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Effect of PVDF dope rheology on the structure of hollow fiber membranes used for CO_2 capture

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Abstract

In this paper, poly(vinylidene fluoride) (PVDF) hollow fiber membranes were prepared to make membrane contactors for CO_2 capture. The hollow fiber membranes were spun with two different dope solutions at different shear rates in order to understand the influences of the rheological characteristics of the dope solution on the membrane structure and the system performance for CO_2 adsorption. The membrane's pore size distribution was characterized using the log normal distribution with the measurement of the rejection characteristics of dextran through the membrane. Lab-scale membrane contractors were finally prepared using resultant PVDF hollow fibers to conduct preliminary study on CO_2 absorption.

With the increase of the shear rate, the water permeation flux was increased and then maintained nearly the same level. The MWCO and CO_2 absorption flux of the hollow fiber membranes spun from 17 wt.% PVDF dope at different shear rates were almost the same. But for the hollow fibers spun from 20 wt.% PVDF dope, increasing the shear rate in the spinning process resulted in bigger geometric mean diameters, larger MWCO and higher CO_2 absorption flux. Compared with the hollow fiber membranes spun with high polymer concentration (20 wt.%), the hollow fibers spun from low PVDF concentration (17 wt.%) had a wider pore size distribution and bigger pores, which dominated the MWCO of hollow fiber membranes and presented a significant influence on the membrane performance.

Keywords: PVDF hollow fibers; Shear rate; Pore size distribution parameters; Membrane contactors; CO_2 capture

1. Introduction

The CO_2 emission from the combustion of fossil fuels in power plants is a big concern from the environmental perspective. The growing evidence for causal links between CO_2 emissions and global climate change highlights the need to develop cost effective CO_2 capture technologies for the combustion processes [1]. Among various CO_2 capture techniques, microporous hollow fiber membrane contactors are expected to have potential to overcome the disadvantages of the conventional equipment and lead the CO_2 capture technology to a new level when integrated with chemical absorption [2]. However, the polymeric membranes in the membrane contactor have to be in direct contact with the absorbent though the most of absorbents with a higher CO_2 loading capacity are highly corrosive. The chemical attack of the absorbents was found to result in performance deterioration of the system [3,4] and only polytetrafluoroethylene (PTFE) membranes showed a stable performance [5]. It suggested that the membrane used as contactors for CO_2 capture should possess a high degree of hydrophobicity and strong chemical resistance except for having certain structural characteristics.

Among popular hydrophobic polymers, poly(vinylidene fluoride) (PVDF) has excellent chemical and thermal resistances, which makes it stable in most of the corrosive chemicals and organic compounds such as acids, alkaline, oxidant and halogens [6]. In addition, PVDF material can be used to prepare asymmetric membranes via phase-inversion method [7,8], while

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commercially available PTFE flat sheet or tubular membranes and polypropylene hollow fiber membranes are symmetric in structure, which are produced by stretching or thermal method. Therefore, the preparation of PVDF and modified PVDF membranes has been an active subject for various membrane-based separation applications including membrane distillation, pervaporation and gas absorption [9–11].

Extensive studies of PVDF membranes are focused on flat sheet configuration and relatively less research on the fabrication of PVDF asymmetric hollow fiber membranes has been carried out. In those studies, the influences of various dope concentration, additives, spinning conditions, coagulations et al. on the membrane morphology and membrane performance were investigated, aiming at identifying optimal polymer dope formations and spinning conditions [7–9,12–15]. However, the effect of dope rheology in the spinning process on the performance and morphology of PVDF hollow fiber membranes has not received much attention though this factor has been studied detailedly for other membrane materials [16–20]. Chung et al. [17–20] found that the hollow fiber membranes had a lower flux and a higher separation with the increase of shear rate. Ismail et al. [21,22] suggested that extrusion shear rate was linked indirectly to the phase inversion through induced molecular orientation and affected the subsequent dry/wet precipitation in the spinning process.

In terms of structural characteristics, the pore sizes and pore size distribution are important parameters for the microporous hollow fiber membranes. In order to characterize them, the rejection characteristics of standard solutes with known molecular weight such as dextran or polyethylene glycol (PEG) were measured and the correlation between the solute size and solute rejection were then linked to different distribution functions and transport theories [23–30]. Zydney et al. have reviewed different forms of the log-normal distributions [26]. From the review, the appropriate equations required to transform between the different functional forms and their statistical means and variances were also provided and evaluated. Singh et al. [29] and Mosqueda-Jimenez et al. [30] gained the log-normal distribution parameters of various ultrafiltration membranes with a geometric standard deviation, by ignoring the dependence of solute separation on the steric and hydrodynamic interactions between solute and pores. However, such a simplification made in the analysis can only provide a rough estimation of the pore size distribution.

In this study, PVDF material was used to prepare two different dope solutions with five components of PVDF, polyvinylpyrrolidone (PVP), *N*-methyl-2-pyrrolidone (NMP), lithium chloride (LiCl) and Tween80 for hollow fiber fabrication. The rheological characteristics of the dope solution within the spinneret, and the dope shear rate were discussed in relation to the morphology and performance of PVDF hollow fiber membranes. Meanwhile, the pore size distribution of PVDF hollow fiber membranes was analyzed by using the log-normal distribution, Poiseuille flow and steric interaction between solute molecules and membrane pores in combination with the measurement of the rejection characteristics of dextran through the membrane. Following these works, lab-scale membrane contractors were prepared using resultant PVDF hollow fibers and the CO_2 absorption in the system was performed accordingly.

2. Experimental

2.1. Membrane material and chemicals

The membrane material, PVDF (Kynar grade 740, Molecular weight: 156,000, pallet form), is a commercial polymer and was purchased from Elf Autochem (USA). *N*-Methyl-2-pyrrolidone (NMP, >99.5%, CAS#872-50-4) supplied by Merck was used as a solvent. PVP (K15) (Fluka, CAS#9003-39-38), lithium Chloride (LiCl, CAS#7447-41-8, 99%, Aldrich Chemical Company Inc.), and polyoxylenesorbitan monooleate (Tween80, 9005-65-5, SIGMA) were the non-solvent additives. Some dextran $(C_6H_{10}O_5)_n$ samples with different molecular weight (1500–200,000; CAS#9004-54-0; from Fluka and Sigma) were used to characterize the molecular weight cut-off (MWCO) of hollow fiber membranes. All the reagents were used as received.

2.2. Fabrication of asymmetric PVDF hollow fiber membranes

Two batches of polymer dope solutions were prepared for hollow fiber fabrication. One consists of 17 wt.% PVDF; 4 wt.% PVP (K15); 79 wt.% NMP/LiCl/Tween80 (99.4/0.5/0.1) and another consists of 20 wt.% PVDF; 4 wt.% PVP (K15); 76 wt.% NMP/LiCl/Tween80 (99.4/0.5/0.1). Tween80 is a surfactant, which can enhance the solvent-water exchange between the dope solution and the coagulant in the phase-inversion process. The PVDF pellets were dried for 2 days at 110 °C under vacuum before use. They were then dissolved in the mixture of NMP, LiCl, PVP and Tween80 and stirred for about 3 days at 65 °C. Prior to spinning, the dope prepared was degassed under vacuum for 3 h and then kept for 1–2 days.

A RheoStress 300 rheometer (HAAKE Instruments Inc.) was used to determine rheological characteristics (the shear stress, viscosity of the dope solutions, etc.) at various shear rates. The experiment was carried out using a 25 mm cone-plate at 25 °C.

Asymmetric PVDF hollow fiber membranes were fabricated by a dry-jet wet spinning process. The spinneret has an outer diameter (OD) of 0.8 mm, inner diameter (ID) of 0.38 mm, and annual length of 1 mm. The pressure inside the spinneret exerted over the polymer solution was controlled at 6–8 bars. The dope flow rate was calculated according to the following equation:

$$\bar{v} = \frac{V}{\pi(R^2 - r^2)} \quad (1)$$

where $\bar{v}$ is the dope flow rate, V the volumetric flux controlled by a digital gear pump, R and r are the outer and inner radius of the spinneret, respectively. The coagulation bath was filled with tap water at room temperature. After coagulation, the hollow fiber was taken up by a roller and stored in a water bath to remove residual solvent for at least 3 days. The outer surface of hollow fiber membranes was a selective skin layer.