

# Investigation of H<sub>2</sub>S and CO<sub>2</sub> Removal from Gas Streams Using Hollow Fiber Membrane Gas–liquid Contactors



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Chemical absorption of H<sub>2</sub>S and CO<sub>2</sub> from CH<sub>4</sub> was carried out in a polypropylene porous asymmetric hollow fiber membrane contactor (HFMC). A 0.5 mol L<sup>-1</sup> aqueous solution of methyldiethanolamine (MDEA) was used as chemical absorbent solution. Effects of gas flow rate, liquid flow rate, H<sub>2</sub>S concentration and CO<sub>2</sub> concentration on the H<sub>2</sub>S outlet concentrations and CO<sub>2</sub> removal percentage were investigated.

The results showed that the removal of H<sub>2</sub>S with aqueous solution of MDEA was very high and indicated almost total removal of H<sub>2</sub>S. Experimental results also indicated that the membrane contactor was very efficient in the removal of trace H<sub>2</sub>S at high gas/liquid flow ratio. The removal of H<sub>2</sub>S was almost complete with a recovery of more than 96 %. Using feed gas mixtures containing 5000 ppm H<sub>2</sub>S with CO<sub>2</sub> concentrations in the range of 4–12 vol.%, the outlet H<sub>2</sub>S concentration of less than 1.0 ppm was attained with less than 4.0 vol.% of CO<sub>2</sub> permeated and absorbed.

*Key words:*

hollow-fiber membrane contactor, MDEA, hydrogen sulphide, carbon dioxide

## Introduction

Hydrogen sulfide (H<sub>2</sub>S) and carbon dioxide (CO<sub>2</sub>) are the major impurities of industrial gas mixtures. The presence of these two acid gases in natural gas causes several problems during its processing and usage. CO<sub>2</sub> content reduces the energy efficiency of natural gas, and it has been considered a major contributor to global warming. On the other hand, H<sub>2</sub>S is a toxic and corrosive gas also known as the main sulfur dioxide emission source<sup>1</sup>. Therefore, in order to sustain economic growth besides achieving compliance with environmental protection regulations, it is very important to capture CO<sub>2</sub> and H<sub>2</sub>S from natural gas. Conventional techniques, such as column absorption for CO<sub>2</sub> and H<sub>2</sub>S capture are energy-consuming and not easy to operate because of the frequent problems, including flooding, foaming, channeling, entrainment, and high capital and operating costs<sup>2</sup>.

Hollow fiber membrane contactor (HFMC) is a promising alternative which has been a focus of research for decades because of its advantages over the traditional gas absorption processes, such as independent liquid and gas flow rate manipulation,

much larger gas–liquid interfaces, and the flexibility to scale up or down<sup>3</sup>.

A membrane contactor usually consists of a bundle of hydrophobic microporous symmetric hollow fiber membranes where the fluids flow on each side of the membrane without direct contact<sup>4</sup>. In gas–liquid absorption processes, the membrane contactor mainly acts as a physical barrier between two phases (gas and liquid) without significant effect in selectivity, i.e., the membrane does not change the partition coefficient. As the two phases are separated by the membrane, there is no mixing phase or dispersion phenomena. The gases are transferred from one phase to the other only by diffusion. Hydrophobicity of gas–liquid membrane contactors increases mass transfer rates and separation efficiency. The membranes do not allow the liquid phase to penetrate through the membrane pores, and thus the gas phase fills the membrane pores<sup>3</sup>.

The key issue which usually suggests a membrane contactor to be selected for a given application is the possibility to achieve a significant reduction in the size of the installation without changing the separation performances. A so-called process intensification effect as high as 10–30 has been reported in some cases when membrane contactors are compared to packed columns, especially for gas–liquid absorption operations<sup>5</sup>.

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A large number of studies dealing with CO<sub>2</sub> absorption by membrane contactors involve hydrophobic microporous hollow fibers for which impressive intensification factors have been reported<sup>4,6</sup>.

The present work was performed to achieve an efficient removal of H<sub>2</sub>S and CO<sub>2</sub> from CH<sub>4</sub>. The absorption medium used was an aqueous solution of methyldiethanolamine (MDEA) and the contactor employed was a hollow-fiber hydrophobic membrane module. The effects of various operating conditions on the selective removal of H<sub>2</sub>S and CO<sub>2</sub> were investigated. This study attempts to assess the influence of liquid absorbent flow rate, gas feed flow rate, CO<sub>2</sub> and H<sub>2</sub>S concentration on the removal efficiency of H<sub>2</sub>S and CO<sub>2</sub>, as well as the overall mass transfer coefficients.

This research aims at studying an efficient and selective removal of H<sub>2</sub>S from gas streams containing high concentrations of CO<sub>2</sub> using a hollow fiber membrane module to reduce the amount and thus the re-generation process capacity of absorbent used.

## Experimental

### Hollow fiber module

The shell-and-tube type asymmetric polypropylene hollow fiber membranes used in this study were obtained from Liqui-Cell. The membrane was found to have an average pore size of 0.05 micron and porosity of approximately 25 percent. The fibers outer and inner diameters were 300 and 200 microns, respectively. The complete specifications of hollow fiber membrane module are listed in Table 1. Two SEM images of the hollow fiber membrane used are shown in Figure 1.

Table 1 – Membrane contactor parameters

| Item                    | Value                                 |
|-------------------------|---------------------------------------|
| Membrane area           | 1.4 m <sup>2</sup>                    |
| Porosity percent        | 25 %                                  |
| Fiber dimensions        | (o.d.: 300 μm, i.d.: 200 μm)          |
| Fiber inside volume     | 150 cm <sup>3</sup>                   |
| Shell material          | polyethylene                          |
| Shell dimensions        | (o.d.: 77.4 mm, length: 282.5 mm)     |
| Surface/volume ratio    | 9333.3 m <sup>2</sup> m <sup>-3</sup> |
| Maximum liquid pressure | 7.2 bar                               |
| Maximum gas pressure    | 0.7 bar                               |
| Max liquid flowrate     | 0.7 m <sup>3</sup> h <sup>-1</sup>    |
| Shell inside volume     | 400 cm <sup>3</sup>                   |

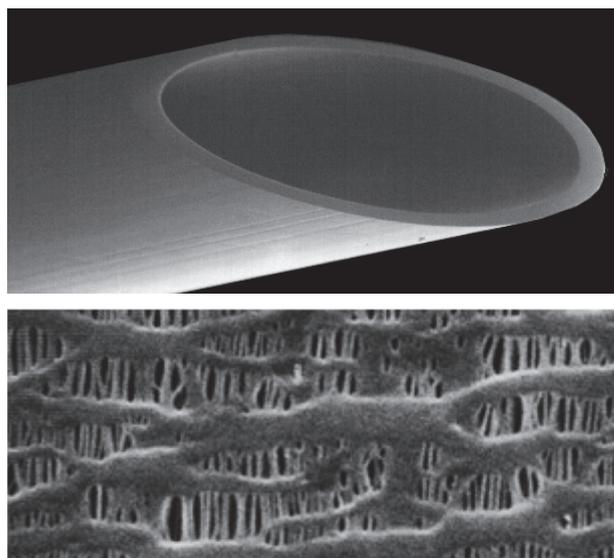


Fig. 1 – Scanning Electron Microscope (SEM) images of hollow fiber membrane used. The porous surface can be seen in the lower photo.

### Experimental set-up

A schematic of experimental set-up used in this study is shown in Figure 2. The feed gas mixtures of various concentrations of H<sub>2</sub>S, CO<sub>2</sub> and CH<sub>4</sub> were prepared by mixing pure gas streams adjusted with mass flow controllers. The CO<sub>2</sub>, H<sub>2</sub>S and CH<sub>4</sub> gas cylinder with purity of 99.9 % were prepared from Roham Gas Corp. The feed gas mixtures were passed through a mixing vessel, and then a secondary mass flow controller was used in order to adjust accurate gas flowrate. The feed stream was passed through the lumen side of the hollow fibers. A 0.5 mol L<sup>-1</sup> concentration aqueous solution of MDEA was used as absorbent. The 99 % pure MDEA solution was prepared from Sarakhs petrochemical complex and deionized water was used for making the aqueous solutions. An accurate PTFE penetrating pump (Jesco) with a maximum flowrate of 15 L h<sup>-1</sup> was used as liquid pump. The liquid flowrates were controlled by a flow meter, and then fed into the shell side of the membrane module in counter-current direction.

The module was set at a constant temperature, and the experiments were conducted at room temperature (25 °C). The feed gas operating pressure was kept constant at 0.5 bar and the liquid operating pressures were consistently 1.5 bar higher than that at the gas phase.

The CO<sub>2</sub> concentrations in feed and retentate streams were measured using Gas Chromatography (Varian 3800). The H<sub>2</sub>S concentrations in the feed and retentate streams were monitored using Tutwilmer apparatus plus an online gas detector (GFG, Germany) which provided accurate measurements (± 1 ppm) of the gas components.

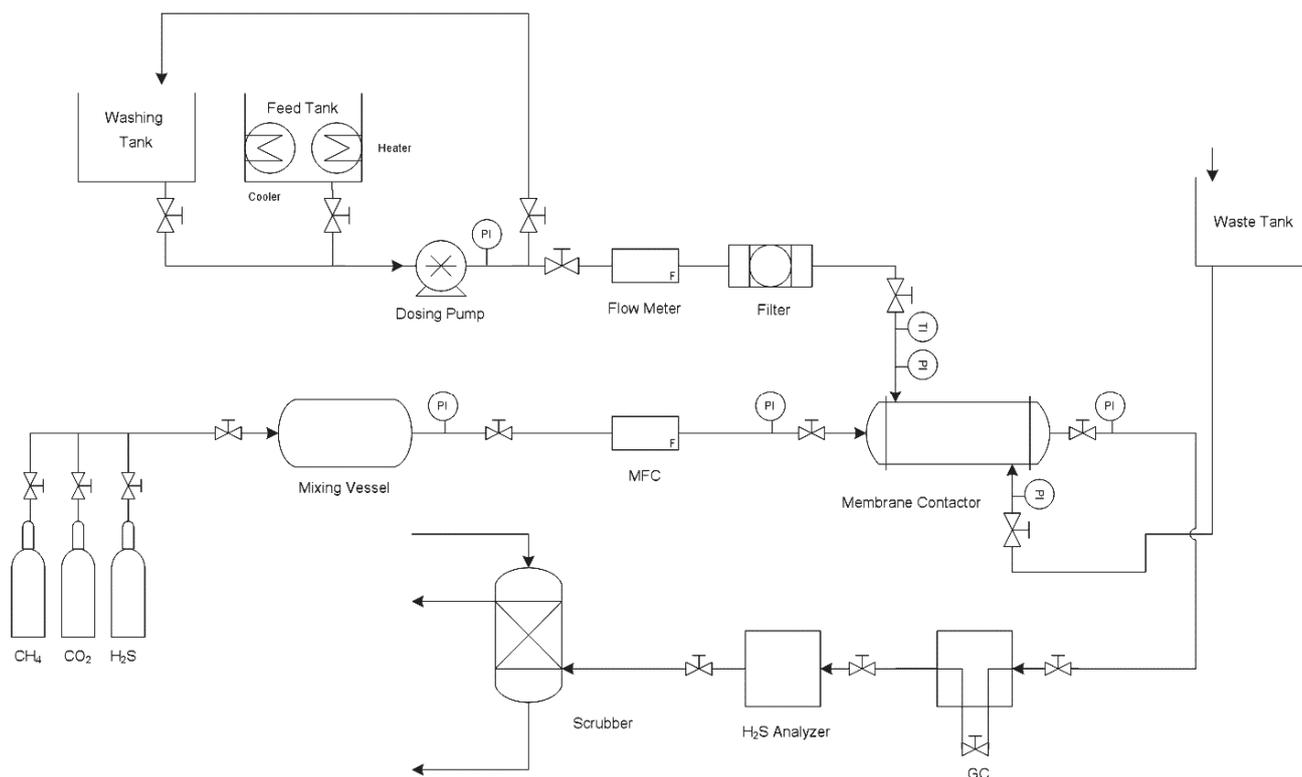


Fig. 2 – Schematic representation of the experimental set-up

The Tutwiler method is widely applied for the determination of hydrogen sulfide in gas mixtures for control purposes. It consisted of a 100- or 500-mL Tutwiler burette, with two-way glass stopcock at bottom and three-way stopcock at top which connect either with inlet tube or glass-stoppered cylinder, 10 mL capacity, graduated in 0.1 mL subdivision. The used reagents were iodine stock solution, 0.05 mol L<sup>-1</sup>, standard iodine solution (1 mL = 0.001771 g iodine) and starch solution. The H<sub>2</sub>S was determined by two-step titration reagents.

At the final stage, the retentate stream exited from membrane module was passed through a packed gas absorbent column to remove the toxic gases.

In order to evaluate the effects of the investigated parameters on CO<sub>2</sub> and H<sub>2</sub>S absorption performances, gas mixtures containing three different CO<sub>2</sub> (4, 12 and 20 vol.%) and H<sub>2</sub>S (5000, 15000 and 25000 ppm) concentrations at pressure of 0.5 bar with various flow rates of 360, 420 and 480 L h<sup>-1</sup> were used as feed stream. A 0.5 mol L<sup>-1</sup> MDEA aqueous solution at flow rates of 0.5, 1.5 and 2.5 L h<sup>-1</sup> at pressure of 1.5 bar were also used as absorbent liquid. As a result, the gas flow ratios were varied in three limited ranges as (144, 168 and 192), (240, 280 and 320) and (720, 840 and 960). All these ratios are much higher than those reported for packed towers.

## Results and discussion

### Effect of H<sub>2</sub>S feed concentrations

The effect of H<sub>2</sub>S concentrations on the H<sub>2</sub>S retentate concentration and percentage of CO<sub>2</sub> removal for different feed flow rates are shown in Figure 3. These experiments were carried out using 0.5 mol L<sup>-1</sup> aqueous MDEA solution. The CO<sub>2</sub> concentrations in the feed were kept constant at 4 vol.% during all experiments. All other operating conditions were adjusted as explained previously in Experimental section. Experimental results revealed that, with an increase in H<sub>2</sub>S concentration from 5000 to 25000 ppm, the retentate concentration steadily increased from 2.0 to 217.0 ppm, and from 0 to 24.5 ppm for gas flowrate of 360 L h<sup>-1</sup> and liquid flowrate of 0.5 L h<sup>-1</sup>, respectively.

The results also indicated that the maximum H<sub>2</sub>S retentate concentration was measured for feed containing 25000 ppm H<sub>2</sub>S, with highest gas/liquid flow ratio of 960. At these conditions, the minimum CO<sub>2</sub> removal percentage was achieved (19.25 %). It was also found that with increasing H<sub>2</sub>S concentration in the range from 5000 to 25000 ppm, the CO<sub>2</sub> removal declined from 100 to 51.25 %, and from 100 to 78.50 % for gas flowrate of 360 L h<sup>-1</sup> and liquid flowrate of 0.5 L h<sup>-1</sup>, respectively.

An increase in H<sub>2</sub>S concentration generally had a negative effect on separation performance, which

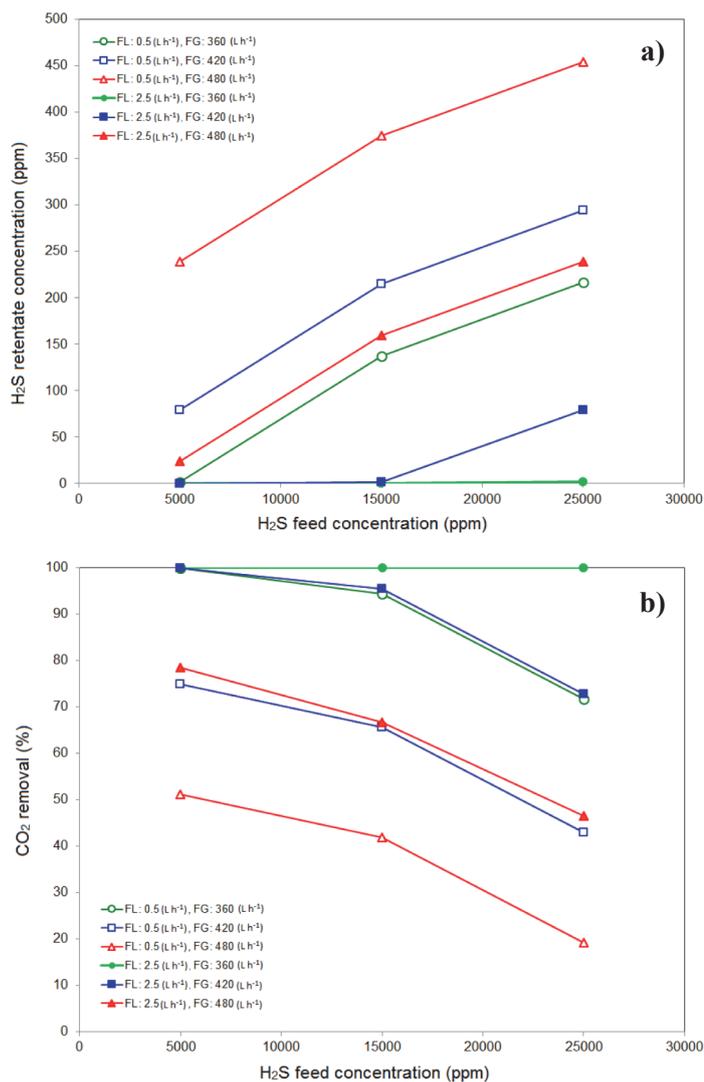


Fig. 3 – Effect of H<sub>2</sub>S feed concentrations on the H<sub>2</sub>S retentate concentration (a) and CO<sub>2</sub> removal percent (b): MDEA 0.5 mol L<sup>-1</sup> and CO<sub>2</sub> feed concentration 4 vol.%

decreased both the H<sub>2</sub>S (and/or) CO<sub>2</sub> removal efficiency, and the mass transfer coefficient. This indicated that the additional H<sub>2</sub>S was accumulated in the transfer path.

The reaction rate of H<sub>2</sub>S with the aqueous solutions of alkanolamines can be considered instantaneous with respect to mass transfer, while the reaction rate of CO<sub>2</sub> in these solutions decreased considerably going from primary to secondary to tertiary amines<sup>7</sup>. Thus, when using MDEA as a tertiary amine, the CO<sub>2</sub> molecules are not absorbed and stay in the gas–liquid interface within the membrane. In this situation, the increase in H<sub>2</sub>S feed concentration reduced the absorption rate of CO<sub>2</sub> molecules.

According to the literature<sup>8</sup>, in the absence of CO<sub>2</sub>, the increase in H<sub>2</sub>S feed concentration has no negative effect on the removal efficiency, but, in the presence of CO<sub>2</sub>, when both acid gases concentra-

tions are increased, the removal efficiencies decrease strongly. It should be noted that the negative effect of H<sub>2</sub>S feed concentration has the same effect on CO<sub>2</sub> removal efficiency compared to that of H<sub>2</sub>S. Therefore, it can enhance the H<sub>2</sub>S selectivity despite reducing its removal efficiency.

As a result, it can be concluded that aqueous MDEA solution, because of its ability to absorb H<sub>2</sub>S in the presence of CO<sub>2</sub>, could be a suitable choice for selective separation of H<sub>2</sub>S from natural gas streams which do not have too much CO<sub>2</sub> content.

### Effect of CO<sub>2</sub> feed concentrations

The effect of CO<sub>2</sub> concentrations on the H<sub>2</sub>S retentate concentration and CO<sub>2</sub> removal percentage are shown in Figure 4.

The increase in CO<sub>2</sub> concentrations from 4 to 20 vol.% obviously decreased CO<sub>2</sub> removal performance for gas flow rate of 360 L h<sup>-1</sup> from 100 to 51.25 % and from 100 to 81.00 % at liquid flow rates of 0.5 and 2.5 L h<sup>-1</sup>, respectively. However, in the case of H<sub>2</sub>S retentate concentration, it remained approximately constant in the range 0–2 ppm at gas flow rate of 360 L h<sup>-1</sup>, while it increased slightly up to 79.5 ppm at gas flow rate of 480 L h<sup>-1</sup>.

The comparison of CO<sub>2</sub> removal efficiency in Figures 3 and 4 revealed that the presence of H<sub>2</sub>S lowers the average removal efficiency of CO<sub>2</sub>. This is due to the competition of H<sub>2</sub>S and CO<sub>2</sub> for being absorbed by the solvent. As it is found from the literature<sup>9,10</sup>, the increase in H<sub>2</sub>S concentration decreases the overall mass transfer coefficient of CO<sub>2</sub>. Therefore, with increasing H<sub>2</sub>S concentration or H<sub>2</sub>S partial pressure in the feed gas phase, more H<sub>2</sub>S molecules dissolve and react with the amine absorbent. The increased consumption of the MDEA results in a decrease in the absorption of CO<sub>2</sub> which was present even at much higher concentrations.

Since MDEA is a tertiary amine and does not have hydrogen attached to the nitrogen, the CO<sub>2</sub> reaction can only occur after the CO<sub>2</sub> dissolves in the water to form a bicarbonate ion<sup>11</sup>. The chemical reactions determine the composition of the different ions in the liquid phase, and as a result, the enhancement of the mass transfer. Equilibrium reactions are fast enough to assume chemical equilibrium throughout the entire liquid phase. This assumption is acceptable if reaction kinetics is significantly faster than mass transport in the liquid phase. A certain number of equilibrium reactions occur within the system CO<sub>2</sub> – H<sub>2</sub>S – alkanol amines<sup>12</sup>.

### Effect of gas and liquid flow rate

The effect of gas flow rates on the H<sub>2</sub>S retentate concentration for various feed compositions is

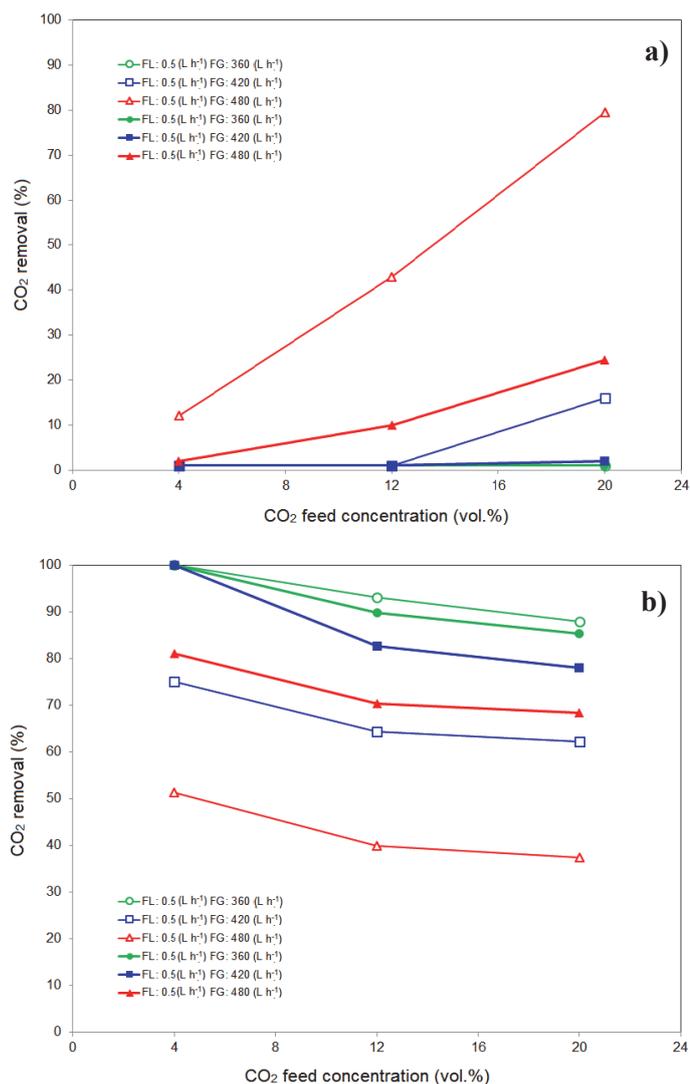


Fig. 4 – Effect of CO<sub>2</sub> feed concentrations on the H<sub>2</sub>S retentate concentration (a) and CO<sub>2</sub> removal percent (b): MDEA 0.5 mol L<sup>-1</sup> and H<sub>2</sub>S feed concentration 5000 ppm

presented in Figure 5a. As is observed, the H<sub>2</sub>S retentate concentration increases rapidly with increasing gas flow rate. Higher feed concentration causes higher increasing rate of H<sub>2</sub>S retentate concentration. In addition, it seems that the increasing rates enhanced at higher gas flow rates.

The results showed that the increase in the gas/liquid flow ratio caused an increase in gas velocity, which decreased the contact time between the gas and liquid phases, and thus limited the reactions of the acid gases with amine solution. This observation is also reported in references<sup>9,13</sup>. Therefore, it will reduce the removal performance of both CO<sub>2</sub> and H<sub>2</sub>S.

On the other hand, when the liquid absorbent flow rate increases, the mass transfer rate of acid gases into the liquid phase increases because the concentration gradients of H<sub>2</sub>S (CO<sub>2</sub>) and absorbent

in the liquid phase increase, which in turn results in reduction of the H<sub>2</sub>S (CO<sub>2</sub>) outlet concentration in the gas phase. It can also be observed that the increase rate of H<sub>2</sub>S (CO<sub>2</sub>) outlet concentration is much sharper at lower gas/liquid flow ratios.

The effect of gas and liquid flow rate on the CO<sub>2</sub> removal percentage versus feed concentration is shown in Figure 5b. The experiments were carried out with H<sub>2</sub>S feed concentration of 5000 and 25000 ppm using 0.5 mol L<sup>-1</sup> MDEA aqueous solution at flow rates of 0.5 and 2.5 L h<sup>-1</sup>. As would be expected, the CO<sub>2</sub> removal decreased slightly with increasing gas flow rate. It can be seen that, at higher gas flow rates, the decreasing rate of CO<sub>2</sub> removal is higher than that of lower gas flow rates. It can be concluded that the decrement of resident time for higher gas flow rates has more significant effects on CO<sub>2</sub> removal.

It is obvious that the increase in H<sub>2</sub>S absorption flux with increasing gas flow rate was more significant than that of CO<sub>2</sub>. This implied that the gas phase resistance for mass transfer of H<sub>2</sub>S played a more important role than that of CO<sub>2</sub>.

Figure 5b also shows that the results of the experiments were in the range of 65–100 % regardless of CO<sub>2</sub> feed concentration. This indicates that in the presence of low H<sub>2</sub>S content (5000 ppm), varying the CO<sub>2</sub> feed concentrations has no significant effect on its absorption performance. Therefore, it can be concluded that MDEA could be a suitable chemical absorbent even for CO<sub>2</sub> in case of low concentrations of H<sub>2</sub>S.

## Conclusions

In this work, the performance of simultaneous absorption of CO<sub>2</sub> and H<sub>2</sub>S from CH<sub>4</sub> using hollow fiber membrane contactor was investigated. The experimental results showed that both CO<sub>2</sub> and H<sub>2</sub>S removal performance using MDEA solution were much higher than those reported for packed towers. The increase in evaluated parameters, including CO<sub>2</sub> and H<sub>2</sub>S feed concentration and gas flow rate, significantly decreased the CO<sub>2</sub> removal percent while increasing the H<sub>2</sub>S retentate concentration. A reverse effect was observed for liquid flow rate. Due to the large difference in CO<sub>2</sub> and H<sub>2</sub>S concentrations in this study, the H<sub>2</sub>S absorption should be strongly influenced by CO<sub>2</sub> absorption. However, the use of MDEA as a selective amine solution neutralized this effect and kept the H<sub>2</sub>S selectivity at high levels.

The results revealed that using feed gas mixtures containing 5000 ppm H<sub>2</sub>S with CO<sub>2</sub> concentrations ranging from 4 to 12 vol.%, the H<sub>2</sub>S remov-

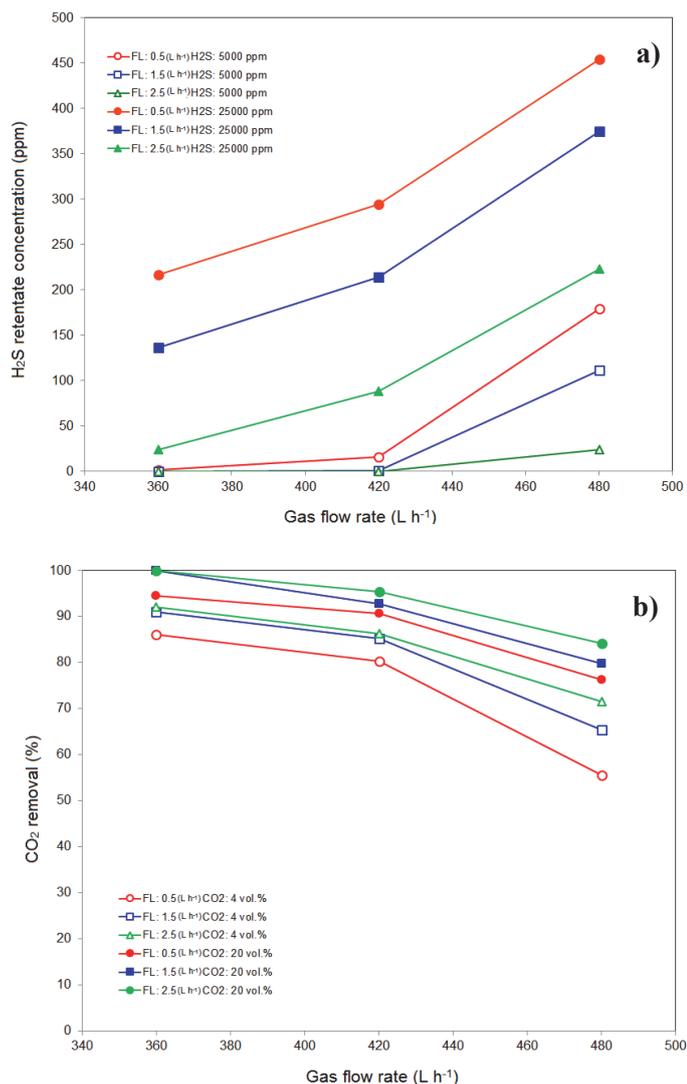


Fig. 5 – Effect of gas and liquid flow rates on the H<sub>2</sub>S retentate concentration (a) and CO<sub>2</sub> removal percent (b): MDEA 0.5 mol L<sup>-1</sup>, CO<sub>2</sub>: 4 vol.% (a) and H<sub>2</sub>S: 5000 ppm (b)

al efficiency of 100 % was attained with less than 4 vol.% of CO<sub>2</sub> remaining in the retentate stream. The influence of CO<sub>2</sub> feed concentration on the H<sub>2</sub>S removal is not significant and even diminishes with decreasing gas/liquid flow ratio.

#### ACKNOWLEDGMENTS

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