



CO₂ Selective Carbon Tubular Membrane: The Effect of Stabilization Temperature on BTDA-TDI/MDI P84 co-polyimide

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ABSTRACT

Membranes offer remarkable attributes such as possessing small equipment footprints, having high efficiency and are environmentally friendly, with carbon membranes progressively investigated for gas separation applications. In this study, carbon tubular membranes for CO₂ separation are prepared via dip-coating method with P84 co-polyimide as carbon precursor. The prepared membranes were characterized using Thermogravimetric Analysis (TGA), pore structure analysis Brunauer-Emmett-Teller (BET), Fourier Transform Infrared Spectroscopy (FTIR) and pure gas permeation system. The permeation properties of the carbon membranes are measured and analyzed using CO₂, CH₄ and N₂ gases. The P84-based carbon tubular membrane stabilized at 300°C and featured excellent permeation properties with permeance range of 2.97±2.18, 3.12±4.32 and 206.09±3.24 GPU for CH₄, N₂ and CO₂ gases, respectively. This membrane exhibited the highest CO₂/CH₄ and CO₂/N₂ selectivity of 69.48±1.83 and 65.97±2.87, respectively.

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Greek Symbols

μ	Micro (0.000001)
γ	Gamma
$(P/l)_i = \frac{Q_i}{\Delta p \cdot A} = \frac{Q}{\pi D l \Delta P}$	Permeance, P
$\alpha_{A,B} = \frac{P_A}{P_B} = \frac{(P/l)_A}{(P/l)_B}$	Selectivity, α

1. INTRODUCTION

Nowadays, gas separation is one of the premier applications of membrane technology. The improvement of gas separation membranes in past years have accelerated for gas refining applications, especially natural gas [1,2]. For the past 30 years, membrane technology has been prominently used as a method to obtain various types of gases with high purity. In order to attain membranes that exhibit high selectivity, high

permeability, high chemical and thermal steadiness, membranes are developed using polymeric materials [3]. Nevertheless, it also believed the reduction in polymeric membrane effectiveness with time can be affected by fouling, compaction, chemical degradation and thermal instability [4]. Because of the limited thermal stability and lack of resistance towards abrasions and chemical attacks, polymeric membranes encountered a drawback when applied in separation processes where hot reactive gases are present [5]. This has brought about a movement

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to explore inorganic membranes to separate gas mixtures [6]. Carbon membrane provides better permeability and selectivity over polymeric membrane, while being able to withstand harsh environmental conditions (high temperature, etc.) [7,8].

Recently, researchers have developed an interest in using various kinds of polymeric materials such as polyimides for carbon membrane precursor [4,9]. P84 co-polyimide can withstand temperatures of more than 300°C without losing its shape; because it does not undergo a melting phase transition [10,11]. Mangindaan et al. [12] reported that the new development of polyimide P84 co-polyimide blended with TAEA cross-linked membranes have exhibited good separation performance for acetone dehydration. Furthermore, Choi et al. [13] had investigated the chemical cross-linked asymmetric P84 co-polyimide hollow fibre membranes using the dry-wet spinning process. The results showed an enhancement in the separation performance, as well as, in the gas transport properties of the fabricated membranes. Regarding the membrane thickness, Ren et al. [11] had investigated the thickness on the formation of asymmetrical flat sheet membranes prepared with P84 (BTDA-TDI/MDI co-polyimide)/N-methyl-2-pyrrolidone (NMP)/GBL (γ -butyrolactone) casting solutions. The results showed that high flux and a large MWCO were exhibited by membranes fabricated via the wet spinning process [11]. Previous researchers have prepared asymmetrical membranes based on P84 co-polyimide by the phase inversion technique. The asymmetrical membrane prepared from acetone/NMP/P84 chemical mixture exhibited the best gas separation performance with a permeance of 17, 1.8, 0.82 and 0.092 GPU for He, CO₂, O₂ and N₂, respectively; along with a selectivity of 200, 20 and 9 for He/N₂, CO₂/N₂ and O₂/N₂, respectively [14]. It is believed that the development of a carbon membrane from excellent polymer precursor would significantly improved the final membrane properties. Therefore, P84 co-polyimide was selected to be used in this study.

Carbon membranes are more suitable for gas separation processes at high temperatures between 500-900°C [15,16]. Further studies regarding the stabilization condition by using polyimides as a precursor membrane are promising since they offer greater stability among other materials [17]. During the stabilization process, a chemical reaction is initiated during the isothermal step, and it was suggested that the majority of nitriles take part in the cyclisation and trimerisation reactions below 400°C [18]. Cipriani et al. [18] performed carbonization on a thin film polyacrylonitrile (PAN) at a stabilization temperature below 400°C where the final structure of the samples resembled graphitised structures. Barbosa-Coutinho et al. [19] had indicated that at the stabilization temperature of above 500°C, an intensive degradation of the polyetherimide-based carbon membrane was

observed. This is because the extent of membrane exposure under maximum temperature of stabilization was decisive in the final membrane morphologic characteristics and properties [19]. Furthermore, Hameed et al. [20] had investigated the effect of oxidative stabilization and carbonization processes on the structure, mass and mechanical properties of polyacrylonitrile (PAN) precursor fibres. The results revealed that after stabilization at a maximum temperature of 255°C and carbonization at a maximum temperature of 800°C, the tensile strength and modulus of the fibres had increased.

Different precursors would require different stabilization conditions due to the chemical structure and thermal behaviour of those particular precursor materials. Despite their impact on carbon membrane properties, researches specifically on the stabilization conditions are very limited in the current literature since most researches focusing on carbonization or pyrolysis conditions. Therefore, this work aims to investigate the effect of the stabilization temperature on CO₂ separation of the prepared carbon membrane. Furthermore, majority of gas separation membranes are framed into support membranes for higher mechanical steadiness as compared to unsupported carbon membranes [21]. Considering that supported carbon membranes exhibited superior gas permeation properties, supported carbon tubular membranes was utilised in this study [22,23]. Based on the author's knowledge, the effects of stabilization temperatures on P84-based carbon membranes have not been reported in the current literature. The investigation was conducted by performing the stabilization process at various temperatures (250, 300, 350, 400 and 450°C) with constant heating rate of 2°C/min under N₂ atmosphere, and a flow rate of 200 ml/min. The characterization methods employed were thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR) and Brunauer-Emmett-Teller (BET). It is expected that the findings from this study would help bridge the literature gap in the understanding of the influence of stabilization temperature for the improvement of gas separation properties.

2. EXPERIMENTAL

2. 1. Materials

Commercially available co-polyimide BTDA-TDI/MDI (P-84) procured from Sigma Aldrich (CAS#: 58698-66-1) was chosen as a precursor for the fabrication of carbon-based membranes. The measured density of P84 co-polyimide was 1.31g/cm³. Additionally, the glass transition temperature (T_g) of this polymer was 315°C [14]. N-Methyl-2-Pyrrolidone was purchased from Merck (Darmstadt, Germany) and employed as a solvent in the preparation of the dope

solution. Porous tubular ceramic, TiO₂ (4.5-5.5mm), with a coating of ZrO₂ (2-3nm) on the inner surface was purchased from Shanghai Gongtao Ceramics Co., Ltd (China). 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 0.2µm. All chemicals were utilised 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 P84 co-polyimide and 85wt% of NMP over the external surface of the tubular support. This composition was obtained based on our previous study [24, 25]. The ceramic support was dipped into the dope solution for 15 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 cycles were repeated three times to eliminate possible pinhole presences on the surface of the prepared carbon tubular membranes. The dried supported precursor membranes were then placed inside a Carbolite horizontal tubular furnace for stabilization and carbonization processes. In this study, two steps of the heat treatment were involved. In the first step, the membranes were treated at different stabilization temperatures (250, 300, 350, 400 and 450°C) with a heating rate of 2°C/min under N₂ atmosphere (200ml/min). In the second step, the membranes were carbonized up to 800°C at the same heating rate and gas flow as mentioned in step 1. The nomenclature of the resultant carbon membranes was given in the form of (CM-stabilization temperature);CM-250/CM-300/CM-350/CM-400/CM-450. Carbon membranes without substrate were also prepared via similar procedure for characterization purposes.

2. 3. Membrane Characterization

Several characterization methods were used to study the carbon membranes fabricated at different stabilization temperatures. The weight loss of carbon membranes during the heat treatment process was characterised using thermogravimetric analysis (TGA 2050). The analysis was carried out with a ramp of 10°C/min with temperature ranging from 50°C to 800°C. The purge gas was N₂ and its flow rate was controlled at 20ml/min. A small piece of the tested membranes was cut and conditioned in liquid nitrogen to leave an unreformed structure to be mounted on sample stubs. The samples were then sputter coated with gold under a vacuum. Fourier Transform Infrared Spectroscopy (FTIR) and Single Reflection Diamond for the Spectrum Two (PerkinElmer, L1600107) were used to distinguish the actuality of the functional groups in a membrane. The

FTIR sequences displayed the variation of the functional groups in the membranes once heated from room temperature to carbonization temperature. The apparent surface area of the carbon membrane particles was calculated using Brunauer–Emmett–Teller (BET) equation (Micromeritics ASAP 2010) obtained from the equipment software. The sample was heated at 130°C for 1 h to remove any trapped moisture.

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

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

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), D is the outer diameter of the membrane (cm) and l is the effective length of the membrane (cm). The permeate volumetric flow rate was measured by the soap bubble flow meter reading of 1.0ml. This permeation test was repeated with two other different membrane samples. The gas permeation test was conducted at ambient temperatures. Similar gas permeation was also used in previous studies [24,25].

3. RESULTS AND DISCUSSION

3. 1. Thermal Behaviour Analysis

The weight loss of P84-based polymeric membranes during the carbonization process was assessed by TGA by measuring the changes in the physical and chemical properties of the membranes as a function of increasing temperatures. Figure 1 illustrated the weight variation of polymers during the heating process, from 50°C to 800°C. As seen in Figure 1, P84- based polymeric membranes exhibited two distinct weight loss patterns. The first degradation of precursor membrane from its original weight to 94% started at approximately 40°C to 460°C, which was due to moisture evaporation. The second stage of precursor membrane degradation began at temperature range of 460°C to 800°C, which represented the degradation temperature of P84 co-polyimide. According to the TGA thermogram obtained, the degradation temperature (Td), which was defined as the temperature corresponding to 5-10% weight loss of the precursor, was observed at 470°C. This explained the high thermal resistance exhibited by P84 co-polyimide. Studies have found that stabilization between the temperature range of glass transition temperature, T_g, and degradation temperature, T_d, can effectively prevent melting during carbonization of thermal plastic

polymers, such as polyimides (PI) [26]. The glass transition temperature of P84 co-polyimide, as reported in previous research, was 315°C [11]. Therefore, in this study, stabilization temperatures in the range of 250°C-450°C were investigated.

3. 2. Fourier Transform Infrared Spectroscopy (FTIR)

Molecular orientation analysis of P84-based carbon membranes under various stabilization temperatures was performed using FTIR; as illustrated in Figure 2. The chemical structural changes that took place through the transformation of polymer to carbon were observed. The results indicated that the intensity of the prepared carbon membranes decreased compared to the prepared precursor membranes. The most significant difference was found at a lower wave number, from 400 to 1900 cm^{-1} . The peak at 3442 cm^{-1} was attributed to the O-H stretching vibration of the OH functional group. The intensity of this peak was reduced due to the evaporation of water molecules at higher stabilization temperatures.

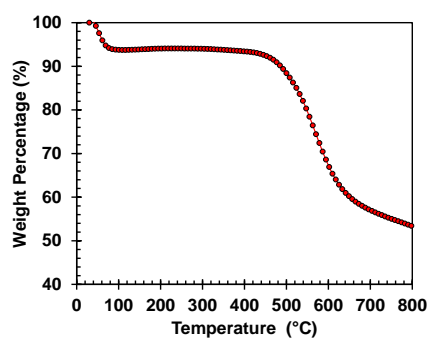


Figure 1. TGA profile of P84-based polymeric membrane

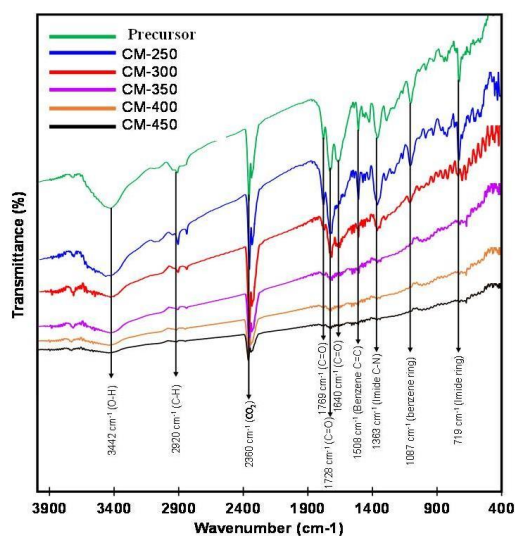


Figure 2. Molecular orientation analysis of precursor and carbon membrane prepared at different stabilization temperature.

The absorption peak at 2920 cm^{-1} corresponded to the symmetric and asymmetric stretching vibrations of CH_2 groups [27]. The doublet at 2360 cm^{-1} was due to atmospheric CO_2 . The absorption peak at 1769, 1728 and 1640 cm^{-1} was associated to symmetric C=O stretching and asymmetric C=O stretching of imide [28, 29]. The peaks at 1508 cm^{-1} and 1087 cm^{-1} were attributed to the symmetric stretching vibrations of C-C groups in the benzene rings. In addition, the stretching of C-N in the imide group can be found at 1363 cm^{-1} . The aforementioned absorption peaks' intensity significantly reduced with the increment of stabilization temperatures, from 250°C to 350°C. This phenomenon indicated that the demolition of P84-based polymeric membrane structure prior to the formation of P84-based carbon membrane was at a higher stabilization temperature, followed by carbonization temperature at 800°C.

Based on TGA analysis, it can be observed that P84-based polymeric membranes undergone thermal degradation during the heat treatment process. Upon carbonization, precursor membranes may degrade via a number of mechanisms including random scission, cross-linking and side group elimination [30]. The existence of free radicals along the backbone of a polymer or any other locations on the chain could result in random scission. Cross-linking generally resulted after stripping of some substituent, and involves the creation of bonds between two adjacent polymer chains [31]. These processes are very important during char's formation as higher molecular weight structures that are less easily volatilised are generated. During chain elimination reaction, the bonds connecting the side groups of polymer chain to the chain itself were broken giving products which are small enough to be volatilised. Specifically, the weight loss of the precursor membranes after the carbonization process were attributed to the release of ammonia (NH_3), hydrogen cyanide (HCN), methane (CH_4), hydrogen (H_2), nitrogen (N_2), oxygen (O_2), carbon monoxide (CO), carbon dioxide (CO_2), benzene, phthalimide and others [32]. As mentioned previously, cross-linking occurs more dominantly compared to scission reaction in P84-based polymeric membranes due to their thermal stability in which greater cross-linking density will give rise to higher Tg. As temperature increased above Tg, the polymer packing density increases [33].

3. 3. Pore Structure Analysis The surface area and pore volume of porous materials were observed from the isotherm adsorptions where it was measured at -196°C, with a relative pressure of around 0.03 due to the molecular size of the N_2 , along with low running temperature. Total pore volume and the volume of the micropores were estimated from the absorption measurements where they were automatically analyzed by the instrument software. Generally, porous materials

are characterised in terms of pore size derived from gas sorption data and IUPAC conventions; this was proposed in order to classify pore sizes and gas sorption that reflect the relationship between porosity and sorption [34]. Figure 3 presented the N₂ adsorption isotherms for the carbon membrane prepared at different stabilization temperatures. The N₂ adsorption result displayed the characteristics of Type III isotherm. Membranes with a high possibility of microporous materials have low adsorption energy [33]. Initially, at a relative pressure of 0 to 0.9, the increment of nitrogen volume was slow and this was consistent for all stabilization temperatures. However, from 0.9 to 1, each stabilization temperature exhibited a different value where all of them made an abrupt increase in the high pressure region. This type of isotherm illustrated the existence of the multi-layered formation [35]. It was also revealed that there was no flattish portion in the curve which indicated that monolayer formation was missing from the carbon membrane sample (Mangindaan *et al.*, 2014). The result for N₂ adsorption obtained for this study can be considered as low in value, and all the samples had a similar trend of results. It was observed that the higher N₂ uptake was exhibited for CM-300 in comparison to other stabilization temperatures applied.

Table 1 demonstrated the effect of stabilization temperatures on the membrane pore structure. It was observed that when the stabilization temperature was increased from 250°C to 450°C, the pore size average radius decreased. This occurred because rigid chains tend to shrink and stress, which results in smaller pore size with the increment of stabilization temperature [36]. The lowest surface area was exhibited by the carbon membrane prepared at 300°C.

It was reported that the reduction in BET surface area may be due to the deterioration of the original polymer backbone and the increment in the formation of activated

points composed of oxygen-containing groups during the stabilization process; this affects the developed pore system of the carbon membrane produced [21].

According to previous studies, the optimum pore size range for carbon membrane is between 3 to 5 Å [10]. In this study, the pore size range obtained ranged between 3 to 10 Å which showed that the pore size of the carbon membranes was still in range with the gas molecular size. The pore size range (Å) was measured using the standard Barrett-Joyner-Halenda (BJH) analysis that refers to the pore size distribution determination method [37]. Previous researchers suggested that the amount of ultra micropores (< ~7 Å) must exceed the amount of the micropores (> ~7 Å) in order to obtain high results in gas separation performance [25].

3. 4. Gas Permeation Measurements The gas permeation properties of the prepared precursor and carbon membranes were measured using the gas permeation test apparatus at room temperature. The permeance of three pure gases with different molecular sizes, CO₂ (3.30 Å), N₂ (3.64 Å) and CH₄ (3.80 Å), through the resulted precursor and carbon membranes prepared at different stabilization temperatures were measured and shown in Table 2. The results revealed that stabilization parameters can essentially influence the execution of the subsequent carbon membrane performance. It can be indicated that carbon membranes provide excellent performance compared to the precursor membranes in terms of gas permeation and selectivity. This was due to the arrangement of pore structure by cross-linking and volatilisation of minor vaporous particles delivered by thermal degradation during stabilization. Carbon membrane, which was stabilized at 300°C, showed superior selectivity. This was because its pore system consists of extensive openings with narrow constriction [38]. The results demonstrated that gas permeance of the prepared membranes follow the order of CO₂ > N₂ > CH₄, which are in accordance to their kinetic diameters [39]. These findings are in agreement with work accomplished in previous studies [36].

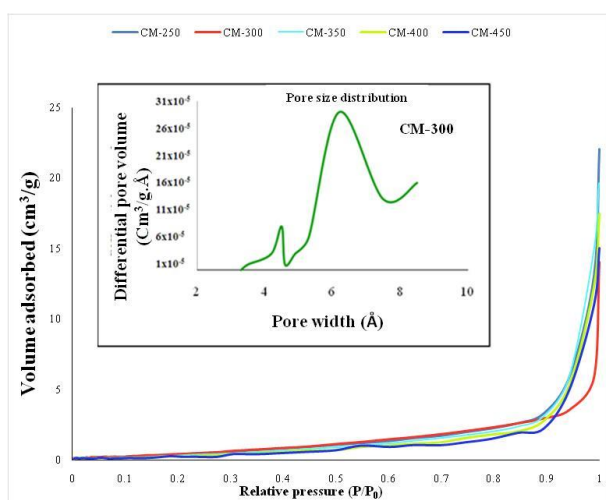


Figure 3. N₂ adsorption isotherms of P84-based carbon membranes

TABLE 1. Effect of stabilization temperature on the membrane pore structure

Stabilization Temperature (°C)	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	Micropore volume (cm ³ /g)
CM- 250	2.8176	0.0248	0.0017
CM-300	2.2875	0.0276	0.0015
CM-350	2.7419	0.0197	0.0011
CM-400	2.5854	0.0157	0.0013
CM-450	2.3111	0.0118	0.0010

TABLE 2. Gas permeation properties of P84-based polymeric and carbon membranes

Membrane	Permeability			Selectivity	
	CH ₄	N ₂	CO ₂	CO ₂ /CH ₄	CO ₂ /N ₂
Precursor	0.76 ± 4.57	0.78 ± 5.23	2.01 ± 6.32	2.64 ± 1.76	2.59 ± 2.33
CM-250	2.73 ± 5.32	2.90 ± 4.98	174.40 ± 5.21	63.96 ± 2.53	60.15 ± 2.76
CM-300	2.97 ± 4.49	3.12 ± 5.13	206.09 ± 5.78	69.48 ± 1.83	65.97 ± 2.87
CM-350	2.86 ± 5.76	3.02 ± 6.22	183.81 ± 4.51	64.22 ± 2.64	60.90 ± 3.01
CM-400	2.64 ± 22	2.76 ± 18	164.66 ± 4.23	62.37 ± 5.19	59.66 ± 5.72
CM-450	2.58 ± 19	2.74 ± 61	158.77 ± 3.54	61.54 ± 3.76	57.96 ± 1.22

In addition, as the stabilization temperature was increased, the degree of deterioration and cross-linking in the membrane increased, which resulted in different micropore structures of carbon membranes; as evident via the N₂ adsorption analysis. Thus, controlling the stabilization temperature can be used as a means to fine-tune the gas separation properties of the derived carbon membranes. It is believed that the stabilization processes offer the potential to prevent melting and fusion of polymeric membranes and avoid excessive volatilisation of carbon elements in the following carbonization process. As a result, the final carbon yielded from the precursor can be maximised; as reported in previous studies [7]. Numerous researchers have noted that the microstructure of carbon membranes (pore size, pore volume and pore distribution) could be customised by controlling the states of the heat treatment process.

4. CONCLUSION

Carbon tubular membranes were successfully prepared by heat treatment with the use of commercially available P84 copolyimide. Carbon membranes were stabilized at different stabilization temperatures before carbonized at 800°C. The stabilization temperatures have prominent effect on the membrane properties especially their pore structure, and ultimately their gas separation properties. The carbon membrane stabilized at 300°C possessed greater permeation properties with CO₂ permeability of 206.09±3.24 GPU, and with the selectivity of 69.48±1.83 and 65.97±2.87 for CO₂/CH₄ and CO₂/N₂, respectively. The gas permeation properties of the carbon membranes were markedly increased in magnitude compared to the polymeric precursor membranes. This was due to the formation of pore structures by cross-linking and volatilisation of small gaseous molecules produced by

minor thermal degradation during stabilization. The overall results demonstrated that the P84-based carbon membrane is a promising material for CO₂/CH₄ and CO₂/N₂ separation.

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CO₂ Selective Carbon Tubular Membrane: The Effect of Stabilization Temperature on BTDA-TDI/MDI P84 co-polyimide

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غشا پیشنهاد مناسبی برای فرایندهایی که دستگاه و تجهیزات کوچکی و بازدهی بالایی هستند و با محیط زیست سازگارند می باشند. با کربنی پیشرفت قابل ملاحظه ای در جداسازی گازها صورت گرفته است. در این تحقیق غشای کربنی لوله ای شکل بروش لایه گذاری با پی-84 و بکمک کو پلی امید بعنوان پیش درآمد برای جداسازی گاز کربنیک تهیه گردید. غشای تهیه شده بروش طیف سنجی و آنالیز ترموگراومتری و آنالیزهای ساختاری سطح با خلل و فوج تعیین مشخصات گردید. پایداری و مختصات نفوذ پذیری عالی غشا برای غشا کربنی لوله ای و آنالیز گازهای کربنیک، متان، و نیتروژن به ترتیب در محدوده 2.97 ± 2.18 , 3.12 ± 4.32 and 206.09 ± 3.24 GPU و در دمای 300 سانتیگراد CH_4 , N_2 و CO_2 می باشند. چنین غشایی نمایش مناسبی از گرینش پذیر ی گازهای CO_2/N_2 و CO_2/CH_4 به ترتیب 65.97 ± 2.87 و 69.48 ± 1.83 می باشند.

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