Absorption of CO₂ Form Natural Gas via Gas-liquid PVDF Hollow Fiber Membrane Contactor and Potassium Glycinate as Solvent

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Graphical abstract
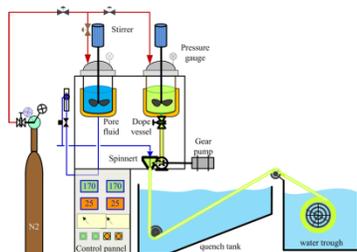
Abstract

PVDF hollow fiber membranes were fabricated using Thermally Induced Phase Separation (TIPS) method. 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 and then reacted in the presence of solvent such as aqueous sodium hydroxide or amine solutions. Nowadays, Monoethanol amine (MEA) and Diethanolamine (DEA) are the most commonly used solvents. In the present work potassium glycinate is used as an alternative liquid absorbent. A comprehensive two-dimensional mathematical model was developed for the transport of carbon dioxide-methane gas mixture through the in lab-made hollow fiber membrane contactor. Potassium glycinate is found to be a promising liquid absorbent. Model predictions were validated with experimental data. Results revealed that mass transfer rate generally increased with the absorbent concentration and that aqueous potassium glycinate solution performs better than MEA and DEA. The model equations were solved using COMSOL software package, model predictions were in good agreement with experimental data.

Keywords: Membrane contactor; gas absorption; PVDF; TIPS method; modeling and simulation; COMSOL

∎1.0 INTRODUCTION

Ethanolamine compounds (MEA, DEA, MDEA, DGA) and hot potassium carbonate are chemical solvent processes which rely on chemical reactions to remove acid gas constituents from sour gas streams.[1] The regeneration of chemical solvents is achieved by the application of heat whereas physical solvents can often be stripped of impurities by reducing the pressure without the application of heat. Physical solvents tend to be favored over chemical solvents when the concentration of acid gases or other impurities is very high. 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; conversely, the drawback of membrane contactor is that the membrane is subject to fouling. Membrane can introduce another resistance to mass transfer, membrane pores must be small to prevent the penetration of absorbents into the pores, the smaller the pore radius, the larger the liquid entry pressure.[2,3] Over the conventional gas absorption and gas separation approaches, membrane contactor affords some advantages such as high surface area per unit volume, operational flexibility, low cost and being easy to scale up. Actually, membrane absorption is thought to be a promising technology to decrease the emission of greenhouse gas.[4] Despite the advantages of membrane contactor, the deterioration of CO₂ absorption performance due to membrane wetting by absorbents during the operation has seriously obstructed the practical application of this technology.[5] In order to prevent aqueous absorbents from passing through membrane pores into the gas side, membrane used in membrane absorption is usually hydrophobic. However, commercially available hydrophobic polymer membranes such as PP, polyethylene (PE), poly (vinylidene fluoride) (PVDF) are not strong enough to withstand the gradual wetting due to swelling by absorbent, and surface deformation. Many efforts have been made to resolve the wetting problem by the development of new membrane materials or hydrophobic modification of available membranes. PTFE membrane is proven to have a high resistance to wetting, but the complicated processing procedure and high cost limit its attractiveness.[6] The preparation of hollow fiber membranes involves large numbers of spinning parameters (the structure and dimension of the spinneret, polymer dope viscosity, and flow rate of the bore fluid, the dope extrusion rate, the length of the air-gap and take-up speed). The membrane structure and performance depend upon different factors such as methods of fabrication, polymer choice composition, quenching bath temperature and other

operating factors.[7,8] These factors are dependent on each other, changing one or more of these variables can affect membrane structure and performance; furthermore, spinning factors such as dope extrusion rate, take-up speed, bore fluid type and flow rate must be optimized at the best condition in order to produce high performance membrane. The primary aim of the present work was to investigate the effect of various solvents on the membrane separation performance. Membrane performance was tested in gas-liquid membrane contactor modules used in the absorption of CO_2 from CO_2/CH_4 gas mixture in aqueous 0.5 M potassium glycinate, MEA, DEA solution. Furthermore, the experimental data was compared with the simulation results for the CO_2 flux on the basis of non-wetted model to validate the model predictions.

■2.0 EXPERIMENTAL

Hollow fiber membranes were fabricated using a prepared 1000 gram of dope solutions consist of 28% PVDF polymer and 72% triacetin liquid solvent. Thermally induced phase separation (TIPS) method was used for this purpose (Figureeq 1). The dope solution was prepared and extruded at a temperature of 170 °C. The pore fluid used was triacetin and water was used as the quenching tank fluid. The mixture was kept at each extrusion temperature for 3 hours; 1 hour under gentle mixing and 2 hours without mixing for degassing purpose. The uniform solution is then extruded by gear pump under the pressure of nitrogen (1–1.2 bars) through the spinneret (outer/inner diameter is 1.5/1.1 mm) to the quenching water tank at room temperature and then winded by a take up winder rotated in a water trough. The solvent left over in the hollow fiber membrane was extracted by ethanol which was removed by transferring the fibers from ethanol tank into distilled water container.
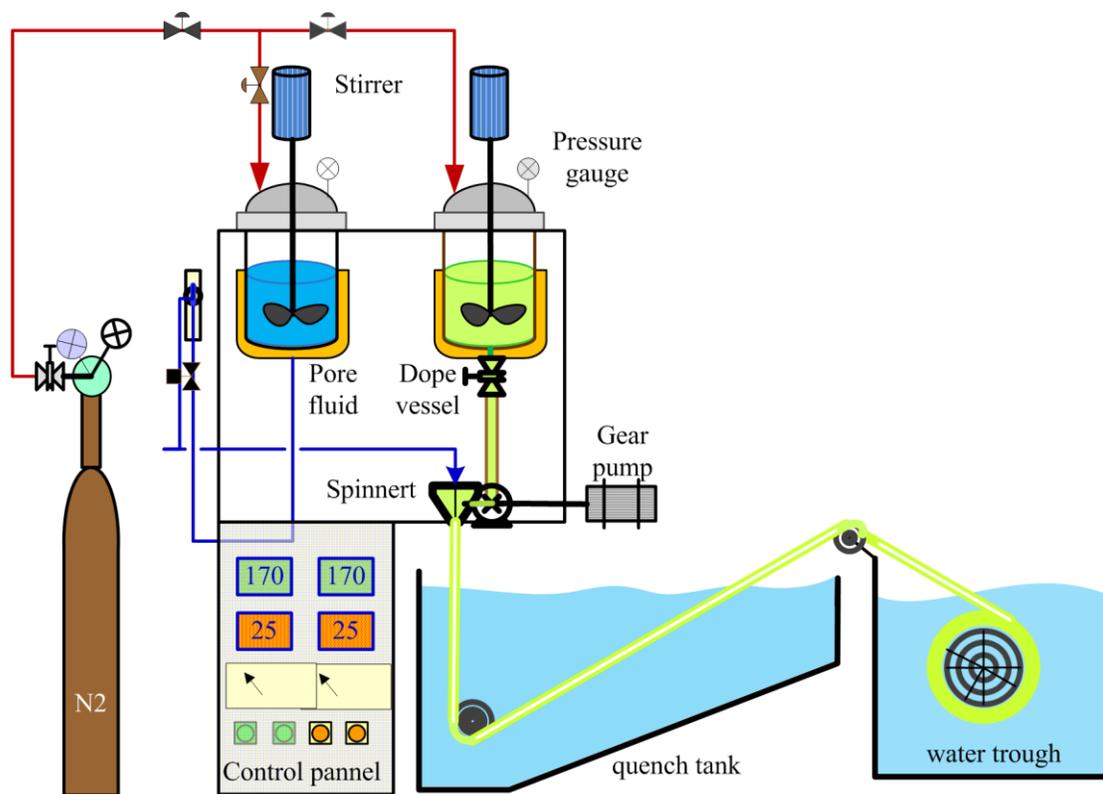
Figure 1 Schematic diagram of the thermally induced phase separation (TIPS) process

The gas absorption was carried out using the experimental setup shown in Figure 2. The system consists of membrane module consists of 6 fibers 0.26 m long. Temperature indicator is inserted in inlet and exit gas and liquid streams to measure the system temperatures. 10% CO_2/90%CH_4 gas mixture was applied to the membrane contactor module and different gas inlet flow rate (10 to 100 ml/min). Liquid flow rate was fixed to 10 ml/min. Exit gas concentration was measured using gas chromatography. Three different solvents were used in the CO_2 absorption process, the solvents were potassium glycinate, MEA

and DEA. Various concentration were used to study the effect on carbon dioxide removal performance.

■3.0 MODLEL EQUATIONS

A steady state mathematical model that described the material balance has been carried out on a shell-and-tube membrane contactor system. The model is developed for a segment of a hollow fiber, as shown in Figure 3, through which the solvent flows with a fully developed laminar parabolic velocity profile.
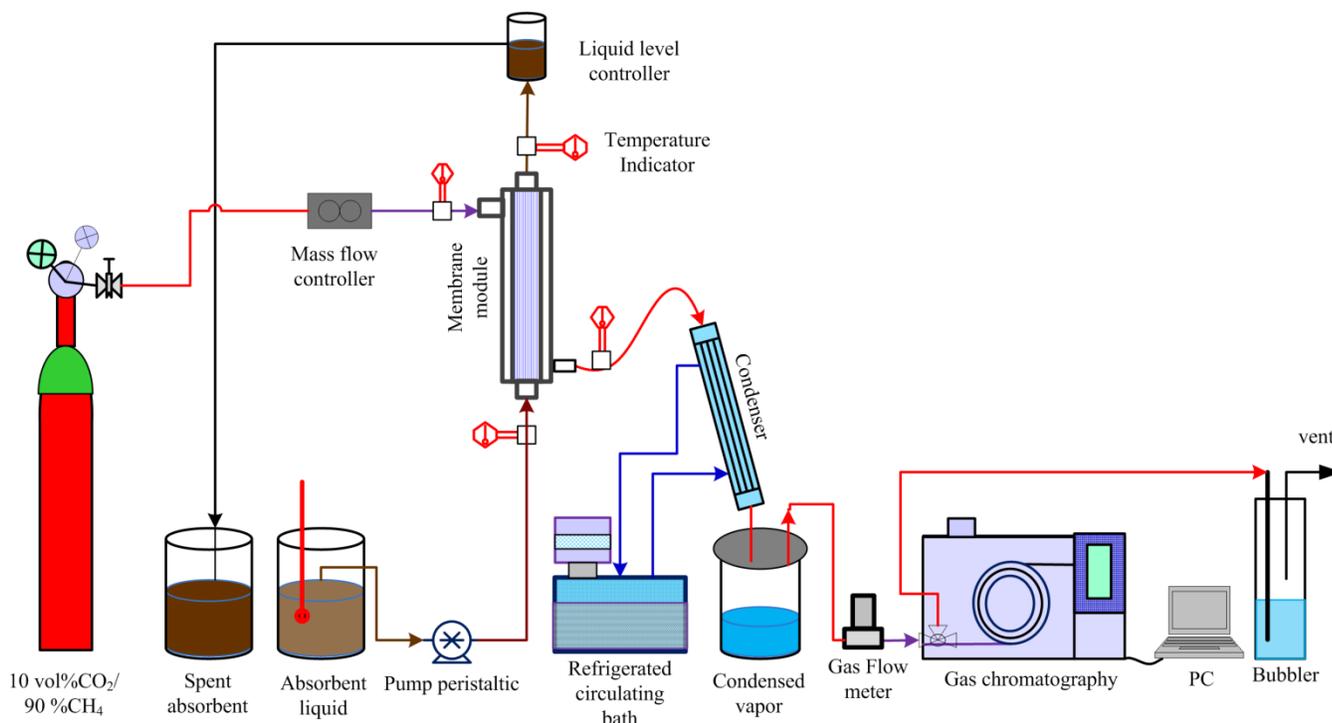
Figure 2 Schematic diagram of gas absorption unit
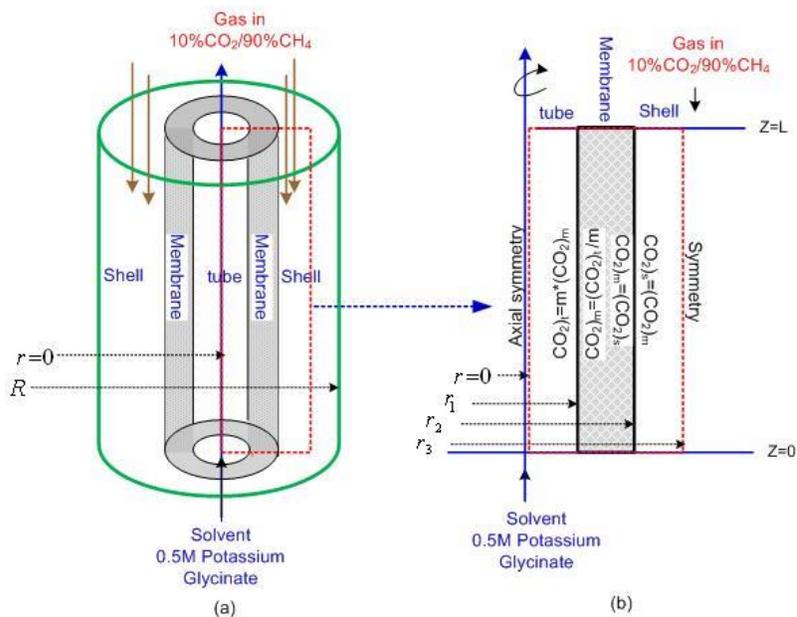
Figure 3 schematic diagrams of the hollow fiber section (a) and boundary conditions (b)

The fiber is surrounded by a laminar gas flow in an opposite direction to that of the liquid. Based on Happel's free surface model, [9] only portion of the fluid surrounding the fiber is considered which may be approximated as circular cross section. Thus, symmetry may be considered at the outer portion of the fluid surrounding the fiber (at $r = r_3$). The steady state material balance for the transport of gas mixture in the shell side may be written as follows ($i = CO_2$ and CH_4):

$$D_{i,s}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_{i,s}}{\partial r}\right)+\frac{\partial^2 C_{i,s}}{\partial z^2}\right]=\frac{\partial}{\partial z}\left(V_{zs}C_{i,s}\right)+\frac{1}{r}\frac{\partial}{\partial r}\left(rv_{rs}C_{i,s}\right)$$

(1)

Considering the active area around each fiber calculated from the hypothetical radius bearing in mind a hexagonal–shaped unit cell of the fiber assembly around each fiber.

$r_3 = r_2\sqrt{1/(1-\varphi)}$ where φ is the volume void fraction of the membrane contactor module. Assuming Happel's free surface model, the boundary conditions:

$$r = r_2, \quad C_{i,s} = C_{i,m} \tag{2}$$

$$r = r_3, \quad -\frac{\partial C_{i,s}}{\partial r} = 0 \tag{3}$$

$$z = 0, \quad -\frac{\partial C_{i,s}}{\partial r} = 0 \tag{4}$$

$$z = L, \quad C_{CO_2,s} = C^\circ_{CO_2} \quad , \quad C_{CH_4,s} = C^\circ_{CH_4} \tag{5}$$

The steady state material balance for the transport of CO_2 and CH_4 across the membrane skin layer for non-wetting mode of operation is considered to be due to diffusion only; no reactions are taking place in the gas filled pores (i = CO_2 and CH_4).

$$D_{i,m}\left[\frac{\partial^2 C_{i,m}}{\partial r^2} + \frac{1}{r}\frac{\partial C_{i,m}}{\partial r} + \frac{\partial^2 C_{i,m}}{\partial z^2}\right] = 0 \tag{6}$$

Boundary conditions:

$$r = r_1, \quad C_{i,m} = C_{i,t}/m_i \tag{7}$$

$$r = r_2, \quad C_{i,m} = C_{i,s} \tag{8}$$

$$z = 0, \ z = L, \ \frac{\partial C_{i,m}}{\partial z} = 0 \tag{9}$$

where m_i is the solubility of CO_2 and CH_4 in aqueous sodium hydroxide solution.

The steady state material balance for the transport of CO_2 and aqueous potassium glycinate (PG) in the lumen side of the hollow fiber membrane tubes is considered to be due to diffusion, convection and reaction as well:

$$D_{i,t}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_{i,t}}{\partial r}\right) + \frac{\partial^2 C_{i,t}}{\partial z^2}\right] + r_{i,t} = \frac{\partial}{\partial z}\left(v_{zt}C_{i,t}\right) + \frac{1}{r}\frac{\partial}{\partial r}\left(rv_{rt}C_{i,t}\right) \tag{10}$$

where the subscript "*i*" indicates carbon dioxide and sodium hydroxide. Reaction rates for CO_2 and PG are shown in equations 11 and 12, respectively:

$$r_{CO_2,t} = -k_r C_{CO_2,t} C_{PG} \tag{11}$$

$$r_{PG} = -k_r C_{CO_2,t} C_{PG} \tag{12}$$

Physical and chemical parameters used to model the absorption of CO_2 in potassium glycinate aqueous solutions in a hollow fiber membrane contactor can be found elsewhere. [10-12]
The boundary conditions for liquid flowing in lumen side of the fibers (i = CO_2 and PG):

$$r = 0, \quad -\frac{\partial C_{i,t}}{\partial r} = 0, \text{ tube center, axial symmetry.} \tag{13}$$

$$r = r_1, \quad C_{i,t} = m_i C_{i,m}, \quad \text{gas solubility in solvent at liquid-membrane interface.} \tag{14}$$

$$z = 0, \quad C_{NaOH,t} = C^\circ_{NaOH} \quad , \text{ solvent initial feed concentration.} \tag{15}$$

$$z = L, \quad -\frac{\partial C_{i,t}}{\partial z} = 0, \text{ convective flux at the exit liquid stream.} \tag{16}$$

The simultaneous partial differential equations were solved using software COMSOL®.[13]

■4.0 RESULTS AND DISCUSSION

The effect of solvent type (PG, MEA, and MDEA) and concentration on CO_2 removal flux is shown in Figure 4.
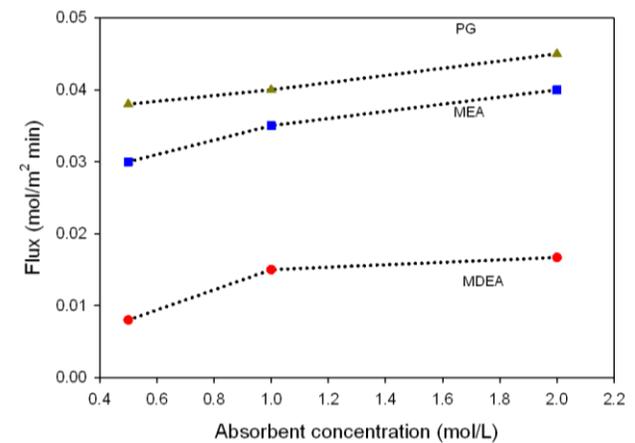
Figure 4 Effect of absorbent concentration on CO_2 removal flux for various solvents. Solvent flow rate = 10 ml/min, gas flow rate=200 ml/min, module length 0.26 m, 30 fiber, fiber radius (inner = 2.1×10^{-4}, outer =5.5×10^{-4} m)

Overall as absorbent concentration increases removal flux increases. This is related to the increase in reaction rate with solvent concentration. According to solvent type, the diagram revealed that with potassium glycinate (PG) as solvent better removal flux of carbon dioxide is achieved than MEA and MDEA, that's attributed to the higher reaction rate constant of PG. Mass transfer rate generally increases with the absorbent concentration and aqueous PG solution performs better than MEA and MDEA. The change in flux using as MDEA was insignificant for concentration change between 1 and 2 mol/liter. By contrast a monotonic increase is achieved with PG with solvent concentration. The effect of absorbent inlet flow rate on percent removal efficiency is shown in Figure 5. The diagram shows the absorbent flow rate has insignificant effect on the percentage of removal efficiency after gas velocity of 0.04 m/s. High velocity means less residence time and consequently less removal of carbon dioxide.
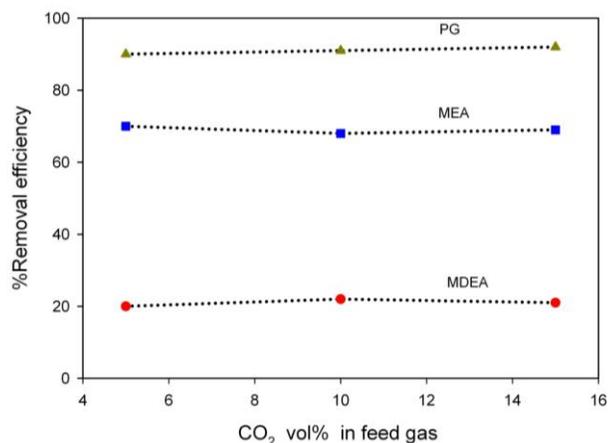
Figure 5 Effect of CO_2 volume percent in feed gas on percent removal efficiency. Solvent flow rate = 10 ml/min, gas flow rate=200 ml/min, module length 0.26 m, 30 fiber, fiber radius (inner = 2.1×10^{-4}, outer = 5.5×10^{-4} m)

The surface diagram generated for the set of model equations generated from the mass balance around the membrane module was solved via COMSOL software package and depicted in Figure 6. The diagram depicts the CO_2 concentration across the membrane module. The diagram revealed a complete removal of carbon dioxide is achieved within the first 0.16 m of the membrane length as shown from the blue color on the shell side at a dimensionless length of 0.4, as the gas is entering counter currently with liquid solvent, accordingly the length of the fiber is 0.6 of the 0.26 m length of fibers (0.156 m).
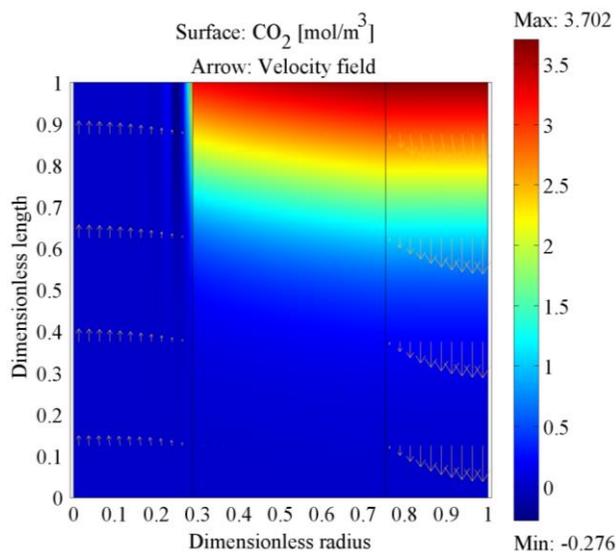
Figure 6 Surface diagram of CO_2 concentration using PG as solvent via membrane contactor, liquid flow rate=10 ml.min, gas flow rate=200 ml/min, module length 0.26 m, 30 fiber, fiber radius (inner = 2.1×10^{-4}, outer = 5.5×10^{-4} m)

The CO_2 enters the shell side of the membrane module at initial concentration around 3.5 mol/m^3, from the surface plot it can be noticed that the CO_2 concentration at the exit of the membrane is almost null. The model predications were in good agreement with experimental data. The modeling predictions for the effect of solvent velocity (0.02, 0.04, 0.06, 0.08 m/s) on percent CO_2 removal rate is shown in Figure 7. The figures revealed that as the PG solvent velocity increased, %CO_2 removal rate increased, the rate of increase in the percent CO_2 removal rate with solvent velocity is attributed to the increase in reaction rate with solvent velocity.[14]
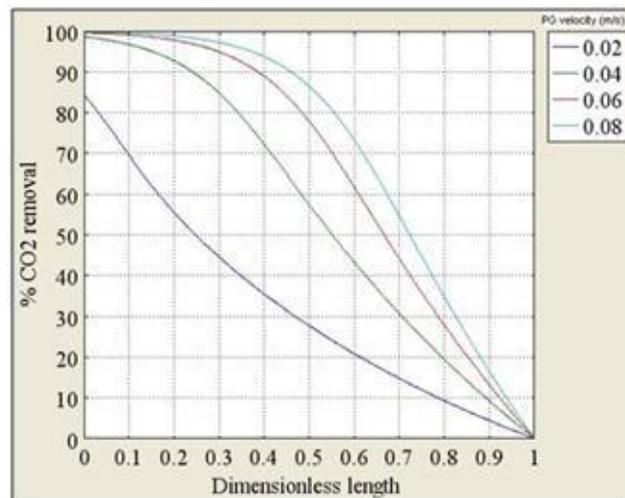
Figure 7 Model predictions for the effect of solvent velocity on % removal CO_2 versus module dimensionless length. Variable solvent velocity, gas flow rate=200 ml/min, module length 0.26 m, 30 fiber, fiber radius (inner = 2.1×10^{-4}, outer = 5.5×10^{-4} m

■**5.0 CONCLUSION**

PVDF hollow fiber membrane was fabricated successfully via thermally induced phase separation technique. The in-house fabricated membrane was utilized in a gas-liquid membrane contactor module. The constructed module was used for the removal of CO_2 from natural gas using three different solvents; potassium glycinate, MEA and DEA as solvents. Complete removal was achieved using potassium glycinate as solvent. The potassium glycinate shows higher CO_2 removal flux than DEA and DEA solvents. The model prediction and experimental results were in good agreement. It is clearly seen from the results that the performance of CO_2 absorption using PG is always better than MEA and DEA under the identical operating circumstances.

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