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Hydrophobic and hydrophilic hollow fiber membranes for Co$_2$ stripping via gas-liquid membrane contactor

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Prolonged operation hours and hydrophobic features are privilege in membrane contactor application as it can retained membrane from wetting. Although there are many available commercial membrane (PTFE, PP and PE) that can be applied in contactor system, severe wetting problem which is due to reaction with alkanolamine liquid absorbent [1] thus allowing the search for suitable membrane in contactor application is wide open. Polyvinylidene fluoride (PVDF) polymer have proven to be reliable membrane material in CO_2 absorption due to several advantages [2]. Having a similar theory of absorption process but in a reverse mode, potential of membrane in CO_2 stripping has started to emerge as it produce promising results as it is in the absorption process. In order to be suitable for CO_2 capture in industrial gas processing plant, membrane material should be able to withstand high temperature in the range of 70°C to 110°C [3]. Previous work on hollow fiber PVDF membrane for CO_2 stripping process showed enhancement of CO_2 stripping flux and removal efficiency by incorporating non-solvent additive [4]. An attempt to study hydrophilic material; polyetherimide (PEI) is highlighted here as it was observed that PEI hollow fiber membrane has high wetting pressure and proven to be applicable for CO_2 absorption [5]. Therefore, a comparative study on structure and performance of PVDF and PEI hollow fiber membranes for stripping CO_2 is highlighted in this paper.

Removal of flue gases (CO_2 and H_2S) from industrial processing plant is vital since emission of flue gases indirectly contribute to greenhouse effects thus triggering to climate change worldwide. In natural gas processing plant, corrosive effluent caused significant loss in profit due to reduction of fuel energy content and corrosion in pipeline equipments. Therefore, intensive study has been carried out to improve the performance of membrane contactor by modifying the membrane properties, liquid absorbent compatibility and durability of the membrane system in harsh operating condition. Commercially available membrane material such as polypropylene, polytetrafluorethylene and polyethylene are diversely tested in contactor system for flue gases removal and post combustion treatment [6] despite being costly and having complicacy in fabrication. Hydrophobic criteria is seen as a significant requirement to ensure efficient operation of membrane contactor system as liquid intrusion into membrane pores would increase membrane mass transfer resistant. Several study in CO_2 stripping highlighted on the application of commercial membrane such as PTFE membrane in the membrane contactor system [7,8]. Operated at prolong hours at 100°C, the stripping flux of these commercial membrane was declined continuously due to membrane wetting by amine solution. Meanwhile, recently Naim et al [4] reported on in-house fabrication of PVDF membrane for CO_2 stripping from DEA solution and it produces promising results as the increase composition of additives enhanced the stripping efficiency of the membrane. Alternatively, Bakeri et al [9] studied on hydrophilic polyetherimide (PEI) hollow fiber membrane for CO_2 absorption using different non-solvent additives. The result showed higher absorption performance of PEI membrane than that of PVDF membrane. Polyetherimide membranes have been used diversely in microfiltration [10], ultrafiltration [11] and gas separation [12] where it may be applied solely or hybrid with other additives or non-additives to produce a new composite membrane or mixed matrix membranes [13]. Having several options for fabricating the asymmetric membrane via conventional phase inversion [14] ,this polymer is believed to have excellent performance in term of thermal resistance and chemical resistance towards acidic environment due to its high glass transition (215 °C).

Polymer dope solution of 17 wt.% with 5 wt.% of additive were wet spun at dope extrusion rate of 4 ml/min and bore fluid rate of 2 ml/min with solvent composition of 70 wt.%. Water contact angle of fibers were measured using a technique called sessile drop using

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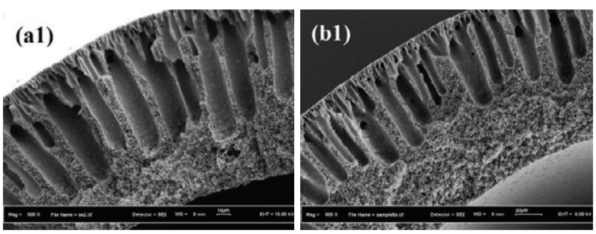
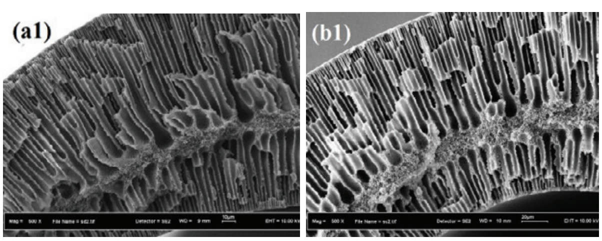
goniometer (Krauss, Germany). Gas permeability was measured using a simple but reliable soap bubble flow meter and the data were then used to determine the mean pore sizes and the effective surface porosity. Field emission scanning electron microscope (FESEM) analysis were carried out to examine membrane morphology at various magnifications. Membrane wetting pressure was determined by supplying liquid medium into the membrane pores until the first water droplet appear on the outer membrane skin. Ten hollow fibers were installed in a stainless steel membrane module and preloaded diethanolamine was used as liquid absorbent for CO_2 stripping test. Stripping test was operated in a counter-current mode as liquid flows in the lumen and gas on the outer shell with nitrogen as sweep gas. By using double chemical titration method [15], concentration of CO_2 in the inlet and outlet of the stripper module were measured to determine stripping flux and efficiency. The overall mass transfer coefficients of the membrane system were calculated based on non-wetted mode of operation.

As observed from the morphology analysis, formation of combined finger-like and sponge-like structure was formed on the outer skin layer and inner layer of plain PVDF and PVDF/PEG-400 membrane. In contrast to former membranes, both plain PEI and PEI/PEG-400 membrane possessed thin finger-like morphology stretching from the outer skin layer to inner layer separated by sponge-like structure in the middle. Since both polymers have the properties of hydrophobic and hydrophilic which are utterly opposite behaviours, it is expected that morphology of the membranes would be differed where the formation of membrane structures depend on the interaction of polymer solution with the coagulation bath medium (water) and bore fluid composition used [16]. Despite having lower contact angle compared to PVDF membrane, wetting pressure of PEI/PEG-400 membrane was significantly higher than that of PVDF membrane with water and aqueous DEA as testing medium. A stripping flux of 3.62×10^{-2} mol/m^2.s was achieved for PEI membrane at 0.77 m/s which is only 10% lower than stripping flux of PVDF membrane. All tested membrane showed stripping efficiency of more than 50% with PVDF membrane reached the highest value of 56%. Therefore, it can be concluded from this study that the hydrophilic hollow fiber membrane could be potentially attractive in CO_2 stripping through gas-liquid membrane contactors.



Morphology of PVDF hollow fiber membranes (a) plain (b) with PEG-400



Morphology of PEI hollow fiber membranes (a) plain (b) with PEG-400

Membrane	LEPw (10^5 Pa)	LEP_{DEA} at 80°C (10^5 Pa)	N_2 permeance at 1×10^5 Pa (10^{-3} cm^3/cm^2 s.cmHg)	Effective surface porosity, ε/Lp (m^{-1})	Mean pore size (μm)	Water contact angle
Plain PVDF	5.0	4.5	34.78	153.71	0.35 ± 0.05	88.7 ± 1.35
PVDF/PEG-400	6.5	5.0	31.66	175.13	0.30 ± 0.02	84.9 ± 1.58
Plain PEI	9.0	7.0	0.53	35.62	0.04 ± 0.05	78.0 ± 1.05
PEI/PEG-400	11	9.0	13.13	357.27	0.08 ± 0.06	75.0 ± 1.43

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