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The Study of Carbon Dioxide Removal in Membrane Module by Single and Mixture of Alkanolamine Aqueous Solutions

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ABSTRACT

This work presents an investigation on the performance of CO_2 absorption into aqueous alkanolamine solution using a hollow fiber membrane gas-liquid contactor. Aqueous solution of ethanolamine (MEA), diethanolamine (DEA), 2-amino-2-methyl-1-propanol (AMP) and piperazine anhydrous (PZ) were chosen as the absorption liquids. A microporous hollow fiber membrane made of polyvinylidene fluoride (PVDF) was used as the medium for gas-liquid absorption process. In this study, the operating temperature is fixed at 30°C, while the flowrate of CO_2 and alkanolamine were in the range of 1000-5000 ml/min and 50-280 ml/min respectively. The feed gas was introduced directly to the shell of the module at 1-1.5 bar and the liquid flowed through the fiber lumen side. The CO_2 transfer through the membrane was found to be reaction controlled and dependent on the type of amine used. The use of piperazine as an accelerator in the mixture of the absorption liquids gives a good impact on increasing the performance for the rate of CO_2 transfer.

Keywords: Microporous hollow fiber membrane, carbon dioxide, piperazine, gas loading, mass transfer coefficient

1.0 INTRODUCTION

Carbon dioxide can be selectively removed from flue gasses using commercially available absorption process and conventional equipment like packed towers, bubble columns and spray towers. Although the conventional absorbers have been used in the chemical industry for decades, there are several disadvantages such as flooding at high flow rates, unloading at low flowrates and channeling as well as foaming, which lead to difficulties in mass transfer between gas and liquid.

Microporous hollow fiber membrane contactors are expected to overcome the disadvantages of the conventional equipment when incorporated into the acid gas treating process. Membrane-based gas absorption technology in the recovery of CO_2 from process gas streams was introduced because membrane gas-liquid contactors is characterized by operational flexibility, high mass transfer rate, and more economic easy linear scale-up [1]. Instead of that, hollow fiber membrane is conveniently

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used for gas-liquid contacting because it does not function as a species selective barrier and offer much smaller size in comparison to conventional equipment which requires a larger space to scale up. Commercially available membrane modules can provide interfacial area as high as 3000 m^2m^{-3} [2].

In microporous membrane contactors, the gas stream flows on one side and the absorption liquid flows on the other side of the membrane without phase dispersion which can avoid the problems often encountered in the conventional equipment. The compact modular structure of membrane contactors also provides much larger gas-liquid interfaces with known area at the pore mouth of the membrane, as well as the flexibility to scale up or down [3]. In order to avoid any phase dispersion, pressure plays an important role in the gas-liquid absorption system. The gas pressure needs to be maintained lower than the liquid pressure to prevent dispersion of gas as bubbles in the liquid. Liquid does not enter the pores unless a certain critical pressure is exceeded. This mode of operation is identified as the non-wetted mode since the liquid does not wet the membrane and the membrane pores are gas filled. The wetted mode is another mode of operation which leads to have absorbent liquid fills the membrane pores. In this mode, the gas pressure has to be higher than the liquid pressure to prevent the liquid from dispersing as drops in the gas (Karoor, 1985).

There are several options available for removing CO_2. The most well-established method for CO_2 removal is by absorption into amine based solvents such as monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), 2-amino-2methyl-1-propanol (AMP) or even by the use of their mixtures. The absorption of CO_2 by solutions of alkanolamine is mainly through chemical reactions where both kinetic and thermodynamic equilibrium play important roles in determining the ultimate gas loading that can be achieved. Amines are weak basic compounds that react with CO_2 to form weak chemical bonds. These chemical bonds are easily broken upon mild heating, leading to regeneration.

Primary and secondary amines such as MEA and DEA respectively are very reactive and therefore exhibit high rates of absorption. However, the formation of stable carbamate with CO_2 causes a stoichiometric gas loading limitation of 0.5 mole CO_2 per each mole of amine. To achieve high CO_2 absorption rates, reactive absorbents are widely employed in practice. Recently, the use of AMP is preferred to other amines since it is capable to give higher loading because its carbamate is relatively unstable [4]. When AMP reacts with CO_2, the formation of carbamates is inhibited due to the bulkiness of the group that is attached to its tertiary carbon atom. Therefore, the only significant reaction between CO_2 and the hindered amine is the formation of a bicarbonate ion, of which the stoichiometry allows CO_2 loading up to 1 mole per each mole of hindered amine. Consequently, high loading and fast reaction rates can be expected.

During the last three decades, many studies have been performed to improve the performance of CO_2 absorption in the aqueous alkanolamine. Sartori and Savage (1983) identified the advantage of using aqueous sterically hindered amines such as AMP to absorb CO_2. Chakravarty *et al.* (1985) proposed the use of blended amine, typically a mixture of tertiary and primary or secondary amines in order to gain better characteristics for each solution. Mandal *et al.* (2003) investigated on CO_2 absorption into blends of AMP and DEA through a wetted wall contactor. Another important development is the use of activated amine solutions, which consists of a conventional amine doped with small amounts of an accelerator (activator) that enhances the overall CO_2 absorption rates. An example of such activator is piperazine (PZ). Bishnoi and Rochelle (2000) studied on CO_2 absorption into aqueous solutions of piperazine in a wetted wall contactor. It was found that PZ has a significant effect on CO_2 loading.

It was observed that most of the works have employed water, NaOH or even some typical amines solutions as absorbent in removing CO_2 either from the mixture with N_2, SO_2 or air. Although increasing interest in the separation by membrane contactor is shown in recent years and exciting results have been reported, there is still a long way ahead before this technique is commercially applicable. Therefore, this research is conducted to study the performance of pure CO_2 absorption into aqueous alkanolamines through a hollow fiber membrane contactor. The effects of gas and liquid flowrates, inlet gas pressure, concentration of amine solutions and also the use of activated amines on the removal behavior of CO_2 were investigated as a basis for further experimental study.

2.0 METHODOLOGY

Experimental membrane module was fabricated using Microza microporous hydrophobic PVDF (polyvinylidene fluoride) hollow fiber module (Pall Corp., NY, USA) with 0.65 μm fiber ratings. Specifications of the hollow fiber membrane module used in this study are as given in Table 1. Test absorbents were prepared by mixing distilled water with aqueous solutions of methylethanolamine (MEA), diethanolamine (DEA), 2-amino-2-methyl-1-propanol (AMP) or piperazine (PZ).

Table 1 Specification for the hollow fiber membrane

Fiber pore size (μm)	0.65
Fiber diameter (cm)	0.11
Membrane nominal inner surface area (m^2)	0.02
Nominal module length (cm)	31.0
Typical cross flowrate (l/min)	2.30

A schematic diagram of the experimental setup is shown in Figure 1. The reaction gas was saturated in a water saturator before being passed through the shell side of the membrane module at pressure 1.0 or 1.5 bar and diffused through membrane pores into the liquid absorbent. The operating temperature was held constant at 30°C with uncertainty of ±0.01. The temperature of inlet gas and

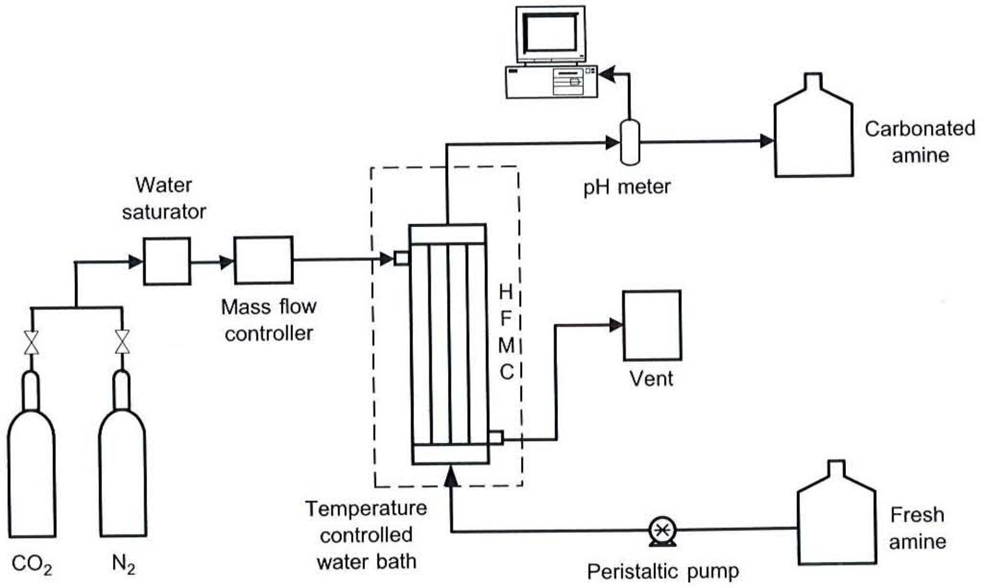

Figure 1 Schematic diagram of experimental setup

liquid was controlled using a circulating water bath to match the experimental temperature. A mass flow controller (Brooks) is used to regulate flow rates of CO_2 gas. In this study, the gas flowrates were varied from 1000 to 5000 ml/min. For the liquid stream, absorbent was pumped counter currently to the fiber lumen by using a peristaltic pump. The pump (Heidolph PD 5201) at the same time was used to control liquid flowrates from 50 to 280 ml/min. The pH of the CO_2 loaded solution is continuously monitored using a PC controlled pH meter (Metrohm 716 DMA Titrino). The pH decreased gradually, as more CO_2 gas is being absorbed by the alkanolamine solution.

The experiment was stopped when steady state was reached as indicated by a constant pH with uncertainty of ±0.003 for a period of about 30 minutes. Four samples of carbonated alkanolamine were analyzed by mixing in excess with solutions of 0.5 M $BaCl_2$ and 0.5 M NaOH and kept for about three hours under a temperature of 70°C and atmospheric pressure. NaOH was used in order to convert free dissolved gas into non volatile ionic species while $BaCl_2$ was used to precipitate all CO_2 existing in the sample. Another carbonated liquid sample was taken and neutralized with a solution of 1 M HCl in order to determine the final concentration of amine after reaction. Finally, results were averaged to find out the CO_2 loading of absorption with uncertainty of ±0.005.

3.0 RESULTS AND DISCUSSION

As for feasibility studies, low concentration of amines was used in order to test the experimental setup without loss of large amounts of solvents. All the experimental runs were carried out at constant temperature of 30°C by using a microporous hydrophobic hollow fiber membrane. The microporous membrane-based device acts as a gas absorber, with gas flows in the shell side and absorption liquid flows in the tube side of the membrane. The effects of gas and liquid flowrates on CO_2 permeation flux through the membrane for 0.1 M AMP at inlet gas pressure of 1.0 bar is depicted in Figure 2. In general, it shows that the CO_2 permeation flux does not change significantly with the liquid and gas flowrates at 3000 to 5000 ml/min. However, at lower flowrates of gas such as 1000 and 2000 ml/min, it shows that the CO_2 permeation flux increases as well as rise of liquid flowrates.

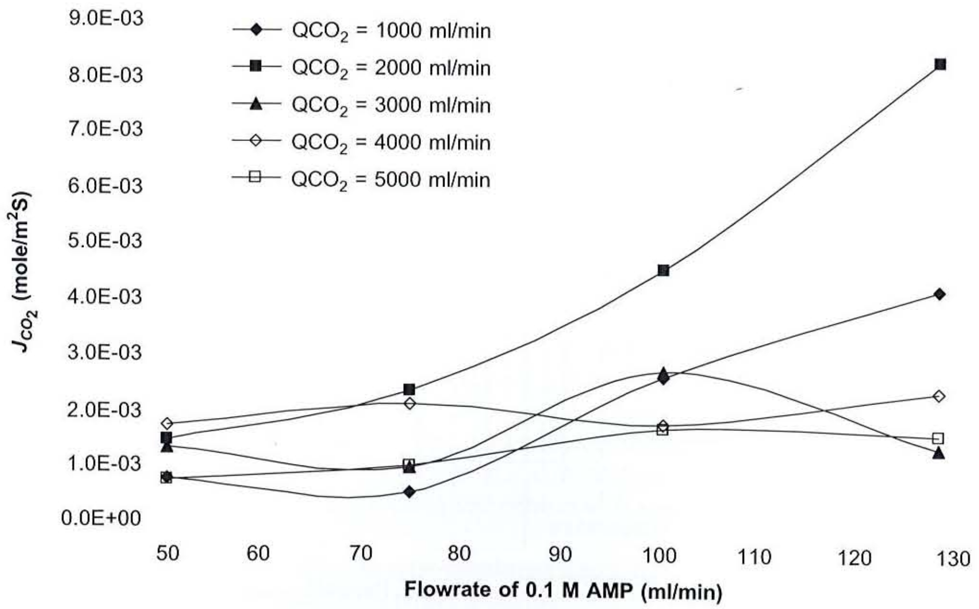

Figure 2 CO_2 permeation flux using 0.1 M AMP at 1.0 bar

These results indicate that the CO_2 mass transfer in the membrane contactor at the inlet gas pressure of 1.0 bar is found diffusion controlled especially when the gas flowrate is above 3000 ml/min. This is may be due to the low concentration of amine used. From observation, it was found that moistures appeared in the gas ventilation tubing. Therefore, this condition strongly supported the fact that the membrane pores are absorbent liquid filled which is called wetted mode of operation.

In order to avoid liquid dispersion, experiments then were carried out by increasing the inlet gas pressure to 1.5 bar and this is indicated by Figure 3. Although the inlet gas pressure has been increased, it needs to be maintained lower than the liquid pressure to prevent dispersion of gas as bubbles in the liquid stream. Based on observation, no more moisture appeared in the gas ventilation tubing and also no bubbles emerged in the liquid outlet tubing. Hence, this condition indicated that the removal process is now reaction controlled. Results in Figure 3 show that the fluxes of CO_2 increase with liquid flowrates, almost for all cases of gas flowrates. However, due to inconsistent increment especially when using gas flowrates above 3000 ml/min, therefore absorption of CO_2 then was investigated by increasing the liquid flowrates to the maximum level that the peristaltic pump able to operate which is up to 280 ml/min.

Figure 4 illustrates the behavior of CO_2 removal in both wetted and non-wetted mode by using 0.1 M AMP at a constant gas flowrate of 5000 ml/min. It is clearly seen that the transfer of CO_2 in the wetted mode is lower than that in the non-wetted mode. This effect is more apparent as the flowrate of amine was increased. By filling the pores with the absorbent liquid (wetted mode), the membrane-phase resistance is increased as the liquid offers additional resistance to the transport;

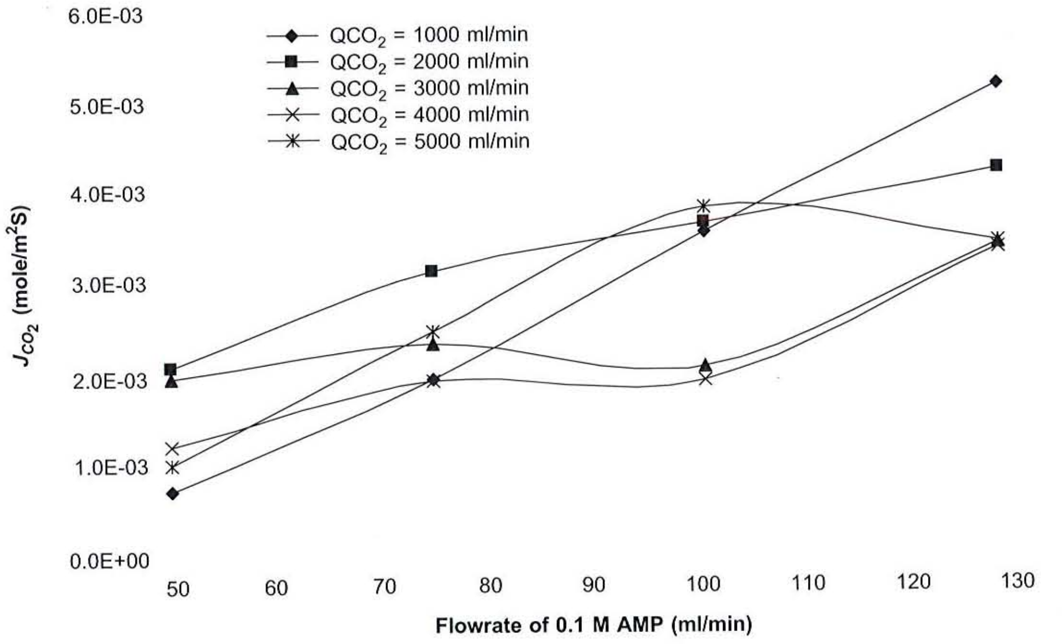

Figure 3 CO_2 permeation flux using 0.1 M AMP at 1.5 bar

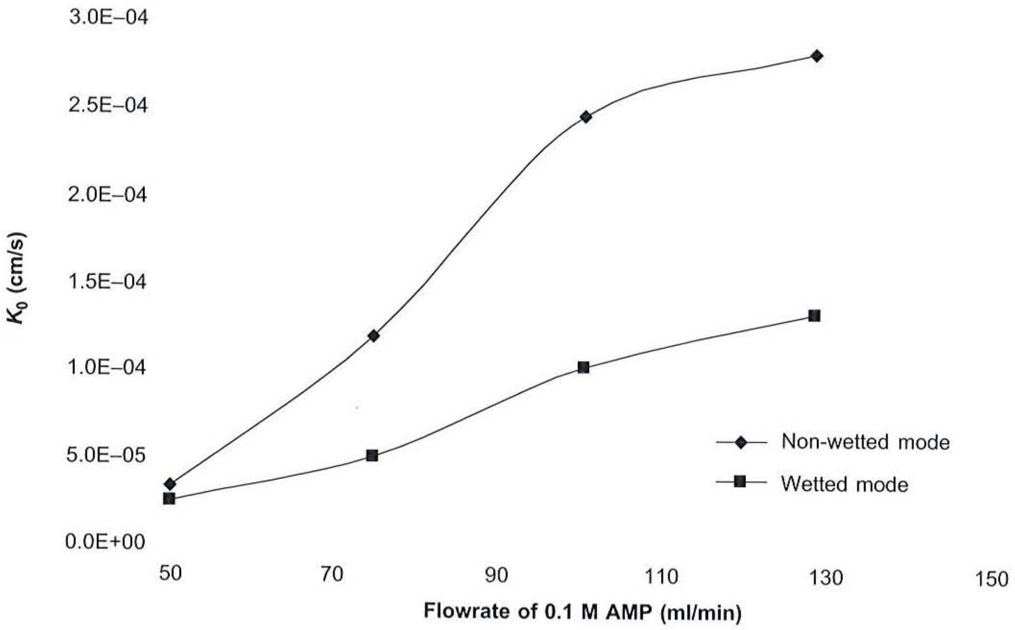

Figure 4 Overall mass transfer coefficient at various operation mode for CO_2 absorption using 0.1 M AMP (Q_{CO_2} = 5000 ml/min)

this behavior highlights the fact that this is liquid phase-controlled process. Hence it would not be advantageous to operate this system under wetted mode. For non-wetted mode of pure CO_2 absorption, the pores of fibers are filled with CO_2 and the gas-liquid interface lies at the pore mouth of the hydrophobic fiber on the absorbing liquid side. There is no transport resistance in the gas phase. Thus, the mass transfer inside the pores of membrane is governed by gas diffusion and membrane structure.

In a membrane contactor, the gas and liquid phases flow on the opposite sides of the membrane. For this study, amine which contains in the liquid flow was passed through the lumen side, while the gas flow contains of pure CO_2 filled the shell side of the membrane. The absorption occurred at the pore mouth of the membrane through a chemical reaction. As illustrated in Figure 5, the overall mass transfer coefficient is plotted against the liquid flowrates. This result shows the effect of higher liquid flowrate on the CO_2 absorption at higher inlet gas pressure (1.5 bar). As the liquid flowrate increases, the CO_2 mass transfer increases as well. Obviously, an increase in liquid flowrate results in a lower liquid mass transfer resistance and hence, more efficient gas removal is obtained. This effect is more pronounced when the gas flowrate is low which is at 1000 ml/min. For higher gas flowrate, an equivalent gas removal can be achieved if a higher volume module is used providing more gas-liquid contact area. The membrane contacting process shows an excellent performance in terms of mass transfer. Therefore, further studies are preferable by fixing the gas flowrate at 5000 ml/min and the use of higher concentration at higher flowrate of amine should show different rates of CO_2 transfer.

In the presence of AMP as absorbent, absorption is facilitated by chemical reaction. This fact proved that the use of chemical aqueous solution enhances absorption rate of CO_2 and therefore, the scrubbing capacity of the liquid absorbent improves. Figure 6 shows the overall mass transfer coefficient as a function of liquid flowrate for a constant gas flowrate of 5000 ml/min. In this case, the CO_2 mass transfer appreciably increases even for low AMP concentration. By increasing AMP concentration from 0.1 to 4 M, the CO_2 mass transfer was expected to be increased because of the reaction rate increased. Results in this figure have supported the fact that higher concentration of amine solution as absorbent improves the performance of CO_2 absorption in membrane contactor [11].

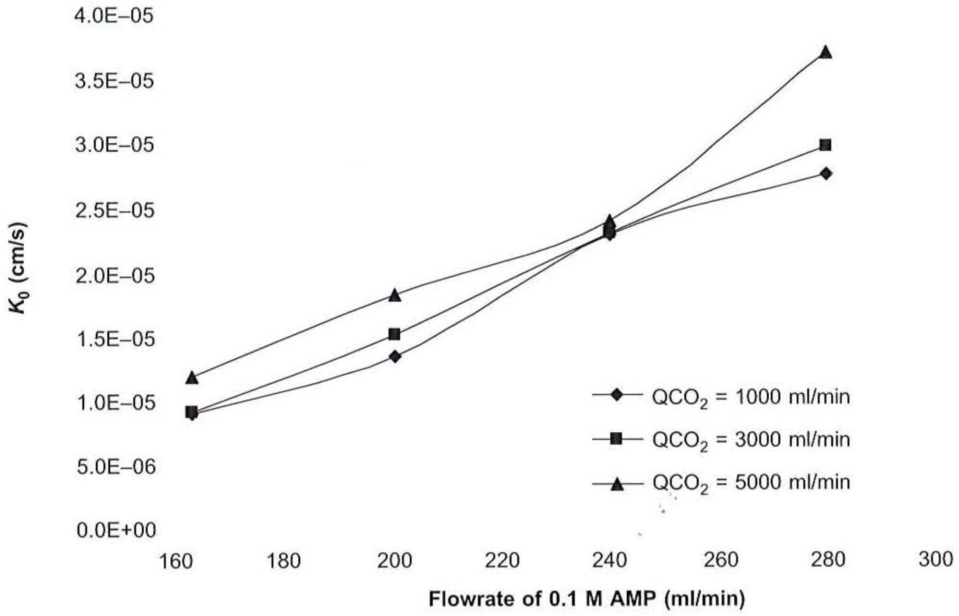

Figure 5 Overall mass transfer coefficient at various gas flowrates (P_{in} = 1.5 bar)

The rate of CO_2 absorption is found to be the highest at the amine flowrate of 279.9 ml/min. This is may be due to the highest usage of gas flowrate, which affect the rate of CO_2 absorption. At the highest amine flowrates, a fast reaction is taking place as the speed of pure CO_2 applied to the system is very fast. At this stage, the CO_2 solubility in AMP is very high as more CO_2 being absorbed by AMP at fast speed causing an increase in the rate of mass transfer. Whereas at low liquid flowrates, the solution becomes saturated with CO_2 since the membrane pores are filled with the reaction gas at very fast speed while AMP as absorbent is flowed in the membrane lumen at much slower speed. At this stage, a slow reaction is taking place and therefore the mass transfer rate decreases.

Instead of using single alkanolamine as the liquid absorbent in the absorption of CO_2, most of open literatures also discussed on the addition of a primary (MEA) or secondary amine (DEA) to a tertiary amine (MDEA) which have been applied in the gas treating processes. However, the main interest in this study is more on the mixture with piperazine (PZ) in order to enhance the CO_2 mass transfer rate. A mixture of any conventional alkanolamine with PZ is usually known as activated alkanolamines. Normally, only a small amount of piperazine is added to improve the performance of the alkanolamine solution by increasing the rate of CO_2 absorption. In this study, the piperazine concentration is in the range of 0.1 and 0.5 M and the total concentration of the activated alkanolamines is kept constant at 2.0 M. It has to be noted here that piperazine has a symmetrical diamino cyclic molecule structure; therefore 1.0 M solution of PZ is actually equal to 2.0 M of any other conventional alkanolamines.

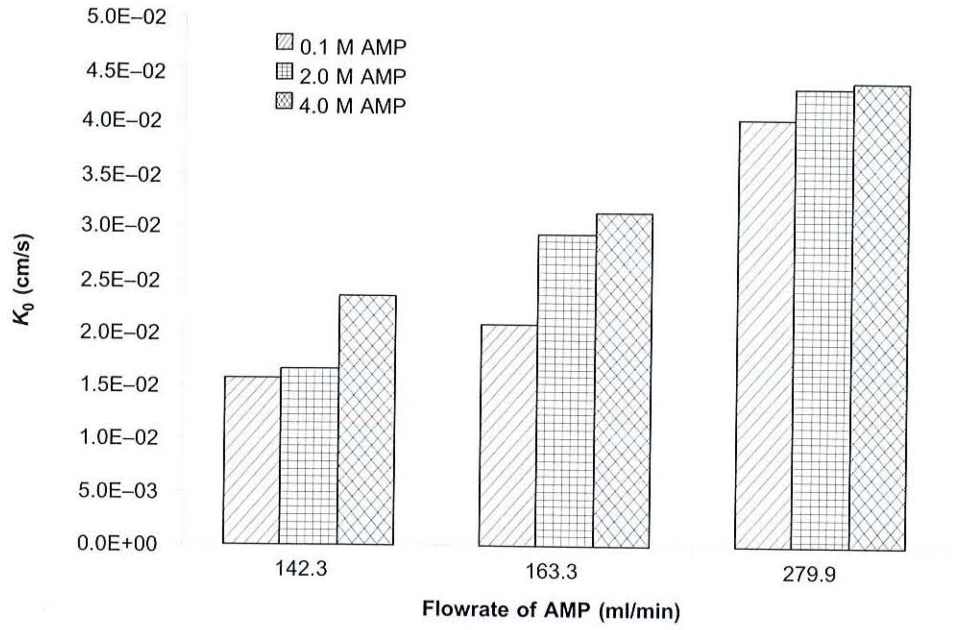

Figure 6 Overall mass transfer coefficient using various concentration and flowrate of AMP (Q_{CO_2} = 5000 ml/min and P_{in} = 1.5 bar)

The results of CO_2 absorption using both single and mixture of amines are given in Table 2 in which the removal of CO_2 in both aqueous alkanolamine solutions is expressed in terms of CO_2 total (mol of CO_2 absorbed/l of amine used). This table shows results for single amine at 0.1 and 2.0 M and activated amine at total concentration of 2.0 M in order to identify and compare the efficiency of each absorbent. These results obviously show that single MEA is not preferable as absorbent because even when the concentration is increased from 0.1 to 2.0 M, the total CO_2 absorbed are only slightly increased. However, activated MEA shows much greater amount of CO_2 absorbed rather than by the use of MEA alone.

Table 2 Total CO_2 absorbed by conventional and activated aqueous alkanolamine solutions (Q_{CO_2} = 5000 ml/min, Q_{amine} = 163.3 ml/min and P_{in}=1.5 bar)

Amines	Concentration	CO_2 total, $(CO_2)_t$ (mol/l)
Conventional	0.1 M MEA	0.0223
	0.1 M DEA	0.0269
	0.1 M PZ	0.0273
	0.1 M AMP	0.0386
	2.0 M MEA	0.0233
	2.0 M DEA	0.0454
	1.0 M PZ	0.0557
	2.0 M AMP	0.0560
Activated	0.1 M PZ + 1.8 M MEA	0.0494
	0.1 M PZ + 1.8 M DEA	0.0586
	0.1 M PZ + 1.8 M AMP	0.0705
	0.5 M PZ + 1.0 M MEA	0.0651
	0.5 M PZ + 1.0 M DEA	0.0830
	0.5 M PZ + 1.0 M AMP	0.0820

Table 2 also indicates that both DEA and AMP are preferable to be used as the absorption liquid for CO_2 removal. This is due to the fact that both amines have performed well either as single or with the addition of piperazine. It is clearly shown in Table 2 that the total CO_2 absorbed using DEA as well as AMP, are gradually increased as the concentration increases from 0.1 to 2.0 M. Furthermore, the total CO_2 absorbed using activated DEA and activated AMP at 2.0 M are greater than both single amines. These results imply that the use of piperazine as an accelerator in the mixture with conventional amines gives a good impact in increasing the rate of CO_2 transfer. In addition, the use of higher inlet gas pressure of gas is found to be a requirement to obtain the rate of CO_2 transfer under reaction control regime together with the improvement of the absorption capacity.

4.0 CONCLUSION

A membrane rig was constructed to study the CO_2 transfer into a solution of alkanolamine. The CO_2 transfer through the membrane has shown to be reaction controlled at 1.5 bar of the inlet gas pressure. The experimental results show that removal of CO_2 using mixture of amine as absorption liquid gives higher CO_2 transfer rather than by single amine. The use of piperazine as an accelerator in the mixture of the absorption liquids gives a good impact in increasing the rate of CO_2 transfer. The absorption capacity was found to be improved when the highest flowrates of amines and gas was applied to the system.

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NOMENCLATURE

AMP	2-amino-2-methyl-1-propanol
MEA	Monoethanolamine
DEA	Diethanolamine
MDEA	N-Methyldiethanolamine
PZ	Piperazine
l, g	Liquid and gas phase respectively
in, *out*	Inlet and outlet respectively
n	Number of moles (mol)
x	Mole fraction (mol/mol)
P	Pressure (bar)
T	Temperature (°C)
V	Volume (l)
P_{in}	Inlet gas pressure of CO_2 (bar)

P_{CO_2}	Partial pressure of CO_2 (bar)
P_{gas}	Gas pressure (bar)
P_{aq}	Aqueous liquid pressure (bar)
M_{amine}	Concentration/molarity of aqueous amine solutions (mol/l)
A_m	Internal area of hollow fiber membrane (m^2)
Q_{CO_2}	Flowrate of CO_2 gas (ml/min)
Q_{amine}	Flowrate of alkanolamine solution (ml/min)
K_i	Equilibrium constant (l/mol)
m	Dimensionless solubility
a	CO_2 loading (mol CO_2/mol amine)
J_{CO_2}	CO_2 permeation flux (mol/m^2.s)
$(CO_2)_t$	Total CO_2 absorbed by amine solution (mol CO_2/l)
K_o	Overall mass transfer coefficient (cm/s)

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