Polyacrylonitrile (PAN)-based carbon hollow fiber membrane for O_2/N_2 gas separation

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Abstract

Polyacrylonitrile (PAN) was used as an alternative precursor for making carbon membranes for gas separation. Nitrogen gas pyrolysis system was applied in order to convert the PAN polymer membranes into PAN based carbon hollow fiber membranes. The effect of pyrolysis temperature on the separation performance of carbon membranes for gas separation was studied. The temperature range from 500-800°C was studied during pyrolysis process. The resultant carbon hollow fiber membranes were tested with pure oxygen and nitrogen as test gases. The highest selectivity of PAN carbon membrane for O_2/N_2 separation is about 1. These permeation data represents the first reported data for PAN as a precursor in literature. Such data can be a useful guide to tailor made the separation performance of PAN based carbon membrane in the future.

Keyword : Carbon Membrane, Pyrolysis, PAN, Gas Separation

Introduction

Gas separation technology by using membrane system has emerged as a promising alternative in the recent years. Beginning from synthesizes of polymeric membrane until the development of inorganic membrane, continuous effort is still ongoing in order to find superior properties of membrane materials that were suitable for gas separation. Inorganic molecular sieves membrane such as carbon molecular sieves, zeolites, and ceramic membrane not only have an ability to give high separation performance, but their performance can be retain in the severe environment where the use of polymeric membrane is limited (i.e. such as high temperature and high acidic) [1]. In addition, the new development of mixed-matrix membrane, which is believed to give the best properties for gas separation, also uses this kind of molecular sieves membrane material in their preparation [2].

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Among molecular sieving material, carbon molecular sieve have show more attractive characteristics and they were more feasible to be fabricate in the membrane form [3]. In the recent years, many studies have been conducted in order to tailor the separation performance of carbon membrane by changing the pyrolysis process parameter, and it was found that such attempt was successful in producing different kind of carbon membrane by using the same precursor. However, the drawback factor is the cost of the precursor itself. Although polyimide precursor gives better performance [4], but it cost is relatively high and the availability is limited. Therefore, current studies are directed to find an alternative precursor for carbon membranes.

Therefore, we have introduced the usage of polyacrylonitrile (PAN) as a new precursor for manufacturing carbon hollow fiber membrane for gas separation [5, 6]. PAN has been known as a primary precursor for producing high performance carbon fiber for the composite material. In the membrane application, they were widely use for the liquid separation (i.e. reverse osmosis and nanofiltration) rather than the gas separation membranes. In carbon membranes area, the using of PAN as precursor to form carbon membrane starting in early 1990's when Schindler and Maier [7] and Yoneyama and Nishihiro [8] have prepared porous carbon membrane with PAN. Later, Linkov et al. [9, 10] expand the use of PAN precursor by blending it with other polymers and also coated their PAN carbon membrane with zeolites to form composite membranes [3]. However, the detail of the separation performance offered by PAN based carbon membrane was not reported in those studies.

In our previous paper [5], we had successfully developed PAN hollow fiber membrane and characterized the membrane in term of morphology, the functional group existence and also the properties of the porous structure in the carbon membrane. Therefore in the present paper, we extended the work by reporting the separation performance of PAN carbon hollow fiber membrane for O_2/N_2 and H_2/N_2 gas separation. Hopefully, this result may encourage further research on PAN as a new precursor for carbon membrane, and subsequently their performance can be competing with other precursor.

2. Experimental

2.1. *PAN polymeric hollow fiber membrane*

The polymer solution consisting of 15 wt% PAN (Aldrich18131-5) is dissolved in 85wt% DMF was used as a spinning dope. The homogenous dope solution was degassed in ultrasonic bath before going to spinning process in order to remove the gas bubble existed in the solution. The presence of gas bubble will lead to the formation of poor polymeric hollow fiber membrane. The dry/wet spinning technique has been used with the spinneret located about 9 cm from the water bath. The fully formed hollow fiber membrane has a dimension of 600μm and 300μm of outside and inside diameter respectively. Before undergoes drying process, the membrane was subjected to the

solvent exchange process in water, methanol and hexane for 2 days in each bath respectively.

2.2. Nitrogen inert gas pyrolysis system

Nitrogen inert gas pyrolysis system was set up as shown in Figure 1 [5]. Around 25-30 pieces of PAN fiber were pyrolyzed for each run. Before starting the pyrolysis, the PAN membrane was subjected to the thermostabilization in air at 250°C for 30 minute at heating rate of 5°C/min. After thermostabilization, the inert gas needed to be purged into the pyrolysis system to remove the unwanted air or oxygen. This was to prevent the oxidation from occurring during high temperature pyrolysis process. Then, the precursor was heated to a required pyrolysis temperature in the range of 500-800°C and maintained at that temperature for 30 min by setting up the temperature control systems. The heating rate was set at 3°C/min and nitrogen gas flow rate was maintained at 200 cm^3/min. The resulting carbon membrane was cooled down to ambient temperature in an inert gas atmosphere.

2.3. Permeation test

Before the permeation test was run, the carbon hollow fiber membrane must be potted in a bundle consisting about 5 to 10 fibers. One end of the fiber bundle was sealed into a stainless steel tube of 5/8 inch outer diameter, while the dead end part was potted in an aluminium cap. Loctite E-30CL epoxy adhesive was used as a potting resin

The entire single gas permeation system used during this study is illustrated in Figure 2. Pure O_2 and N_2 were introduced into the system at feed pressure of 5 bar at ambient temperature. The permeate side of membrane was maintained at atmospheric pressure. Simple soap film flow meter was used to obtain the permeation properties of the gas owing to its suitability for the measurement of small and wide range flow rates [11].
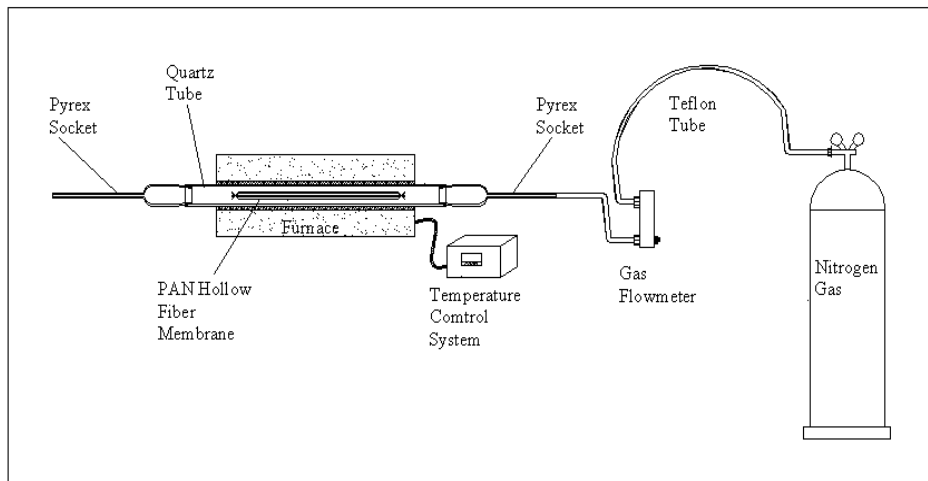

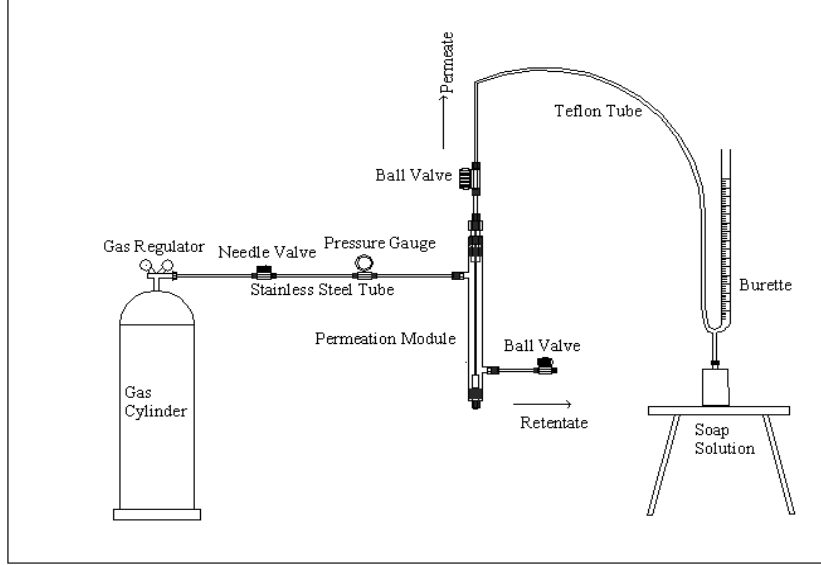
Figure 1: Inert gas pyrolysis system

Figure 2: Schematic diagram of pure gas permeation testing system.

The pressure-normalized flux and selectivity of the carbon membrane was calculated from the collected data by using equation (1) and equation (2) respectively.

$$\left(\frac{P}{l}\right)_i = \frac{Q_i}{\Delta p.A} \tag{1}$$

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{\left(\dfrac{P}{l}\right)_A}{\left(\dfrac{P}{l}\right)_B} \tag{2}$$

Where; $(P/l)_i$ is pressure-normalized fluxes, Q_i is volumetric flow rate of gas, Δp is transmembrane pressure drop, A is surface area of membrane and $\alpha_{A/B}$ is ideal separation factor or selectivity. The permeability unit that was usually applied in membrane research is gas permeation unit (GPU) and Barrer. In this study, GPU (1 GPU = 1×10^{-6} $cm^3(STP)/cm^2.s.cmHg$) was used due to the facts that the exact value of membrane skin thickness is difficult to attain and determine since the membrane is in asymmetric form.

3. Results and discussion

Table 1 summarizes the gas permeation data of PAN carbon hollow fiber membrane pyrolysis at different temperature for the O_2 and N_2 gases. Respectively Figure 3 and Figure 4 show the pressure-normalized flux and selectivity of the PAN carbon

hollow fiber membrane plotted at different pyrolysis temperature for O_2/N_2 gas separation.

As shown in Figure 3, both O_2 and N_2 pressure-normalized flux decreased with increasing the pyrolysis temperature. The extent of this reduction is more noticeable between pyrolysis temperatures of 500°C to 700°C. The reduction in pressure-normalized flux of gases depicted that the pore structure in PAN carbon membrane become smaller with increasing pyrolysis temperature. According to Suda and Haraya [12], high temperature pyrolysis would cause a higher crystallinity, density and narrower interplanar spacing of graphite layers of the carbon, which produces a carbon membrane with small pore size structure. Furthermore, the asymmetric structure of the membrane becomes dense due the physical shrinking of the membrane with a decomposition and evolution of the byproducts as the pyrolysis temperature increases. All of these factors were contributed to a reduction of pressure-normalized flux in PAN carbon hollow fiber membrane as the pyrolysis temperature increases.

Table 1
Effect of pyrolysis temperature on the gas permeation properties of PAN carbon hollow fiber membrane for O_2/N_2

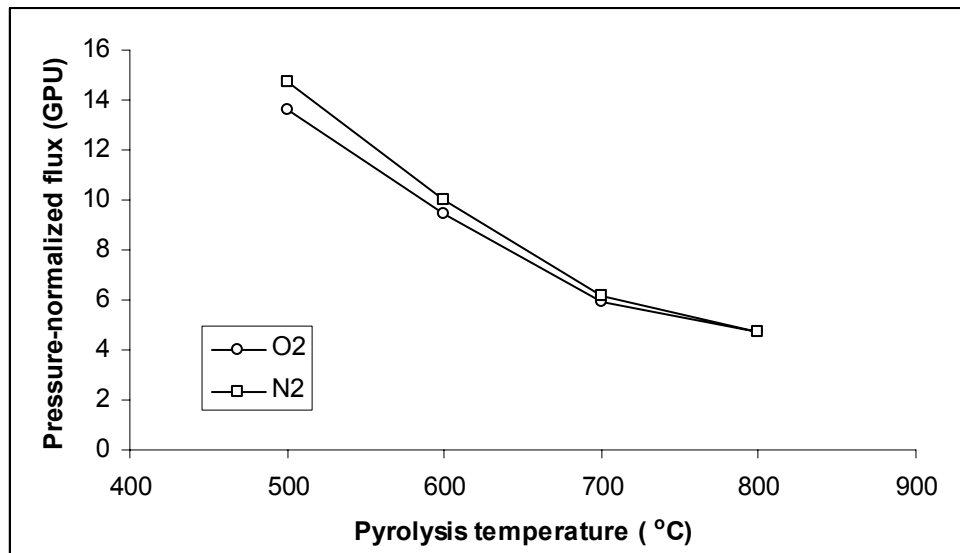| Pyrolysis Temperature (°C)	Oxygen (GPU)	Nitrogen (GPU)	Selectivity O_2/N_2
500	13.62	14.74	0.92
600	9.47	10.00	0.95
700	5.92	6.20	0.96
800	4.74	4.70	1.01

Figure 3: Pressure-normalized flux of O_2 and N_2 for PAN carbon hollow fiber membrane at different pyrolysis temperature
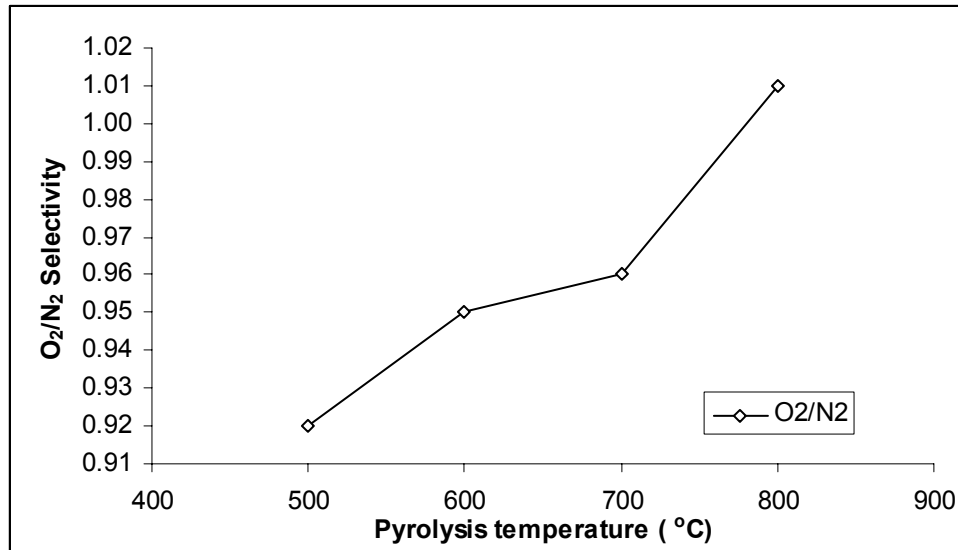
Figure 4: O_2/N_2 selectivity of PAN carbon hollow fiber membrane at different pyrolysis temperature

At early stage of pyrolysis process, it was believed that the selectivity of the membranes decreased due to the pore formation on the surface of the membrane that is induced by the evolution of the volatilities in the polymer [13]. However, based on the result shows in Figure 4, pyrolysis temperature of 500°C already contributed to the increment of selectivity in PAN carbon hollow fiber membrane. This means that the pore formation in PAN carbon hollow fiber membrane already started below this temperature, thus it is also feasible to pyrolysis the PAN membrane below 500°C.

Obviously from Figure 4, the increasing of pyrolysis temperature will produce more selective carbon hollow fiber membrane. Highest selectivity for O_2/N_2 by was achieved at 800°C which is around 1, but we believe that further increment can be achieved by further increasing pyrolysis temperature. This is because as the pyrolysis temperature is increases, gradual destruction of crosslinks in polymeric membrane occurs which leads to clustering of the aromatic units and subsequent rearrangement of stacking graphite planes. The alignment of graphitic structures leads to micropores closing on increasingly severe thermal treatment conditions [14]. Moreover, at high temperature, it was proposed that a thin layer of carbon could be deposited inside the pores without sealing them. As a result, average pore size was being modified or reduced without complete pore blocking, thus the increment of membrane selectivity and reduction of permeability could be detected [15].

Based on the permeation results obtained, all the selectivity value achieved by PAN carbon hollow fiber membrane is just slightly above the Knudsen selectivity (i.e. α O_2/N_2= 0.94). One of the probable reasons for the low selectivity of the PAN carbon membrane was due to the lower selectivity of the initial PAN precursor. Although the pyrolysis process had improved the selectivity of the membrane as reported with other precursor, but this increment was not pronounced in the case of the PAN based carbon

hollow fiber membrane. One way that can be considered in the future is to fully optimize the preparation condition of the PAN polymeric precursor to give better precursor properties. This area of the research especially with PAN hollow fiber membrane used for gas separation is still not fully explored yet.

Another possibility that contributed to lower selectivity in PAN carbon membrane is the presence of surface defects in the membrane surface which diminish the ability of membrane to perform molecular sieving characteristic. Thus, further study on the mechanism of pore formation in PAN polymer degradation during pyrolysis is important in order to tailor made the pore structure in the PAN carbon membrane. Precise control of pore formation in PAN membrane may result in significant improvement in PAN carbon hollow fiber membrane for gas separation.

4. Conclusion

For the first time the separation performance of PAN carbon hollow fiber membrane was reported for the gas separation at different pyrolysis temperature in the literature. Such data can be very useful as a guide to prepare PAN carbon membrane in the future study. The highest selectivity of PAN carbon membrane for O_2/N_2 gas separation is about 1. Although the separation performance is not as competitive compared to the available precursor, we had discussed in details the science behind developing carbon hollow fiber membrane from PAN. Perhaps this scientific background can be further explored in order to develop a more competitive carbon hollow fiber membrane from PAN. In addition, we believed that the manipulation of pyrolysis process parameter can give more pronounce effect in order to tailor made the performance of PAN carbon membranes.

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