2/N_2 at 800°C. In the next experiment, the pyrolysis under argon environment will be conducted taking into account both physicochemical properties as well as the efficiency of gas separation.

4. Conclusions

From this work, the pyrolysis environment effect on the efficiency of PI/NCC tubular carbon membrane (TCM) was identified. Nanocrystalline cellulose (NCC) blended with BTDA-TDI/MDI (P-84) polyimide resulted in TCM's with superior gas separation performance. Further study on the pyrolysis conditions showed the significance of pyrolysis environment on the morphologies of the membrane as well as its capabilities in separation process. In contrast to helium and nitrogen, preparation of membrane under argon environment involved less weight loss while demonstrated high selectivity for all gas pairs tested. Pyrolysis under helium environment produced membrane that resulted in high permeability and low selectivity compared to the resultant membrane under argon environment pyrolysis due to massive loss of weight. Among the TCM's investigated in this study, the most desirable separation performance was resulted from the membrane formed under argon environment

Acknowledgements

Author would gratefully acknowledge the financial support from the Ministry of Higher Education and Universiti Malaysia Pahang under Fundamental Research Grant Scheme (RACER/1/2019/TK10/UMP/2).

References

- [1] Nasir, Atikah Mohd, Pei Sean Goh, Mohd Sohaimi Abdullah, Ng Be Cheer, and Ahmad Fauzi Ismail. "Adsorptive nanocomposite membranes for heavy metal remediation: Recent progresses and challenges." *Chemosphere* (2019).
- [2] Kumar, Annamalai Pratheep, Dilip Depan, Namrata Singh Tomer, and Raj Pal Singh. "Nanoscale particles for polymer degradation and stabilization—trends and future perspectives." *Progress in polymer science* 34, no. 6 (2009): 479-515.
- [3] Stern, S. A., Y. Mi, H. Yamamoto, and Anne K. St Clair. "Structure/permeability relationships of polyimide membranes. Applications to the separation of gas mixtures." *Journal of Polymer Science Part B: Polymer Physics* 27, no. 9 (1989): 1887-1909.
- [4] Rao, MadhukarB, and Shivaji Sircar. "Nanoporous carbon membranes for separation of gas mixtures by selective surface flow." *Journal of Membrane Science* 85, no. 3 (1993): 253-264.



- [5] Robeson, Lloyd M. "Correlation of separation factor versus permeability for polymeric membranes." *Journal of membrane science* 62, no. 2 (1991): 165-185.
- [6] Robeson, Lloyd M. "The upper bound revisited." *Journal of membrane science* 320, no. 1-2 (2008): 390-400.
- [7] Zhang, Bing, Lin Li, Chunlei Wang, Jing Pang, Shouhai Zhang, Xigao Jian, and Tonghua Wang. "Effect of membranecasting parameters on the microstructure and gas permeation of carbon membranes." *RSC Advances* 5, no. 74 (2015): 60345-60353.
- [8] Geiszler, Vincent C., and William J. Koros. "Effects of polyimide pyrolysis conditions on carbon molecular sieve membrane properties." *Industrial & engineering chemistry research* 35, no. 9 (1996): 2999-3003.
- [9] Aguilar-Vega, M., and Donald R. Paul. "Gas transport properties of polycarbonates and polysulfones with aromatic substitutions on the bisphenol connector group." *Journal of Polymer Science Part B: Polymer Physics* 31, no. 11 (1993): 1599-1610.
- [10] Favvas, E. P., E. P. Kouvelos, G. E. Romanos, G. I. Pilatos, A. Ch Mitropoulos, and N. K. Kanellopoulos. "Characterization of highly selective microporous carbon hollow fiber membranes prepared from a commercial co-polyimide precursor." *Journal of Porous Materials* 15, no. 6 (2008): 625-633.
- [11] Li, Dan, Huai Yong Zhu, Kyle R. Ratinac, Simon P. Ringer, and Huanting Wang. "Synthesis and characterization of sodalite–polyimide nanocomposite membranes." *Microporous and mesoporous materials* 126, no. 1-2 (2009): 14-19.
- [12] Sazali, N., W. N. W. Salleh, A. F. Ismail, K. C. Wong, and Y. Iwamoto. "Exploiting pyrolysis protocols on BTDA-TDI/MDI (P84) polyimide/nanocrystalline cellulose carbon membrane for gas separations." *Journal of Applied Polymer Science* 136, no. 1 (2019): 46901.
- [13] Menendez, Ivan, and Antonio B. Fuertes. "Aging of carbon membranes under different environments." *Carbon* 39, no. 5 (2001): 733-740.
- [14] Bernardo, Paola, Enrico Drioli, and G. Golemme. "Membrane gas separation: a review/state of the art." *Industrial* & engineering chemistry research 48, no. 10 (2009): 4638-4663.
- [15] Sazali, N., W. N. W. Salleh, and A. F. Ismail. "Carbon tubular membranes from nanocrystalline cellulose blended with P84 co-polyimide for H2 and He separation." *international journal of hydrogen energy* 42, no. 15 (2017): 9952-9957.
- [16] Liang, Can Zeng, Tai-Shung Chung, and Juin-Yih Lai. "A review of polymeric composite membranes for gas separation and energy production." *Progress in Polymer Science* (2019).
- [17] Lu, G. Q., JC Diniz Da Costa, Mikel Duke, S. Giessler, R. Socolow, R. H. Williams, and T. Kreutz. "Inorganic membranes for hydrogen production and purification: a critical review and perspective." *Journal of colloid and interface science* 314, no. 2 (2007): 589-603.
- [18] Saeidi, Samrand, Nor Aishah Saidina Amin, and Mohammad Reza Rahimpour. "Hydrogenation of CO2 to valueadded products—A review and potential future developments." *Journal of CO2 utilization* 5 (2014): 66-81.
- [19] Abe, J. O., E. Ajenifuja, and O. M. Popoola. "Hydrogen energy, economy and storage: review and recommendation." *International Journal of Hydrogen Energy* (2019).
- [20] Favvas, Evangelos P., Nikolaos S. Heliopoulos, Sergios K. Papageorgiou, Athanasios Ch Mitropoulos, George C. Kapantaidakis, and Nick K. Kanellopoulos. "Helium and hydrogen selective carbon hollow fiber membranes: The effect of pyrolysis isothermal time." Separation and Purification Technology 142 (2015): 176-181.
- [21] Sazali, N., W. N. W. Salleh, N. Arsat, Z. Harun, and K. Kadirgama. "P84 Co-Polyimide-based tubular carbon membrane: effect of pyrolysis temperature." *Journal of Applied Membrane Science & Technology* 23, no. 1 (2019).
- [22] Sazali, Norazlianie, Wan Norharyati Wan Salleh, Ahmad Fauzi Ismail, Kumaran Kadirgama, Mohamad Shahrizan Moslan, Faten Ermala Che Othman, Nor Hafiza Ismail, Mahendran Samykano, and Zawati Harun. "Effect of heating rates on the microstructure and gas permeation properties of carbon membranes." *Malaysian Journal of Fundamental and Applied Sciences* 14, no. 3 (2018): 378-381.
- [23] Sharip, Mohd Syafiq, Norazlianie Sazali, Ahmad Shahir Jamaludin, Muhammad Atif Mohamed, Farhana Aziz Azmi, and Wan Norharyati Wan Salleh. "Current advancement by membrane technology: a review." *Journal of Advanced Research in Fluid Mechanics and Thermal Sciences* 59: 283-290.