J. Applied Membrane Science & Technology, Vol. 12, December 2010, 1–6
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CO_2 Absorption with NaOH Solution through the Porous PVDF Hollow Fibre Membrane Contactor

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ABSTRACT

In this study, porous hydrophobic polyvinylidene fluoride (PVDF) hollow fiber membranes were fabricated via a wet phase inversion process. In order to improve the phase inversion rate and provide porous membranes, 4 wt.% lithium chloride (LiCl) was used in the spinning dope. The prepared membrane morphology was studied using field emission scanning electron microscopy (FESEM). Chemical CO_2 absorption by NaOH solution (1M) was conducted through the PVDF hollow fiber membrane contactor. The effect of the main operating condition such as absorbent temperature, CO_2 pressure and absorbent flow rate on the performance of CO_2 absorption was investigated. From FESEM examination, the membrane possesses an almost sponge-like structure with ultra thin skin layer. Results of CO_2 absorption test showed that by increasing the absorbent flow rate the CO_2 flux increased which confirmed the existence of liquid side mass transfer resistance. It was found that by increasing the absorbent temperature the CO_2 flux considerably improved. Meanwhile, the effect of CO_2 pressure on the absorption rate was insignificant. Therefore, it can be concluded that by applying a porous hydrophobic membrane with improved structure and optimizing the operating conditions, high CO_2 removal efficiency can be achieved through gas-liquid membrane contactors

Keywords: PVDF hollow fiber membrane, CO_2 absorption, membrane contactor

1.0 INTRODUCTION

CO_2 is the most important component of greenhouse gases, which has been associated with global climate change. One-third of CO_2 emission comes from combustion of fossil fuels in power plants worldwide. In addition, presence of CO_2 in natural gas can cause pipeline and equipment corrosion, reduction in the heating value, occupying the volume in the pipeline and CO_2 is also able to solidify in cryogenic process [1]. Several techniques have been improved for CO_2 removal from the gas streams such as chemical and physical absorption, solid adsorption, cryogenic distillation, membrane separation [2].

Alkanolamine based gas absorption systems have gained approximately 90% of the acid gas treating processes in operation due to their flexibility and ability to remove the acid gas to very low level [3]. Although, these devices have attained significant success in the industries, they suffer from some operational drawbacks such as foaming, flooding, channeling and entrainment. In addition, because of their relatively smaller mass transfer coefficient, they tend to be large and costly to build. Therefore, in order to minimize overall environmental impacts and cost of CO_2 capture, the priority will be given to the

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technologies with improved CO_2 removal efficiency.

Hollow fiber gas-liquid membrane contactor is a promising alternative to conventional gas absorption systems for CO_2 capture from the gas streams. In this system, membrane separation is not only combined with an absorption process, but both processes are fully integrated into one piece of equipment. The porous membrane acts as a fixed interface between the gas and the liquid phase without dispersing one phase into another. The membrane offers a flexible modular device with a high specific surface area. The absorption process can offer a very high selectivity and a high driving force for transport even at very low concentrations [4].

The membrane is the most important element of the membrane gas absorption process. In order to minimize the membrane mass transfer resistance, not only the membrane should possess high permeability but also the pores of membrane must be completely gas-filled over the prolonged periods of operational time. This can be achieved by using hydrophobic membrane with small pore size. PVDF is the only hydrophobic polymer soluble in the organic solvents, which can be used in the phase-inversion process for asymmetric membrane fabrication. It was found that the addition of polyvinylpyrrolidone (PVP) in the PVDF dope resulted in the membranes with a slight decrease in the mean pore size and a drastic increase in the effective porosity as compared to that without addition of PVP [5]. Since, the PVP has a high molecular weight, it can not completely wash out from the membrane structure during solvent/non-solvent exchange and later washing process then a trace of it in the membrane can seriously affect the membrane hydrophobicity. Therefore, using water soluble additives with small molecular weight, which can easily wash out during membrane preparation, is preferred to fabricate PVDF membranes with high permeability and good hydrophobicity.

In present study, asymmetric PVDF hollow fiber membranes were prepared via a wet phase-inversion process. In order to provide porous membranes, 4 wt.% lithium chloride (LiCl) was introduced into the spinning dope as phase inversion promoted additive. The performance of the prepared membrane for CO_2 absorption was evaluated through the gas-liquid membrane contactor at different operating conditions.

2.0 EXPERIMENTAL

2.1 Materials

Commercial PVDF polymer pellets (Kynar® 740) were supplied by Arkema Inc., Philadelphia, USA. 1-methyl-2-pyrrolidone (NMP, >99.5 %) was used as polymer solvent without further purification. Lithium chloride (LiCl, ≥ 99 %) (Sigma-Aldrich®) was used as non-solvent additives in the polymer dopes. Methanol (GR grade, 99.9 %) and n-Hexane (99 %) were purchased from MERCK and used for post-treating the prepared membranes. Tap water was used as coagulation bath in the spinning process. NaOH solution (1M) was used as liquid absorbent in the CO_2 absorption experiments.

2.2 Fabrication of Porous Hollow Fibre Membrans

The PVDF polymer was dried at 60 ± 2 °C in a vacuum oven for 24 h to remove moisture content. The spinning dope (PVDF 18 wt.%, LiCl 4wt.%, NMP 78 wt.%) was prepared at 60 °C using stirring until the solution became homogeneous. The spinning solution was degassed using 30 min ultra-sonic and maintained 24 h at room temperature before spinning. The hollow fiber spinning apparatus by the dry-jet wet phase-inversion was explained elsewhere [6]. Table 1 lists the detailed spinning parameters.

Table 1 Hollow fibre spinning conditions

Dope extrusion rate (mL/min)	4.5
Bore flow rate (mL/min)	1.55
Bore composition (wt.%)	NMP/H_2O 80/20
External coagulant	Tap water
Air gap distance (cm)	0.50
Spinneret o.d./i.d. (mm)	1.2/0.55
Spinning dope temperature (°C)	25
External coagulant temperature (°C)	25

The spun fibers were immersed in water for 3 days to remove the residual NMP and the additive. Then they were post-treated using methanol and n-hexane as non-solvent exchange to minimize fiber shrinkage and pores collapse before drying at room temperature.

2.3 Field Emission Scanning Electron Microscopy Examination

Field emission scanning electronic microscopy (FESEM) (ZEIZZ SUPRA 35VP) was used to examine the morphology of the spun PVDF hollow fiber membranes by the standard methods. The membrane samples were immersed in liquid nitrogen and fractured carefully. Then the samples were dried in a vacuum oven and coated by sputtering platinum before testing. The FESEM micrographs of cross-section, internal surface, external surface and outer skin layer of the hollow fibers were taken at various magnifications.

2.4 CO_2 Absorption Experiment

The gas-liquid membrane contactor was employed to determine CO_2 absorption flux of the membranes, where a total of 10 hollow fibers were packed randomly in the stainless steel module. The specifics of the membrane contactor module were given elsewhere [7]. Pure CO_2 as the feed gas and NaOH solution (1M) as the liquid absorbent were flowed in the shell side and lumen side of the membrane contactor, respectively. A counter-current flow was used for the gas and the liquid absorbent at continues mode of operation. In all the experiments, the liquid side pressure was controlled 0.2×10^5 pa higher than the gas side in order to prevent bubble formation in the liquid phase. Using the titration method, CO_2 concentration in the liquid outflow at various operating conditions was measured to determine the CO_2 flux. Before taking the samples, all the experiments were carried out for 30 min to achieve a steady state condition. The flow diagram of the experimental setup was shown elsewhere [8].

3.0 RESULTS AND DISCUSSION

3.1 Morphology of the Hollow Fibre Membranes

It was proven that increasing phase inversion rate could result in more porous asymmetric membranes [9]. Therefore, in order to fabricate porous membranes with small pore sizes, which are favorable for gas absorption application, LiCl was introduced into the spinning dopes as a phase inversion promoter. The morphology of the prepared PVDF membranes was examined through field emission scanning electron microscopy (FESEM) and the micrographs are given in Figure 1. The hollow fiber membranes possess outer diameters ranging from 740 to 750 μm, inner diameters ranging from 415 to 420 μm and the wall thickness ranging from 120 to 135 μm. As it can be seen from the cross-sectional morphology (Figure 1a), the membrane has an almost sponge-like structure. On the other hand, addition of 4 wt.% LiCl in the spinning dope provided very small finger-likes (up to 30 μm) close to the outer surface. This morphology can be related to the spinning dopes viscosity and enhanced phase inversion rate. It was observed that by adding LiCl, viscosity of the spinning dopes drastically increased. In general, addition of non-solvent additives in the polymer dopes results in enhancement of phase inversion process which can provide membranes with finger-like structure. Meanwhile, the additives can also increase the polymer dopes viscosity which generates membranes with sponge-like structure [10, 11]. A decrease in mutual diffusion between solvent in the spinning dope and non-solvent (water) in the coagulation bath due to high viscosity of the spinning dope (4 wt.% LiCl) provided an almost sponge-like structure. However, the small finger-likes generated can be a result of enhanced phase inversion.

The skin layer, inner surface and outer surface of the PVDF membrane are presented in Figure 1(b,c,d). The prepared membranes showed an ultra thin skin layer (80-100 nm). Since the PVDF polymer has a high molecular weight the resulted solutions for asymmetric membrane preparation have relatively high viscosity. Therefore, during phase inversion process, the solvent and non-solvent could not rapidly diffuse out of the polymer solution and prevented the polymer concentration on the outer surface. This phenomenon provided the membranes with ultra thin skin layer, high surface porosity and very small pore sizes (13-90 nm) which are favorable parameters for gas absorption applications.

As for the inner surface formation, using 80 wt.% NMP solution as the bore fluid induced delay phase-inversion and provided an inner skinless surface with open microporous structure (Figure 1c). The same morphology was also obtained for the polysulfone membranes using 95 wt.% NMP as the bore fluid [7]. In fact, removing inner skin layer can minimize the membrane mass transfer resistance during gas absorption process.

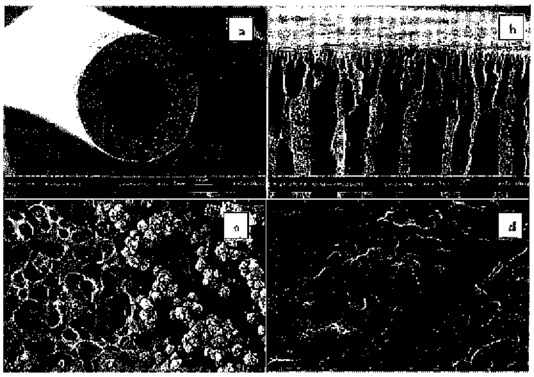

Figure 1 FESEM micrographs of the PVDF hollow fiber membrane: (a) cross-section; (b) skin layer; (c) inner surface; and (d) outer surface

3.2 Effect of Absorbent Flow Rate on CO_2 Flux

Chemical CO_2 absorption with NaOH solution (1M) was conducted in the gas-liquid membrane contactor at 25 °C. The liquid absorbent passed through the lumen side and pure CO_2 flowed counter-currently through the shell side of the hollow fiber membrane module. The CO_2 absorption flux of the prepared PVDF membrane as a function of the absorbent flow rate is shown in Figure 2.

As it can be seen, the CO_2 flux increased with an increase in the absorbent flow rate. A similar trend was also reported for CO_2 absorption by typical amines in the PVDF and PTFE hollow fiber membrane contactors [12]. Although the absorption concentration is relatively high, significant OH^- depletion was occurred due to the high CO_2 concentration in the gas phase (pure CO_2). Therefore, at this case, the OH^- concentration at the gas-liquid interface may reach to zero and liquid saturation occurred can increase the liquid mass transfer resistance. By increasing the absorbent flow rate the supply rate of NaOH was increased and OH^- depletion could be reduced which resulted in the enhancement of the CO_2 flux.

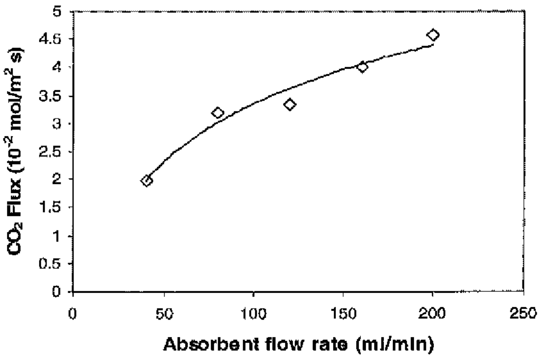

Figure 2 Effect of absorbent flow rate on CO_2 flux of the PVDF hollow fiber membrane (Q_g=100 mL/min, T=26 °C, $P_g=1\times10^5$ Pa, $P_l=1.2\times10^5$ Pa)

3.3 Effect of Absorbent Temperature on CO_2 Flux

Figure 3 shows the measured CO_2 flux as a function of the liquid absorbent temperature. The results were obtained at constant CO_2 and the absorbent flow rate (100 ml/min) through the membrane contactor. The CO_2 flux approximately 65% increased when the absorbent temperature increased from 10 to 40 °C. A significant increase of CO_2 flux with temperature (from 30 to 50 °C) was also reported for chemical absorption of CO_2 using methyldiethanolamine (MDEA) in the PP hollow fiber membrane contactor [13]. The increase in the absorption performance with temperature can be attributed to the enhancement of the species diffusivity and the reaction rate constant according to the Arrhenius expression. On the other hand, at high temperature, water vapors can fill the membrane pores and eventually result in capillary condensation. It must be mentioned that the smaller pore size is more suitable for capillary condensation of water vapor based on the Kelvin equation, which dictates that even under-saturated vapors can be condensed in channels with very small dimensions [14]. Therefore, membrane wetting can be occurred due to capillary condensation in the membrane pores which results in improvement of the membrane mass transfer resistance during long-term operation. In fact, membrane wetting can drastically affect the absorption performance [15].

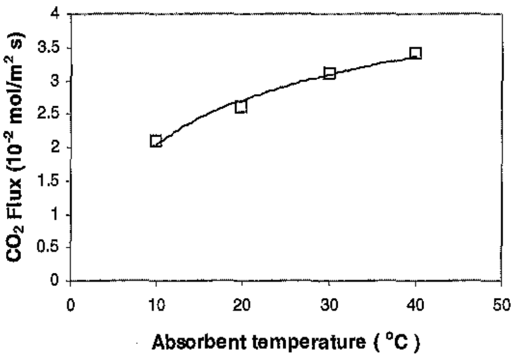

Figure 3 Effect of absorbent temperature on CO_2 flux of the PVDF hollow fiber membrane (Q_l=100 mL/min, Q_g=100 mL/min, P_g=1×10^5 Pa, P_l=1.2×10^5 Pa)

3.4 Effect of CO_2 Pressure on CO_2 Flux

The measured CO_2 flux of the membrane verses CO_2 pressure is shown in Figure 4.

By increasing the CO_2 pressure, the CO_2 concentration in the gas phase increases which can improve the absorption driving force. However, as the results showed the enhancement in the CO_2 flux was not significant. Once the CO_2 pressure increased from 1×10^5 to 6×10^5 pa, an approximate 14% increase in the CO_2 flux was observed. Since the absorbent flow rate is constant, an increase in the CO_2 concentration with pressure resulted in the liquid saturation on the lumen side which higher increment of the CO_2 pressure could not increase the CO_2 flux. Therefore, it can be said that the reaction rate was almost independent from CO_2 concentration and can be considered as pseudo first order. This indicates an instantaneous absorption regime which the OH^- concentration controls the CO_2 absorption flux.

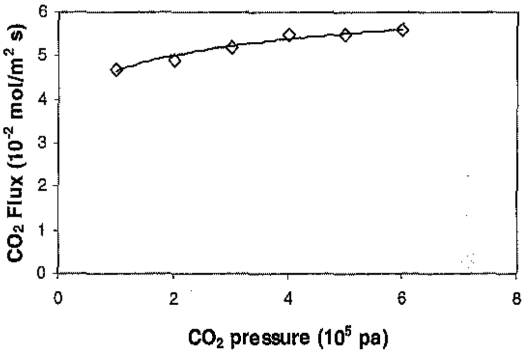

Figure 4 Effect of CO_2 pressure on CO_2 flux of the PVDF hollow fiber membrane (Q_l=100 mL/min, Q_g=100 mL/min, T=26 °C)

4.0 CONCLUSIONS

Porous hydrophobic PVDF hollow fiber membranes were fabricated via a wet phase inversion process. In order to improve the membrane structure for CO_2 absorption, 4 wt.% of LiCl was introduced into the spinning dope as phase inversion promoter and 80% NMP solution was used as the neutral bore fluid. Chemical CO_2 absorption by NaOH solution (1M) was conducted through the prepared PVDF hollow fiber membrane contactor. The effect of the main operating condition such as absorbent temperature, CO_2 pressure and absorbent flow rate on the performance of CO_2 absorption was investigated. FESEM micrographs indicated that the membrane had a sponge-like structure with inner skinless layer and ultra thin outer skin layer. From the CO_2 absorption experiments, it was found that increasing the absorbent temperature significantly enhanced the CO_2 flux due to an increase in the reaction rate constant and the reactive species diffusivity. However, the effect of CO_2 pressure on the CO_2 flux was insignificant because of the liquid absorbent saturation in the lumen side. In addition, by increasing the absorbent flow rate the CO_2 flux increased which confirmed the existence of liquid side mass transfer resistance. It can be concluded that high CO_2 removal efficiency can be achieved through gas-liquid membrane contactors by applying an improved membrane structure and optimizing the operating conditions.

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