

CO₂ Absorption in Membrane Contactor using Piperazine, Monoethanolamine and Diethanolamine: A Mass Transfer and Performance Study

H. N. Mohammed^{a,b}, A. L. Ahmad^{a*}, B. S. Ooi^a, C. P. Leo^a

^aSchool of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Pulau Pinang, Malaysia

^bChemical Engineering Department, Tikrit University, Saladdin, Iraq

*Corresponding author: chlatif@eng.usm.my

Article history

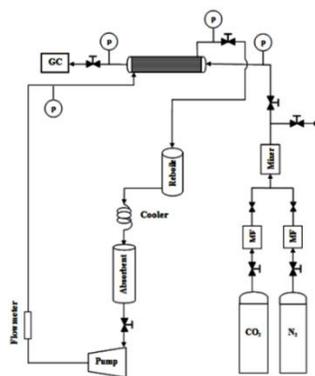
Received :15 September 2013

Received in revised form:

17 November 2013

Accepted: 15 January 2014

Graphical abstract



Abstract

Carbon dioxide has been demonstrated to be the largest component of greenhouse gases, which increases the temperature of the earth's surface. Therefore, much effort has been endeavor to recover CO₂. Recently, polymeric micro-porous membrane contactors have been proposed as an alternative technology for the conventional gas absorption equipments such as bubble column, packed tower and sieve trays column. In this work, three concentrations of aqueous piperazine (PZ) solutions namely 0.2 M, 0.6 M and 1 M in contact with polyvinylidene fluoride (PVDF) capillary membrane. Moreover, the absorption performances were compared with the aqueous solution of 1M monoethanolamine (MEA) and 1 M diethanolamine (DEA). The results revealed that the efficiency of amine solutions in CO₂ absorption were according to the order of 1 M PZ > 1 M MEA > 0.6 M PZ > 1 M DEA > 0.2 M PZ. It was found that the efficiency of the system was controlled by the liquid phase resistance which could be improved with the increased of the liquid flow rate.

Keywords: CO₂ absorption; mass transfer; PVDF capillary membrane; membrane contactor

© 2014 Penerbit UTM Press. All rights reserved.

1.0 INTRODUCTION

Carbon dioxide (CO₂) has been demonstrated to be the largest component of greenhouse gases present in atmosphere than others such as methane, water vapour, nitrous oxide and ozone. It was proven that CO₂ is responsible to the increasing temperature of the earth's surface. CO₂ acting like a thick blanket which trap the heat within the atmosphere [1]. Many techniques had been proposed to reduce the CO₂ emission to the atmosphere such as gas absorption, adsorption, membranes and cryogenic.

The choosing of the suitable technique depends on the conditions of CO₂ streams. In general, conditions of flue gasses streams are at low pressure, high gas flow rate and low CO₂ concentrations (4–14%, v/v) [2]. Gas absorption technique is a desirable method to capture CO₂ from flue gas streams. However, the conventional equipments used in gas absorption systems such as bubble-column, venture-scrubber, packed-tower and sieve-tray columns have disadvantages such as flooding,

loading, foaming and channeling. An alternative is the membrane gas absorption system, which was developed to overcome these disadvantages. The advantages and disadvantages of membrane contactor have been discussed in more detail by (Gabelman and Hwang) [3].

Basically, the microporous polymeric membranes used as gas-liquid contactor are not selective medium; the CO₂ selectivity is dominated by the absorbent liquid. The conventional absorbents used in CO₂ absorption are aqueous alkanolamine solutions such as monoethanolamine (MEA), monodiethanolamine (MDEA) and diethanolamine (DEA) [4]. In selecting absorbent, the chemical compatibility of absorbents with membrane material should be taken in considerations to avoid membrane wetting. Membrane pores wetting could increase the membrane resistance thus decrease the CO₂ absorption flux. Absorbents of low surface tension property are easily penetrate membrane pores especially with increasing absorbent concentration [5-7]. Recently, concentrated aqueous solutions of piperazine (PZ) was proposed as a novel absorbent

for CO₂ capture by absorption due to high reaction rate and relatively high surface tension [8-10].

In this paper, the effect of PZ, MEA and DEA aqueous solutions on the performance of the CO₂ absorption and their compatibility with PVDF capillary membrane was evaluated. The mass transfer resistances of system were determined through the membrane module.

2.0 THEORY

The film model has been applied to describe the mass transfer in membrane contactor using the resistance-in-series model [11]. Resistances of CO₂ transport from gas bulk to liquid bulk have been divided into gas film, membrane and liquid film resistance. Therefore, the overall mass transfer resistance can be expressed as follows [12]:

$$\frac{1}{K_{og}} = \frac{1}{Hk_l} + \frac{d_o}{k_m d_{ln}} + \frac{d_o}{k_g d_i} \quad (1)$$

where K_{og} (m/s) is the overall mass transfer coefficient based on gas phase; k_l , k_m , k_g are the liquid, membrane and gas mass transfer coefficient, respectively, (m/s). The dimensions d_i , d_o and d_{ln} represent inner, outer and logarithmic mean diameters of membrane, respectively, and H is Henry's constant (dimensionless). K_{og} have been determined as [13,14]:

$$K_{og} = \frac{Q_g \ln(C_{g,i}/C_{g,o})}{A} \quad (2)$$

where Q_g is gas volumetric flow rate (m³/s); $C_{g,i}$, $C_{g,o}$ are the inlet and outlet CO₂ concentration in gas phase, respectively, (mol/m³) and A is the total contact area (m²).

3.0 EXPERIMENTAL

3.1 Materials

Commercial-grade PVDF capillary membranes supplied by Pall Co. (UMP-153) were used in all experiments. PZ ($\geq 99\%$), MEA (≥ 98), and DEA (≥ 99) were purchased from Sigma-Aldrich. Distilled water was used to prepare different amine solutions.

3.2 Characterizations

Scanning Electron Microscope (SEM) (ZEISS SUPRA 35VP) was used to investigate the surface morphology of PVDF membrane before and after immersion in absorbent solution.

3.3 Experimental Set-up for Absorption Process

Capillary membranes were cleaned using distilled water and then dried at 60°C for 24 hr. Three capillaries were packed in glass housing and sealed with epoxy resins at the module ends. Two Teflon flanges were put on both sides of the membrane module to avoid leakage during the experiments. The specifications of the modules are listed in Table 1.

Table 1 Capillary membrane module specifications

Specification	Value
Module i.d (cm)	2.6
Capillary o.d. (mm)	3.6
Capillary i.d. (mm)	2.4
Effective capillary length (cm)	18
Number of capillaries	3

A gas mixture of 20% (v/v) CO₂ balanced with N₂ gas was introduced into the lumen side of the membrane module at 143 kPa. The gases flow rates were adjusted via mass flow controller (AALBORG 0-500 ml/min). The liquid absorbent was pumped to the shell side of module via digital peristaltic pump (Cole-Parmer, MasterFlex L/S) at 160 kPa to avoid the formation of bubbles in the liquid phase. The absorbent flow rate was controlled by a rotameter with a counter-current flow to the gas. Online gas chromatography (GC) (Agilent Technologies 7890A) was used to analyze the outlet gas stream. A schematic diagram of the experimental setup is shown in Figure 1.

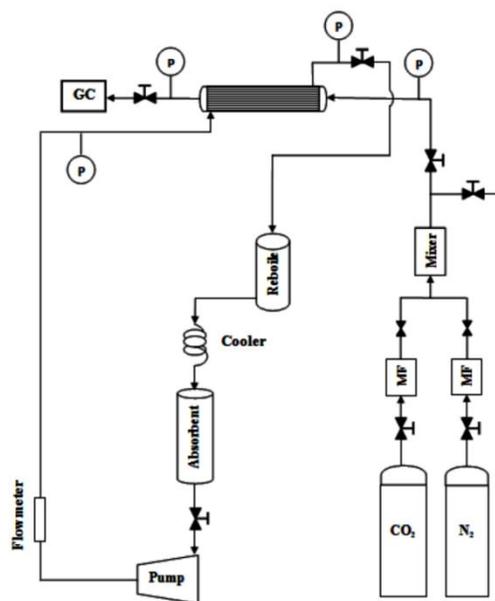


Figure 1 Schematic drawing of experimental setup

3.4 Absorption Rate of CO₂

The performance of capillary membrane module for gas absorption in terms of the CO₂ absorption flux (J_{CO_2}) (mol/m².s) was calculated as [15]:

$$J_{CO_2} = \frac{(Q_{g,in} \times C_{g,in} - Q_{g,out} \times C_{g,out}) \times 273.16}{0.0224 \times T \times A} \quad (3)$$

where $Q_{g,in}$ and $Q_{g,out}$ are the inlet and outlet gas flow rates, respectively, (m³/s); $C_{g,in}$ and $C_{g,out}$ represent the volumetric ratios of CO₂ in the gas phase at the inlet and outlet, respectively, (%); T is the temperature of the gas (K).

4.0 RESULTS AND DISCUSSION

The effect of liquid velocity on the J_{CO_2} was assessed for three amine solutions in PVDF membranes module. The Q_g was fixed at 250 ml/min thus the gas velocity (u_g) in module was 0.30826 m/s. In contrast, the liquid volumetric flow rate (Q_l) was varied 200-400 ml/min thus the liquid velocity (u_l) was 0.0065-0.013 m/s in shell side. Figure 2 illustrates the effect of the liquid velocity on the J_{CO_2} . As shown in Figure 2, the J_{CO_2} in PVDF membrane module increased according to the following order PZ > MEA > DEA. This sequence could attributable to the high reaction rate of PZ than others. The similar experimental work had carried out by the Tan and Chen who indicated that the PZ was the superior absorbent for CO₂ absorption compared to

AMP and DMEA [16]. Dugas and Rochelle pointed out that the CO₂ absorption rate of PZ was 2-3 times faster than the MEA at same concentration [17-18].

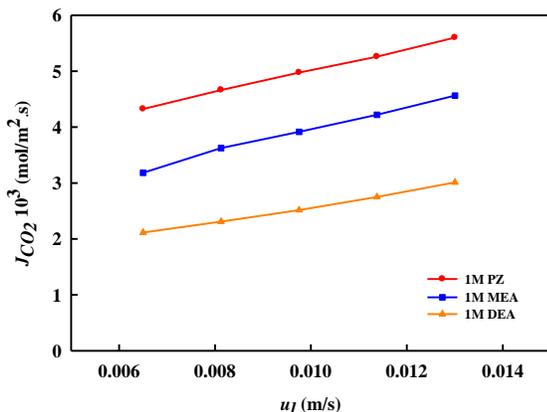


Figure 2 Effect of liquid velocity on the CO₂ absorption flux

Lin *et al.* investigated the effect of the gas flow rate on the performance of PP hollow fiber membrane module using 0.1M PZ + 1M MDEA as absorbent [19]. They pointed out that the rate controlling step was gas-film diffusion in the condition of gas volumetric flow rate less than 400 cm³/min. However, the rate controlling step was changed to be liquid-film diffusion for gas volumetric flow rate higher than 400 cm³/min at constant liquid flow rate. Based on this case of study, we can infer that the mass transfer resistance in liquid phase significantly affects in the J_{CO_2} in PVDF module for all amine solutions used in this case study.

The Q_l of 250 ml/min (0.00812 m/s) was fixed in order to investigate the effect gas velocity on the CO₂ absorption flux. Q_g was varied within 200-400 ml/min wherein u_g was 0.247-0.554 in the lumen side. Figure 3 demonstrates that the impact of gas velocity on the J_{CO_2} were less significant. However, at high u_g the absorption flux has a declining tendency. High gas velocity resulted in the reduction of CO₂ residence time into the module thus reduce the contact time with the solvent. Therefore, solvent with high reaction rate is preferable to capture the CO₂ at high gas velocity.

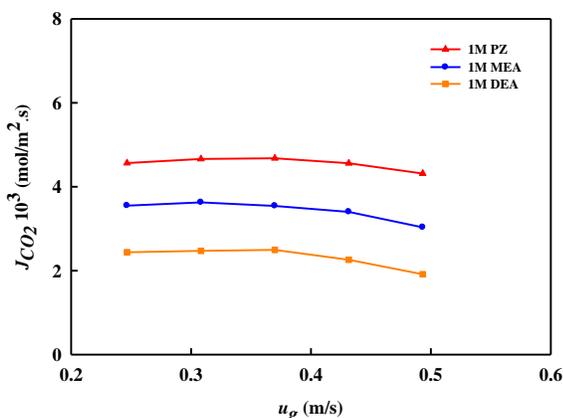


Figure 3 Effect of liquid velocity on the CO₂ absorption flux

As mention earlier, the mass transfer of CO₂ through the membrane module was dominated by the liquid phase velocity;

thereby the mass transfer resistance in the gas phase was neglected. As such, the resistance in series model can be writing as follows:

$$\frac{1}{K_{og}} = \frac{1}{Hk_l} + \frac{d_o}{k_m d_{in}} \quad (4)$$

Thus, the mass transfer coefficient in the liquid phase is proportional to the liquid velocity as follows:

$$\frac{1}{k_l} = C_1 u_l^{-\alpha} \quad (5)$$

The Wilson plot method was considered to determine the membrane resistances. Plotting $\frac{1}{K_{og}}$ vs. $\frac{1}{H u_l^\alpha}$ with the substituting the α value of 0.93 which provided the straight lines. Same α value was used by many researchers to achieve best straight line pass through the experimental overall mass transfer resistance in the Wilson plot [12,20,21]. Figure 4 demonstrates the Wilson plot for three amine solutions in membrane module. The high R^2 value obtained indicates the correctness of Wilson method.

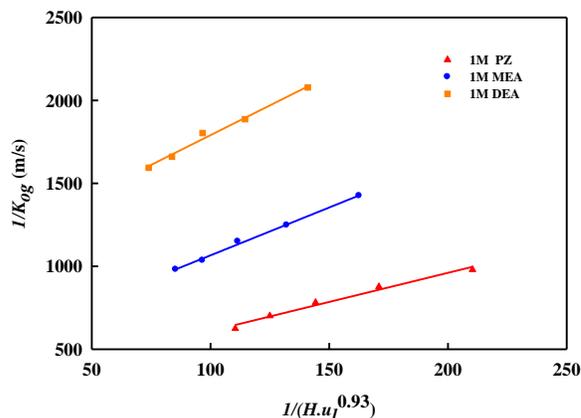


Figure 4 Wilson plot for CO₂ absorption using PZ, MEA and DEA

As shown in Figure 4, the PZ had lower overall mass transfer resistance because the decreasing of the mass transfer resistance in the liquid phase with high CO₂ reaction rate. In addition, mass transfer coefficient in the liquid phase increase with increase the liquid velocity thus decreases the liquid phase mass transfer resistance. The slope of Eq. 4 represents the C_1 value, while the intercept is the membrane mass transfer resistance. Table 2 presents the Wilson equation and membrane mass transfer coefficient.

Table 2 Wilson equation and membrane mass transfer coefficient for different amines solutions

Amine	Wilson Equation	R^2	$k_m \times 10^3$ (m/s)
PZ	$3.511 \frac{u_l^{-0.93}}{H} + 258.2$	0.982	4.71
MEA	$5.611 \frac{u_l^{-0.93}}{H} + 513.2$	0.996	2.37
DEA	$7.17 \frac{u_l^{-0.93}}{H} + 1073$	0.988	1.13

As demonstrated in Table 2, the k_m increase when reactive absorbent was used. Esquiroz-Molina *et al.* recorded that the k_m increased when pH of sodium hydroxide increased to absorb

hydrogen sulphide in hollow fiber membrane contactor [22]. The high CO₂ absorption efficiency of PZ compare to the other amines lead to the study of PZ concentrations effect. Two concentrations of PZ namely 0.2 and 0.6 M were used and compared to 1M of MEA and DEA. Figure 5 illustrates the CO₂ removal efficiency at Q_g and Q_l of 250 and 400 ml/min, respectively.

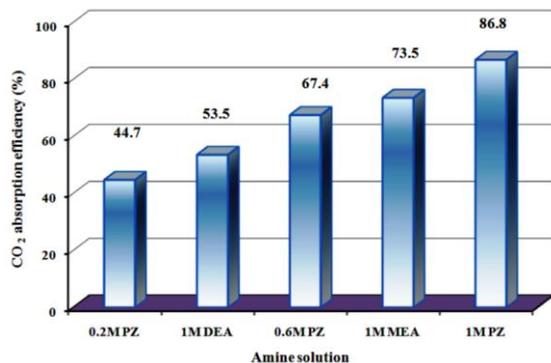


Figure 5 CO₂ absorption efficiency for different amine solutions

As shown in Figure 5, 0.6 M PZ was provided absorption efficiency 13.9% higher than 1M DEA. On the other hand, 1 M MEA provided 6.1% efficiency higher than 0.6M PZ and 13.3% efficiency lower than 1 M PZ. The solvent of 0.2 M PZ was exhibited absorption efficiency lower than high concentration of 1 M DEA by 8.8%. This difference is small compare with amine concentration range. This is could attributable to the high surface tension value of the 0.2 M PZ solution with respect to the DEA solution which reduces the membrane wetting as well as the high reaction rate of PZ. Wherein, the surface tension of 0.2 M PZ is 71.48 mN/m and 57.95 mN/m for 1 M DEA at 30°C.^{23,24}

Samples of PVDF membrane were immersed in the solution of 1M PZ for 30 days to assess the surface stability of membrane towards PZ under long operating how. Figure 6(a) & (b) show the SEM images of membrane surfaces before and after immersing in PZ solution for 30 days, respectively. The images unveiled that the PVDF membrane can maintain surface morphology with long period time of operating due to inherent high chemical resistance property.

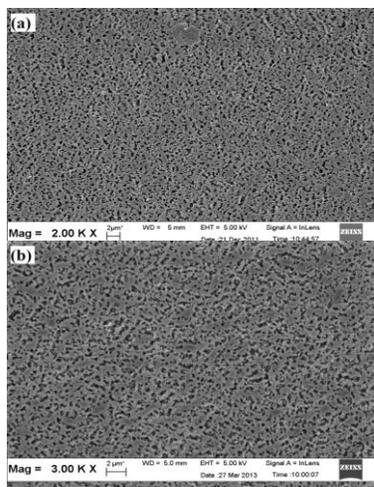


Figure 6 SEM image for PVDF membrane surface (a) before immersion; (b) after immersing in 1M PZ for 30 days

5.0 CONCLUSION

CO₂ capture from CO₂-N₂ stream was carried out using capillary PVDF membrane contactor. The absorption performance was assessed for PZ, MEA and DEA solutions. PZ solution exhibited higher absorption rate compared to other amine solutions at same concentration and operating conditions. The results revealed that the CO₂ absorption efficiency following the order of 1 M PZ > 1 M MEA > 0.6 M PZ > 1 M DEA > 0.2 M PZ. The overall mass transfer resistance was controlled by the liquid phase resistance when the gas velocity is high value. Stability test shows that PVDF membrane could maintain its surface morphology after exposed to the solution of 1 M PZ for 30 days.

Acknowledgement

The authors wish to thank the financial support granted by MOSTI Science Fund (No. 305/PJKIMIA/6013386), FRGS fund (No. 203/PJKIMIA/6071234), RU-PRGS fund (No. 1001/PJKIMIA/8045029) and Universiti Sains Malaysia Membrane Science and Technology Cluster.

References

- [1] A. Arenillas, K.M. Smith, T.C. Drage, C.E. Snape. 2005. *Fuel*. 84: 2204–2210.
- [2] A. A. Olajire. 2010. *Energy*. 35: 2610–2628.
- [3] A. Gabelman, S. T. Hwang. 1999. *J. Membr. Sci.* 159: 61–106.
- [4] A. B. Rao, E. S. Rubin. 2002. *Environ. Sci. Technol.* 36: 4467–4475.
- [5] J. G. Lu, Y. F. Zheng, M. D. Cheng, L. J Wang. 2007. *J. Membr. Sci.* 289: 138–149.
- [6] G. Va'zquez, E. Alvarez, J. M. Navaza, R. Rendo, E. Romero. 1997. *J. Chem. Eng. Data*. 42: 57–59.
- [7] G. Va'zquez, E. Alvarez, R. Rendo, E. Romero, J. M. Navaza. 1996. *J. Chem. Eng. Data*. 41: 806–808.
- [8] G. Rochelle, E. Chen, S. Freeman, D. V. Wagener, Q.A. Voice. 2011. *Chem. Eng. J.* 171: 725–733.
- [9] X. Chen, G. T. Rochelle. 2011. *Chem. Eng. Res. Design*. 89: 1693–1710.
- [10] G. Murshid, A. M. Shariff, L. K., Keong, M. A. Bustam. 2011. *J. Chem. Eng. Data*. 56: 2660–2663.
- [11] H. A. Rangeala. 1996. *J. Membr. Sci.* 112: 229–240.
- [12] S. Khaisri, D. deMontigny, P. Tontiwachwuthikul, R. Jiraratananon. 2009. *Sep. Purif. Technol.* 65: 290–297.
- [13] H. Kreulen, C. A. Smolders, G. F. Versteeg and W. P. M. van Swaaij. 1993. *J. Membr. Sci.* 78: 217–238.
- [14] A. Esquiroz-Molina, S. Georgaki, R. Stuetz, B. Jefferson, E. J. McAdam. 2013. *J. Membr. Sci.* 427: 276–282.
- [15] Y. Shui-ping, F. Meng-Xiang, Z. Wei-Feng, W. Shu-Yuan, X. Zhi-Kang, L. Zhong-Yang, C. Ke-Fa. 2007. *Fuel Proc. Technol.* 88: 501–511.
- [16] C. S Tan, J. E. Chen. 2006. *Sep. Purif. Technol.* 49: 174–180.
- [17] R. Dugas, G. Rochelle. 2009. *Energy Procedia*. 1: 163–1169.
- [18] R. Dugas, G. Rochelle. 2009. *J. Chem. Eng. Data*. 56: 2187–2195.
- [19] S. H. Lin, K. L. Tung, W. J. Chen, H. W. Chang. 2009. *J. Membr. Sci.* 333: 30–37.
- [20] S. Atcharyawut, C. Feng, R. Wang, R. Jiraratananon, D. T. Liang. 2006. *J. Membr. Sci.* 285: 272–281.
- [21] S. Atcharyawut, R. Jiraratananon, R. Wang. 2008. *Sep. Purif. Technol.* 63: 15–22.
- [22] A. Esquiroz-Molina, S. Georgaki, R. Tuetz, B. Jefferson, E. J. McAdama. 2013. *J. Membr. Sci.* 427: 276–282.
- [23] A. Muhammad, M. I. A. Mutalib, T. Muregesan, A. Shafeeq. 2009. *J. Chem. Eng. Data*. 54: 2317–2321.
- [24] G. Vazquez, E. Alvarez, R. Rendo, E. Romero, J.M. Navaza. 1996. *J. Chem. Eng. Data*. 41: 806–808.