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## PI/NCC Carbon Membrane: Effect of Heating Rates Towards Oxygen Separation Performance

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# PI/NCC Carbon Membrane: Effect of Heating Rates Towards Oxygen Separation Performance

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**Abstract.** Separation of oxygen and nitrogen gas was considered by utilizing tubular carbon membrane (TCMs) arranged from polymeric precursors. A coating methodology called dip coating strategy was utilized to manufacture the TCMs utilizing P84 co-polyimide and Nanocrystalline cellulose (NCC) as the primary precursor and added additives individually. Past examination has demonstrated that properties of PI/NCC can be adjusted by changing the carbonization parameter i.e. time, temperature and condition. The statement of PI/NCC on the tubular supported help was utilized to deliver an assortment of TCMs for gas separation by basic carbonization process. In this examination, the heating rates was controlled to watch the impact of TCMs on gas permeation by setting the heat rates at 1, 3, 5, and 7 °C/min. It was demonstrating that the gas separation performance was profoundly influenced by the carbonization heating rates amid the manufacture of PI/NCC-based carbon membrane. Likewise, heat rates at (3 °C/min) demonstrates an enhancement in the membrane selectivity and separation performance.

## 1. Introduction

The oxygen-advanced air is fundamentally required in parts, for example, medicinal, synthetic and mechanical. A case of the utilization of oxygen-advanced air in the business is for improving ignitions and to better the air course in sewerage treatment plant [1]. The inside ignition motor will profit by utilizing advanced oxygen to help ignition as it can enhance fuel consuming productivity. Purging oxygen in the space could likewise enhance the indoor air quality [2]. Oxygen-improved air is routinely created by either cryogenic refining or weight swing adsorption (PSA). High virtue oxygen with in excess of 100 tons of day by day generation is attainable by the cryogenic refining while with PSA, the medium creation limit of 20 – 100 tons can be delivered day by day [1, 3]. Indeed, even with the way that this innovation has developed since it has been utilized in the business for the greater part decades, still, its high vitality use and exorbitant activity fill in as a disadvantage from this procedure.

Membrane innovation is viewed as a promising substitute for gas filtration innovation at a little creation limit of 10 to 25 tons for each day at 25 – 40% virtue [4-6]. Nonetheless, at high generation volume, there is still no membrane innovation could provide food the requirements for vast scale creation. membrane utilized for this reason ought to likewise support great mechanical strength under enthusiastic long-haul activity in sets with unrivalled permeability and selectivity performance [7-10]. Membrane technology progression, particularly for gas separation purposes draws in consideration for its favourable circumstances over other separation techniques, for example, absorption and adsorption. This innovation is viewed as practical as membrane activity is vitality escalated, easy to work at a lower add up to cost and the procedure can undoubtedly be versatile without the requirements for thorough recovery technique [11-13]. Synthetic membranes can be made utilizing either earthenware or polymer materials where the determination of beginning material would influence the virtue of the separation. For a large portion of 10 years, polymeric materials stay positive because of its financial esteem and separation performance. It is bound to show signs of improvement separation utilizing this material for their capacity to offer high porousness and selectivity in accordance with their high additives and mechanical quality [14, 15].



To accomplish high separations, a couple of ordinary techniques have been utilized mechanically, for example, weight swing adsorption, cryogenic refining and amine adsorption. Shockingly, these strategies confronting difficulties to limit the negative effects on nature, generally costly and required high vitality loadings to run [16]. Thus, using membranes could counter the impediments of the conventional strategies. Membranes act to give a physical hindrance between various part either in fluid stages, gas stages or among fluid and gas stage. The customized semipermeable structures could control the permeation of particles at various rates relying upon the span of the pores and main thrust engaged with the task [17, 18]. Early investigations found that carbon membranes are especially appealing for their capacities for high selectivity and permeability [8, 19]. Contrasted with its polymeric partners, carbon-based membranes likewise indicated prevalent preferences as far as its physical protection from defilement, and ageing with a deferred plasticization process [11]. Separation productivity for gases with comparable atomic sizes like  $\text{CO}_2/\text{CH}_4$ ,  $\text{O}_2/\text{N}_2$  and  $\text{CO}_2/\text{N}_2$  additionally higher for carbon membranes because of their high pore volume [20-23]. Additionally, the cooling procedure after carbonization happens can be dispensed with in the manufacture arrange which add to the bringing down handling cost [24, 25]. The introduction separation of aromatic microdomains makes ultra-smaller scale porosity structure with a glasslike matrix, would expand the free volume. Moreover, the created micropores were regularly in the slit-shaped geometry, and the pores opening size was relatively like the gas atom measurement [26, 27].

Numerous investigations have demonstrated that carbonization conditions influence the gas permeation performance of carbon membranes. The vehicle system of gas atoms is exceedingly identified with the pore structures of the membranes. As separation depends on sub-atomic strainer impacts, the way structures should be custom fitted cautiously, and this should be possible by controlling the carbonization heating rates [7, 10, 13, 28]. The heating rates could decide the rates of carbonization advancement dependent on the vanishing of the unstable segments from the polymeric materials. In spite of the fact that the detailed typical scope of heating rates is inside a scope of 1 – 13 °C/min, the rates are as yet one of a kind to the beginning polymeric materials utilized. Centeno et al. (2004) [29] ) explored the creation of carbon membrane at an alternate heating rates. Phenolic gum was utilized as the beginning material with carbonization temperature up to 700 °C. The heating rates at 10 °C/min was accounted for to deliver the littlest pore measure which would profit the separation with atomic sifter impacts. The separation performance was dissected utilizing perpetual gas sets of ( $\text{O}_2/\text{N}_2 = 5$ ,  $\text{CO}_2/\text{N}_2 = 27$ , and  $\text{CO}_2/\text{CH}_4 = 23$ ) and olefin/paraffin ( $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6 = 3$  and  $\text{C}_3\text{H}_6/\text{C}_3\text{H}_8 = 6$ ). In an alternate report directed by Salleh and Ismail, they announced 1–5 °C/min as the ideal heating rates on account of PEI/PVP-based carbon empty fiber membranes. At the low heating rates,  $\text{CO}_2/\text{CH}_4$  and  $\text{CO}_2/\text{N}_2$  selectivity were expanded with diminished ( $\text{N}_2$ ,  $\text{CH}_4$ ,  $\text{CO}_2$ ) permeation rates, lamentably [10]. The carbon membranes structure and the gas permeation transport were influenced by the heating rates, and 3 °C/min was accounted for having the most elevated  $\text{CO}_2/\text{CH}_4$  and  $\text{CO}_2/\text{N}_2$  separation for PEI/PVP carbon-based membranes. With the primary goal to control the carbonization heating rates, any impacts of this parameter to the  $\text{O}_2$  advancement was broke down. The heating rates of 1 – 7 °C/min and carbonization at 800 °C under Argon condition were chosen. The outcomes from gas permeation properties of TCM at various heating rates will give knowledge into general rules of process parameters should be considered for  $\text{O}_2$  separation purposes.

## 2. Experimental section

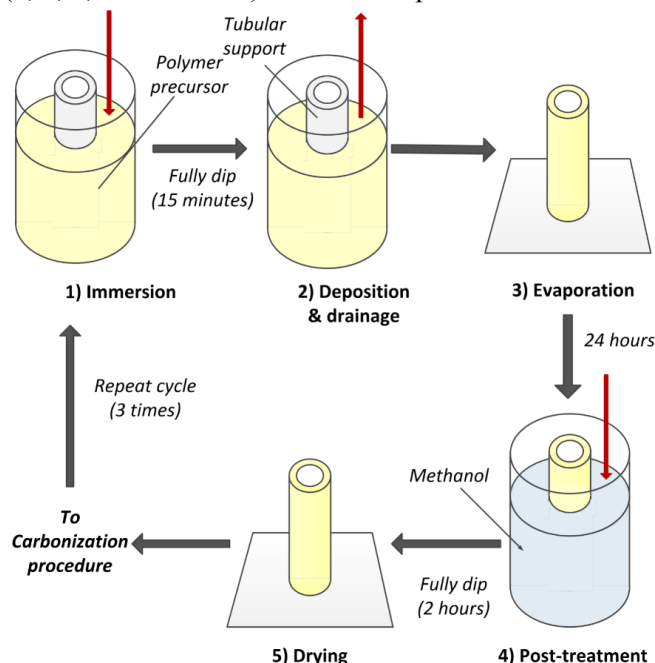
### 2.1 Materials

P84 co-polyimide was bought from Sigma Aldrich while the polymer solvent, N-methyl-2-pyrrolidone (NMP) was obtained from Merck. All chemicals were used as purchased. A nanocrystalline cellulose (NCC) was initially prepared in our previous study [5]. A porous  $\text{TiO}_2$  tubular support (dimension: 8 cm x 3 cm; overall pore size: 0.2  $\mu\text{m}$ ; porosity: 40-50%) has been procured from Shanghai Gongtao Ceramic Co., Ltd.

### 2.2 Preparation of tubular carbon membrane

The experimental procedures were based on the study by Sazali et al. (2017)[5]. A dope solution was

prepared by dissolving 15 wt% of P-84 in NMP at the temperature of 80°C under a constant stirring while 7 wt% of NCC was gradually added. Afterwards, ultrasonication was performed on the dope solution for a few hours to discard the presence of air bubble. Subsequently, the supported membrane was prepared via dip-coating method as tabulated in **Figure 1**. This technique is popularly known as a simple approach to make a very thin layer at the top of the membrane. Firstly, the tubular support was dip-coated into the prepared dope solution for 45 minutes. Next, it was later immersed in methanol for 2 hours and finally, the dip-coated membrane was dried in an oven at 100°C overnight to discard the remaining solvent. Carbon membranes emerged after the supported polymeric membrane undergoes carbonization process in a carbolite horizontal tubular furnace under the flow of argon gas (200 ml/min) with different heating rates (1, 3, 5, and 7°C/min) until the temperature stabilized at 800°C.



**Figure 1:** Dip-coating method

### 2.3 Pure gas permeation measurements

The gas permeation system used for measuring the permeation performance of the prepared membranes can be found elsewhere [5, 8]. A 14 cm-length stainless-steel (tubular in shape) was used as membrane module housing. Rubbery O-ring was carefully placed on the module to prevent leakage. O<sub>2</sub> (0.280 nm) and pure N<sub>2</sub> (0.364 nm) have been channelled separately into the module, at a trans-membrane pressure of 8 bars. Both membrane permeation, P/I (GPU) and selectivity,  $\alpha$  were calculated using the respective equations as shown in our previous study [5].

## 3. Results and discussion

### 3.1 Gas Permeation Measurements

In some report, the heating rates value during the carbonization process could affect the microstructure of the carbon membranes since volatile compound evolution rates is controlled by this parameter [30]. **Table 1** shows that the gas separation performance on the PI/NCC carbon membranes were affected by the heating rates parameter.

**Table 1:** Gas separation results for PI/NCC carbon membranes carbonized at a different heating rates ( $n = 3$ , error analysis =  $\pm 10\%$ )

Sample	Carbon membrane		
	Permeance (GPU)		Selectivity
	N <sub>2</sub>	O <sub>2</sub>	O <sub>2</sub> /N <sub>2</sub>
PI/NCC 1°C/min	3.08±3.65	22.67±1.84	7.36±2.11
PI/NCC 3°C/min	3.22±3.21	29.91±2.98	9.29±2.54
PI/NCC 5°C/min	3.18±4.16	25.53±3.51	8.03±2.43
PI/NCC 7°C/min	3.11±3.98	24.48±2.44	7.87±3.19

In light of **Table 1**, the gas permeance of N<sub>2</sub> and O<sub>2</sub> dropped when the heat rates of 5 and 7°C/min were connected. This has happened because of the limited pore estimate dispersion and the carbon structure densification. Prior, numerous works expressed that the expansion in carbonization heat rates may make littler measured pores which constrains the level of gas revolution opportunity [31, 32]. At higher heat rates, the quick evacuation of unstable mixes in the polymer amid the carbonization prompts the development of littler pore estimate. Be that as it may, past some point, any further increment of the heat rates may make pinholes and tiny break or imperfection on the film surface. The carbon film arranged at the most reduced heat rates encountered a diminished gas permeance. Contrasted with different membranes, this film indicates low separation esteem. Notwithstanding that, the esteem acquired is worthy as it is still keeping pace with past examinations on hydrogen separation [33]. The carbon membrane at that point accomplished the most noteworthy O<sub>2</sub>/N<sub>2</sub> separation at the ideal carbonization heat rates of 3°C/min. It was trusted that the more drawn out contact time between the membrane and the inert gas has consequently limited the pore measure circulation. Nonetheless, the film O<sub>2</sub>/N<sub>2</sub> selectivity began to diminish as the carbonization heat rates was expanded to 5 and 7°C/min. In our past examination, we have referenced that the pore measure appropriation is likewise influenced by various polymer precursor types, contingent upon their compound synthesis [34,35].

#### 4. Conclusion

With regards to the findings, it was proven that tubular carbon membrane prepared by blending NCC with PI improved the H<sub>2</sub>/N<sub>2</sub> separation. Besides, the impacts of adding different types of thermally labile additives on membrane performance were studied and discussed. Generally, incorporation of either additive (NCC, MCC and PVP) reduced the thermal resistance of the polymer blend. Among the three additives, NCC provides the membrane with optimized physicochemical properties due to its nanocrystalline structure. The results showed a substantial increase of membrane gas permeance after the addition of additives. It appears that PI/NCC carbon tubular membrane has the best H<sub>2</sub>/N<sub>2</sub> selectivity of 434.68±1.39. In conclusion, the use of NCC as thermally labile additive resulted to positive impacts on the development of high-performance carbon membrane. These whole findings may provide a strong foundation for future endeavors using natural resources as polymeric additives.

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