

## Controlled Dip-coating Times for Improving CO<sub>2</sub> Selective of PI/NCC-based Supported Carbon Membrane

Sazali N<sup>1,2</sup>, Salleh WNW<sup>1,2\*</sup>, Ismail AF<sup>1,2\*</sup>, Ismail NH<sup>1,2</sup>, Yusof N<sup>1,2</sup>, Aziz F<sup>1,2</sup>, Jaafar J<sup>1,2</sup> and Nordin NAHM<sup>3</sup>

<sup>1</sup>Advanced Membrane Technology Research Centre (AMTEC), Universiti Teknologi Malaysia, 81310 Skudai, Johor Darul Takzim, Malaysia

<sup>2</sup>Faculty of Chemical and Energy Engineering (FCEE), Universiti Teknologi Malaysia, 81310 Skudai, Johor Darul Takzim, Malaysia

<sup>3</sup>Department of Chemical Engineering, Universiti Teknologi PETRONAS (UTP), 32610 Bandar Seri Iskandar, Perak, Malaysia

\*Corresponding authors: WNW Salleh, Faculty of Chemical and Energy Engineering (FCEE), Universiti Teknologi Malaysia, 81310 Skudai, Johor Darul Takzim, Malaysia, Tel: (+60) 75 535 388; E-mail: [hayati@petroleum.utm.my](mailto:hayati@petroleum.utm.my); Ismail AF, Faculty of Chemical and Energy Engineering (FCEE), Universiti Teknologi Malaysia, 81310 Skudai, Johor Darul Takzim, Malaysia, Tel: (+60) 75 535 592; E-mail: [afauzi@utm.my](mailto:afauzi@utm.my)

Received date: February 12, 2018; Accepted date: March 5, 2018; Published date: March 12, 2018

Copyright: ©2018 Sazali N, et al. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.

### Abstract

Carbon membrane can be regarded as the future separation media in gas separation process due to its high gas separation performance, easy processability, and moderate energy requirement compared to conventional separation process. In this study, the fabrication of tubular carbon membrane prepared from PI blends with nanocrystalline cellulose (NCC) was investigated. The influence of dip-coating duration (15, 30, 45, and 60 min) towards the physicochemical properties and CO<sub>2</sub>/CH<sub>4</sub> and O<sub>2</sub>/N<sub>2</sub> separation was explored. The process of carbonization was conducted at 800°C with rate of heating at 3°C/min under argon gas flow (200 mL/min). Pure gas permeation tests were performed to investigate the prepared carbon membrane's mechanism of transport at ambient temperature and a feed pressure of 8 bar. The carbon membrane with CO<sub>2</sub>/CH<sub>4</sub> and O<sub>2</sub>/N<sub>2</sub> selectivity of 68.23 ± 3.27 and 9.29 ± 2.54 and CO<sub>2</sub> and O<sub>2</sub> permeance of 213.56 ± 2.17 and 29.92 ± 1.44 GPU, respectively, were obtained when applying 45 min dip-coating.

**Keywords** Tubular carbon membrane; Dip-coating; Nanocrystalline cellulose (NCC); P84 co-polyimide (PI); Gas separation

### Introduction

Nowadays, gas separation is one of the premier applications of membrane technology. The application of membrane in gas separation has drawn much attention from researchers around the world due to their advantages, including ease of operation (no moving parts), low energy requirements, and small footprint [1]. Membrane for gas separation technology can be marked as a competitive industrial gas separation technique especially for CO<sub>2</sub> separation [2,3]. CO<sub>2</sub> capture from power plant flue gas and subsequent sequestration is expected to play a key role in mitigating global climate change. It is known that CO<sub>2</sub> is not only the main greenhouse gas but also an important potential carbon source, therefore, the capture and separation of CO<sub>2</sub> has attracted worldwide attention [3,4].

Both CO<sub>2</sub> and O<sub>2</sub> separation are based on a pressure driven process, where the driving force is induced by the variation of pressure between upstream and downstream sides. In gas separation, the membrane with nonporous structure is more preferable to prevent leakage of gas across the membrane layer. Up to now, the production of large-scale commercial gas is still in the middle of searching for feasible membranes that possess high selectivity and permeability. Principally, membrane should possess high selectivity and permeability as well as mechanical and chemical stability under the long-term operation conditions. Previously, most review articles discussed the chronology of the membrane development in gas separation and also the separation progress of various binary pairs of gases. Differ from previous reported articles, this paper aims to study the recent and

updated progress of carbon membrane utilized in CO<sub>2</sub> and O<sub>2</sub> separation, by manipulating fabrication condition.

Carbon membranes have begun to have potential as candidates to be applied in separation of gas due to the attractive characteristics such as excellent thermal endurance, chemical stability in eroding surroundings, and possess advantageous balance of gas selectivity and permeability compared to polymeric membranes [5,6]. Carbon membranes are prepared by carbonization of polymeric membrane under controlled inert atmosphere at temperatures of up to 900°C [7,8]. In the case of polymeric precursor membrane selection, the material should withstand high temperature treatment without much shrinkage and produce high carbon yield. The microstructure and gas permeation properties of the carbon membranes depend on the type of polymer precursor, fabrication techniques, and carbonization conditions [9]. In this study, dip-coating method was applied to fabricate the supported tubular carbon membrane. Until now there is no studies reported on the effect of coating condition towards gas diffusion characteristic of the tubular PI/NCC-based carbon membrane.

The main focus of this research study was to provide better understanding in dip-coating processes to control the morphology of the tubular supported carbon membrane. The main parameter of coating time has been identified as the major influence on the dip-coating processes. Dip-coating techniques show great potential for large scale production and to replace the conventional spin coating and spray coating methods, as there is no limitation in the supported size and the utilization of polymers is low [10]. Overall, the methods described in the literature to obtain tubular supported carbon membranes are complex and the coating time must be increased to achieve crack-free carbon membrane, which needs several cycle and

exceptional care. Only a few researchers have reported on the advancement of membranes that are free of defects by a single step dipping-drying-carbonization [11-14]. This work focused on the incorporation of NCC as an additive towards carbon membrane superior performance by different dip-coating times of 15, 30, 45, and 60 min. Defect-free supported carbon membranes were prepared at the carbonization end temperatures of 800°C under argon environment (200 mL/min). The characterization of the material was performed using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD) analysis.

## Experimental Procedures

### Materials

Sodium Chloride (NaCl, M.W=58.44 g/mole) Sodium Sulphate anhydrous (Na<sub>2</sub>SO<sub>4</sub>, M.W=142.036 g/mole), Calcium Chloride dihydrate (CaCl<sub>2</sub>·2H<sub>2</sub>O, M.W=147.008 g/mole), and Magnesium Sulphate hepta-hydrate (MgSO<sub>4</sub>·7H<sub>2</sub>O, M.W=246.466 g/mole) salts, commercial-grade chemicals were obtained from El-Gomhoreya Company for chemicals, Egypt. A commercial polyamide TFC flat sheet brackish water (BW) membrane (model: GE Osmonics Flat Sheet membrane, Thin Film RO SG, YMSGSP4205, Sterlitech) was used for reverse osmosis desalination process.

### Methods

In this study the precursor for polymer that has been chosen was P84 co-polyimide, otherwise known as PI, acquired from Sigma Aldrich [15]. Fabricated nanocrystalline cellulose (NCC) together with additive which was newspaper has been acquired from preceding study [16]. Both polymers were desiccated at 100°C overnight to eliminate any humidity in advance of preparation of membrane. The solvent used in this study was N-Methyl-2-pyrrolidone (NMP) procured from Merck (Germany). Porous tubular support was purchased from Shanghai Gongtao Ceramics Co., Ltd. The tubular support with 3 mm in thickness and 8 cm in length was employed. The tubular support mean size of the pore is roughly 0.2 μm with 40%-50% porosity.

### Carbon membrane preparation

NMP was used to dissolve the PI by means of a mechanical stirrer and the trapped bubbles were removed through sonication during the stirring process. The tubular support was immersed into the polymeric solution at different coating periods. The supported polymeric membrane was then desiccated at 80°C for 24 h and subsequently immersed in methanol for 2 h. The reinforced polymeric membrane was desiccated at room temperature for 24 h and was proceed to heat treatment process. The coating-carbonization process was reiterated twice to make sure that the defect-free carbon membrane was attained. The carbonization process of the polymeric membranes was done to prepare the membrane through Carbolite horizontal tubular furnace at 800°C in argon environment (200 mL/min). The heating rate was uniformed at 3°C/min during the course of the experiment. Upon completion of the heating cycle, the prepared membranes' temperature was naturally lowered to ambient temperature. Unsupported carbon membranes (flat sheet) were put in order similarly for characterization.

### Membrane characterization

NMP The observation of the morphological structure of the membrane by means of scanning electron microscopy (SEM)

(TM3000, Hitachi) was performed. Prior to imaging and photographing with a potential of 10 kV, the samples were coated with gold. Fourier transform infrared spectroscopy (FTIR) (PerkinElmer, L1600107) was used to distinguish the functional groups present in the membrane samples. The FTIR spectra show the changes of the functional groups in the membranes as they are heated from room temperature to carbonization temperature. The microstructure properties of the prepared carbon membranes were analyzed using X'Pert PRO X-ray different diffractometer (XRD) from PANalytical with the diffraction angle 2θ of 10° to 50°. Ni-filtered CuKα radiation with a wavelength of λ=1.54 Å was applied in the experiments. The interplanar distance (d-spacing) of the carbon membranes were calculated using the Bragg equation as stated in previous studies [17,18].

### Pure gas permeation measurements

NMP In this study, we employed the gas permeation system to assess the carbon tubular membranes as explained in our preceding study [19]. The membrane tubular stainless-steel module that is 14 cm-long was employed to position the 8 cm carbon tubular membrane. The membranes were fitted using rubber O-ring to prevent leakages as the membranes are fitted into the module. Pure gases CH<sub>4</sub> (0.380 nm), CO<sub>2</sub> (3.30), N<sub>2</sub> (3.64), and O<sub>2</sub> (3.46) were individually supplied into the module correspondingly at 8 bar of transmembrane pressure. The selectivity (α) and permeability (P/l) of the membranes were calculated using the following equations: where P/l is the membrane permeability, Q<sub>i</sub> the gas i's volumetric rate of flow at standard temperature and pressure (cm<sup>3</sup> (STP/s), p the changes in pressure between the feed at the membrane permeation border (cmHg), A the membrane surface area (cm<sup>2</sup>), n is the quantity of fiber in module, D the outer diameter of the membrane (cm), and l the operative length of the membrane (cm). The selectivity is described as the ratio of permeation of fast gas permeation to slow gas permeation.

### Permeance, P:

$$(p/l)_i = \frac{Q_i}{\Delta p \cdot A} = \frac{Q}{\eta \pi D l \Delta P}$$

### Selectivity, α:

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{(P/l)_A}{(P/l)_B}$$

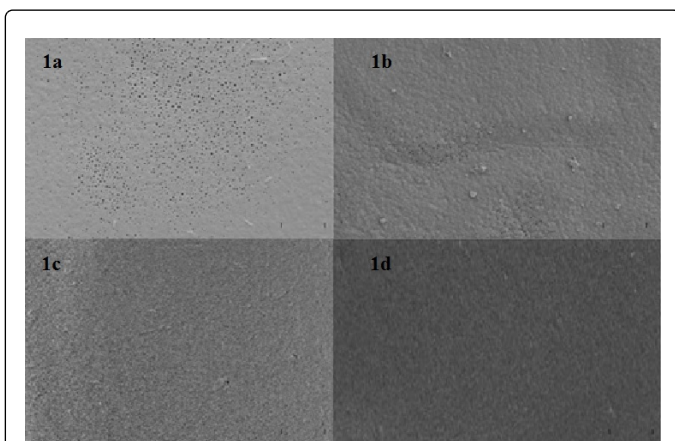
where P/l is the membrane permeance, Q<sub>i</sub> the gas i's volumetric flow rate of at standard temperature and pressure (cm<sup>3</sup> (STP/s), p the difference in pressure between the feed the permeation side of the membrane (cmHg), A the area of membrane surface (cm<sup>2</sup>), n the fiber quantity in module, D the membrane's outer diameter (cm), and l the membrane's effective length (cm). The selectivity is defined as the permeation ratio of fast gas permeation to slow gas permeation.

## Results and Discussions

### Characterization of tubular carbon membrane

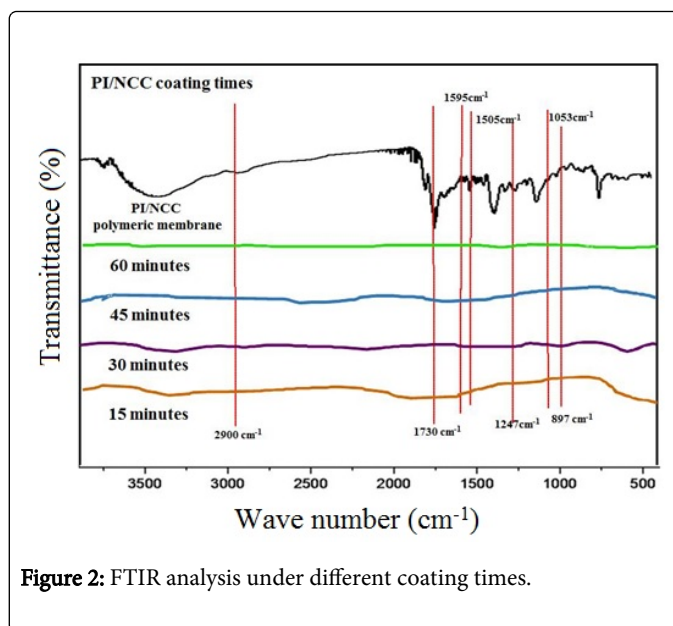
**Morphological structure analysis:** Morphological structures of the resultant carbon membranes of different coating times were observed (Figure 1). Although the same technique was applied for all the carbon membranes, different micrograph views were attained. Figure 1(a) shows the carbon membrane coated for 15 min contains a lot of empty

spots that can be seen clearly from the micrographs. Comparing with Figure 1(b), the empty spot is almost covered and the surface is smoother compared to Figure 1(a). As shown in Figures 1(c) and 1(d) a smooth surface with no presence of cracks was obtained after the coating times of 45 and 60 min were applied, respectively. However, the membrane in Figure 1(c) is smoother compared to that prepared for 60 min of coating due to the longer coating time will make the surface becomes too thick. This is due to the increased mass transfer resistance because of the deep penetration of the polymeric solution on the supporting material surface, hence reducing the gas permeation performance.



**Figure 1:** SEM microphotographs of PI/NCC-based carbon membrane prepared at different coating times; (a) 15 minutes, (b) 30 minutes, (c) 45 minutes and (d) 60 minutes.

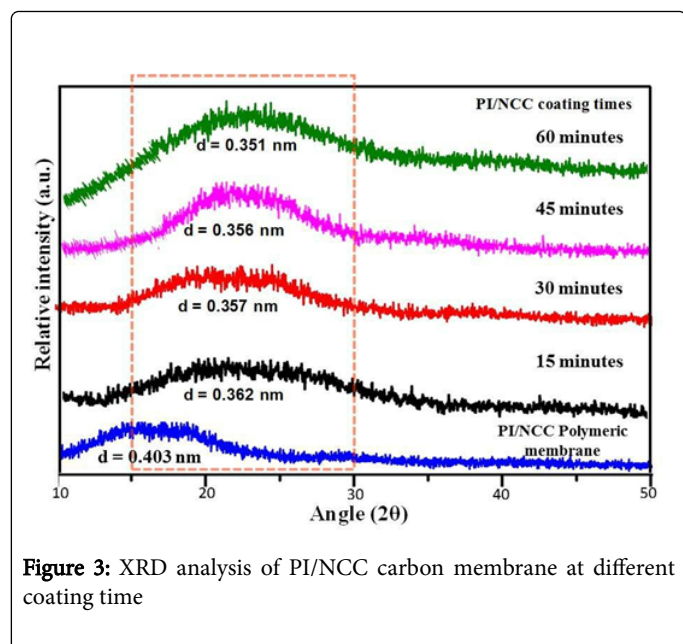
**Functional group analysis:** Figure 2 illustrates the functional group analysis for PI/NCC-based polymeric and carbon membranes prepared at different coating times. After the heat treatment, the chain of the polymeric membrane, where most of the heteroatoms were removed, left a cross-linked and stiff carbon behind [20]. This phenomenon is proven by the functional group left in the carbon membrane. Most of the atoms were dominated by C and H, along with a weak bond of O-H, as most of the O atoms from the polymer precursor were released. This situation suggests the existence of the amorphous structure in the carbon membrane [21,22]. In addition, the FTIR results exhibit that the amount of the functional groups presence in the membranes decreased with the increasing carbonization temperature, indicating that the duration of heat treatment was sufficient to break the polymer chain in the original backbones of the polymeric precursor membranes [23,24]. However, no significant difference can be seen in the FTIR spectra for all samples because all membranes were fabricated from the same polymeric material and fully converted into carbon membrane; hence all peaks were reduced. During carbonization, the bonds connecting side groups of the polymer chain to the chain itself were broken. The products of this reaction are generally small enough to be volatile [25].



**Figure 2:** FTIR analysis under different coating times.

**X-ray diffraction patterns:** The XRD spectra were stacked accordingly to show clear X-ray diffraction results without affecting the diffraction angle. XRD was employed to confirm the amorphous nature of the carbon structure. The average d-spacing between the individual layers of the carbon were calculated using the Bragg's Law. These d-spacing values were determined at the maximum of the broad peaks and only reflected the average space between the centers of the chain segments in the polymer matrix. The d-spacing value of the PI/NCC polymeric membrane was 0.403 nm. Meanwhile, for all carbon membranes with different coating times, the d-spacing values were in the range of 0.35 to 0.36 nm as illustrated in Figure 3. It is revealed that the d-spacing value decreased after the carbonization process. The microstructure of the polymeric was slightly different from that of carbon membranes due to the similar layer distance that could be considered as a divisional path for gas molecules. All samples exhibited broad peak and amorphous structures [26,27]. The values of the d-spacing for polymeric and carbon membranes were different. The value refers to the space dimension for a small gas molecule to penetrate through membrane and it is very helpful information to determine the permeability and selectivity of a membrane. It has been suggested that a decrease in d-spacing value would result in narrow pore sizes. The small reduction in the average d-spacing of the carbon membranes resulted in a very strong molecular sieving effect [28]. However, the results indicated that there is no significant difference in d-spacing value when different coating times were applied. The lowest d-spacing value was exhibited when 60 min of coating time was applied.





**Gas permeation properties:** The gas permeability performances of the carbon membrane fabricated at different coating times are presented in Table 1. It is revealed that 45 min coating times produced the best better gas permeation performance compared to other coating times. This is due to the better sealing of pinholes and the penetration through the membrane pores was complete with enough coating time [29]. For all the tested membranes, the gas permeance of the selected gases were in the order of CO<sub>2</sub>>O<sub>2</sub>>CH<sub>4</sub>>N<sub>2</sub>. The differences in gas permeation performance were determined by differences in the carbon microstructure that directly affected the transport mechanism of the membrane. Based on the results, the high selectivity at 45 min may be due to the reduction of pores than those at 60, 30, and 15 min. In fact, differences in pore characteristics result in the predominance of different transport mechanisms on the membrane [30]. Moreover, it will have enough time for improving the surface condition and repairing the cracks of a highly porous support.

Sample	Carbon membrane					
	Permeance				Selectivity	
	CH <sub>4</sub>	N <sub>2</sub>	CO <sub>2</sub>	O <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>	O <sub>2</sub> /N <sub>2</sub>
15 minutes	2.17 ± 3.22	2.62 ± 1.67	134.28 ± 2.09	20.02 ± 2.19	61.88 ± 2.33	7.64 ± 4.52
30 minutes	2.39 ± 5.61	2.77 ± 2.17	150.91 ± 3.19	22.18 ± 1.27	63.14 ± 2.18	8.00 ± 2.45
45 minutes	<b>3.13 ± 1.56</b>	<b>3.22 ± 3.21</b>	<b>213.56 ± 2.17</b>	<b>29.90 ± 2.98</b>	<b>68.23 ± 3.27</b>	<b>9.29 ± 2.54</b>
60 minutes	2.53 ± 32.19	2.86 ± 1.28	162.11 ± 3.29	24.71 ± 4.55	64.08 ± 4.56	8.64 ± 3.28

**Table 1:** Gas permeation performance of carbon membranes produced from different coating time.

## Conclusion

Tubular carbon membrane was successfully obtained by single-step dip-coating under argon atmosphere at the carbonization temperature of 800°C with the introduction of PI/NCC membrane. The factor of dip-coating time during coating method was explored in this study. The results demonstrated that the best coating time was exhibited by the carbon membrane dip-coated for 45 min. Shorter dip-coating time made it impossible for the polymeric solution to cover the defect formation on the supporting material. However, longer dip-coating time resulted in a thicker membrane layer that reduced the carbon membrane. Based on the result, the highest CO<sub>2</sub>/CH<sub>4</sub> and O<sub>2</sub>/N<sub>2</sub> selectivities of 68.23 ± 3.27 and 9.29 ± 2.54 were obtained with CO<sub>2</sub> and O<sub>2</sub> permeance of 213.56 ± 2.17 and 29.92 ± 1.44 GPU, respectively.

## Acknowledgments

The authors gratefully acknowledge the financial support from the Ministry of Higher Education and Universiti Teknologi Malaysia under Higher Institution Centre of Excellence Scheme (Project Number: R.J090301.7846.4J188), Fundamental Research Grant Scheme (Project Number: R.J130000.7846.4F846) and Research University Grant Scheme (Project Number: Q.J130000.2546.03G69). The authors would

also like to acknowledge technical and management support from Research Management Centre (RMC), Universiti Teknologi Malaysia.

## References

1. Rezakazemi M, Sadrzadeh M, Matsuura T (2018) Thermally stable polymers for advanced high-performance gas separation membranes. Prog Energy Combust Sci 66: 1-41.
2. Baker RW (2002) Future Directions of Membrane Gas Separation Technology. Ind Eng Chem Res 41: 1393-1411.
3. Castel C, Favre E (2018) Membrane separations and energy efficiency. J Membr Sci 548: 345-357.
4. Belaissaoui B, Moullec YL, Hagi H, Favre E (2014) Energy Efficiency of Oxygen Enriched Air Production Technologies: Cryogeny vs Membranes. Energy Procedia 63: 497-503.
5. Kim SJ (2018) Preparation of carbon molecular sieve membranes on low-cost alumina hollow fibers for use in C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> separation. Sep Purif Technol 194: 443-450.
6. Ahmad F (2012) Process simulation and optimal design of membrane separation system for CO<sub>2</sub> capture from natural gas. Comp Chem Eng 36: 119-128.
7. Ismail NH, Salleh WNW, Sazali N, Ismail AF (2018) Disk Supported Carbon Membrane via Spray Coating Method: Effect of Carbonization Temperature and Atmosphere. Sep Purif Technol 195: 295-304.

8. Sazali N, Salleh WNW, Nordin NAHM, Ismail AF (2015) Matrimid-based carbon tubular membrane: Effect of carbonization environment. *J Ind Eng Chem* 32: 167-171.
9. Salleh WNW, Ismail AF (2012) Effects of carbonization heating rate on CO<sub>2</sub> separation of derived carbon membranes. *Sep Purif Technol* 88: 174-183.
10. Kargari A, Shamsabadi AA, Babaheidari MB (2014) Influence of coating conditions on the H<sub>2</sub> separation performance from H<sub>2</sub>/CH<sub>4</sub> gas mixtures by the PDMS/PEI composite membrane. *Int J Hydrogen Energy* 39: 6588-6597.
11. Ismail NH, Salleh WNW, Sazali N, Ismail AF (2018) Development and characterization of disk supported carbon membrane prepared by one-step coating-carbonization cycle. *J Ind Eng Chem* 57: 313-321.
12. Wang C, Hu X, Yu J, Wei L, Huang Y (2014) Intermediate gel coating on macroporous Al<sub>2</sub>O<sub>3</sub> substrate for fabrication of thin carbon membranes. *Ceram Int* 40: 10367-10373.
13. Teixeira M, Rodrigues SC, Campo M, Tanaka PDA, Tanco LMA, et al. (2014) Boehmite-phenolic resin carbon molecular sieve membranes - Permeation and adsorption studies. *Chem Eng Res Des* 92: 2668-2680.
14. Rodrigues SC, Whitley R, Mendes A (2014) Preparation and characterization of carbon molecular sieve membranes based on resorcinol-formaldehyde resin. *J Membr Sci* 459: 207-216.
15. Shao L, Chung TS, Wensley G, Goh SH, Pramoda KP (2004) Casting solvent effects on morphologies, gas transport properties of a novel 6FDA/PMDA-TMMDA copolyimide membrane and its derived carbon membranes. *J Membr Sci* 244: 77-87.
16. Mohamed MA, Salleh WNW, Jaafar J, Asri SEAM, Ismail AF (2015) Physicochemical properties of "green" nanocrystalline cellulose isolated from recycled newspaper. *RSC Adv* 5: 29842-29849.
17. Ismail NH, Salleh WNW, Sazali N, Ismail AF, Yusof N, et al. (2018) Disk supported carbon membrane via spray coating method: Effect of carbonization temperature and atmosphere. *Sep Purif Technol* 195: 295-304
18. Sazali N, Salleh WNW, Ismail AF, Nordin NAHM, Ismail NH, et al. (2018) Incorporation of thermally labile additives in carbon membrane development for superior gas permeation performance. *J Nat Gas Sci Eng* 49: 376-384.
19. Sazali N, Salleh WNW, Md Nordin NAH, Harun Z, Ismail AF (2015) Matrimid-based carbon tubular membranes: The effect of the polymer composition. *J Appl Polym Sci* 132: 42394.
20. Saufi SM, Ismail AF (2004) Fabrication of carbon membranes for gas separation- A review *Carbon*. 42: 241-259.
21. Zhang C, Geng Z, Ma J (2013) Self-assembly synthesis of ordered mesoporous carbon thin film by a dip-coating technique. *Microporous and Mesoporous Mat* 170: 287-292.
22. Teixeira M, Campo MC, Tanaka PDA, Tanco LMA, Magen C, et al. (2011) Composite phenolic resin-based carbon molecular sieve membranes for gas separation. *Carbon* 49: 4348-4358.
23. Zhao L, Riensche E, Menzer R, Blum L, Stolten D (2008) A parametric study of CO<sub>2</sub>/N<sub>2</sub> gas separation membrane processes for post-combustion capture. *J Membr Sci* 1: 284-294.
24. Zhao S, Wang Z, Wei X, Tian X, Wang J, et al. (2011) Comparison study of the effect of PVP and PANI nanofibers additives on membrane formation mechanism, structure and performance. *J Membr Sci* 385-386: 110-122.
25. Soroko I, Makowski M, Spill F, Livingston A (2011) The effect of membrane formation parameters on performance of polyimide membranes for organic solvent nanofiltration (OSN). Part B: Analysis of evaporation step and the role of a co-solvent. *J Membr Sci* 381: 163-171
26. Lua AC, Su J (2006) Effects of carbonisation on pore evolution and gas permeation properties of carbon membranes from Kapton® polyimide. *Carbon* 44: 2964-2972.
27. Haider S (2018) CO<sub>2</sub> separation with carbon membranes in high pressure and elevated temperature applications. *Sep Purif Technol* 190: 177-189.
28. Salinas O, Ma X, Litwiller E, Pinnau I (2016) High-performance carbon molecular sieve membranes for ethylene/ethane separation derived from an intrinsically microporous polyimide. *J Membr Sci* 500: 115-123.
29. Wu T, Diaz MC, Zheng Y, Zhou R, Funke HH, et al. (2015) Influence of propane on CO<sub>2</sub>/CH<sub>4</sub> and N<sub>2</sub>/CH<sub>4</sub> separations in CHA zeolite membranes. *J Membr Sci* 473: 201-209.
30. Ma QS, Gao AJ, Tong YJ, Zhang ZG (2016) The densification mechanism of polyacrylonitrile carbon fibers during carbonization. *New Carbon Mater* 31: 550-554.