Measurement of Mass Transfer Coefficient of CO₂–Amine System from Absorption Process

Thanakornkan Limlertchareonwanit¹, Kreangkrai Maneeintr³⁺, Tawatchai Charinpanitkul¹

¹Center of Excellence in Particle Technology, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand.
²Carbon Capture, Storage and Utilization Research Group, Department of Mining and Petroleum Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand.

*Krengkrai.M@chula.ac.th

Abstract. Carbon dioxide (CO₂) is one of the main factors for climate change issues. Absorption is the technology to remove CO₂ from various industries. The equipment used is the packed column to promote high mass transfer rate and to study the overall mass transfer coefficient (K_Gav). The K_Gav is an important parameter for designing and scaling up of packed column. Therefore, the objective of this work is to measure K_Gav for CO₂ absorption into the aqueous solution of monoethanolamine (MEA) in a random-packed column and to investigate effect of parameters on K_Gav. The parameters are the solvent flow rate from 5.3-15.9 m³/m²h, CO₂ initial loading from 0.0-0.2 mole/mole and CO₂ content in gas phase from 5-15 %v/v. The results show that K_Gav increases as the solvent flow rate and solvent concentration increase. The CO₂ content in gas phase provides relatively high impact on K_Gav with an increase in the CO₂ content.

1. Introduction

Currently, the major problem of global warming is an increase in the amount of greenhouse gases (GHGs) in the atmosphere. Carbon dioxide (CO₂) is the main component of GHGs up to 81% [1]. CO₂ is usually produced from three main processes; pre-combustion, post-combustion and oxy-fuel combustion. Coal-fired power plant is the major industry to release the CO₂ to the atmosphere. Thus, there are many researchers interested in carbon dioxide capture and storage (CCS) from post-combustion process in coal-fired power plant. Absorption technology is commonly used absorption solution, like monoethanolamin (MEA). MEA is a primarily chemical solution because of high reactivity, rapid reaction rate, low cost [2], low molecular weight and uncomplicated structure whereas the disadvantages are high energy consumption and corrosion [3]. The packed column is a basic equipment to study the mass transfer coefficient which is important for designing and scaling up of packed absorption column in the future. The features of this column can be operated in the ambient temperature and pressure.

Two Film Theory is suggested by Whitman [4] about the chemical reaction between gases into liquid phase. The liquid is soaked onto the packing with a thin film and the gas is dissolved and reacted with the liquid on the packing. The gas-phase mass transfer coefficient can be calculated in
terms of $K_G$. However, the overall volumetric mass transfer coefficient is more useful based on the unit volume of the packed column. The overall volumetric mass transfer coefficient can be determined using equation (1);

$$K_{Gav} = \left( \frac{G_i}{P(y_{CO_2,g} - y_{CO_2,i})} \right) \left( \frac{dY}{dZ} \right)$$

where

- $K_{Gav}$ is the overall volumetric mass transfer coefficient (kmol/m$^2$·h·kPa)
- $a_v$ is specific area of contactor (m$^2$/m$^3$)
- $G_i$ is inert gas flow rate (kmol/m$^2$·h)
- $P$ is total pressure (kPa)
- $y_{CO_2,g}$ is mole fraction of CO$_2$ in the bulk gas phase
- $y_{CO_2,i}$ is mole fraction of CO$_2$ in bulk liquid that equilibrium with CO$_2$ concentration in bulk gas

Maneeintr et al. [5] investigated the mass transfer coefficient of MEA solution in a laboratory-scale absorption column packed with DX structured packing. It is reported in terms of mass transfer to the overall mass transfer coefficient. It is found that inert gas flow rate has an insignificant effect on mass transfer.

Halim et al. [6] studied the mass transfer coefficient of MEA at high-pressure condition (5.0 MPa). The experiment is conducted in the absorption packed column with Sulzer metal gauze packing. The results show that the temperature at 40°C is the optimum condition to remove the CO$_2$. $K_{Gav}$ has increased with an increased solvent flow rate and solvent concentration. At the 5.0 MPa, it can be explained that the performance to remove CO$_2$ is similar at the atmosphere.

Naami et al. [7] studied of the mass transfer coefficient in a lab-scale packed absorption column with high-efficiency DX structured packing. The experiment has conducted at pressure atmosphere and 14.9 v/v% gas mixture. This study compares the mass transfer between MEA and MDEA. The result show that $K_{Gav}$ increase as the liquid flow rate increased. $K_{Gav}$ of MEA is higher than MDEA because MEA is a primary amine and high reactivity than tertiary amine.

Therefore, the objective of this study is to measure overall volumetric mass transfer ($K_{Gav}$) for CO$_2$ absorption into the aqueous solution of monoethanolamine (MEA) in a random-packed column and to investigate effect of parameters on $K_{Gav}$ and design a random packed column in the future.

2. Experimental

2.1. Chemical

Monoethanolamine (MEA) with purity of 99.0% is purchased from Sadara Chemical Company. Hydrochloric acid (HCl) with purity of 99% is purchased from RCI Labscan Limited. De-ionized water from Purelab Classic is used to prepare a MEA solution. N$_2$ and CO$_2$ with the same purity 99.5% are purchased from Praxair, Thailand.

2.2. Experimental apparatus

The absorber column is in 1.8-m high and 25-mm diameter with randomly packed column. The packed column is made of borosilicate glass. Raschig rings (with stainless steel, AISI304) are used as packing for this study. The advantages of stainless steel raschig rings are inexpensive, low pressure drop, free volume more than ceramic, resistance to temperature and physical force and resistance to amine and alcohol compared with ceramic raschig rings [8]. Amine solution is prepared to the desired concentration by mixing deionized water. 1M HCl is used to verify the amount of CO$_2$ in amine solution after the absorption process in a column by titration with methyl orange as an indicator. The CO$_2$ loading of each solution is determined by the Association of Official Analytical Chemists [9] and can be calculated from mole CO$_2$ / mole amine [10].
2.3. Operating procedure
The flue gases (N₂ and CO₂) is entered to the mass flow controller (Aalborg) and fed to the bottom of the column, while the amine solution is pumped by a peristaltic pump ( Longer) and the flow rate is controlled with rotameter (Cole-Palmer) to the top of the column. The gas outlet leaves at the top and the liquid outlet leaves at the bottom of the column. The CO₂ content in gas phase is checked with the IR analyzer within a reliable measurement range of 0-20 v/v%. The operating condition is shown in Table 1.
For this column, there are 11 sampling points along the height of the column. At each point, there are pressure gauges, temperature probes and CO₂ sampling point to measure the concentration of CO₂ in gas phase. The column is filled with raschig rings for increasing contact area between the gas-liquid phases. Flue gas and amine solution contact each other within the column. When the steady state is reached, flue gas is sent to analyzer to measure the amount of CO₂ in the system at each point. After amine solution has already reacted with CO₂, it leaves to the bottom of the column. Flue gas leaves at the top of the column.

Table 1. Operating condition of the experiments.

| Variable                              | Range       |
|---------------------------------------|-------------|
| Solvent flow rate, m³/m²·h            | 5.3, 10.6, 15.9 |
| CO₂ content in gas phase, v/v%        | 5, 10, 15   |
| CO₂ initial loading, mole CO₂ / mole amine | 0.0, 0.1, 0.2 |

3. Results and discussion

3.1. Effect of solvent flow rate
The solvent flow rate strongly affects the mass transfer coefficient. The effect of solvent flow rate on $K_{G\text{a}}$ is shown in Figure 1. It can be seen that the solvent flow rate at 15.9 m³/m²·h provides the highest $K_{G\text{a}}$ at 0.37 kmol/m³·h·kPa. The solvent flow rate is a direct relationship with the $K_{G\text{a}}$ [11], the $K_{G\text{a}}$ increase as the liquid flow rate increase. The reasons for this behaviour are (i) an increase in the solvent flow rate can cause more amine molecules available for reacting with CO₂ molecules, (ii) an increase in the mass transfer in liquid phase which is directly proportional to the $K_{G\text{a}}$ increase, and (iii) an increase in the solvent flow rate leads to increasing the wet surface area between gas and liquid phase on the packing [12].

Figure 1. Effect of solvent flow rate on $K_{G\text{a}}$. Solvent concentration = 3 kmol/m³; solvent flow rate = 5.3-15.9 m³/m²·h; CO₂ content in gas phase = 15 v/v%; CO₂ loading = 0.0 mole CO₂/mole amine.

3.2. Effect of CO₂ content in gas phase
The effect of CO₂ content in gas phase is the concentration of CO₂ in the gas stream after burning the fossil fuel. According to Figure 2, the CO₂ content at 5 v/v% has the highest $K_{G\text{a}}$ because of the
partial pressure of CO\textsubscript{2} increase leads to K\textsubscript{Gav} decrease. It can represent to two-film theory, k\textsubscript{L} is a main of mass transfer coefficient due to CO\textsubscript{2} absorption is controlled by the liquid phase. An increase in the driving force results in CO\textsubscript{2} partial pressure as K\textsubscript{Gav} decrease. This result corresponds well with Dey et al. [13], for the K\textsubscript{Gav} of CO\textsubscript{2} absorption into MEA solution in a structured packed column.

Figure 2. Effect of CO\textsubscript{2} content in gas phase on K\textsubscript{Gav}. Solvent concentration = 3 kmol/m\textsuperscript{3}; solvent flow rate = 10.6 m\textsuperscript{3}/m\textsuperscript{2}h; CO\textsubscript{2} content in gas phase = 5-15 v/v%; CO\textsubscript{2} loading = 0.0 mole CO\textsubscript{2}/mole amine.

3.3. Effect of CO\textsubscript{2} initial loading
For the effect of CO\textsubscript{2} initial loading of MEA, it can be found in Figure 3. CO\textsubscript{2} initial loading is defined as mole of CO\textsubscript{2} absorbed per mole of amine due to the absorptions [10]. The results show that the CO\textsubscript{2} initial loading at 0.0 mole/mole give the highest K\textsubscript{Gav} and 0.2 mole/mole is the lowest K\textsubscript{Gav}. The CO\textsubscript{2} loading from the liquid in the bottom of the column over range of 0.20-0.35 mole/mole. MEA can absorb the CO\textsubscript{2} around 0.5 mole/mole with absorption process [11]. There are more fresh-amine molecules in amine solution with 0.0 mole/mole for reacting with dissolved CO\textsubscript{2} whereas CO\textsubscript{2} initial loading at 0.2 mole/mole could provide less amine molecules for reacting with CO\textsubscript{2}. Therefore, an increase in CO\textsubscript{2} loading within amine solution leads to after decrease amount of fresh amine molecules and K\textsubscript{Gav}, because of a driving force from the gas to the liquid phase will decrease.

Figure 3. Effect of CO\textsubscript{2} initial loading on K\textsubscript{Gav}. Solvent concentration = 3 kmol/m\textsuperscript{3}; solvent flow rate = 10.6 m\textsuperscript{3}/m\textsuperscript{2}h; CO\textsubscript{2} content in gas phase = 15 v/v%; CO\textsubscript{2} loading = 0.0-0.2 mole CO\textsubscript{2}/mole amine.
4. Conclusion
Overall mass transfer coefficient on the CO₂ absorption in MEA solution is experimentally determined by using a random-packed absorption column. The operating conditions are conducted by solution flow rate, CO₂ content in gas phase and CO₂ initial loading. The results show that the mass transfer increase as solution flow rate increases whereas decreases as CO₂ initial loading increase. It can be concluded that 15.9 m³/m²·h is the best CO₂ absorption condition because there are free amine molecules to react with CO₂ molecules more than other solution flow rate. However, an increase solution flow rate effect to high energy and high cost in the system.

Acknowledgments
The authors would like to gratefully acknowledge the Malaysia-Thailand Joint Authority (MTJA) for financial support of this project.

References
[1] EPA 2017 United States Environmental Protection Agency
[2] Kim S, Shi H and Lee J 2016 International Journal of Greenhouse Gas Control 45 186
[3] Wang Y, Zhao L, Otto A, Robinius M and Stolten, D 2017 Energy Procedia 114 650
[4] Welty J R, Wicks C E, Wilson R E and Rooror G L Fundamentals of momentum, heat, and mass transfer. 2009: John Wiley & Sons.
[5] Maneeintr K, Idem O R, Tontiwachwuthikul P and Wee G H A 2010 Industrial & Engineering Chemistry Research 49 2857
[6] Halim H N A, Shariff A M, Tan L S and Bustam M A 2015 Industrial & Engineering Chemistry Research 54(5) 1675
[7] Naami A, Sema T, Edali M, Liang Z, Idem R and Tontiwachwuthikul P 2012 Industrial & Engineering Chemistry Research 51(18) 6470
[8] Jintai metal raschig ring 2005 China Jintai. Retrieved June 30, 2019, from www.ceramic-honeycombs.com/tower_packing/Raschig_Ring_Tower_Random_Column_Packing
[9] Horwitz W Association of Official Analytical Chemists (AOAC) Methods, 12th ed.; George Banta: Menasha, WI, 1975.
[10] Wen L, Liu H, Rongwong W, Liang Z, Fu K, Idem R and Tontiwachwuthikul P 2015 Chemical Engineering & Technology 38 1435
[11] deMontigny D, Tontiwachwuthikul P, Chakma A 2001 The Canadian Journal of Chemical Engineering 79 137
[12] Morteza A and Masoud M 2017 RSC Advances 7(29) 17857
[13] Dey A and Aroonwilas A 2009 Energy Procedia 1 211