Preparation of defect-free Polysulfone membrane: optimization of fabrication method

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Abstract: Separation of CO_2 from natural gas is a crucial process in oil and gas industry in order to produce high-quality natural gas prior to its utilization. This paper reports the preparation of defect-free asymmetric polysulfone membrane by manipulating ultimate membrane fabrication parameters. These parameters include the membrane thickness, the forced-convection evaporation duration, and the post-treatment drying method. Membranes obtained were characterized using Field Emission Scanning Electron Microscope (FESEM) and Fourier Transform Infrared (FTIR). The defects of the resulting membranes were verified using single gas permeation of CO_2 and CH_4. The results showed that optimum parameters in obtaining defects free polysulfone membrane were casting of the membrane with a thickness of 0.25 mm, then, left for forced-convective evaporation for 30 seconds and drying of the membrane in open air for 3 days. The permeability values for CO_2 and CH_4 were 12.33 Gas Permeation Unit (GPU) and 4.69 GPU, respectively, with a CO_2/CH_4 ideal selectivity of 2.63, which are consistent with the results reported in the literature.

Key words: Polysulfone; CO_2 separation; Forced-convection evaporation; Post-treatment method

1. Introduction

There has been an increase in demand of natural gas in recent years because of its advantage as a highly efficient form of energy and cleaner fuel. It is estimated that the world market for natural gas is about ES$22billion per annum with 23.5% usage as source of energy in 2004 (Adewole et al., 2013). Thus, the need to process natural gas has become an importance. The two major processes in raw natural gas processing are gas dehydration and gas sweetening (Brunetti et al., 2014). Gas sweetening or also known as acid gas removal is a process of removing CO_2 and hydrogen sulfide (H_sS) from natural gas to increase its calorific value (Hussain and Hägg, 2010). The assisting technologies for CO_2 removal are absorption, adsorption, membrane separation and cryocell method (Brunetti et al., 2014). Since there is a need to obtain a cost effective and energy efficient technology, membrane separation has been extensively researched due to its ability to achieve higher efficiency of separation with a lower capital cost and operating in simple modern compact modules (Adewole et al., 2013).

The performance of membrane-based CO_2 gas separation process is strongly dependent on the permeability and selectivity of the membrane (Ismail and Lai, 2003). Other requirements are thermally and chemically resistance, cost effective, and the ability to be manufactured and produced into different membrane modules (Brunetti et al., 2010).

The study of the polymeric membrane has been extensively reported for the removal of CO_2 from natural gas. Researchers have been focusing on the structure, flux and selectivity of the membrane polymers (Ismail and Rahman, 2003). Thus, there is significant progress found in fabricating a membrane including membrane material, dope formation, fabrication method and fundamental understanding of membrane formation (Ismail et al., 2003).

The first integrally skinned asymmetric membranes had successfully developed by Loeb and Sourirajan in 1960 (Ismail and Lai, 2003). This type of membrane is formed of a very thin and dense skin layer overlying a thicker and highly porous sublayer. The above dense layer represents the actual selective barrier while the porous sublayer gives mechanical support for the membrane (Ismail and Lai, 2004). The thin dense layer is formed by evaporating the membrane on open air for a few seconds before submerging into water bath. In the water bath, the porous layer of the membrane will form. For a variety of membrane-based separation processes, the widely employed one is the asymmetric membrane prepared via phase inversion technique. However, there's a trade-off between permeability and selectivity according to Robeson upper bound (Aroon et al., 2010; Kulprathipanja et al., 2010), in which both parameters exhibit a contradiction relation that proves to be an obstacle in productions and applications of asymmetric membranes for the gas separation process.

Polysulfone is chosen in this study as it contains several advantages, apart from being a well-known polymeric membrane, which has been frequently used by researchers in the production of industrial and commercial membranes (Ismail and Lai, 2004; Rafiq et al., 2011; Scholes et al., 2010). CO_2 is

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preferentially adsorbed in polysulfone rather than CH_4 mainly due to the similarity of chemical structure to sulfonyl and the higher critical temperature of CO_2 compared with CH_4 (Wang et al., 2014). Besides, polysulfone also exhibits few profitable properties such as high chemical stability, excellent mechanical strength, compaction resistance and thermal resistance (Rafiq et al., 2012).

According to the earlier studies (Ismail and Shilton, 1998; Junaidi et al., 2014; Kim et al., 2007; Reverchon and Cardea, 2005; Temtem et al., 2006; Won et al., 1998), various methods have been reported in fabricating a thin asymmetric polysulfone membrane. To our best knowledge, the methods have not been explained in detail. Furthermore, variations in the dope formation using different kinds of solvents in the fabrication of polysulfone membrane were also reported (Aroon et al., 2010; Ismail et al., 2003; Junaidi et al., 2013). The solution was tailored to be close to thermodynamic instability limit and approaching phase transition boundary (Ismail and Lai, 2004). After the membrane was cast, forced-convective evaporation was applied before the membrane was submerged in coagulant bath, which was an important step in membrane fabrication.

Based on Ismail et al. (2003), the time taken for the evaporation duration will affect the thickness of the dense layer and thus, determine the structure of the membrane (Ismail et al., 2003). The thickness of dense layer and membrane structures are important in obtaining a membrane with high selectivity. The thickness of the membrane itself plays an important role in maintaining the mechanical support for the membrane in order to avoid the membrane from getting crinkled (Khulbe, 2008).

The purpose of this research is to fabricate defects free polysulfone membrane with chemical structure as shown in Fig. 1. Few membranes have been fabricated based on different parameters. The structural property of the membranes was studied using FESEM. The performance of each polysulfone membranes in CO_2 separation from CH_4 has also been studied.

In this study, three critical fabrication parameters including the thickness of the membrane, forced-convection evaporation duration and post-treatment drying methods were varied in order to obtain defects free polysulfone membrane.
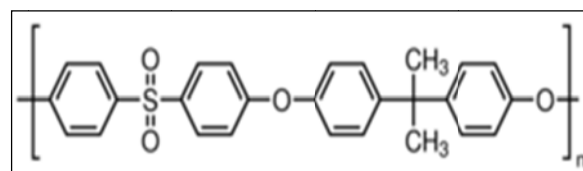

Fig. 1: Chemical structure of Polysulfone

2. Experimental section

2.1. Materials and membranes preparation

The pure polysulfone membrane is prepared via phase inversion method with composition of 25wt.% of polysulfone and 75 wt.% of NMP. The polysulfone was supplied in pellets form (Aldrich, Mw ~ 35,000 by LS). NMP (N-Methyl-2-pyrrolidone) used in this study was supplied by Merck.

The polysulfone pellets were first dried under vacuum for 24 hours at 90°C to remove excess moisture. Then, it was mixed in NMP solution at ambient temperature for 10 hours. Prior to casting, the solution was degassed for 4 hours and left for free standing for another 24 hours to eliminate microbubbles trapped in the solution. The casting solution was then poured onto a clean glass plate and cast using a casting knife at ambient temperature. The membrane thickness was varied by adjusting the gap of the casting knife of 0.15 mm and 0.25mm. After that, the membrane was left for forced convection evaporation, and the duration was varied at 15s, 30s, and 45s. Then, the glass plate with the flat layered membrane was immersed in Deionized (DI) water for 24 hours before solvent-exchanged with methanol for 2 hours. The membrane was dried using three different post-treatment methods: i) drying under vacuum at 110°C for 1 day, ii) open air drying for 1 day before drying under vacuum for 1 day at 110°C and iii) open air drying for 3 days. The performance testing using CO_2 and CH_4 gasses was then conducted. All the membranes fabricated in the present work were listed in Table 1. Total seven membranes were cast based on different fabrication parameters including a reproducible test for defects free polysulfone membrane.

Table 1: PSf membranes synthesized in the present work using different fabrication parameters

Membranes	Membrane Thickness (mm)	Forced-convection Evaporation Duration (s)	Post-treatment Drying Method
M1	0.15	15	110°C for 1 day under vacuum
M2	0.25	15	110°C for 1 day under vacuum
M3	0.25	30	110°C for 1 day under vacuum
M4	0.25	30	1 day air-dried, 1 day under vacuum oven 110°C
M5	0.25	30	3 days air-dried
M5*			
M6	0.25	45	3 days air-dried

M5* - reproducibility testing

2.2. Sample characterization

2.2.1. Variable pressure field emission scanning electron microscope (VPFESEM)

Membrane samples were sent for characterization using Variable Pressure Field Emission Scanning Electron Microscope (VPFESEM, Zeiss Supra55 VP) in order to determine the membrane morphology. The membrane was cut into half using liquid nitrogen before scanning.

2.2.2. Fourier transform infrared (FTIR)

The Fourier Transform Infrared (FTIR) spectroscopy was used to characterize the membrane sample (PerkinElmer, USA). The membrane was scanned with wave numbers ranging from 500 to 4000 cm^{-1}.

2.3. Gas performance testing

The performance of the resultant polysulfone membrane was tested by conducting a single gas permeation test for CO_2 and CH_4 gasses using membrane permeation test rig. The test was carried out using a constant pressure method with a feed pressure of 2 bar at ambient temperature. The volumetric flow rate of the permeate gas was measured using a bubble flow meter attached to the membrane permeation test rig at a constant temperature of 32°C. A membrane was cut into circle with an area of 0.6362 cm^2 and placed in between the feed gas chamber and the permeate gas chamber. The membrane will be supported by a porous metal support and rubber O-rings that acted as a seal. In this study, the unit for gas permeation measurement used is Gas Permeation Unit (GPU), where 1 GPU is equal to 10^{-6}cm^3 (STP)/cm^2 s cm Hg. The permeability of CO_2 and CH_4 in the gas mixture is determined using Eq. 1 and 2 as follows (Mirfendereski et al., 2008).

$$Pi = \frac{Ji}{\Delta P}$$
(1)

$$\alpha \frac{CO_2}{CH_4} = \frac{P_{CO_2}}{P_{CH_4}}$$
(2)

Where P_i (GPU) is a ratio of flux (J_i, cm^{3}s^{-1}(STP)) to pressure drop (ΔP, cmHg) through the membrane, while $\alpha \frac{CO_2}{CH_4}$ is the ratio of CO_2 permeance to CH_4 permeance.

3. Results and discussion

3.1. Characterization of polysulfone membrane

Fig. 2 shows the cross-sectional FESEM images of PSf membranes synthesized in the present work with the magnification of 500x. It can be observed from Figure-2 that membranes fabricated using a longer evaporation duration (30 s and 45 s) produce a thicker dense layer with the thicknesses of 826.3 nm, 893.3 nm, 815.1 nm, and 848.6 nm for M3, M4, M5, and M6 membranes respectively, while membrane produced using a shorter evaporation duration (15s) resulted in thinner dense layer with the thickness of 781.6 nm and 759.3 nm for M1 and M2 membranes respectively. The thickness of the dense layer is important to determine the membrane structure. Both the thickness of dense layer and the membrane structure are significant in the selectivity of the membrane.

The thickness Table 2 summarizes the result of the effect of evaporation duration on the thickness of the dense layer formed.
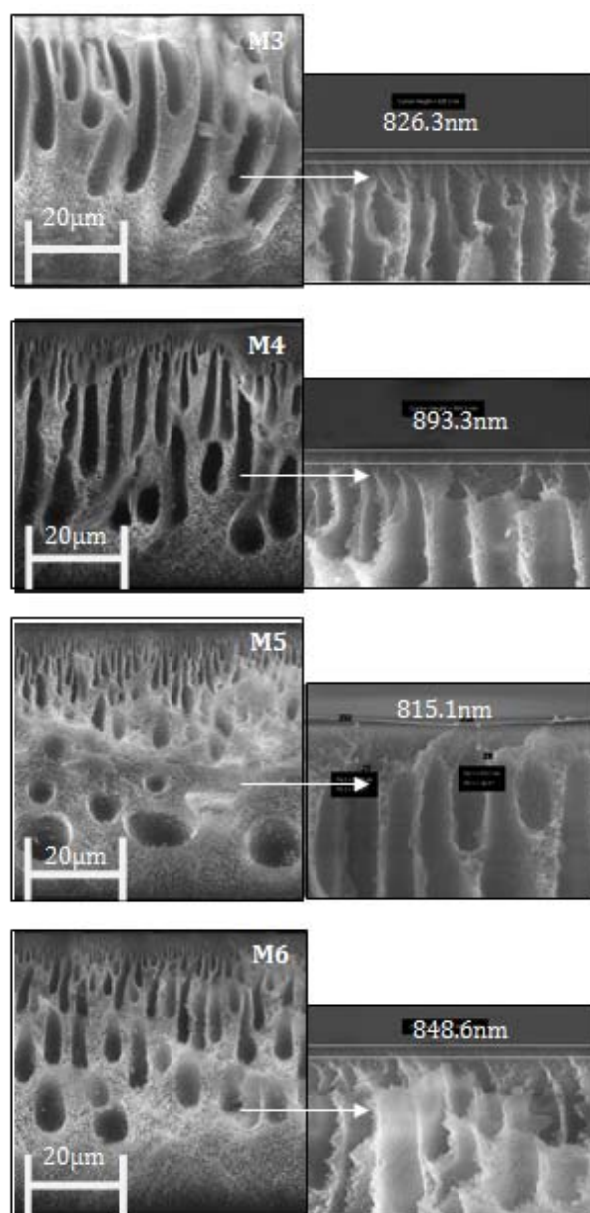

Fig. 2: Cross-sectional View of FESEM Micrographs for PSf Membranes Synthesized in the Present Work.

Meanwhile, the thicknesses of the membranes were varied at 0.15 mm for M1 membrane and 0.25

mm for M2 membrane in order to study its effect towards the thickness of the dense layer formed. As shown in Fig. 1 (M1 and M2), the thicknesses of the dense layer for resultant membranes were similar to each other, proving that the thickness of the membrane did not affect the thickness of the dense layer.

However, the membrane cast with a thickness of 0.15 mm under the same fabrication technique (M1) folded easily due to its thin and weak porous sub-layer which reduced the mechanical support of the membrane, compared to a much thicker M2 membrane as revealed in Fig. 3.
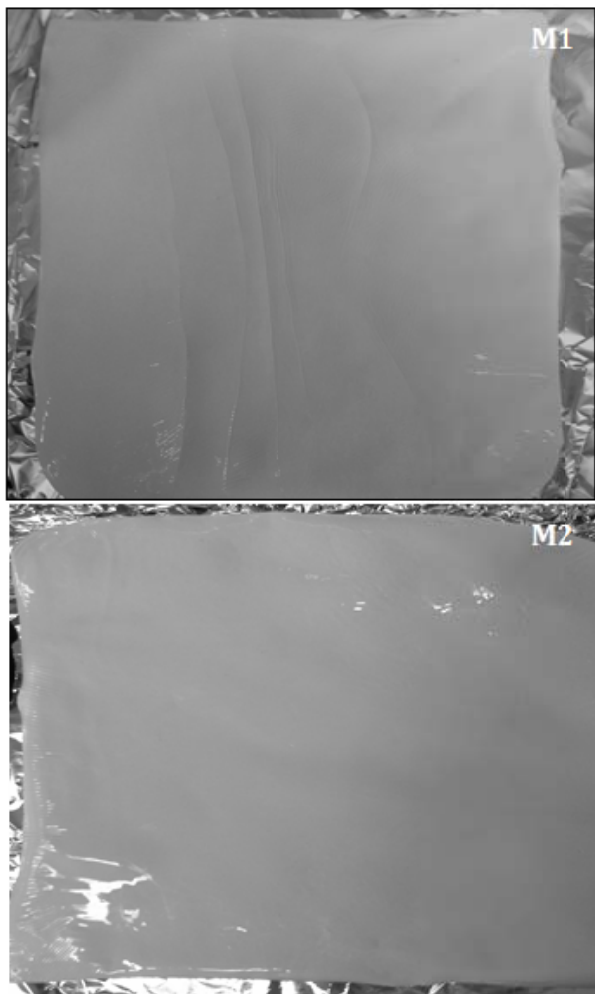

Fig. 3: Membranes Synthesized with Difference in the Thickness of Membrane

Referring to Fig. 1, the only membrane dried in open air for 3 days (M5) demonstrates different morphology than the other membranes. Membrane dried in open air for 3 days showed oval-like structures with the presence of finger-like structure near the dense layer, which differs from the finger-like structures shown by other membranes dried under vacuum. This can be mainly due to the force of the vacuum suction which resulted in different morphology of those membranes dried under vacuum.

The PSf membrane was further characterized by using FTIR as shown in Fig. 4. The FTIR spectrum displayed band at 1050 cm^{-1} which showed the C=C-

O-C stretching. The band occurring at 1230 cm^{-1} signified C-O stretching while the O=S=O stretching was shown at the bands 1105.8 cm^{-1} and 1150 cm^{-1}. The C=C conjugation benzene ring for aromatic ring shows a band at 1579 cm^{-1}. The band at 1390 cm^{-1} signified the presence of asymmetric –CH_3.
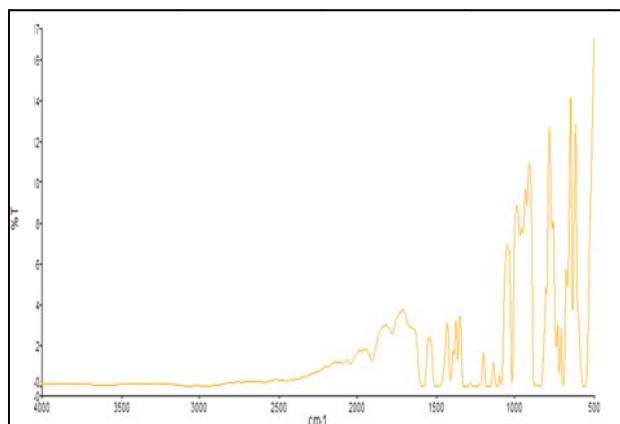

Fig. 4: The FTIR Spectra for PSf Membranes Synthesized in the Present Work.

Table 2: All membranes synthesized in the present work with difference in the thickness of dense layer

Membranes	Forced-convection Evaporation Duration (s)	Thickness of Dense Layer (nm)
M1	15	781.5
M2	15	759.3
M3	30	826.3
M4	30	893.3
M5	30	815.1
M6	45	848.6

3.2. Gas Performance Analysis

Single gas permeation measurements for CO_2 and CH_4 gasses were performed for all the membranes and the results are tabulated in Table 3. Referring to Table-3, the CO_2/CH_4 ideal selectivity for M1 and M2 with different membrane thicknesses of 0.15 mm (M1) and 0.25 mm (M2), respectively, are nearly similar, confirming that the membrane thickness did not play an important role in producing a defect-free membrane.

Meanwhile, lower selectivity of CO_2/CH_4 (near to 1) was obtained for all membranes cast in the present work except for M5 (thickness of 0.25 mm, forced convection evaporation duration of 30 seconds and dried in open air for 3 days). This could be due to the enhancement of free volume in ultrathin skin layer, and increasing the evaporation duration from 15 s to 30 s has caused the membrane skin to mature properly with lesser defects. However, after an optimum evaporation time has been reached, the selectivity of CO_2/CH_4 decreases with the increase in evaporation duration. The membrane cast with evaporation time of 45 seconds (M6) exhibits a lower selectivity of 0.61 compared to the membrane cast with evaporation time of 30 seconds (M5) with a selectivity of 2.63.

Referring to Table 3, all the membranes dried under vacuum as post-treatment drying method

show very low selectivity (near to 1) towards CO_2/CH_4. This could be due to the usage of the vacuum suction which caused defects on the membrane, and thus deteriorates its selectivity.

Table 3: Gas permeation data and CO_2/CH_4 ideal selectivity of all the membranes synthesized in the present work tested at ambient temperature and feed pressure of 2 bar

Membranes	Permeability (GPU)		CO_2/CH_4 Selectivity
	CO_2	CH_4	
M1	14.40	17.10	0.84
M2	23.99	28.90	0.83
M3	8.03	5.78	1.39
M4	17.20	28.50	1.60
M5	12.33	4.69	2.63
M5*	12.80	4.90	2.61
M6	14.70	24.30	0.61

M5* - reproducibility testing

On the other hand, the gas permeation data obtained for M5 is comparable with the result reported in the literature (Aroon et al., 2010). As reported by Aroon et al. (Aroon et al., 2010), the permeability of polysulfone was 9.64 GPU for CO_2 and 4.02 GPU for CH_4, whereas the CO_2/CH_4 ideal selectivity obtained was 2.39. In the present work, the permeability for CO_2 is 12.33 GPU while the permeability for CH_4 is 4.69 GPU. The CO_2/CH_4 ideal selectivity obtained in this work is 2.63. The membrane reproducibility test was conducted and the gas permeation data is reproducible (M5*, Table 3).

4. Conclusions

Place Defects-free polysulfone membrane has been fabricated by mixing NMP with polysulfone pellets. Parameters were varied during the fabrication of membrane including the thickness of membrane, forced-convection evaporation duration, and post-treatment drying methods. The resultant membranes were characterized using FESEM in order to observe the morphology of each membrane. The membranes were further characterized using FTIR to The resultant membranes were tested for their separation performance using CO_2 and CH_4 gasses. The method in fabricating a defect-free polysulfone membrane was obtained by casting the membrane with the thickness of 0.25 mm, forced-convection evaporation duration of 30 seconds before submerging in coagulation bath and left for drying in open air for 3 days. The gas permeation result of CO_2 and CH_4 and CO_2/CH_4 ideal selectivity obtained in the present work were comparable with those results reported in the literature.

Acknowledgment

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