

Polyimide-based Carbon Membrane: Effect of Coating Times on Helium Separations

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ABSTRACT

In this study, fabrication of tubular carbon membrane prepared from BTDA-TDI/MDI (P-84) polyimide are investigated. Carbon membrane can be observed as the forthcoming of the separation media in gas separation process due to its tremendous gas separation performance, ease process ability, and conservative energy requirement as compared to conventional separation. The consequences of the dip-coating methods to produce high performance tubular carbon membrane by manipulating the coating times (15, 30, 45, and 60 minutes) which have been identified as an influence on the outcome of dip-coating method. Based on above-mentioned studies, we formulated the hypothesis that tubular carbon membrane performance can be controlled by manipulating the carbonization conditions which was conducted with a heating rate of 3°C/min, a final temperature of 800°C and stabilization time of 300°C. Pure gas permeation tests were performed by single gas permeation test at room temperature and at 8 bars. Helium (He), and Nitrogen (N₂) gas are used to investigate the transport mechanism in the carbon membrane separation process. From this study, the highest selectivities of 305.86±2.21 for He/N₂; He permeance of 984.92±1.65 GPU were achieved by applying 45 minutes coating times.

Keywords:

Carbon membrane; dip-coating times;
BTDA-TDI/MDI(P-84) polyimide; Helium
separation

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1. Introduction

Utilization of membrane in order to separate gas is a dynamic method and currently undergoes expeditious growth in the industry. They received enormous attention because they offer quite a few advantages such as easy to operate due to it having no moving parts, requires low energy and economical for low-scale operation. Gas separation is among the primary applications in membrane technology these days. In the past few years, advancements on gas separation have quicken for gas refining purposes particularly natural gas. Gas separation technology incorporating membrane can be considered as contending gas separation technique in the industry [1-3]. In chemical inertness, helium has high productivity, it is lighter than air property and it able to achieve cryogenic at temperatures that is near to zero degrees. Helium has found in various application in electronic,

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industries, and fiber optics fabrication, it acts as a heat transfer agent in rocket technology, and it also used in medical such as MRI scanners [4]. Traditionally, to separate the helium from the natural gas, it need three stage process to purify the helium. The first stage is the initial recovery of helium from natural gas. The next stage is the upgrading of the helium to ~70%, and finally is the purification of helium [5]. By virtue of its high condensability, He has higher solubility coefficient compared to other lightweight gases like H₂, N₂ and CH₄. Another thing to note, He has affinity with polar groups for instances carbonyl, ether and acetate groups hence polymer that contains these groups has the possibility to get high selectivity for He [6]. Carbon membranes have desirable features such as outstanding resistance towards heat, exceptional chemical stability even in corrosive environments, great permeability and tremendous selectivity in comparison to polymeric membranes which make them a favourable candidate for gas separation purposes [7,8].

Being one of the possible techniques to isolate He from natural gas, supported carbon membrane has enticed immense attention because it is strong mechanically and has great performance in He separation. In harsh environments such in the existence of strong acid and base and high temperatures as well as pressures, carbon membranes strive due to their stability. Carbonization of polymeric precursors in regulated inert atmosphere was employed to prepare carbon membranes [9,10], such that the precursor should endure high heat treatment without shrinking excessively and should yield high amount of carbon. The microstructure and gas permeable characteristics of carbon molecular sieve membranes are determined by several parameters in carbonization conditions (heating rate, end temperature, soaking time and gas atmosphere) and pre or post treatment conditions (thermostabilization, oxidation and chemical vapor deposition) [11]. In spite of this, coating techniques are potentially having a role of deciding the final carbon membranes structure given that different time of coating although carbonized in the same conditions will result in different carbon membrane features.

One of the ways to construct carbon membrane is in tubular form in order to diminish flaws and to yield high performance for gas separation [12]. This research study is principally emphasized in providing enhanced understanding on parameters that are appropriate in dip-coating processes in contemplation of controlling the tubular supported carbon membrane morphology. It has been determined that the main parameter has the most influences on the dip-coating process and the said parameter is coating times. On the grounds that there is no impediment in supported size and low utilization of polymers in dip-coating techniques, it appears to have considerable potentiality to be applied in large scale production as well as to take over the current spin coating and spray coating techniques [13]. On the whole, techniques to construct tubular supported carbon membranes described in the literature are complicated while coating times are necessary to expand for obtaining carbon membrane that is free from cracks, which requires several cycle and exceptional attention. The development of membranes without defect by single dipping -drying-carbonization process has only been reported by a few researchers [14-17] however reports on coating are scarce. Defect-free supported carbon membranes were prepared successfully at carbonization end temperatures of 800 °C (CM-800) and stabilization temperature of 300°C (S-CMSM 300) under Argon environment (200ml/min). End temperatures for carbonization at 800°C (CM-800), temperature for stabilization at 300°C (S-CMSM 300) and Argon environment (200ml/min) are the conditions to successfully prepare a defect-free supported carbon membrane.

2. Experimental Section

2.1 Materials

Chemicals such as polyimide BTDA-TDI/MDI (P-84), polyvinylpyrrolidone (PVP) and microcrystalline were obtained from Sigma Aldrich while N-methyl-2-pyrrolidone (NMP) was acquired from Merck (Germany). These chemicals were utilized as is with no additional purification step. An 8 cm long porous tubular ceramic support (Al_2O_3) was bought from Shanghai Gongtao Ceramics Co., Ltd. It has 0.2 μm average pore size, inner and outer diameter of 10 mm and 13mm respectively as reported from previous study [10].

2.2 Preparation of Carbon Membrane

Preparation of polymer solution was done under continuous stirring at 80°C and it contained 15wt.% of P-84 in NMP. In order to eliminate trapped bubbles in the solution, sonication was performed and the solution was let to rest for 12 hours. Plunged the tubular support into the polymer solution prepared earlier for 45 minutes and allowed it to go through aging at 80 °C for 24 hours. Immersed the membranes in methanol for 2 hours then rested them inside an oven for 24 hours long and temperature of 100°C. Carbon membranes were produced from carbonized polymeric membranes. In order to go through carbonization process, the supported polymeric membranes were positioned at the centre of Carbolite horizontal tubular furnace. Throughout the whole process of carbonization, 3°C/min heating rate was enforced as per reported by previous study [18]. Temperature of the processed membranes was then decreased to room temperature naturally upon the end of every heating cycle.

2.3 Preparation of Carbon Membrane

Carbon tubular membranes have been experimented in the gas permeation system as depicted in our preceding study [19]. The carbon tubular membrane was mounted inside a 14 cm long stainless-steel tubular frame. With the aim of avoiding leakages while housing the membrane inside the module, the membrane was equipped with rubber O-rings. To calculate the membranes permeance, P/l (GPU) and the membrane selectivity, α , these equations were used:

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 membrane permeance, Q_i is the gas i volumetric flow rate at standard temperature and pressure (cm^3 (STP/s)), p is the difference of pressure between feed and permeation sides of membrane (cmHg), A is the surface area of membrane (cm^2), n is the fibers quantity in the module, D is the membrane outer diameter (cm), and l is the effective membrane length (cm). Definition of selectivity can be described as the permeation ratio of fast gas permeation to slow gas permeation.

3. Results and Discussion

In dip-coating procedure, it has been found that in this type procedures might have extremely recommended to some of application due to their relative simplicity. The transfer properties of the carbon membranes are influence by the coating parameters [20]. By manipulating the coating cycles, it has created a high solidness of carbon membrane while manipulating the coating time it enhances the membrane selectivity and the porousness of the membranes decrease. Along the dip coating process, one way to restrain the development of complicates structure is by interfacial stress among polymer and aiding that reduce the Tg of polymer [21]The distinction of the microstructure if carbon happened due to the dissimilar at the homogeneous polymer surface and it happened during the carbonization process [21].

3.1 Effects of Coating Times on Gas Permeation Properties

Gas separation performance for some gases at room temperature for membranes attained at various time of coating are shown in Table 1. Membrane that has been processed through dip coating procedure has highest selectivity against all other samples in 45 minutes coating time. This owes to the fact that this coating condition caused its pinholes to be well sealed and the penetrate across pores of the membrane was complete [22]. Altogether, the performance was descending in the sequence of 45, 60, 30 and 15 minutes. Gas separation performance disparities were decided by carbon microstructure differences which has a direct effect on transport mechanism in membrane. From the result, 45 minutes coating time has high selectivity probably attributable to more pores reduction compared to 60, 30, and 15 minutes coating time. As a matter of fact, the prevalence in transport mechanisms differences is facilitated by pore characteristics differences [23].

Table 1
 Gas separation performance of carbon membranes produced from different coating time.

Sample (CM-PI)	Carbon membrane		
	Permeance (GPU)		Selectivity
	He	N ₂	He/N ₂
15 minutes	704.76±1.76	2.62±1.67	268.99±3.22
30 minutes	821.98±3.21	2.77±2.17	296.74±1.98
45 minutes	984.92±1.65	3.22±3.21	305.86±2.21
60 minutes	795.66±2.74	2.86±1.28	278.20±1.72

Coating time of 45 minutes has evidently higher gas separation performance than the rest of the samples from different coating times due to enhanced carbon membranes morphology [24]. Furthermore, it provides enough time for surface condition improvement as well as for cracks adjustment on extremely porous substrate produced via particle-stabilized direct forming approach. In favour of producing a preeminent material with extremely porous core but comparatively fewer pores on the surface, improvements made on the supported surface resolve around filling in heterogenous defects and mending cracks which then elevate substrate's compressive strength and debris resistance. Nevertheless, the presented method can be assured in pursuance of attaining

competitive membranes for gas separation. 60 minutes of coating times show reduction on selectivity reading due to the sample exceed the accurate time for surface condition development.

4. Conclusions

Based on this study, it is being investigated to find out the influence of coating time for dip-coating method on Polyimide carbon membrane. From this investigation, it shows that the optimum coating time for superior gas separation is at 45 minutes. It is show that the highest selectivities of He/N₂ is 305.86±2.21 and the Helium permeance achieved with value of 984.92±1.65 GPU.

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