Hydrogen Separation Through Pi/NCC Carbon Membrane: Effect of Stabilization Environment and Heating Rates

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EXTENDED ABSTRACT

A study on tubular carbon membrane (TCMs) formed from polymeric precursors is reported for separation of hydrogen with nitrogen. TCMs were fabricated by dip coating process using P84 co-polyimide as a main precursor with blending of Nanocrysttaline cellulose (NCC) as an additives. Previously, it was shown that changing the time, temperature, or environment of the carbonization protocol for a commercially available PI/NCC altered the final properties of the carbons produced. A large variety of TCMs for gas separation have been developed by simple carbonization of a PI/NCC deposited on a ceramic tubular support. In this study, heating rates (1, 3, 5, and 7 ^{o}C/min) and stabilization environment (Argon, Nitrogen, and Helium) were investigated and the effect on permeation were determined for all resultant TCMs. In recent study, the modifications on the carbonization parameters such as stabilization conditions and heating rates during fabrication of PI/NCC-based carbon membranes could affect their gas separation performance. It was observed that stabilization under Argon environment produced carbon membranes with high separation performance while heating rates of 3°C/min improved the membrane selectivity but reduced the membrane's permeability. In literature, the rate of evolution of the volatile compounds can be determined by carbonization heating rate as it is believed could affect the microstructure of the carbon membranes [1]. The variation in carbonization heating rates have showed different gas separation results on the PI/NCC carbon membranes as represented in Table 1. The data obtained showed an average value from at least three different PI/NCC carbon membranes with small error analysis of ±10% for both selectivity and permeance value.

Table 1: Gas separation results for PI/NCC carbon membranes carbonized at different heating rate

Sample	Carbon membrane		
	Permeance (GPU)		Selectivity
	N_2	H_2	H_2/N_2
PI/NCC 1°C/min	3.08±3.65	1283.43±2.77	416.70±2.24
PI/NCC 3°C/min	3.22±3.21	1399.66±5.22	434.68±1.39
PI/NCC 5°C/min	3.18±4.16	1344.31±2.77	422.74±3.87

PI/NCC 7oC/min   3.11±3.98   1305.22±4.52   419.68±2.87

As tabulated in Table 1, it can be seen that the gas permeance of N_2 and H_2 decreasing when the heating rate increasing from 5 to 7oC/min and was believed due to the decreasing in pore size distribution and concurrently, due to the carbon structure densification. Previously, numerous studies have reported that increases in carbonization heating rate can affect the pore size distribution by producing pores with smaller size and this is believed to cause another limitation in the degree of gases rotation freedom [1-3]. According to Centeno et al. (2004), they found that random smaller pore size distribution polymer-based carbon membranes can be affected by the higher carbonization heating rate [2]. This is might due to the loss of most of the volatile compounds during the increases in the heating rate and subsequently, the partial carbon vapor deposition occurred in the pores that were formed previously. Moreover, it is believed any further increment to the heating rate might cause pinholes creation and microscopic crack on the membrane surface. During the heat treatment, the membrane are expected to deform.

The implement of low heating rate to the carbon membrane have resulting reduction in the values of gas permeance as shown in Table 1. In comparison to the other tested membranes, these membranes possessed lower separation value, however the value obtained is acceptable as its value is still comparable with previous hydrogen separation studies [2]. Furthermore, the highest H_2/N_2 separation was obtained by carbon membrane carbonized at heating rate of 3oC/min as compared to 5 and 9oC/min. This was caused by long contact of membrane with the inert gas that consequently, narrow down the pore size distribution. The increment of carbonization heating rate from 5 to 7oC/min will decreasing the selectivity of the H_2/N_2. Sazali and co-workers (2017) have also stated that the pore size distribution was also attributed by selection of types of the polymer precursors such as the chemical composition of the polymer precursor[4].

Keywords: Heating rates, stabilization environment, P84 co-polyimide, Nanocrystalline cellulose (NCC), and Hydrogen separation

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