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# Preparation of porous hydrophobic poly(vinylidene fluoride-co-hexafluoropropylene) hollow fiber membrane contactors for CO<sub>2</sub> stripping

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## ABSTRACT

Porous hydrophobic poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) hollow fiber membranes were prepared via a wet spinning process using polyethylene glycol (PEG-400) and ortho-phosphoric acid (PA) in the spinning dope. CO<sub>2</sub> stripping from diethanolamine (DEA) solution was conducted through the gas-liquid membrane contactor modules. By obtaining cloud point diagrams, higher phase inversion rate was confirmed for the solution with PA. The smaller finger-like macrovoids were resulted when using the non-solvent additives. The membranes with higher surface porosity and smaller mean pore size were produced when using the additives in the spinning dope. The improved PVDF-HFP/PA membrane had the mean pore size of 0.015 μm and permeability of 13,100 GPU. This membrane showed a minimum mass transfer resistance of 15,982 (m/s)<sup>-1</sup> which is about 68% less than the resistance of plain PVDF-HFP membrane. The improved PVDF-HFP/PA membrane showed CO<sub>2</sub> stripping flux of about 9 × 10<sup>-3</sup> mol/m<sup>2</sup> s at the liquid velocity of 0.045 m/s.

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## 1. Introduction

Using hydrophobic polymers for porous membrane preparation has been a research interest due to the wide range of applications such as microfiltration, ultrafiltration, nanofiltration, membrane distillation, and membrane contactor [1–4]. Polyethylene (PE), polypropylene (PP), polytetrafluoroethylene (PTFE) as hydrophobic polymers are not soluble in organic solvents at low temperature. Therefore, the asymmetric membranes cannot be produced by non-solvent induced phase separation (NIPS) process. Thermal and stretching methods which are highly energy consuming have been used to prepare these membranes. The only hydrophobic polymer soluble in common organic solvents at room temperature is polyvinylidene fluoride (PVDF). PVDF has extensively used for membrane preparation by NIPS owing to good chemical and thermal stability, and easy processing. However, insufficient hydrophobicity of PVDF has resulted in partial wetting of the porous membranes during the gas absorption process which could significantly deteriorate the separation performance [5]. So far, several costly methods such as blending, cross-linking and grafting have been introduced to enhance surface hydrophobicity of the PVDF membranes [6]. Due to the higher hydrophobicity,

commercial copolymer of polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) has been used as a promising material for porous asymmetric membrane preparation [7–11]. In fact, by addition of HFP group, fluorine content increases which generates a higher hydrophobic structure compared to PVDF. Moreover, PVDF-HFP copolymer has higher solubility, lower crystallinity, and smaller glass transition temperature compared to PVDF material. PVDF-HFP has a larger free volume because of the addition of HFP as an amorphous phase into the main vinylidene fluoride (VDF) blocks [12,13], which can also cause more open membrane structure. These properties can produce a high porosity and hydrophobicity structure which are promising factors for gas-liquid membrane contactor applications. Indeed, a reduction in the membrane resistance and the improvement of wetting stability of the membrane can be a result of these factors. Shi et al. [7] improved the structure of PVDF-HFP hollow fiber membranes for CO<sub>2</sub> absorption considering polymer dope rheology. The improved membrane presented a significantly higher CO<sub>2</sub> flux than the commercial PVDF membrane. The effect of concentration and molecular weight of polyethylene glycol (PEG) as non-solvent additive in the spinning dope on the structure and performance of PVDF-HFP hollow fiber membrane was investigated by Wongchitphimon et al. [8]. Increasing molecular weight of PEG from 200 to 600, resulted in a higher pure water permeability (PWP) due to the more open morphology. A similar result for PWP also was obtained by increasing PEG-200 concentration from 3% to 10% in

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the polymer dope. Poly (vinyl pyrrolidone) (PVP), lithium chloride (LiCl) and glycerol were also used as non-solvent additives by the same research group to enhance the membrane structure and performance [9]. Addition of the non-solvents in the polymer dope significantly improved PWP. The addition of LiCl or glycerol also resulted in a narrow pore size distribution. Moreover, the membrane hydrophobicity was less affected by LiCl and glycerol compared to PVP. In another study, surface modification of PVDF-HFP hollow fiber membranes was conducted using Fluorolink® S10 (FS10) and TEOS in order to enhance the outer surface hydrophobicity [10]. The dynamic contact angle of modified membrane increased from 95.5° to 127.8° while the mean pore size reduced from 32.7 nm to 25.2 nm. The prepared membranes were used in a membrane contactor system and the CO<sub>2</sub> absorption flux of the modified membrane was improved about 20%. The effect of PVDF-HFP concentration on the structure and performance of the hollow fiber membranes for direct contact membrane distillation (DCMD) was investigated by García-Payo et al. [11]. By increasing the copolymer concentration, the pore sizes of both the internal and external surfaces of the hollow fibers decreased. When copolymer concentration was more than 20%, the pore size distribution of the external surface reached to a minimum value. In addition, DCMD permeate flux increased when the copolymer concentration decreased.

Membrane contactor provides a non-dispersive contact between the gas and liquid phases which offers several advantages over traditional contacting devices [14,15]. Gas absorption and separation using gas-liquid membrane contactors has been extensively studied in the literature since it was introduced by Qi and Cussler in 1985 [16,17]. However, membrane contactor for gas stripping, which is a highly energy consuming process, was introduced in 2009 by Koonaphapdeert et al. [18] followed by a narrow body of research [19–23]. In fact, by improving membrane structure and separation efficiency it is possible to minimize the energy required for regeneration of the liquid phases with dissolved gases. CO<sub>2</sub> stripping from water through a developed PVDF hollow fiber membrane contactor was investigated by Mansourizadeh and Ismail [19]. The effect of different operating conditions on the CO<sub>2</sub> stripping flux of the membrane was studied. It was found that the liquid flow rate and temperature were the main factors that influenced the stripping flux. The structure of PVDF hollow fiber membranes for CO<sub>2</sub> stripping from diethanolamine (DEA) was improved by addition of different non-solvent additives in the polymer dope [21]. The PVDF/PEG-400 membrane showed a higher stripping flux of  $4.03 \times 10^{-2}$  mol/m<sup>2</sup> s due to the higher surface porosity. In another study, CO<sub>2</sub> stripping from monoethanolamine (MEA) through PTFE hollow fiber membrane contactor was investigated [20]. It was found that velocity of the gas phase had insignificant effect on the mass transfer coefficient and CO<sub>2</sub> stripping flux. On the other hand, increasing the operating temperature, the liquid phase velocity, and MEA concentration resulted in the improvement of the CO<sub>2</sub> stripping flux. Since membrane wetting is the main drawback of the gas-liquid membrane contactors, the membrane structure and properties play important roles on a prolonged stable operation. Indeed, the CO<sub>2</sub> stripping performance of the membrane can be improved by preparing membranes with high hydrophobicity and surface porosity, and small pore sizes.

Due to high hydrophobicity and open structure, PVDF-HFP can be a promising alternative for preparation of porous membrane contactors for gas absorption/stripping. In fact, using a membrane with good wetting resistance and high porosity can minimize the mass transfer resistance during the gas-liquid membrane contacting process. Although some studies on the gas absorption by PVDF-HFP hollow fiber membrane contactors have been conducted, there is no research in the literature regarding gas stripping by PVDF-HFP membranes. In the present work, an attempt was made to improve the structure of porous PVDF-HFP hollow fiber mem-

**Table 1**

Polymer dope composition and viscosity.

Polymer dope	Composition (wt.%)	Viscosity (cp at 25 °C)
PVDF-HFP/NMP	18/82	1840
PVDF-HFP/PEG-400/NMP	18/4/78	2550
PVDF-HFP/PA/NMP	18/4/78	3070
PVDF/PA	18/4/78	3970

**Table 2**

Hollow fiber spinning conditions.

Dope extrusion rate (ml/min)	2.0
Bore flow rate (ml/min)	0.4
Bore composition (wt.%)	NMP/H <sub>2</sub> O 80/20
External coagulant	Tap water
Air gap distance (cm)	0.0
Spinneret o.d./i.d. (mm)	0.7/0.3
Spinning dope temperature (°C)	25
External coagulant temperature (°C)	25

branes for CO<sub>2</sub> stripping from DEA solution. For this purpose, the low molecular weight pore forming additives such as PEG-400 and ortho-phosphoric acid were used in the polymer solution. The membranes were characterized in terms of morphology, hydrophobicity, wetting resistance, mass transfer resistance, N<sub>2</sub> permeability, collapsing pressure and overall porosity. CO<sub>2</sub> stripping tests were conducted through the prepared gas-liquid membrane contactor modules.

## 2. Experimental

### 2.1. Materials and chemicals

Commercial PVDF-HFP powder (Kynar® 2801) with 12 wt.% HFP were purchased from Arkema, Japan. Commercial PVDF polymer pellets (Kynar® 740) were supplied by Arkema Inc., Philadelphia, USA. The polymer solvent was 1-methyl-2-pyrrolidone (NMP, >99.5%) (Merck) and used without further purification. Ortho-phosphoric acid 85% (PA) and PEG-400 were provided by Merck and used as non-solvent additives in the polymer dopes. Ethanol (>99.8% GC) was purchased from Sigma-Aldrich and used for post-treatment of the fresh membranes. Diethanolamine (99%) from Merck was used to prepare the absorbent solution for the CO<sub>2</sub> stripping tests. Barium chloride (BaCl<sub>2</sub>), sodium hydroxide (NaOH) and hydrochloric acid (HCl) were provided by Merck and used as the titration chemicals.

### 2.2. Preparation of hollow fiber membranes

In order to prepare homogeneous solutions, weighted non-solvent additive was added to NMP in a flask under constant stirring at 60 °C followed by addition of the polymer. The stirring was continued until homogenous solutions were achieved. The viscosity and composition of prepared solutions are given in Table 1. PEG-400 was used as a weak non-solvent and PA as a strong non-solvent to prepare membranes at different phase separation rates. The solutions were degassed using 30 min ultrasonication and kept overnight at room temperature before spinning. An aqueous solution of 80 wt.% NMP was used as the bore fluid to produce inner skinless layer hollow fiber membranes with minimum mass transfer resistance. To prepare membranes with high surface porosity, a wet spinning process was employed which is explained elsewhere [24]. Table 2 lists the details of spinning conditions. The prepared fibers were immersed in tap water for 3 days to remove the residual solvent and non-solvents from the membrane matrix. The hollow fiber membranes were post-treated

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