

ADVANCED IN CARBON MEMBRANE BY RELATING TO COATING-CARBONIZATION-CYCLES FOR OXYGEN PERFORMANCE

N Sazali^{1,2*}, W N W Salleh^{1,2*}, N H Ismail^{1,2}, K Kumaran^{1,2}, M H D Othman³, and Z Harun⁴

¹Centre of Excellence for Advanced Research in Fluid Flow (CARIFF), Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia.

²Faculty of Mechanical Engineering, Universiti Malaysia Pahang, 26600 Pekan, Pahang, Malaysia.

³Advanced Membrane Technology Research Centre (AMTEC), School of Chemical and Energy, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor Darul Takzim, Malaysia.

⁴Advanced Manufacturing and Materials Centre (AMMC), Faculty of Mechanical and Manufacturing Engineering, University Tun Hussein Onn Malaysia, 86400 Parit Raja, Johor, Malaysia.

Abstract. This work discusses the creation and assessment of rounded carbon membrane arranged from P84 co-polyimide mixes with Nanocrystalline cellulose (NCC). In light of earlier examinations, it defined the theory that rounded carbon membrane execution can be controlled by controlling the carbonization parameters. The focal point of this investigation is to acquaint compelling dip-coating strategies with deliver superior rounded carbon membrane. In light of the result of this examination, the coating carbonization cycle (1, 2, 3, and multiple times) has been distinguished as real effect on the separation productivity. Gas separation performance and transport instrument of the carbon membranes were enough assessed by single gas permeation of O₂, and N₂. In this exploration, use of 2-cycles of coating carbonization has brought about carbon membrane with the most elevated selectivity and O₂ penetrability which are 9.29±2.54 and 29.92±1.44 GPU, individually.

1. Introduction

Membrane innovation has pulled in extensive consideration in the gas separation enterprises, for example, hydrogen re-coating, air separation, olefin/paraffin separation, CO₂ capture, nature gas drying out, and oxygen separations [1-3]. Oxygen generation has a genuinely high effect on a few enterprises as it is one of the real reagents in compound procedures. The most well-known approach to get high virtue oxygen is by cryogenic refining of air [4]. Be that as it may, this procedure necessities high energy and substantial plant estimate. One of the options is by using the gas-separation carbon membrane, which permits the particular pervasion of the oxygen by dissemination through the carbon cross section. Carbon membrane innovation is at present being quickly produced for these reasons because of the expanding requests on inorganic membrane which showed extraordinary thermal and compound resistance [5-7]. The exceptionally specific atomic sieving instrument of carbon membrane that can even recognize gases with relatively comparative dynamic sub-atomic size is especially helpful to accomplish brilliant separation [8, 9]. This empowers membrane procedures to be more energy productive and, along these lines, more sparing than different gas separation techniques. Extensive measure of research is being attempted to decide new materials and manufacture techniques for carbon membrane. Rounded supported carbon membranes are best as they can withstand higher temperature and weight, anyway they are more inclined to abandon than unsupported carbon membrane because of the similarity of the carbon membrane and the supporting material [10-12].

Extraordinary compared to other approaches to enhance the oxygen separation ability of carbon membrane without limited by material science is through the abuse of membrane geometry and microstructures. In this investigation, the above was accomplished by means of the presentation of PI/NCC. Permeable cylindrical alumina ceramic was dip coating with PI/NCC arrangement and afterward carbonized to get carbon membrane in a reproducible way. This is the primary examination detailing the utilization of NCC to accomplish high performing carbon membrane through a basic and adaptable dip-coating system [2, 12-14]. Cellulose is a characteristic direct polymer of b-(1/4)- D-glucopyranose, which has different extraordinary highlights, for example, nontoxic, great biocompatibility, biodegradable, high mechanical quality and solid adsorption conduct [15-17]. By



utilizing cellulose as an added substance, the exceptional local properties of cellulose are promptly acquainted with the mixing materials [18, 19]. To maintain a strategic distance from negative, self-get together of cellulose began from the surface hydroxyl gatherings, hydrophobization of cellulose is fundamental. NCC is a standout amongst the most generally utilized hydrophobized cellulose got from thin cellulose [16]. The whole incorporation process included non-lethal materials and is free from peril of airborne particulate. When arranged, the carbon membranes are stable and require no extraordinary taking care of or capacity.

A perfect help ought to have a deformity free surface with low unpleasantness, high porosity and little pore size to stay away from arrangement of breaks and pinholes absconds amid membrane manufacture. To this end, the decision of the upheld material assumes a critical job and backings with little imperfections are generally utilized in earlier examinations to guarantee best separation results. However, this regularly keep down the selection of upheld carbon membrane by industry because of the staggering expense joined by this best quality help as detailed by past examination [20, 21]. Placing this at the top of the priority list, this examination is persuaded to create carbon membrane utilizing minimal effort supported materials. Tubular macroporous Al_2O_3 supported are chosen because of its high physical quality, high gas diffusivity, high temperature resistance and above all its generally reasonable expense for large scale manufacturing [22]. This work demonstrated that through a straightforward multi-cycle coating carbonization approach, the issue of the imperfection of carbon membrane arranged over the surface the minimal effort support could be attainably survived.

Dip-coating strategy has been generally used in different mechanical procedures because of its effortlessness and straight-imposition. This technique was actualized in saving a thin membrane arrangement onto upheld polymeric membrane for end purposes including controlling refraction record, grease, polarization and assurance. As per Sazali et al. (2015) the standards of dip-coating incorporate the wetting of the upheld with arrangement [23]. In this technique, the supported was submerged into the answer for some time so as to ensure the upheld is totally wetted before taking it out from the arrangement shower. To this far, the upheld utilized can be either a fired, a chamber, a plate or an unpredictable fit as a fiddle. Also, one of the principles includes that separate dip-coating system is the broad variety of the geometry upheld. As per Wang et al., (2014), the uses of dip-coating techniques are because of the straightforward and practical strategy contrasting with others accessible coating strategies[24]. There are various perspectives should be considered in deciding the thickness of the membrane including dissipation rate of the dissolvable, gravitational increasing speed, physical properties of the liquid, surface pressure, add up to dip cycles and withdrawal speed [25]. To the best of our insight, just a predetermined number of articles have been distributed on coating conditions particularly for dip-coating strategy. In this investigation, the impact of coating carbonization-cycles was considered. Along these lines, the focal point of this examination think about is to give better comprehension on the significant parameters in dip-coating procedures to control the morphology of the cylindrical upheld carbon membrane. The coating carbonization cycles of resultant PI/NCC cylindrical carbon membrane were rehashed a few times and the predominant execution will be accomplished all through this investigation. Subsequently, this investigation ought to give better comprehension with respect to the parameter of coating carbonization-cycles strategy.

2. Experimental procedures

2.1 Materials

Commercially available P84 co-polyimide procured from Sigma Aldrich [26: 58698-66-1] was chosen as a precursor for the fabrication of carbon-based membranes. The measured density of P84 was 1.31g/cm^3 . Additionally, the glass transition temperature (T_g) of this polymer was 315°C [27]. N-Methyl-2-Pyrrolidone was purchased from Merck (Germany) and employed as a solvent in the preparation of the dope solution. Nanocrystalline cellulose (NCC) obtained from newspaper was used as an additive by applying the same method from previous study [28]. Porous tubular ceramic, TiO_2 (4.5-5.5mm), with a coating of ZrO_2 (2-3nm) on the inner surface was purchased from Shanghai Gongtao Ceramics Co., Ltd. The dimensions of the porous tubular ceramic were 8cm in length, 13mm for the outer diameter and 10mm for the inner diameter. The porosity of the support was 40-50% with an average pore size of $0.2\mu\text{m}$. The supports were cleaned with distilled water in a sonication bath for 30

min and then dried in air. All chemicals were utilized without further modification.

2.2 Carbon Membrane Preparation

The supported carbon membranes were prepared via dip-coating of the tubular support into a dope solution consisting of 15wt.% of P-84 in an NMP was prepared under constant stirring at 80°C. 7wt% of NCC was gradually added to the solution and continues stirring until homogeneous solution was obtained to form a uniform membrane of polymeric precursor on the external surface of the tubular support. The dope solution was stirred for 24 hours, then sonicated for degassing purposes. The ceramic support was dipped into the dope solution for 45 minutes. The membrane was then dried in the oven at 80°C for 24 hours. Next, the membranes were immersed in methanol for 2 hours, followed by drying at 100°C for 24 hours to allow slow removal of the solvent. The dip-coating-carbonization cycles were repeated for 1, 2, 3 and 4 times. The dried supported precursor membranes were then placed inside a Carbolite horizontal tubular furnace for stabilization and carbonization processes. After completing each heating cycle, the prepared membranes were cooled naturally to room temperature. Carbon membrane without supported also prepared using similar procedure for characterization purposes.

2.3 Gas Permeation Test

There are two parameters involved in the evaluation of membrane performance such as the membrane selectivity and also the permeance of the membrane. In example, in-house gas permeation system has been utilized in order to measure the pure gas permeation rate of the carbon tubular supported membranes [15]. This system was equipped with permeation cell, soap bubble meter, pressure regulator, flexible hose and valve. Carbon tubular membranes with 8cm length were placed inside the 14cm stainless-steel tubular module while the membranes were fitted with rubber O-rings. This is to make sure there is no leaking when the membrane housed into the module.

At 8 bars of trans-membrane pressure, pure gas of N₂(0.364nm) and O₂(0.346nm) have been fed into the module in order to determine the selectivity, α and permeance, P/l (GPU) of the membranes and were calculated by using the equations as follow:

Permeance, P :

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

Selectivity, α :

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{(P/l)_A}{(P/l)_B} \quad (2)$$

where P/l is the permeance of the membrane, Q_i is the volumetric flow rate of gas i at standard temperature and pressure (cm³ (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 (cm²), n is the number of fibers in the module, D is an outer diameter of the membrane (cm), and l is an effective length of the membrane (cm). The selectivity defined as the permeation ratio of fast gas permeation to slow gas permeation.

3. Results and discussion

3.1 Gas permeation results

The correct coating carbonization cycle numbers created carbon membranes with high solidness which have the normal deviations under 10% and additionally enhancing the membrane selectivity and also membrane porousness. It is trusted the Tg of the polymer was lessened because of the interfacial pressure happened between the polymer and the help of the supported membrane and in addition restricting the edifices' development [17, 29]. After carbonization, the varieties in the resultant carbon microstructure were influenced because of the varieties in the development of homogenous polymer surfaces. The porousness of two pure gases with various molecular sizes; O₂ (3.46), and N₂ (3.64) through the

manufactured carbon membranes created from various coating carbonization-cycles were estimated at feed weight of 8 bars and was exhibited in **Table 1**. It tends to be seen that the gas permeance results acquired for the resultant carbon membrane pursued the request of their dynamic width measure, which is O₂ and pursued by N₂ [12, 30]. As arranged in **Table 1**, the selectivity of the most noteworthy selectivity accomplished when multiple times coating carbonization-cycles was connected. As notice, O₂/N₂ selectivity was 9.29±2.54 with permeation of O₂ was 29.90±2.98 and N₂ permeation was 3.22±3.21, separately.

The gases permeance came to just about a steady an incentive after two coatings-carbonization cycles. Expanding the quantities of coating membrane at multiple times coating carbonization cycles, unrivaled gas separation performance was accomplished because of obstructing the surface pinholes of the upheld by PI/NCC membrane came to are about zero. In the dip-coating strategy, selectivity achieved the most noteworthy incentive after two coatings however begin to diminish when expansion of coating cycles. This wonder is expected, the carbon membrane thickness of the readied carbon membrane increments and have expand on the permeance and also the selectivity. At the point when expansion of coating cycles up to 3 and multiple times, the selectivity was drop with 8.49±1.45 and 8.25±3.41, individually. Be that as it may, as announced by Liu and associates [31], four consecutive dip-coating as reasonable for coating of their created membrane when he utilized 28 wt% P84/NMP dope answers for manufacture empty filaments membrane for pervaporation lack of hydration of isopropanol (IPA) . Expanding the quantity of coatings-carbonization to multiple times result in around no adjustment in permeance for dip-coating and membrane throwing systems. Also, the consequences of consecutive coating demonstrated that selectivity in the adjustment of dip-coating conditions marginally impact on the execution of the readied membrane. When all is said in done the membrane selectivity can be enhanced by better fixing of the membrane surface amid subsequence coating [25]. The redundancy of coating cycle results in better fixing of the surface deformities and diminishes unselective permeance from the surface pinholes.

Table 1: Gas separation performance of carbon membranes produced from different coating-carbonization cycles

Carbon membrane			
Sample (CM-PI/NCC)	Permeance (GPU)		Selectivity
	O ₂	N ₂	O ₂ /N ₂
1 cycle	28.03±5.17	3.09±5.82	9.07±2.86
2 cycles	29.90±2.98	3.22±3.21	9.29±2.54
3 cycles	25.21±3.98	2.97±4.37	8.49±1.45
4 cycles	21.87±4.51	2.65±4.25	8.25±3.41

As organized in **Table 1**, the selectivity of the readied membrane by multiple times carbonization-coating cycles was higher than other coating cycles because of 2 coating carbonization-cycles will have better infiltration of PI/NCC arrangement into membrane surface pinholes; consequently, coming about high O₂/N₂ selectivity. In these strategies, as the quantity of rehashed coatings expanded, the revealed pores or deformities on the membrane surface were additionally stopped or fixed and better execution was accomplished for these techniques [13]. In any case, in spite of their detectable deformity free trademark, these membranes are conceivably to have another potential imperfection including the nearness of the little pinholes or minuscule flaws that were framed amid the creation of membrane that may be caused by encompassing residue particles. Because of that, underlying pure gas tests have been led to test the permeance of the membrane and it uncoating these potential imperfections can influence the membrane execution. In this way, it was recommended the creation of the membranes should be done under right weight which is 8 bars. This procedure was prescribed to be create in the smoke hood for cleanness and cleanliness purposes to maintain a strategic distance from these particles sullied the upheld membrane amid dip-coating process [32, 33].

4. Conclusion

From this examination, the impact of coating conditions on PI/NCC carbon membrane was explored. In light of the outcomes, it very well may be inferred that as the coating carbonization cycles were expanded from 1 to 2 cycles, the outcomes acquired demonstrated that the pore structure of the carbon membrane were improved because of mixes decay amid carbonization.

Acknowledgments

(a) The authors would like to acknowledge technical and management support from Research Management Centre (RMC), Universiti Teknologi Malaysia. Authors would also like to extend their gratitude to Ministry of Higher Education Malaysia and Universiti Malaysia Pahang (UMP) with grant number RDU180399 and RDU19115.

(b) The authors would also 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. J090301.7846.4J186).

References

- [1] Lagorsse S, Magalhães FD, Mendes A. 2008. *J. Membr. Sci.*, **310** 494-502.
- [2] Sazali N, Salleh WNW, Ismail AF, Nordin NAHM, Ismail NH, Mohamed MA., 2018. *J. Nat. Gas Sci. Eng.* **49** 376-384.
- [3] Ismail NH, Salleh WNW, Sazali N, Ismail AF, Yusof N, Aziz F. 2018. *Sep.Purif. Technol.* **195** 295-304.
- [4] Hashim SS, Mohamed AR, Bhatia S. 2011. *Renew. Sustain. Energy Rev.* **15** 1284-1293.
- [5] Wang G, Liu M, Du J, Liu L, Yu Y, Sha J. 2018. *App. Surf. Sci.*, **435** 424-431.
- [6] Haider S, Lindbråthen A, Lie JA, Andersen ICT, Hägg M-B. 2018. *Sep.Purif. Technol.* **190** 177-189.
- [7] Haider S, Lindbråthen A, Lie JA, Andersen ICT, Hägg M-B. 2016. *Green Energy & Environment* **3** 222-234
- [8] Yang Z, Ma X-H, Tang CY. 2018. *Desalination.* **434** 37-59.
- [9] Kamath MG, Fu S, Itta AK, Qiu W, Liu G, Swaidan R. 2018. *J. Membr. Sci.* **546** 197-205.
- [10] Sazali N, Salleh WNW, Ismail AF, Kadirgama K, Othman FEC. 2018. *Solid State Phenomena.* **280** 308-311.
- [11] Sazali N, Salleh WNW, Ismail AF, Wong KC, Iwamoto Y. 2018. *J. App. Poly. Sci.* In press.
- [12] Sazali N, Salleh WNW, Ismail AF, Kadirgama K, Othman FEC, Ismail NH. 2018. *Int. J. Hyd. Energy.* In press.
- [13] Sazali N, Salleh WNW, Ismail AF, Ismail NH, Yusof N, Aziz F. 2018. *Int. J. Hyd. Energy.* In press.
- [14] Ogundare SA, Moodley V, van Zyl WE. 2017. *Carbohydrate poly.* **175** 273-281.
- [15] Sazali N, Salleh WNW, Ismail AF. 2017. *Int. J. Hyd. Energy* **42** 9952-9957.
- [16] Sun Y, Liu P, Liu Z. 2016. *Carbohydrate poly.* **142** 177-182.
- [17] Mohamed MA, Salleh WNW, Jaafar J, Asri SEAM, Ismail AF. 2015. *RSC Adv.* **5** 29842-29849.
- [18] Kaboorani A, Riedl B, Blanchet P, Fellin M, Hosseinaei O, Wang S. 2012. *Euro. Poly. J.* **48** 1829-1837.
- [19] Bai H, Wang X, Zhou Y, Zhang L. 2012. *Prog. Nat. Sci.: Mater. Inter.* **22** 250-257.
- [20] Han Y, Ho WSW. 2018. *Chi. J. Chem. Eng.*, In press.
- [21] Lee P-S, Kim D, Nam S-E, Bhave RR. 2016. *Micro. Meso. Mater.* **224** 332-338.
- [22] Zhang B, Li L, Wang C, Pang J, Zhang S, Jian X. 2015. *RSC Advances.* **5** 60345-60353.
- [23] Sazali N, Salleh WNW, Nordin NAHM, Ismail AF. 2015. *J. Ind. Eng. Chem.* **32** 167-171.
- [24] Wang C, Hu X, Yu J, Wei L, Huang Y. 2014. *Ceram. Inter.* **40** 10367-10373.
- [25] Zhang C, Geng Z, Ma J. 2013. *Micro. Meso. Mater.* **170** 287-292.
- [26] Fernández-Barquín A, Casado-Coterillo C, Palomino M, Valencia S, Irabien A. 2016. *Sep. Purif. Technol.* **157** 102-111.
- [27] Lua AC, Shen Y. 2013. *J. Membr. Sci.* **429** 155-167.
- [28] Mohamed MA, Salleh WNW, Jaafar J, Asri SEAM, Ismail AF. 2015. *RSC Advances.* **5** 29842-29849.

- [29] Appiah-Ntiamoah R, Kim H, Gadisa BT, Baye AF, Abebe MW, Kostjuk SV. 2018. *Mater. Chem. Phys.* **219** 468-477.
- [30] Sazali N, Salleh WNW, Ismail AF, Ismail NH, Aziz F, Yusof N. *IOP Conf. Series: Mater. Sci. Eng.* **342** 012027.
- [31] Liu J, Hou X, Park HB, Lin H. 2016. *Chem. A Euro. J.* **22** 15980-15990.
- [32] Ismail NH, Salleh WNW, Sazali N, Ismail AF. 2017. *Sep. Purif. Technol.*, **52** 2137-2149.
- [33] Ismail NH, Salleh WNW, Sazali N, Ismail AF. 2015. *Chem. Eng. Trans.*, **45** 1465-1470.