Application of Methanol Absorbent for CO₂ Removal in Gas-Liquid Hollow Fiber Membrane Contactors

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In the present work, the physical absorption of CO_2 from CO_2/CH_4 mixture using methanol absorbent was explored by neglecting the reaction term in the model equations. In order to calculate the rates of mass transfer through the membrane and axial and radial diffusion inside the shell, through the membrane and within the tube side of the membrane contactor, a computational mass transfer model was used. The effects of operating conditions such as liquid velocity, gas velocity and temperature were analyzed. The calculated removal efficiencies were compared with the case that absorbent is water. It is shown that methanol solvent can successfully be used for removal of CO_2. It is found that the concentration distribution of CO_2 in the gas phase along the fiber length obeys plug flow model whereas in the methanol absorbent deeply affected by the interface concentration of CO_2, absorbent velocity and CO_2 diffusivity. Relative absorption rate of CO_2 using methanol absorbent is in the range of 2.2 to 4.6 in comparison with the case of water absorbent. When the absorbent velocity is increased or gas velocity is decreased, CO_2 concentration decreases, but the concentration changes aren't the same for equally velocity step size in both gas and absorbent. The model results showed that gas velocity has small effect on liquid phase CO_2 concentration.

Key Words: Membrane contactors, CO₂ Removal, Physical absorption, Methanol, Computational mass transfer.

INTRODUCTION

Carbon dioxide is present as an undesirable impurity in many gaseous streams and hence its removal methods are very important[1,2]. Moreover; since CO_2 is one of the important contributors to the greenhouse effect, interest has increased recently in exploring the removal of carbon dioxide from gas mixtures with the implementation of the Kyoto Protocol in many countries[3,4]. Chemical absorbents like amines and amino acid salts are extensively used in the removal of impurities from gas mixtures. Physical absorbent have been of considerable interest in the development of gas treatment solvents, especially when the partial pressure of carbon dioxide is high. Some of the physical solvents used commercially are propylene carbonate, *n*-formyl morpholine, dimethyl ethers of polyethylene glycol, N-methyl-pyrrolidone, *etc.* [5].

The separation process known as membrane contactor is accepted as a low cost, high interfacial area alternative to conventional absorption processes such as packed and plate absorption columns. Membrane contactors are devices that achieve two phases mass transfer through diffusion without dispersed one phase within another. Such a device employs a porous membrane acts as a non-selective barrier between both phases where the gas and the absorbent solution flow on two sides of a membrane[6,7]. Generally, micro porous hydrophobic membranes, made of polyvinylidene fluoride, polytetrafluoroethylene and polypropylene, *etc.* in the forms of capillary or flat-sheet, have been used in membrane contactors[8]. Compared to the other gas absorption processes, the selection of favourable solvent has more important in designing a membrane contactor gas absorption process. Because in addition to the ordinary solvent selection criteria (solubility, thermally stability, ease of regeneration, low cost and low vapour pressure), In membrane processes, membrane-solvent compatibility must be tested. The most important requirements are the membrane long term stability and avoiding wetting phenomena.

Physical solvents can be a possible alternative to chemical solvents in certain areas of applications. Although they are less effective than chemical absorbents (*i.e.* generally, the specific absorption rate into physical absorbents in comparison with chemical solvents is less). But they can be regenerated by just pressure reduction method without large amount of heat supply and thus excessive energy savings can be obtained[5]. They can also be used as pre-treatment solvent in the development of hybrid systems. The well-known physical absorbent is water. However, its economics are limited by the relatively

low solubility which leads to larger amounts of circulation rate *i.e.* the higher investment costs as well as the higher operating costs[9]. But there are good organic solvents, which possess a much higher solvent capacity than water.

The applications of hollow fiber gas-liquid membrane contactor for the removal of carbon dioxide from gas mixtures have been studied by several researchers. In this case, in order to describe the membrane contactors, a large number of experimental absorption studies and theoretical modeling analyses have been performed as reported[2,10-13]. However, the research done so far is mainly limited to using chemical absorbents. There have been few attempts to explore possible physical absorption in hollow fiber membrane contactors[14,15] that mostly describes the water performance.

In the present work, this new process has been applied for CO_2 absorption from carbon dioxide/ methane mixture using methanol absorbent and its potential possibility for carbon dioxide removal has been evaluated. Before to the experiments in order to gain high efficiency and low cost we studied CO_2 removal using CFD tool with respect to solubility behaviour. CFD has been largely used as a powerful tool to model membrane separation processes[16]. It is able to simulate the concentration, temperature and velocity fields as well as the transport parameters and operating efficiency.

EXPERIMENTAL

Model modification: In this work, the steady state two-dimensional mathematical model was developed by Marzouqi *et al.*[17] is modified to describe the physical absorption of carbon dioxide in the polymeric hollow fiber membrane contactor. Absorption of CO_2 from a carbon dioxide/methane mixture into a methanol solvent is used as a model system. Methanol has a high thermal and chemical stability, low vapour pressure and is not corrosive. It is able to absorb acid gases, hydrocarbons, mercaptans and water. Moreover; it is produced in big quantity and readily available[9]. This properties make it highly effective for processing a wide range of compositions.

The model describes the mass transfer in the gas, membrane and liquid phases. Axial and radial diffusion inside the shell, through the membrane and within the tube side of the membrane contactor have been considered in the model equations. This model assumes that the fibers are distributed evenly through the shell space, which allows the results obtained with a single fiber to be generalized to the entire module. The computational domain used for the numerical simulation is shown in Fig. 1.

Dimensions of the selected hollow-fiber membrane contactor are listed in Table-1. The radial position of r = 0 is the center of a fiber and the radial distances r_1, r_2 and r_3 are the inner radius, outer radius and Happel's free model radius of the fiber (Fig. 1). with respect to the packing density of module, the radius of Happel's free surface model (circular approximation around the hollow fiber[18]) is calculated (r_3 = 720 µm). The gas mixture consist of carbon dioxide and methane is fed to the tube side at z = 0, while the liquid (water or methanol) is passed through the shell side at z = L. Carbon dioxide is removed from the gas by diffusing through the membrane due to a concentration gradient and then absorbing with the solvent. It is important to note that since the fiber is 900 times longer
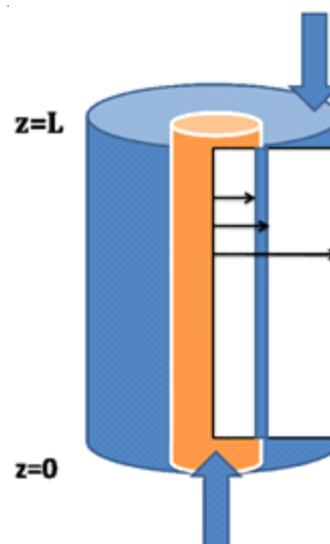

Fig. 1.   Schematic diagram of a membrane hollow fiber and computational domain

TABLE-1
DIMENSIONS OF THE SELECTED MEMBRANE CONTACTOR[19]

Parameters	Value
Module i.d. (m)	4.35×10^{-3}
Module o.d. (m)	6.35×10^{-3}
Fiber o.d. (m)	9.07×10^{-4}
Fiber i.d. (m)	6.07×10^{-4}
Module length (m)	0.3
Fiber length (m)	0.2725
No. of fibers	9

than its radial dimension (in this case 0.3 mm in radius and 27 cm in length), in order to reduce computational cost, a scaling factor of 90 has been applied in the z direction.

Physical properties and numerical solution: Simulation of gas-liquid contactors requires accurate data on physico-chemical properties used as input parameters in the model. The solubility, component diffusivity in each phase, density and viscosity data used in the model were obtained from literature. The temperature dependence distribution coefficient of CO_2 in water was taken from Versteeg *et al.*[20] and its distribution coefficient in methanol was taken from Wang *et al.*[14] Henry's constant of CO_2 for methanol as a function of temperature was reported by Lunsford *et al.*[21]. The temperature dependence diffusivity coefficient of CO_2 in methanol and water were obtained from Frank *et al.*[22]. membrane phase diffusivity was corrected for membrane porosity and tortuosity and gas-phase diffusivity of CO_2 was estimated using the correlation given by Diaz *et al.*[23]. The values for other required data were obtained by previous workers[24].

The work presented here uses the Femlab finite element program in order to solve the coupled partial differential equations for the tube, membrane and shell sides with the appropriate boundary conditions and physical and chemical properties. It runs the finite element analysis together with adaptive meshing and error control using a variety of numerical solvers. These solvers are an implicit time-stepping scheme, which is suited for solving stiff and non-stiff non-linear boundary value problems[25].

RESULTS AND DISCUSSION

Model validation: Due to the lack of literature absorption data for CO_2 removal using methanol solvent in hollow fiber membrane contactors, the model was validated using available CO_2 absorption data in water. The experimental absorptions data of Al-Marzouqi *et al.*[17] in their selected HFMC module was used to validate the accuracy of the simulation for physical absorption mass transfer in hollow fiber membrane contactors as shown in Fig. 2.
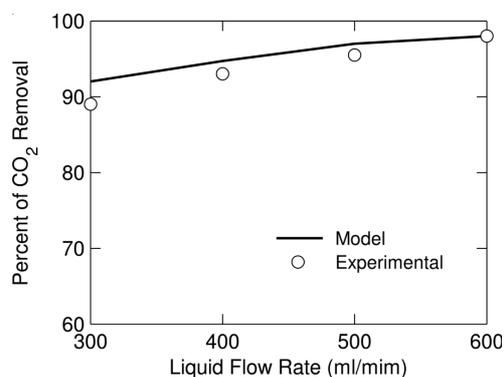

Fig. 2.　Comparison between experimental[16] and simulated CO_2 removal efficiency values

Fig. 2 shows the excellent agreement between the model results and the experimental data indicates the validity of numerical model.

Concentration distribution of CO₂: A component concentration distribution is established inside the shell, membrane and within the tube side of the membrane contactor. Numerically calculated carbon dioxide concentration distribution in each of the three phases is shown in Fig. 3. The solubility of CO_2 in methanol is linearly proportional to the partial pressure of the CO_2 in the gas mixture and, hence, it can be modeled according to Henry's law. As expected, it can be seen that the concentration near the membrane-liquid wall deeply affected by the interface CO_2 concentration, whereas the CO_2 concentrations on the tube side slightly decreases in the radial direction. It is also found that the concentration distribution of CO_2 in the gas phase along the fiber length (tube side) obeys plug flow model.
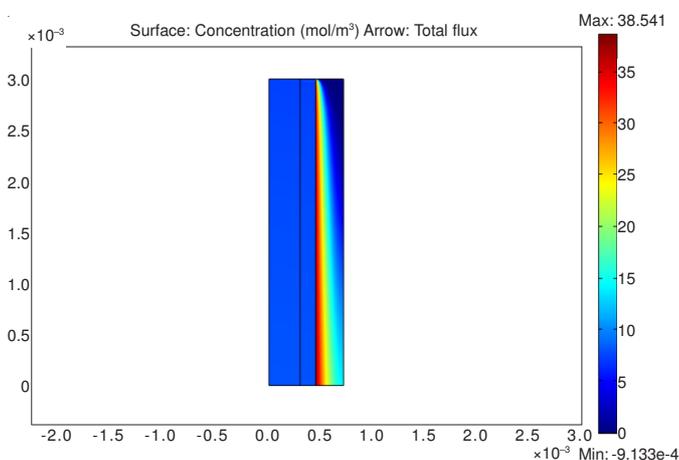

Fig. 3.　CO_2 concentration distribution in computational domain for V_L = 0.1 m/s, V_G = 3 m/s, C_0 = 8 mol/m³, T = 298 K

It is worth mentioning that the sensitivity grid-dependence analysis of the method of solution to the mesh size was performed, In order to ensure that the numerical solution is not affected by the specification of the mesh size. With respect to the carbon dioxide liquid diffusivity, liquid velocity and dimension of fiber. It is seen that penetration depth in radial direction of methanol absorbent increases with distance from liquid entrance (z/L = 1) In order to compare concentration profiles of CO_2 in case of water absorbent and methanol absorbent. Fig. 4 shows the radial concentration profile of CO_2 (in terms of dimensionless) as function of dimensionless radius.
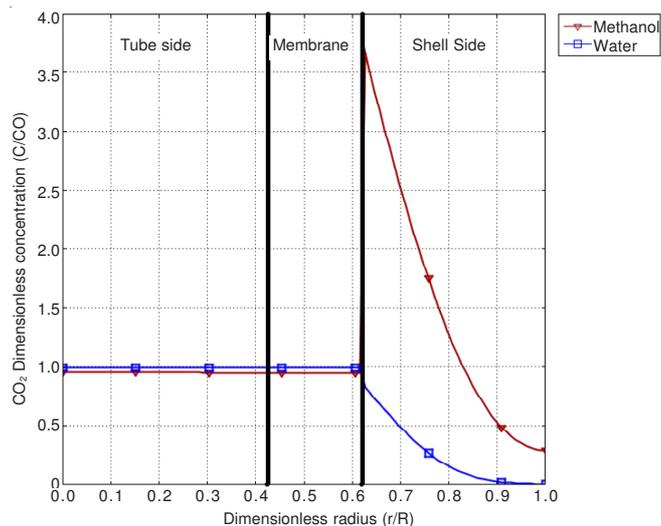

Fig. 4.　Comparison of CO_2 radial concentration profiles for two physical solvents (methanol and water) at V_L = 0.2 m/s, V_G = 3 m/s, z/L = 0.5, C_0 = 8 mol/m³, T = 298 K

As shown in Figs. 3 and 4 the concentration profile is discontinuous at the gas filled membrane-liquid interface based on the Henry's equilibrium relationship. With respect to the higher interface distribution coefficient of CO_2 in methanol, the concentration gradient close to the liquid-membrane interface in the liquid phase becomes sharper. A key parameter in the selection of solvents for CO_2 removal is the solubility. Compared to the other commercially organic solvents except N-methyl-pyrrolidone or methanol has a higher distribution coefficient which increases absorption's driving force and decreases solvent circulation rate, especially at reduced temperatures. The rate of concentration also drop in absorbent liquid is limited by the rate of diffusion of the component.

Comparison of the axial CO_2 concentration profile in absorbent (shell) and gas (tube) phases for methanol and water absorbent is given in Fig. 5. For gas phase tube center's line (r/R = 0) and for liquid phase Happel's radius (r/R = 1) is selected. It can be seen that in the case of water absorbent, the CO_2 concentration depletion in the gas and amount of absorbed are low in comparison with the case of methanol absorbent. It obviously indicates the higher capacity of methanol in absorption of CO_2. Base on the bulk concentration, CO_2 removal efficiency using methanol absorbent is 2.4 times more than removal efficiency with water absorbent in this operating conditions.

Effect of absorbent and gas velocity: Generally, increasing gas flow rate has a negative effect and increasing liquid flow rate has a positive effect on removal efficiency in gas-
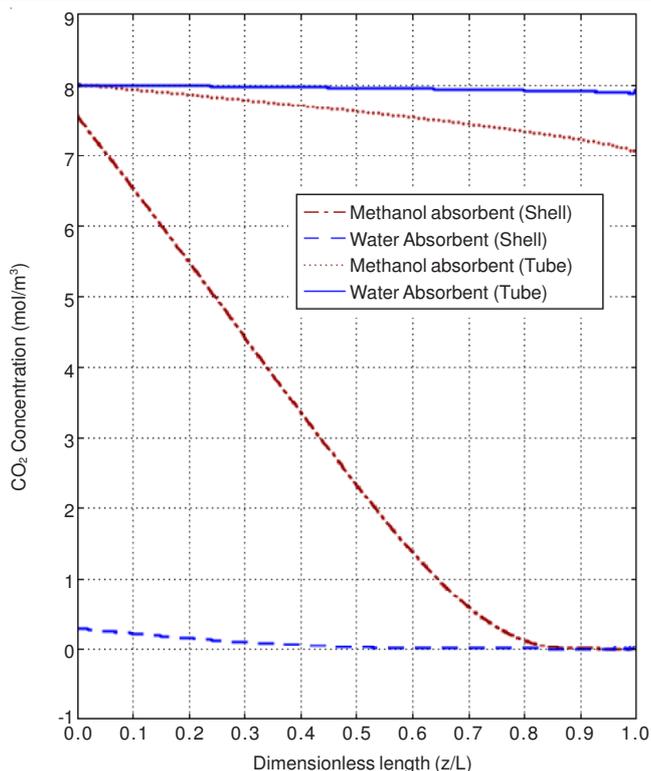
Fig. 5. CO_2 concentration profile in the axial direction for methanol and water absorbent at $V_L = 0.2$ m/s, $V_G = 3$ m/s, $C_0 = 8$ mol/m^3, T = 298 K

liquid membrane contactor devices as reported by previously[15]. However various kinds of chemical and physical absorbents are different in details. Figs. 6 and 7 show liquid phase and gas phase CO_2 concentration profile along the fiber at three different inlet liquid velocities and three different inlet gas velocities, respectively.
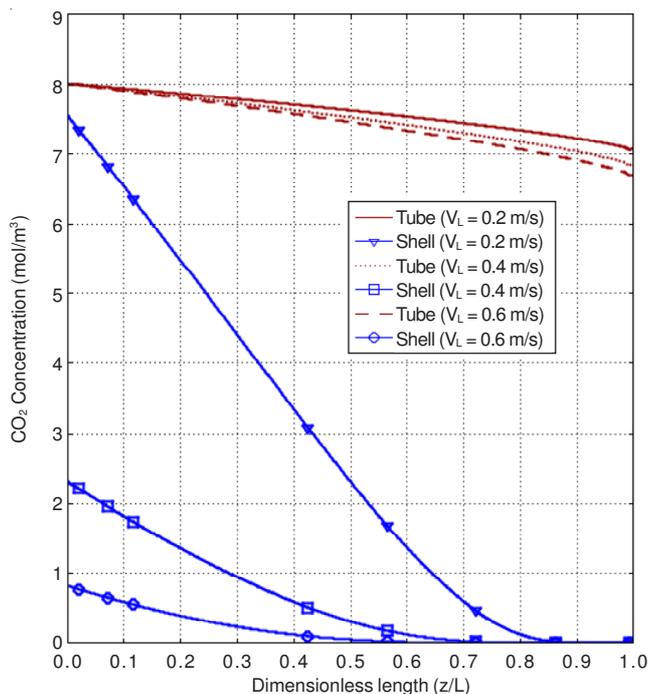

Fig. 6.   Effect of absorbent velocity on the axial concentration profile for $V_G = 3$ m/s, $C_0 = 8$ mol/m^3, T = 298 K
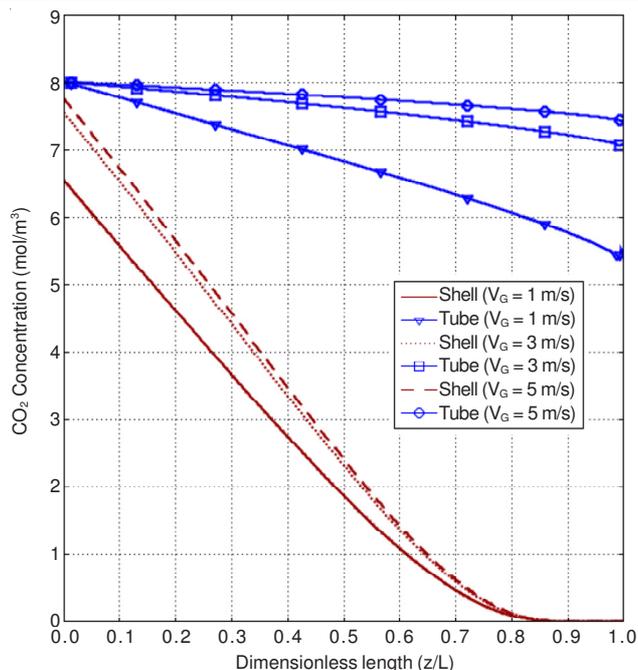

Fig. 7.   Effect of gas velocity on the axial concentration profile for $V_L = 0.2$ m/s, $C_0 = 8$ mol/m^3, T = 298 K

It can be seen from Fig. 6 that the trend of concentration variations for CO_2 in gas and absorbent is the same: the higher liquid velocity, the lower the CO_2 concentration in the gas stream and in the liquid phase in opposite direction (counter current flow). When the liquid velocity (liquid flow rate) is increased, the potential absorption is increased and hence CO_2 concentration decreases. For example, at the lower liquid velocity of 0.2 m/s, saturating methanol absorbent is faster and CO_2 concentration in liquid phase is higher.

It is noted that the concentration changes aren't the same for equally velocity step size in both gas and absorbent due to the different gas-liquid contact time. For example contact time decreases 67 % when velocity changes from 1 to 3 m/s while it decreases 40 % when velocity changes from 3 to 5 m/s. Also at radial direction results indicate that CO_2 penetration depth in methanol absorbent decreases with increasing absorbent velocity. The reason is that the axial convective flow increases in relation to radial diffusion (dimensionless Gz number conception). For example at high absorbent velocity of 5 m/s, absorbed CO_2 does not distribute entirely before about 50 % of fiber length.

The effect of gas velocity on the axial shell and tube side concentration profiles at three different gas velocities of 1 m/s, 3 m/s and 5 m/s was examined. The model results showed that gas velocity has small effect on liquid phase CO_2 concentration. However the CO_2 concentration increased at outlet gas stream in tube side with increasing the gas velocity.

The results show that with increasing the liquid velocity, the overall mass transfer coefficient increases. The reason is that in the case of physical absorption in hollow fiber membrane contactors, the controlling resistance for the mass transfer usually is liquid phase. It has been found that by increasing absorbent velocity up to 3 m/s, relative absorption rate in the case of methanol absorbent increases to 4.3 times more than absorption rate in the case of water absorbent.

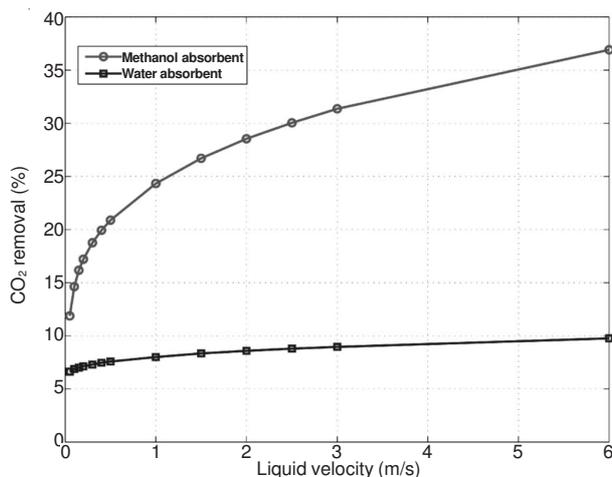Figs. 8 and 9 indicate the effect of methanol absorbent and gas velocity on the removal efficiency of CO_2.

Fig. 8.   Effect of absorbent velocity on the CO_2 removal efficiency for methanol and water absorbent at V_G = 3 m/s, C_0 = 8 mol/m^3, T = 298 K
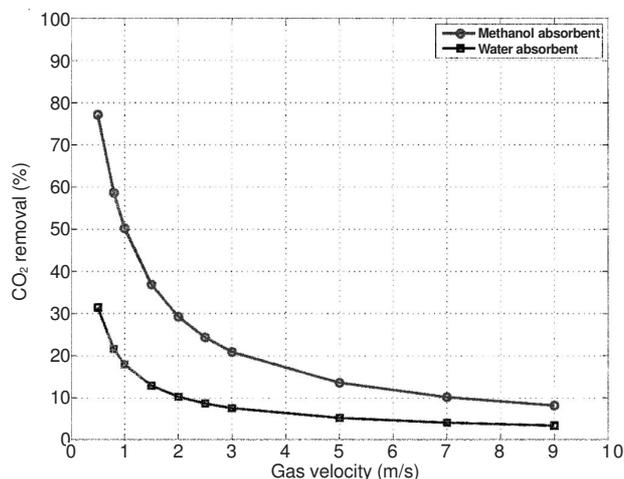

Fig. 9.   Effect of gas velocity on the CO_2 removal efficiency for methanol and water absorbent at V_L = 0.5 m/s, C_0 = 8 mol/m^3, T = 298 K

Wide range of velocities was selected for both absorbent and gas in order to provide a chance to gain a real insight into this effect. With respect to these figures, CO_2 removal efficiency at a given conditions increases with the increase in absorbent velocity. This effect is due to the increasing in driving force with entering fresh absorbent. Therefore, CO_2 concentration in gas phase reduces and removal efficiency improved as a cause of higher absorption rate.

In case of water absorbent CO_2 removal efficiency reaches a relatively constant value, by increasing the liquid velocity whereas in case of methanol absorbent, only increasing rate of CO_2 removal efficiency decreases which leads to higher relative absorption rates. This is because for higher absorbent velocities due to the lower contact time, the absorbent liquid cannot reach saturation and may be leaves the contactor unsaturated. In spite of reducing contact time at higher velocities, water absorbent leaves the contactor saturated with respect to its low potential absorption, whereas for methanol absorbent, the potential absorption is high enough resulting in a unsaturated methanol absorbent at the module exit. Therefore, in design

and application of membrane contactor using methanol absorbent higher flow rate is more efficient. Relative absorption rate of CO_2 using methanol absorbent is in the range 2.2 to 4.6 in comparison with the case of water absorbent. Also methanol in comparison with other commercially available physical solvents has a lower viscosity which increases mass transfer rates and decreases membrane area requirements and pressure drop over the fiber length.

Fig. 9 shows the effect of gas velocity on the CO_2 removal efficiency for methanol and water absorbent at a given conditions. It can be seen that CO_2 removal efficiency decreases considerably with the increase in gas velocity. This effect is due to the fact that by increasing the gas velocity (or flow rate), the amount of input impurity (CO_2) increases at constant absorption ability and also on the other hand, gas-liquid contact time decreases. As a result of these two negative effects, CO_2 removal efficiency decreases in the membrane contactor.

CO_2 removal efficiencies for three flow pattern *i.e.*, counter current flow (gas in shell and absorbent in tube), counter current flow (gas in tube and absorbent in shell) and co current (gas in tube and absorbent in shell) have been compared and results have been shown in Fig. 10. As we expected, counter current flow design leads to higher removal efficiencies than co current due to higher average driving force along the fiber length. In counter current flow condition, the type of flow inside the module has also to be carefully chosen. As it can see from results, when gas stream enter the tube side, counter current flow design leads to higher mass transfer coefficients than counter-current with gas in shell one, but the pressure drops increase too.
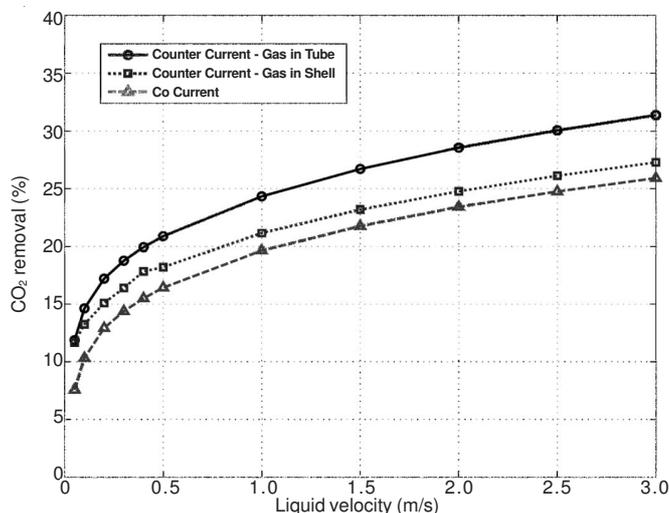

Fig. 10. Comparison of CO_2 removal efficiency for the counter current flow (gas in shell or tube) and co current flow at V_G = 3 m/s, C_0 = 8 mol/m^3, T = 298 K

The membrane length needed to achieve the desired removal efficiency is significant value. By increasing the membrane length, the membrane area for mass transfer increased and thus, higher removal efficiency is achieved. We examine this effect for two membrane length *i.e.*, 27 cm and 54 cm as a result of doubling the length, CO_2 removal efficiency about 60 % increased for V_L = 0.5 m/s, V_G = 3 m/s, C_0 = 8 mol/m^3, T = 298 K.

Effect of temperature: Fig. 11 indicate CO_2 radial concentration profile at three different temperatures *i.e.* 273 K, 293 K and 303 K.
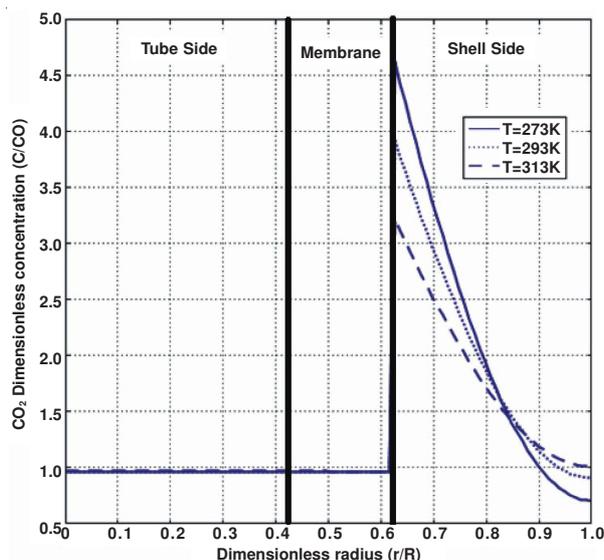

Fig. 11. Effect of temperature on CO_2 concentration profile for V_L = 0.1 m/s, V_G = 3 m/s, z/L = 0. 5

As shown in this figure, CO_2 solubility or similarly interface gas-liquid distribution coefficient decreased with the increase of temperature. High interface leads to a sharp reduction in CO_2 concentration in the liquid phase. But there is an opposite effect that as the temperature increases, liquid-phase diffusion coefficient increases. This affects CO_2 concentration distribution in the radial direction due to faster radial diffusion coefficient in lower temperature as it can be seen in Fig. 11. However, temperature has minor effect on gas and membrane phases CO_2 concentration. As the temperature increased, the gas phase CO_2 concentration slightly increased.

Conclusion

Application of gas-liquid hollow fiber membrane contactors for the removal of carbon dioxide using methanol absorbent was simulated and the effects of liquid velocity, gas velocity and temperature on the concentration distribution inside the shell, through the membrane and within the tube side were studied. In the case, Henry's coefficient, methanol velocity and CO_2 diffusivity in the liquid phase were the most important parameters. It has been found that by increasing absorbent velocity up to 6 m/s, relative absorption rate in the case of methanol absorbent increases to 4.6 times more than absorption rate in the case of water absorbent. The results indicate that methanol has the potential as a low-cost, green physical solvent for CO_2 capture in HFMC. It also revealed that in design and application of membrane contactor using methanol absorbent higher methanol flow rate is more efficient in comparison with water absorbent.

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Nomenclature

C   Concentration (mol m^{-3})
C_0 Initial concentration (mol m^{-3})
L   Filer length (m)
r   Radial coordinate (m)
r_1 Inner tube radius (m)
r_2 Outer tube radius (m)
r_3 Happel's free surface model radius (m)
r_4 Inner module radius (m)
V   Axial velocity (m s^{-1})
z   Axial coordinate (m)
T   Temperature (K)

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