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Effect of Non-Solvent Additive on Effectiveness of Polyvinylidene Fluoride Membrane Fabricated With Thermal Induced Phase Separation Method for Carbon Dioxide Absorption

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Abstract

In the present work porous poly (vinylidene fluoride) (PVDF) hollow fiber membranes were fabricated via thermally induced phase separation (TIPS) method for the application in gas-liquid membrane contactor. For this purpose long air gap distance was used (90 mm). Scanning electron microscopy (SEM) was used for membrane characterization. Gas permeation test was performed using carbon dioxide as test gas. It was observed that the effective surface porosity and membrane pore size increased with increased glycerol concentration. CO_2 absorption using the fabricated hollow fiber membranes were measured in a gas-liquid hollow fiber membrane contactor. The results of the CO_2 absorption rate of the tested fibers revealed that complete removal of CO_2 was achieved using 7% glycerol added to the casted solution at normal operating conditions for equal gas to liquid volumetric flow rates using sodium hydroxide as absorbent liquid.

Keywords: Hollow Fiber Membrane; Membrane Contactor; CO_2 Separation, PVDF

Introduction

Packed bed absorbers have been extensively used in many industries and it is successful in removing undesirable gases and impurities from gas streams. In spite of the success of the packed bed absorbers, there are number of weak points such as flooding at high flow rates and foaming Gabelman and Huang [1]. To overcome this drawback in gas absorbers, microporous hollow fiber membrane contactors for gas separation have been attracting the attention of many researchers as an alternative technology, which overcomes the weaknesses of conventional gas absorption equipments Rangwala [2]. In gas membrane contactor gas–liquid interfacial area remains undisturbed by the change of gas and liquid flow rates. In hollow fiber membrane contactor, phase separation after absorption operation is not necessary because one phase is not dispersed into other phase in the module, by contrast, membrane can introduce resistance to mass transfer Li and cheng [3]. There are several important issues to be considered in the selection of the membrane contactor such that; membrane must be highly hydrophobic to prevent the membrane pores from being filled with aqueous absorbent solutions. Membrane pores must be small to prevent the penetration of absorbents into the pores since the smaller the pore radius, the larger the liquid entry pressure. Membrane porosity must be large so that a large gas–liquid interface is available for gas absorption. The membrane must have enough mechanical strength Kim and Harriot [4]. Several hydrophobic microporous membranes have been used for membrane gas absorption, which include polyethylene (PE), polypropylene (PP), poly (vinylidene fluoride) (PVDF) and (poly(tetrafluoroethylene) (PTFE). Microporous polyethylene and polypropylene membranes have been often used in the membrane contactors since they are cheap and their modules are available commercially. Microporous polyethylene and polypropylene membranes are wetted by some absorbents with low interfacial tensions, which drastically decrease the module efficiency Lawler [5] Wang et al. [6]. Microporous PTFE membrane is showed good gas absorption performance as well as good stability without membrane wetting Nishikawa et al. [7]. Different PVDF hollow fiber membranes were fabricated via non-solvent induced phase separation (NIPS) method. The effect of membrane structure on gas separation was performed and found that the mass transfer coefficients of the membranes estimated from the membrane structure parameters such as pore size, pore size distribution and effective pore length agreed with those observed in the experiments on dilute H_2S absorption in an aqueous NaOH solution under the condition of membrane resistance controlling Kong and Li [8]. Yeon et al. [9] carried out a sequence of tests on the absorption of CO_2 from a CO_2/N_2 mixture into aqueous amine solutions using hollow fiber membrane contactor prepared by using commercially available PVDF membranes. They found that when an aqueous monoethanolamine (MEA) solution was used as absorbent, the membrane was wetted after few hours of operation; by contrast, a high CO_2 removal was maintained for longer period when a mixed solution of MEA and triethanolamine (TEA) was used. Atchariyawut et al. [10-12] studied absorption of CO_2 into water, NaOH and MEA solutions using a commercial microporous PVDF membrane and found that when a 2 molar NaOH solution was used, the membrane mass transfer resistance occupied almost the total resistance. Xu et al. [13] uses PVDF hollow fiber membranes with an inner skinless surface prepared via the NIPS process in the removal of CO_2 from gas mixture. The experiments showed a higher CO_2 absorption rate than other PVDF and polyethylene membranes and attained performance levels equivalent to a PTFE membrane in the experiments of pure CO_2

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absorption into water. As the PVDF membranes, which have been used so far in membrane contactors, were prepared by the NIPS method, their mechanical strength was not so high due to the macrovoid formation. In addition, the formation of skin layer near the inner surface of the membrane is not suitable for membrane contactor application. Khaisri et al. [14] compared the membrane resistances and absorption performances of three different commercial hydrophobic microporous membranes, including PVDF, PP and PTFE membranes, for the CO_2 absorption into aqueous MEA solutions. They found that the CO_2 absorption performance using PTFE membrane had excellent stability compared to other membranes. An alternative method for fabricating microporous membranes without formation of the macrovoids is the thermally induced phase separation (TIPS) method [15,16]. In the TIPS process, the membrane structure was controlled by changing the dope composition and spinning parameters Rajabzadeh et al. [17-19]. Several different PVDF membranes with different structures were prepared and used for CO_2 absorption into aqueous MEA solutions and their efficiencies were compared with that of a commercial PTFE hollow fiber membrane. The effect of the reaction products of the CO_2–MEA reaction on the solubility of CO_2 and diffusivities of CO_2 and MEA in liquid was also discussed [20,21] In the present work porous PVDF hollow fiber membrane is fabricated using predefined concentrations of PVDF/Triacetin/glycerol dope solutions, fabrication of PVDF polymers can be easily performed using TIPS method, by contrast, PTFE is fabricated using stretching and melting method which is not easy method compared to TIPS method, also PVDF is polymer is cheaper than PTFE. The fabricated hollow fibers are used to construct gas liquid membrane contactor module suitable for the removal of CO_2 from CO_2/CH_4 gas mixture using aqueous sodium hydroxide as the absorbent liquid.

Experimental

Materials

PVDF polymer (Solef 6020) was purchased from Solvay, glycerol triacetate (Triacetin) and ethanol from Sigma Aldrich and glycerol from Croda Company, the Netherlands. All chemical were used as received without further treatments.

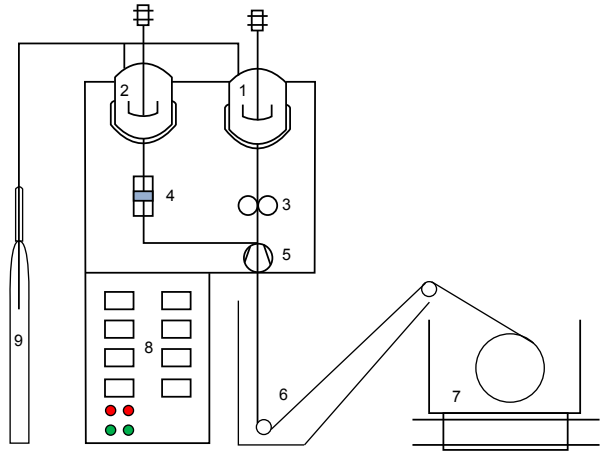


Figure 1: Schematic of thermally induced phase separation (TIPS) process (1) dope vessel, (2) bore liquid vessel, (3) gear pump, (4) bore liquid flow meter, (5) spinneret, (6) quench tank, (7) water trough, (8) control panel, (9) N_2 cylinder

Spinning parameters	Values
Dope composition	30%PVDF/(0,2,5,7)%Glycerol/balance triacetin
Bore liquid	triacetin
Spinneret ID/OD	0.9/2.3 mm
Dope solution flow rate	7 gram/min
Bore fluid flow rate	10 gram/min
Take up winder	10 rpm
Quenching bath temperature	25°C
Air gap	9 cm

Table 1: Hollow fiber spinning conditions.

Preparation of hollow fiber membranes

Hollow fiber membranes were prepared by the device shown in Figure 1. The apparatus consists mainly of two jacked vessels (2 liters each); one vessel is used for dope solution the other vessel is for the bore liquid. The dope vessel is equipped with mixer and jacket filled with high boiling point silicon oil (300°C). The bore liquid is heated with heating mental. The polymer, solvent and additive is stirred manually by spatula for 5 minutes before transferred to the dope vessel. The dope solution is composed of PVDF, triacetin as solvent and glycerol as non solvent additive. The casting solution was heated to 160°C, a temperature of 30°C above the dope solution cloud point to ensure homogeneous solution. The dope solution is heated for 1 hour with continuous gentle mixing. After one hour of the stirring, the stirrer is stopped and the heating continues for 2 more hours without mixing to liberate possible air bubbles. Then, the dope solution is introduced to a spinneret by a gear pump under nitrogen pressure. The spinneret outer and inner diameters were 2.3 and 0.9 mm, respectively. The solvent was introduced into the inner tube to make the lumen of the hollow fiber. The hollow fiber membrane was extruded from spinneret and then immersed in a water quenching bath where the temperature is monitoring at 25°C to induce the separation. Finally the fibers were wounded on a take-up winder. In the spinning process, the variable was the concentration of glycerol. The mass flow rate of the polymer solution and solvent in the spinneret were fixed at 0.9 and 0.7 gram/min, respectively. The take-up speed was fixed at 10 rpm. The fiber membranes were kept in ethanol to extract the solvent remained in the hollow fiber membranes, and then ethanol was detached by immersing the membranes in pure water. The fabrication spinning conditions and parameters are shown in Table 1.

SEM observation

The prepared membranes were freeze-dried with a freeze dryer (EYELA, FD-1000, Japan) to obtain dry hollow fiber membranes without affecting the membrane structure. The dry hollow fiber membranes were fractured in liquid nitrogen and sputtered with gold. The structure of the cross section, the outer and inner surfaces of the hollow fiber membranes were examined through a scanning electron microscopy (SEM, Jeol, JCM-5000 NeoScope, Japan) with an accelerating voltage of 10kV.

Membrane contact angle

The water contact angle of the outer surface of hollow fiber membranes were measured with a drop master (Kyowa, drop master series, Japan). A droplet of 0.5µl was overthrown on the outer surface of the fibers, and then the contact angle was measured.

Membrane mechanical strength

The tensile strength of the hollow fiber membranes were measured by a tensile apparatus (Shimadzu Co, Autograph AG-X, Japan). The hollow fibers were fixed vertically between two pairs of tweezers with the length of 90 mm. The membrane was extended at a constant elongation velocity of 20 mm/min until it was broken. Each data of tensile stress at break was repeated five times.

Gas permeation test

Gas permeation through the hollow fiber membranes were measured using 6 hollow fibers with 17 cm length were glued with epoxy resin at one end and the other side was potted to plastic tubing (Figure 2). The shell inside diameter was 12 mm and length is 200 mm. The CO_2 gas is introduced to the shell side and penetrates through the skin of hollow fiber membranes and leaves from the top of the hollow fibers membrane module. The permeate gas flow rate is measured using digital gas flow meter. The equations used for the calculation of the mean pore size and the effective surface porosity are described below. It was assumed that membrane pores are straight and cylindrical in shape and permeation of gas is under the Poiseuille and Knudsen flow regimes in parallel connection Bakeri et al. [22]. The gas permeance under the Poiselle flow regime is given by:

$$P_p = \frac{1}{8\mu}\frac{r_{p,m}^2}{RT}\frac{\xi}{L_p}\bar{p} \quad (1)$$

The gas permeance under Knudsen flow regime is:

$$P_k = \frac{2}{3}\left(\frac{8RT}{\pi M}\right)^{0.5}\frac{r_{p,m}}{RT}\frac{\xi}{L_p} \quad (2)$$

Hence, the total permeance of permeated gas is:

$$\bar{P} = P_p + P_k = \frac{2}{3}\left(\frac{8RT}{\pi M}\right)^{0.5}\frac{r_{p,m}}{RT}\frac{\xi}{L_p} + \frac{1}{8\mu}\frac{r_{p,m}^2}{RT}\frac{\xi}{L_p}\bar{p} \quad (3)$$

Linearization of equation (3)

$$\bar{P} = A + B\bar{p} \quad (4)$$

Where,

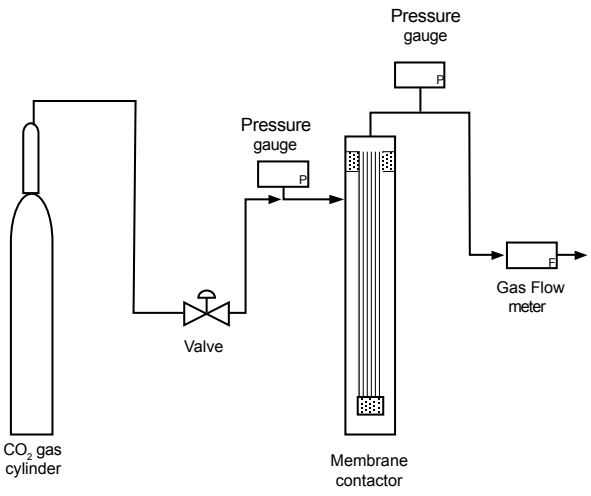


Figure 2: Schematic of the experimental setup used in gas permeation test.

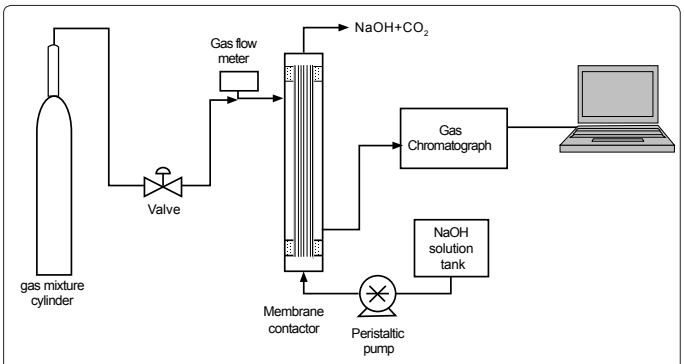


Figure 3: Schematic of the experimental setup used in gas separation test.

$$A = \frac{2}{3}\left(\frac{8RT}{\pi M}\right)^{0.5}\frac{r_{p,m}}{RT}\frac{\xi}{L_p} \quad (5)$$

$$B = \frac{1}{8\mu}\frac{r_{p,m}^2}{RT}\frac{\xi}{L_p} \quad (6)$$

In the above equations, $\bar{P}$ is total gas permeance ($mol.m^{-2}.Pa^{-1}.s^{-1}$), R is universal gas constant ($8.314\ J.mol^{1}.K^{1}$), T is absolute temperature (K), M is molecular weight of gas (g/mol), $r_{p,m}$ is mean pore radius (m), μ is viscosity of gas (Pa.s), ξ is the surface porosity (Ap/A_T) where A_p is area of pores and A_T is total area of membrane, L_p is effective pore length (m) and $\bar{p}$ is mean pressure (Pa):

$$\bar{p} = \left(\frac{Pu + Pd}{2}\right)$$

where P_u is upstream pressure and P_d is downstream pressure. Experimentally obtained gas permeance is plotted versus mean pressure, which should result in a straight line. The intercept (A) of the straight line with the ordinate and slope (B) are used in the following equations to calculate the mean pore size and the effective surface porosity (ξ/L_p).

$$r_{p,m} = \frac{16}{3}\frac{B}{A}\left(\frac{8RT}{\pi M}\right)^{0.5}\mu \quad (7)$$

$$\frac{\xi}{L_p} = \left(\frac{8\mu RTB}{r_{p,m}^2}\right) \quad (8)$$

Gas separation

CO_2 was separated from a gas mixture containing 91% of CH_4 and 9% of CO_2 and 0.5M NaOH aqueous solution was used as liquid absorbent. Five hollow fiber membranes, length of 20 cm were introduced to a plastic tube, the inside plastic tube diameter is 12 mm. The ends of the tube were blocked with epoxy resin. The absorbent liquid was introduced to the tube side and the gas mixture in the shell side of the hollow fiber membranes contactor as shown in Figure 3. The inlet gas volumetric flow rate is adjusted by mass flow controller (Alicat Scientific, USA). The liquid absorbent volumetric flow rate is controlled by peristaltic pump. The CO_2 composition in the exit gas stream is measured using gas chromatography (GC-2014 Shimadzu, Japan).

Results and Discussion

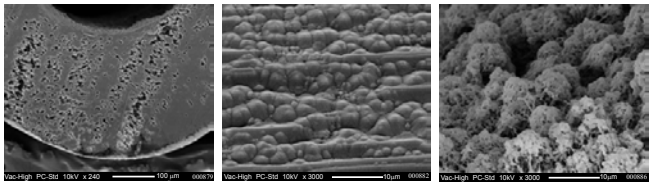
Membrane morphology

Figure 4 is the SEM micrograph of the hollow fiber membrane prepared with 30%PVDF, 70%Triacetin solvent. The SEM micrographs of the cross section, outer surface and inner surface are shown in Figure 4a,4b,4c, respectively. The membrane structure revealed that the porosity at the inner surface is higher than that at the outer surface. This is attributed to two reasons, the long air gap distance (90 mm) compared to previous study which was between 0 to 5 mm Rajabzadeh S et al. [18] and the bore liquid temperature which was 160°C (the same temperature of the dope solution).

Figure 5 shows the membrane structure of the PVDF/triacetin/glycerol system. In this case, 5% Glycerol is added to the dope solution as additive. A difference structure has been observed on the outer surface. The outer surface of the membrane prepared with PVDF/triacetin/glycerol system is more porous than that prepared with PVDF/triacetin system without glycerol additives. This is confirmed in Figure 6, the results of the gas permeability tests as explained in the following section.

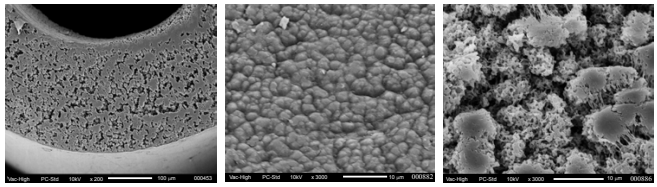
Gas permeation test

Figure 6 shows gas permeability versus inlet gas pressure for hollow fiber membrane fabricated from 30% PVDF and (0%, 2%, 5% and 7% glycerol), the balanced is triacetin. At specific gas pressure, the figure revealed that gas permeability increased as the percent glycerol added to the cast solution increased. Slight increase in gas permeability is observed with increasing inlet gas pressure at fixed percentage of glycerol added to the dope solution. After analysis of gas permeability, it can be disclosed that addition of glycerol increased the porosity of the hollow fiber membrane, that's why the permeability of gas increased with the when the glycerol concentration in the dope solution increased. The addition glycerol was effective to increase gas permeability. This trend is explained by the result shown in Table 2. The table shows the mean pore radius and effective surface porosity for hollow fiber membrane prepared with different concentration of glycerol additive. It is clear from the data disclosed in Table 2 that the pore size increased and effective surface porosity also increased as the percent glycerol added to the dope solution increased. It should be noted that in measuring those values, the assumption is made that the skin layer governs the gas transport. Hence the mean pore size and the effective surface porosity obtained by approach mentioned in section 2.4 are those of the skin layer.



(a) Cross section (b) External surface (c) Inner surface

Figure 4: SEM micrographs for hollow fiber membrane prepared in 30%PVDF/70%triacetin dope solution. (a) Cross-section; (b) External surface; (c) inner surface.



(a) Cross section (b) External surface (c)Inner surface

Figure 5: SEM micrographs for hollow fiber membrane prepared in 30%PVDF/65 %/Triacetin/5% Glycerol cast solution. (a) Cross-section; (b) External surface; (c) inner surface.

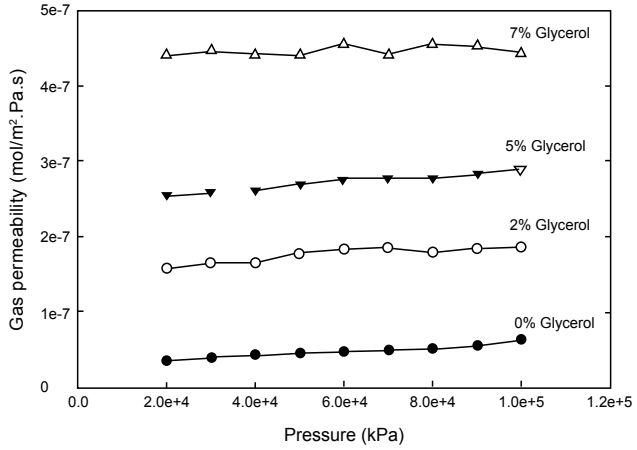


Figure 6: Gas permeability for several hollow fiber membranes prepared with different concentration of glycerol with TIPS method at Bath temperature of 25°C.

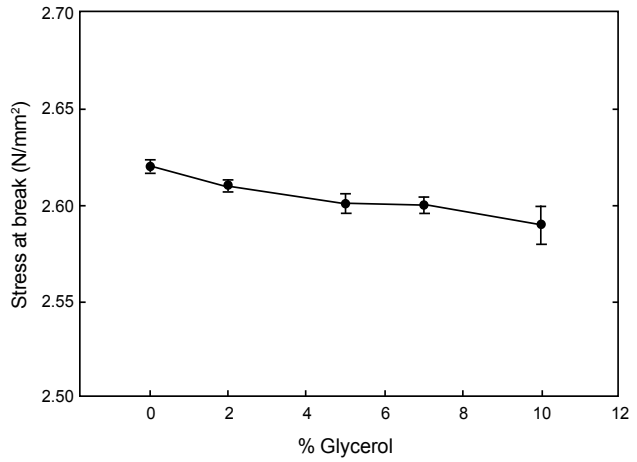


Figure 7: Membrane strength for hollow fiber membrane prepared with different glycerol concentration.

Membrane strength

Figure 7 shows the tensile stress at break for PVDF hollow fiber membranes prepared with various glycerol concentrations. The figure revealed that, tensile strength decreased slightly as glycerol concentration increased. This is attributed to the increase in the membrane porosity of the hollow fiber membranes with glycerol concentrations in the dope solutions. These results agreed with previous studies Rajabzadeh et al. [17-19].

Membrane water contact angle

The effect of percent glycerol added to the dope solution on the average value of the membrane water contact angle is shown in Figure 8. The figure demonstrated sharp increase in the membrane contact angle up to 5% glycerol, further increase in the percent glycerol shows slight increase in the membrane water contact angle.

CO_2 separation

In a membrane contactor for gas absorption, a gas mixture flows on one side of a hydrophobic microporous membrane (in this case shell side) while a liquid absorbent flows on the other side (tube side). The gas–liquid interface is formed at the pore openings adjacent to the liquid. In the membrane contactor module, gas diffuses from the gas side across the membrane and reaches the gas–liquid interface, where gas is absorbed in the liquid. To avoid wetting the membrane pores should not be filled with liquid but with gas; since the liquid phase diffusivity is much lower than gas phase diffusivity, the mass transfer resistance through liquid-filled pores is much larger than that through gas-filled pores. Figure 9 shows the percent removal of CO_2 from CO_2/CH_4 gas mixture versus the inlet gas volumetric flow rate. The gas was inserted to the shell side of the hollow fiber membrane contactor at fixed liquid absorbent (0.5M NaOH) volumetric flow rate (10 ml/min) flows in the tube side of hollow fiber membrane contactor fabricated at different percentage of glycerol additives (0%, 2%, 5% and 7%). The figure shows that, at equal inlet ratio of gas volumetric flow rate to absorbent liquid volumetric flow rate, complete removal of carbon dioxide was achieved. Increasing ratio of gas flow rate at fixed absorbent liquid flow rate decreases the percent CO_2 removal. In other word, when the ratio of gas to liquid absorbent flow rate increased, percent removal of CO_2 decreased. For fiber fabricated with

Glycerol concentration (wt %)	Pore radius (μm)	Effective surface porosity (m^{-1})
0	0.005	20
2	0.011	165
5	0.051	585
7	0.077	907

Table 2: Mean pore radius for hollow fiber membrane prepared with different concentration of glycerol.

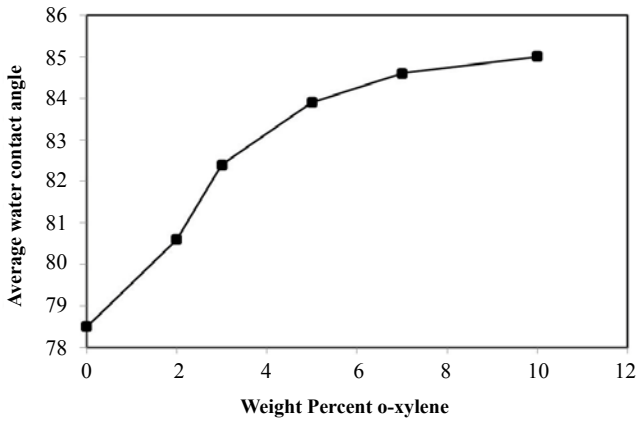


Figure 8: Effect of glycerol concentration in the dope solution on membrane water contact angle.

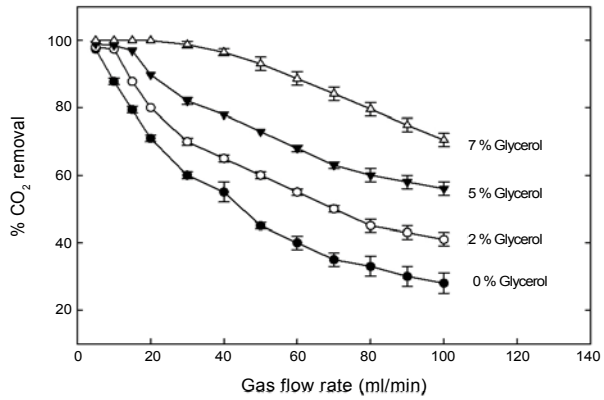


Figure 9: Percent CO_2 removal versus inlet gas flow rate of fabricated hollow fiber membrane prepared with different glycerol concentration.

7% glycerol, it was possible to achieve complete removal for gas to liquid volumetric flow rate up to 3 times, further increase in the gas to absorber ratio resulted in lower percent removal of carbon dioxide, as it is clear from the decline in the curve shown in Figure 9. The percent removal of CO_2 for 0% glycerol was very low. Therefore, in order to investigate the effect of surface property on CO_2 absorption efficiency, we performed experiments for two cases; operation where absorbent flows in the tube and gas mixture flows in the shell side and vice versa. Experimental results revealed that, when gas flowed in the lumen side of the membrane, the percent removal of CO_2 was insignificant and bubbles was observed in the liquid absorbent. That leads to pressure build up of the gas in the tube side and consequently penetrated to the low pressure side and caused bubble formation.

Conclusions

Microporous hollow fiber membranes were prepared via TIPS method using PVDF polymer, triacetin as solvent and varied quantities of glycerol as non solvent additives gas-liquid phase separation. In the case of zero glycerol content in the cast solution; solid-liquid separation covers the structure of the fabricated fibers and liquid-liquid separations governed the cases with glycerol addition to the dope solution. Hollow fiber membranes prepared with PVDF/triacetin/glycerol system, were successfully used to remove CO_2 from CO_2/CH_4 gas mixture. It was found that as the percentage of glycerol increased in the dope solution the removal rate of CO_2 increased where complete removal of CO_2 is achieved at equal ratio of gas to liquid volumetric flow rate. It can be concluded that addition of glycerol to dope solution was efficient to increase the effective surface porosity and pore radius. The effect of glycerol additive to the cast solution on the membrane tensile stress was insignificant.

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