

## Effect of DEA in Membrane Gas Absorption System Using Polymeric Flat Sheet Membrane

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### ABSTRACT

The objective of this study was to investigate the potential process of the removal of carbon dioxide (CO<sub>2</sub>) from flue gases by using developed membrane gas absorption system. The experiments were performed in membrane gas absorption system consisted 0.45 µm pore size microporous polyvinylidene fluoride (PVDF) flat sheet membrane. Diethanolamine (DEA) solution was employed as the liquid absorbent. The operating parameters such as the gas and liquid flow rate were setup at 100 cm<sup>3</sup>/min and 25 cm<sup>3</sup>/min and liquid absorbent was at room temperature. The effect of DEA concentration was studied with variation in range 1 M to 5 M. In addition, the experiments were carried out with 20%, 40% and 100% gas ratio CO<sub>2</sub> to N<sub>2</sub>. The results show that hydrophobic polymeric membranes such as PVDF can be efficiently used for gas absorption with optimized concentration of DEA.

*Keywords:* Membrane gas absorption, CO<sub>2</sub> removal, DEA, polymeric membrane

### 1.0 INTRODUCTION

Membranes have become an established technology for carbon dioxide (CO<sub>2</sub>) removal since their first use in this application in 1981. Initial acceptance was slow and limited to smaller streams, mostly because of the economic risks involved in treating larger streams, but also because many process design parameters were largely unknown. A further factor was the general downturn in the oil and gas industry in the 1980s. The multiple benefits of membrane technology promised by early innovators have since been proven in a wide variety of installations in many locations around the world, and vendors of traditional CO<sub>2</sub> removal technologies have been quick to acquire or develop membrane-based processes to supplement their older processing routes. In some cases, the most economical

approach is to combine membranes with existing technologies or use membranes to debottleneck existing solvent-based plants. Currently, the only commercially viable membranes used for CO<sub>2</sub> removal are polymer based, for example, cellulose acetate, polyimides, polyamides, polysulfone, polycarbonates, and polyetherimide. Polyimide has some potential in certain CO<sub>2</sub> removal applications, but it has not received sufficient testing to be used in large applications.

Flue gas is a gas released to the atmosphere via a flue and quite often refers to the combustion exhaust gas produced at power plants. Its composition generally depends on what is being burned, but usually consist of mostly carbon dioxide (CO<sub>2</sub>) and water vapor as well as nitrogen (N<sub>2</sub>) and excess oxygen. It also contains a small percentage of pollutants such as particulate matter, carbon monoxide (CO), nitrogen oxides (NO<sub>x</sub>) and sulfur oxides (SO<sub>x</sub>). Lately, the removal of CO<sub>2</sub> from flue gases has received

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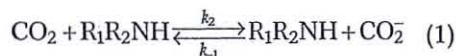
intense attention due to the properties of CO<sub>2</sub>. The CO<sub>2</sub> has long been identified as one of the main green house gasses present in the atmosphere (other green house gases are such as methane and ozone). The accumulation of CO<sub>2</sub> has been well associated with the recent increase in global temperature. A wide variety of acid gas removal technologies are available. They include cryogenic processes; adsorption processes, such as pressure swing adsorption (PSA), thermal swing adsorption (TSA) and iron sponge as well membranes. The conventional method to remove CO<sub>2</sub> is using gas absorption. In gas absorption processes, the gases mixtures are usually dispersed and in direct contact with liquid in absorption devices such as packed or plate columns. Absorption process in these contact devices has many shortcomings like emulsions, foaming, unloading and flooding [1]. An alternative technology that overcomes these disadvantages and also offers more interfacial area than the conventional approaches is a non-dispersive contactor via a microporous membrane or better known as membrane gas absorption (MGA). In MGA system, the fluids to be contacted flow on the opposite side of the membrane, and the gas-liquid interface forms at the mouth of each membrane pore. The available contact area remains undisturbed even at a high or low flow rate because the two fluid flows are independent. Because the absorbent liquid flows on one side and the gas flows on the other side of the membrane, this method is useful in applications where the required solvent/feed ratio is very high or very low [2]. In terms of liquid absorbents, several of them have been studied experimentally. These including pure water and aqueous solutions of NaOH, KOH, amine and amino acid salts [3]. Wang investigated the pure CO<sub>2</sub> absorbed in diethanolamine (DEA), 2-amino-2-methyl-1-propanol (AMP) and methyldiethanolamine (MDEA) aqueous solutions [4]. Dindore tested the process of CO<sub>2</sub> absorbed in propylene carbonate at high gas pressure (1-20 bars) [5]. For Kvaerner, MGA had been used for the removal of acid gases from natural gas and flue gases from conventional gas turbines [3]. However, to achieve high CO<sub>2</sub> absorption rates, higher reactive absorbents are widely used, such as

sodium hydroxide (NaOH) and monoethanolamine (MEA).

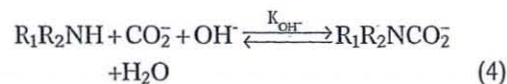
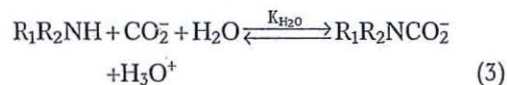
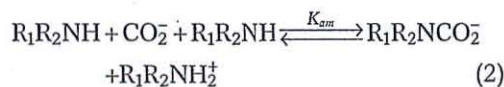
The objective of this paper is to emphasis on effect of DEA concentration in designed MGA system comprising hydrophobic microporous polyvinylidene fluoride (PVDF) flat sheet membrane. It is discussed how the MGA system potential to remove the CO<sub>2</sub> in CO<sub>2</sub>/N<sub>2</sub> mixture.

## 2.0 THEORY

The impact of DEA solutions on the membrane surface would be representative for the cases of primary and secondary amines. It is a widely used absorbent with two ethanol groups attached to a nitrogen atom. The reaction of DEA (R<sub>1</sub>R<sub>2</sub>NH) with dissolved CO<sub>2</sub> is generally described by the zwitterion mechanism in a two-step sequence, i.e. the first step is the formation of intermediate zwitterions [6]:



Then the zwitterion is deprotonated by the bases present in the solution, forming a carbamate ion and a protonated base:



Thus, the components contained in a DEA aqueous solution after reacting with CO<sub>2</sub> include CO<sub>2</sub>, R<sub>1</sub>R<sub>2</sub>NH, R<sub>1</sub>R<sub>2</sub>NCO<sub>2</sub><sup>-</sup> and R<sub>1</sub>R<sub>2</sub>NH<sub>2</sub><sup>+</sup>.

## 3.0 METHODS

The hydrophobic microporous polyvinylidene fluoride (PVDF) flat sheet membrane used in this experiment were purchased from Millipore Asia LTD. The membrane pore size is 0.45 μm and



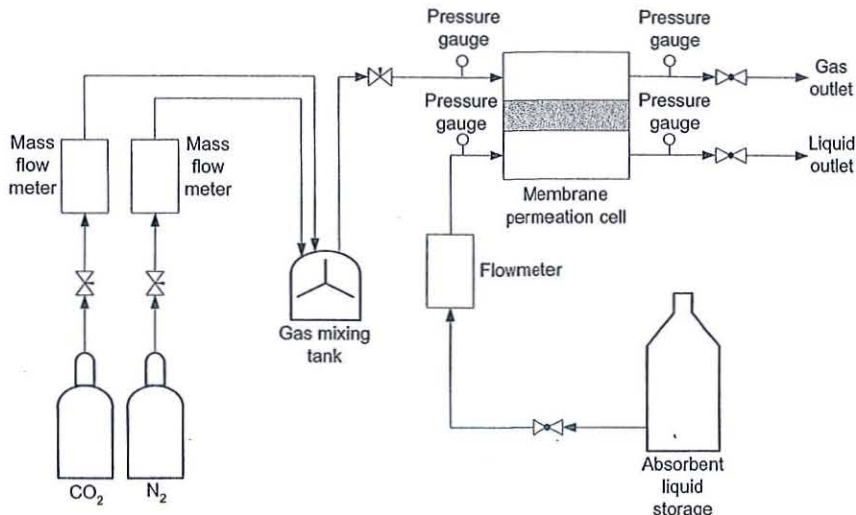


Figure 1 Schematic diagrams of membrane gas absorption system

the membrane porosity is 0.75. A 99% grade Diethanolamine (DEA) purchased from Sigma Aldrich (M) Sdn. Bhd. was mixed with deionized water, respectively to prepare aqueous liquid absorbents with desired concentrations. The experimental setup is schematically shown in Figure 1.

Pure  $\text{CO}_2$  and pure  $\text{N}_2$  were mixed with a volume ratio of 20:80, 40:60 or 100:0, which is in composition range of flue gas, was used as the feed gas while DEA aqueous solution were employed as liquid absorbents. In the experiment, the flow rate of the feed of the feed gas supplied from compressed gas cylinder was adjusted and controlled by Aalborg mass flow controllers, and then it was fed through up side of the membrane module. The inlet and outlet gas volume flow rate were measured by a bubble soap meter. The pressure gauges were used to indicate the inlet and outlet pressure of the gas and liquid. When  $\text{CO}_2/\text{N}_2$  mixture was used as the feed gas, Gas Chromatography (Perkin Elmer, TCD) was used to analyze the inlet and outlet gases compositions. All the data were collected after experiment had been operated for 30 min to ensure the system to reach the steady state. The results of each run were averaged from five times of sampling. The system and operating parameters which influence the process performance such as  $\text{CO}_2$  concen-

tration in the feed, and DEA concentration were varied based on the experimental design. Either pure or mixed gas flow rate were fixed at  $100 \text{ cm}^3/\text{min}$  while liquid absorbent flow rate was fixed at  $25 \text{ cm}^3/\text{min}$ . 1, 2, 3, 4 and 5 M of DEA were studied. All of the experiments were performed at the room temperature; therefore, the gas phase temperature in this work was approximately at  $30^\circ\text{C}$ .

#### 4.0 RESULTS AND DISCUSSIONS

The  $\text{CO}_2$  removal efficiency ( $\eta$ ) and mass transfer rate ( $J_{\text{CO}_2}$ ) were used to describe the running conditions.  $\eta$  and  $J_{\text{CO}_2}$  are determined by the following equations [7, 8, 9, 10]:

$$\eta = \frac{Q_{\text{in}} \times Q_{\text{in}} - Q_{\text{out}} \times C_{\text{out}}}{Q_{\text{out}} \times C_{\text{in}}} \quad (5)$$

$$J_{\text{CO}_2} = \frac{(Q_{\text{in}} \times Q_{\text{in}} - Q_{\text{out}} \times C_{\text{out}}) \times 273.15 \times 1000}{22.4 \times T_g \times S} \quad (6)$$

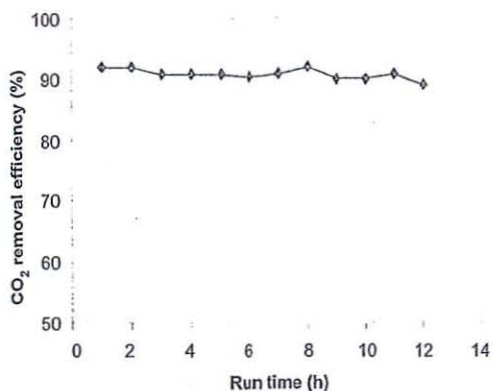
where  $\eta$  is the  $\text{CO}_2$  removal efficiency, %;  $J_{\text{CO}_2}$  is the mass transfer rate of  $\text{CO}_2$ ,  $\text{mol}/(\text{m}^2 \text{ s})$ ;  $Q_{\text{in}}$  and  $Q_{\text{out}}$  are the gas flow rates at the inlet and the outlet of the membrane, respectively,  $\text{cm}^3/\text{s}$ ;  $C_{\text{in}}$  and  $C_{\text{out}}$  are  $\text{CO}_2$  concentrations in the gas

phase at the inlet and the outlet of the membrane, respectively,  $\text{cm}^3$ ;  $T_g$  is the real temperature of the flue gas, K;  $S$  is the gas-liquid interfacial area,  $\text{m}^2$ .

#### 4.1 Effect of Wetting Criteria of DEA on PVDF Membrane

Diethanolamine (DEA) was chosen in this study, as it is a commercial absorbent with reasonable  $\text{CO}_2$  absorption capacity and moderate corrosiveness. Figure 2 shows the experimental results of  $\text{CO}_2$  absorption by 2 M aqueous solution of DEA in the membrane gas absorption system for about 12 h.

For the DEA absorbent, the membrane gas absorption system was successfully operated for about 12 h, maintaining a  $\text{CO}_2$  removal efficiency of about 90%. It was clearly indicated that 2 M aqueous of DEA solution can not wet the PVDF membrane in the long-term operation of about 12 h. It was well known that increasing the concentration of the active species in the solvent will enhance the mass transfer as well. With respect to economics, solvent circulation rate is one of the most important factors in determining the economics of a gas treating process using chemical solvent. So, the relatively higher concentration of DEA could be selected to absorb

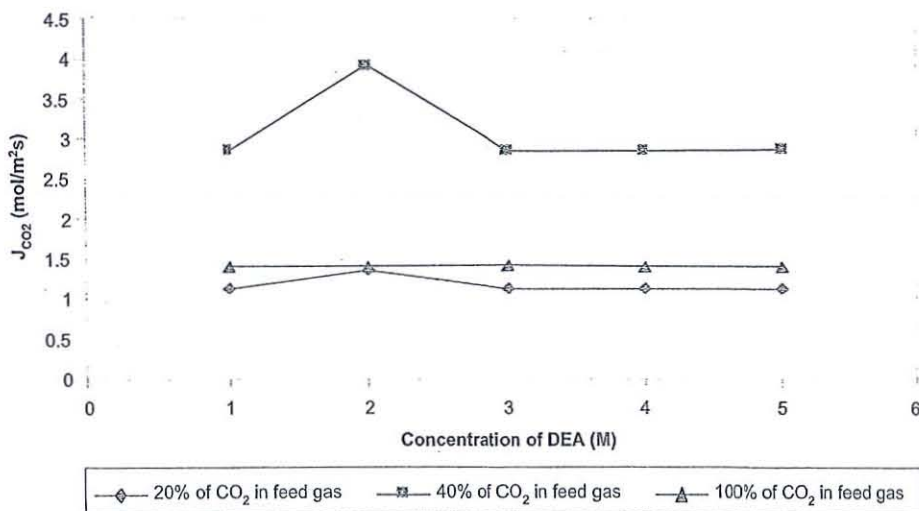


**Figure 2** Long-term performance of the PVDF membrane gas absorption system over 12 h at ambient temperature ( $\text{CO}_2/\text{N}_2$ -DEA system, P gas: 1 bar)

$\text{CO}_2$  from flue gas in order to enhance the mass transfer [3] and reduce the solvent circulation rate.

#### 4.2 Effect of DEA Concentration on Mass Transfer Rate of $\text{CO}_2$

The dependence of mass transfer rate of  $\text{CO}_2$  on initial absorbent concentration was illustrated in Figure 3. It was clearly shown that the mass



**Figure 3** Effect of the liquid absorbent concentration on the mass transfer rate of  $\text{CO}_2$  (gas flow rate: 100 ml/s, liquid flow rate: 25 ml/s, liquid absorbent temperature: 303.15 K)



transfer rate generally increased at 2 M of the absorbent concentration and going to unchange at the end. These trends are similar with research were done by Kumar *et al.* [8] using potassium taurate (PT), S. Yan *et al.* [9] using potassium glycinate (PG), Kim and Yang [11] using 2-amino-2-methyl-1-propanol (AMP) and Wang *et al.* [4] using methyldiethanolamine (MDEA), monoethanolamine (MEA) and AMP with different concentration, respectively. These was because that the active component absorbing CO<sub>2</sub> in the liquid boundary layer increased with the absorbent concentration, which results in higher CO<sub>2</sub> solubility and lower liquid flow rate. However, in this case, liquid flow rate was fixed at 25 cm<sup>3</sup>/min.

As far as the higher CO<sub>2</sub> removal efficiency and the lower liquid flow rate were concerned, it is worthwhile to increase the initial absorbent concentration. However, the absorbent concentration can not be elevated without limitation when using DEA as the absorbent. Other than that, Figure 3 also shows that the mass transfer rate shown the highest reading around 3.9 mol/m<sup>2</sup> s when the DEA concentration at 2 M for 40% of CO<sub>2</sub> in feed gas. Meanwhile, mass transfer for 20% of CO<sub>2</sub> in feed gas also increased with 2 M DEA. It was because CO<sub>2</sub> absorption was enhanced by the chemical reaction. However, a compromise has to be taken among higher mass transfer rate of CO<sub>2</sub>, the potential of membrane wetting problem and crystallization prevention when using DEA as the liquid absorbent.

## 5.0 CONCLUSION

Experiments for PVDF flat sheet membrane were performed extensively to determine the performance of aqueous DEA solution in the removal of CO<sub>2</sub> from flue gas when some key operating factors were fixed. It was clearly seen from the results that the performance of CO<sub>2</sub> absorption using 2 M of was always superior to 40% of CO<sub>2</sub> in feed gas compared to 20% and 100% of CO<sub>2</sub> in feed gas under the same operating conditions. Far from that, long-term performance tests using 2 M of DEA solution as the liquid absorbent shown that the DEA aqueous solution

was suitable to be applied to the PVDF microporous membrane gas absorption because the DEA aqueous solution can provide a higher separation performance and the CO<sub>2</sub> flux was kept almost unchanged over 12 hours of operation especially for flat sheet membrane module.

## ACKNOWLEDGEMENTS

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