PERTANIKA
JOURNALS

Modelling of Carbon Dioxide Absorption into Aqueous Ammonia Solution in a Wetted Wall Column

Ujjal Kumar Ghosh[1]*, Chiu Choon Hong[1], Jobrun Nandong[1] and Shufeng Shen[2]

[1]*Department of Chemical Engineering, School of Engineering & Science, Curtin University CDT 250, 98009 Miri, Sarawak, Malaysia*

[2]*School of Chemical and Pharmaceutical Engineering, Hebei University of Science and Technology, No.70, Yuhua East Road, Shijiazhuang, China 050018*

ABSTRACT

In this paper, a mathematical model is developed based on mass and momentum balance for carbon dioxide absorption into aqueous ammonia solution. The model is simplified based on the assumption that the CO_2 absorption into aqueous ammonia is a pseudo-first-order reaction. Laplace transform method is applied in order to solve the partial differential model equation. Finally, the CO_2 molar flux is expressed as a function of partial pressure of CO_2, concentration of aqueous ammonia, temperature and gas-liquid contact area. Variation of CO_2 molar flux with partial pressure of CO_2 and temperature is discussed and a comparison is performed with experimental data from literature. Variation of CO_2 molar flux is also shown with gas-liquid contact area. The calculated flux from the model follows the same trend as that of the experimental data reported in literature and the accuracy is within the accepted limit. The mathematical model is very helpful to predict the CO_2 molar flux as a function of partial pressure of CO_2, concentration of aqueous ammonia, temperature and gas-liquid contact area.

Keywords: Carbon dioxide capture, absorption, aqueous ammonia, modelling, wetted wall column.

INTRODUCTION

Global warming is one of the most serious environmental problems in this century (IPCC, 2005). It is generally accepted that the issue is closely related to the anthropogenic carbon dioxide (CO_2) emission activities, mainly the combustion of the fossil fuels and chemical transformation. Due to their low cost, availability, existing reliable technology for energy production and energy density, fossil fuels currently supply over 85% of the energy needs of the United States and a similar percentage of the energy

E-mail addresses:
ujjalche@gmail.com, ughosh@qu.edu.qa (Ujjal Kumar Ghosh)
choonhong_88@live.com (Chiu Choon Hong)
jobrun.n@curtin.edu.my (Jobrun Nandong)
shufengshen@gmail.com (Shufeng Shen)
*Corresponding Author

used worldwide (EIA, 2006a, b). Six billion tonnes of CO_2 emission are produced by fossil fuel combustion, while 1.8 billion tonnes of the total are from power plant generation (Diao *et al*., 2004). At present, power plants are one of the biggest discharge points of CO_2 into the atmosphere, whereby the amounts of boiler flue gases are as large as 10 million m^3 hourly (Suda *et al*., 1997). The reduction of CO_2 emission from large industrial point sources such as the power stations and iron- and steel-making plants is considered to be one of the highest priorities by both industry and the lay public. In general, various technologies have been applied to separate CO_2 from the flue gas of conventional fossil fuel fired power plants. These technologies are membrane separation, physical adsorption, chemical absorption, cryogenic methods and biological fixation (Kohl, & Nielsen, 1997; Smith *et al*., 2009; Suda *et al*., 1997). Chemical absorption is the widely applied technology to capture CO_2 from the power plant flue gases (Suda *et al*., 1997; Shen *et al*., 2013). Aqueous alkanolamine solutions are frequently used for the removal of CO_2 from power plants. The current state-of-the-art technology for CO_2 removal from flue gases is considered to be 30 wt% aqueous solution of monoethanolamine (MEA) (Ghosh *et al*., 2009). While amine solution is widely used for CO_2 capture process, it has some drawbacks such as (a) low CO_2 absorption capacity; (b) easier degradation in the presence of acid gases and oxygen; (c) high energy requirement for regeneration, and (d) corrosive nature (Diao *et al*., 2004; Yeh *et al*., 2005). Therefore, it is necessary to develop alternative solvents with higher absorptive capacity and lower reaction energy demands for regeneration.

One of the alternatives is the ammonia solution that provides the advantages of higher CO_2 absorption capacity, no absorbent degradation, as well as low regeneration energy requirement and lower temperature operation (0-10°C, 273-283K) (Yeh & Bai, 1999; Darde *et al*., 2009; Diao *et al*., 2004; Kim *et al*., 2008, 2009; Yeh *et al*., 2005). It allows for precipitation of ammonium carbonate compounds and thereby high carbon dioxide loadings in the slurry. Ammonium salt will be formed due to the presence of sulphur and nitrogen oxide. This salt carries a commercial value as fertilizer (Puxty *et al*., 2010). The vaporization of ammonia during the absorption is limited by low absorption temperature. Thermodynamic and equilibrium based studies have shown the potential of ammonia technology, especially the potential for a low heat requirement in the carbon dioxide desorber and for desorption at elevated pressure that allows for power savings in the subsequent compression of CO_2 (Darde *et al*., 2010). Dave and co-workers (2009) performed an economic assessment on CO_2 capture using aqueous ammonia. The study showed that under operating condition of ammonia concentration less than 5 wt%, temperature less than 10°C and no precipitation of ammonium bicarbonate, aqueous ammonia based CO_2 capture solvent has overall energy requirement comparable to the conventional 30 wt% aqueous MEA based process. Concentration of aqueous ammonia is significant to the system. Liu and co-workers (2009) concluded that the optimum concentration should be in between of 5% to 10% during the experiment at 20°C and 40°C. This range is yielded after the consideration of 90% removal and occurrence of volatilization. Darde and co-workers (2009) had earlier conducted the chilled ammonia process for CO_2 capturing where the operating temperature was between of 2°C to 10°C, whereas Zeng and co-workers (2011) suggested 35°C to 40°C as suitable for column and reactor. A similar experiment of CO_2 absorption was also conducted by Feng and co-workers (2010), whereby the operating temperature ranged from 15°C to 48°C.

Detailed kinetic data are required for the optimal design in terms of gas-liquid contact area and operation of an absorber. The kinetic data are therefore strongly related to the size of the absorber and thereby to the capital costs for capturing carbon dioxide using ammonia. The rate of reaction in a spray tower was given by Diao and co-workers (2004) for temperatures from 28 to 43°C. Puxty and co-workers (2010) presented their latest kinetics results for a reaction in a wetted wall column reactor at temperatures from 5 to 20°C. The zwitterions mechanism was applied to CO_2 absorption in ammonia solution in a stirred cell reactor from 5 to 25°C by Derks and Versteeg (2009). Feng and co-workers (2010) applied the termolecular and zwitterions mechanisms to characterize the kinetics and mechanisms of the absorption of CO_2 in aqueous ammonia solutions having different concentrations and different temperatures, which were determined using a string of discs contactor. In the previous communication, the authors had developed a mathematical model based on mass balance for the carbon dioxide absorption into aqueous ammonia (Ghosh & Yee, 2013). In this paper, a mathematical model was developed based on mass and momentum balance for CO_2 absorption into aqueous ammonia in a wetted wall column. The model was simplified based on the assumption that the CO_2 absorption into aqueous ammonia is a pseudo-first-order reaction. Laplace transform method was applied to solve the partial differential model equation. Finally, the CO_2 molar flux was expressed as a function of partial pressure of CO_2, concentration of aqueous ammonia, temperature and gas-liquid contact area. Variation of CO_2 molar flux with partial pressure of CO_2 and temperature is discussed and a comparison is performed with experimental data from literature. Variation of CO_2 molar flux is also shown with gas-liquid contact area.

WETTED WALL COLUMN

Generally, absorption of carbon dioxide occurs through mass transfer is accompanied by chemical reaction mechanism when a gas mixture consisting of CO_2 is brought into direct contact with the chemical solvent. This paper focuses on the removal of carbon dioxide from inlet gas by aqueous solution of ammonia in a falling film in a wetted wall column as shown in Fig.1. This column has been widely used in theoretical studies of mass transfer rates of components and in analytical distillation.
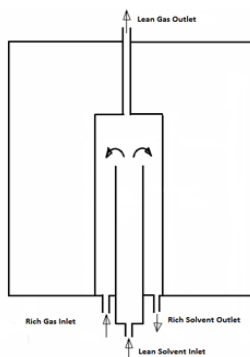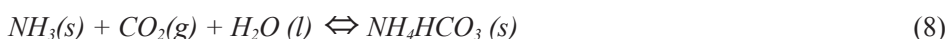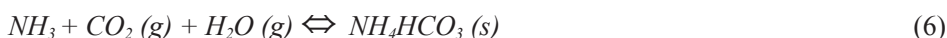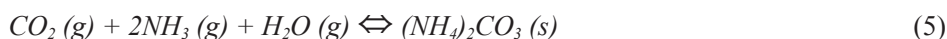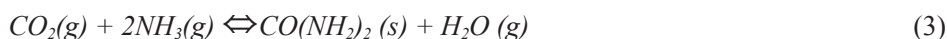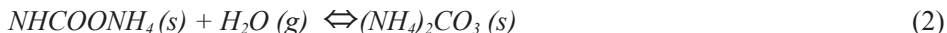

Fig.1: A schematic view of a wetted wall column

In experimental studies which carried out by other researchers, gas mixture was constantly and proportionally injected into the absorber from the bottom and flown upwards. The gas mixture refers to flue gas from typical coal fired power plant. A typical flue gas composition is (in mole %): N_2, 74; H_2O, 7; CO_2, 13.8; O_2, 3.5; CO, 0.2; NO, 0.4; SO_2, 0.07 at 300°C and 1 atm (Strube *et al.*, 2011). The rich gas is contacted with the lean solvent that is falling down from the middle tube. This is the core of the process where the mass transfer and chemical reaction takes place. A fluid layer can be determined whilst the lean solvent is overflowed. This fluid layer plays important role as to enlarge contact surface area and extent of gas penetrate into liquid. In addition, there are numerous factors contributing to the efficiency of the absorption which will be later defined. Generally, the column is rigidly supported to be free from external vibration and is made truly vertical. The liquid flow is merely subjected to gravity force. The surface of the wetted wall column is often cleaned chemically to avoid the possibility of the occurrence of liquid channelling on the tube wall that will later result in the wetting properties. This system is always wrapped up by a temperature protection layer in order to make sure there is neither heat lost nor heat gain by surrounding factors.

CHEMICAL REACTIONS

According to Liu and co-workers (2009), numerous chemical reactions happen in a wetted wall column. The possible reactions are summarized below:

$$CO_2(g) + 2NH_3(g) \Leftrightarrow NH_2COONH_4(s) \tag{1}$$

$$NHCOONH_4(s) + H_2O(g) \Leftrightarrow (NH_4)_2CO_3(s) \tag{2}$$

$$CO_2(g) + 2NH_3(g) \Leftrightarrow CO(NH_2)_2(s) + H_2O(g) \tag{3}$$

$$CO_2(g) + 2H_3(aq) \Leftrightarrow NH_2COO^-(aq) + NH_4^+(aq) \tag{4}$$

$$CO_2(g) + 2NH_3(g) + H_2O(g) \Leftrightarrow (NH_4)_2CO_3(s) \tag{5}$$

$$NH_3 + CO_2(g) + H_2O(g) \Leftrightarrow NH_4HCO_3(s) \tag{6}$$

$$CO_2(g) + 2NH_3(g) + H_2O(l) \Leftrightarrow (NH_4)_2CO_3(s) \tag{7}$$

$$NH_3(s) + CO_2(g) + H_2O(l) \Leftrightarrow NH_4HCO_3(s) \tag{8}$$

These reactions in CO_2-NH_3-H_2O system are also in agreement with the findings of other researchers (e.g., Strube *et al.*, 2011; Puxty *et al.*, 2010; Diao *et al.*, 2004).

To simplify the set of reactions, the total reaction of CO_2 absorption into aqueous ammonia can be represented by Eq. (1) (Liu *et al.*, 2011). Puxty and co-workers (2010) also suggested that the direct reaction between CO_2 and ammonia is immediate and significant. Based on Eq. (1), both the forward and reverse reactions may be considered as first order with respect to each species.

As the concentration of ammonia doesn't change considerably during the course of reaction with CO_2 the reaction can be considered pseudo-first-order irreversible reaction Qin *et al.* (2010). Puxty and co-workers (2010) have agreed that the reaction is pseudo-first-order irreversible reaction based on the surface renewal principles that the concentration of ammonia is not depleted across the liquid film.

MATHEMATICAL MODEL DEVELOPMENT

Model Assumptions

A mathematical model is developed based on mass, energy, and momentum balances. The following are model assumptions:

- One-dimensional diffusion;

- Tube surface is smooth and cleaned chemically. Wetted wall column stands vertically. Therefore, no liquid channelling occurs on tube surface;

- Replenished liquid surface with enough diluted aqueous ammonia solution that allow complete reaction with CO_2;

- Pseudo-first-order reaction of the system;

- Only CO_2 from the flue gas is diffused into liquid layer and reacted with aqueous ammonia solution;

- Constant properties of CO_2.

Mathematical Model Derivation

A mathematical model begins from the component molar balance with subscript A representing CO_2.

$$-\frac{\Delta m_A}{M_A} - R_A \Delta x \Delta y \Delta z = \frac{\delta C_A}{\delta t} \Delta x \Delta y \Delta z \tag{9}$$

Where, $\Delta x \Delta y \Delta z$ represents the axis volume (m³), m_A is mass rate of carbon dioxide (kg s⁻¹), M_A is the molecular weight of carbon dioxide (g mol⁻¹), reaction rate of carbon dioxide, $-R_A$ has unit mol m⁻³s⁻¹, C_A is the concentration of carbon dioxide (mol m⁻³), and the difference

between molar inlet rate and molar outlet rate of system, $-\frac{\Delta m_A}{M_A}$ is shown as:

$$
\begin{aligned}
-\frac{\Delta m_A}{M_A} = &[\ v_x C_A - D_A \frac{\delta C_A}{\delta x})_x - (v_x C_A - D_A \frac{\delta C_A}{\delta x})_{x+\Delta x}]\Delta y \Delta z \\
&+[\ v_y C_A - D_A \frac{\delta C_A}{\delta y})_y - (v_y C_A - D_A \frac{\delta C_A}{\delta y})_{y+\Delta y}]\Delta x \Delta z \\
&+[\ v_z C_A - D_A \frac{\delta C_A}{\delta z})_z - (v_z C_A - D_A \frac{\delta C_A}{\delta z})_{z+\Delta z}]\Delta y \Delta x
\end{aligned} \tag{10}
$$

Substituting Eq. (10) into Eq. (9) and dividing by $\Delta x \Delta y \Delta z$:

$$\frac{\delta C_A}{\delta t} = -(\frac{\delta v_x C_A}{\delta x} + \frac{\delta v_y C_A}{\delta y} + \frac{\delta v_z C_A}{\delta z}) + D_A(\frac{\delta^2 C_A}{\delta x^2} + \frac{\delta^2 C_A}{\delta y^2} + \frac{\delta^2 C_A}{\delta z^2}) + R_A \tag{11}$$

Assume constant density due to the insignificant pressure changes.

$$\frac{\delta C_A}{\delta t} = -(v_x \frac{\delta C_A}{\delta x} + v_y \frac{\delta C_A}{\delta y} + v_z \frac{\delta C_A}{\delta z}) + D_A(\frac{\delta^2 C_A}{\delta x^2} + \frac{\delta^2 C_A}{\delta y^2} + \frac{\delta^2 C_A}{\delta z^2}) + R_A \quad (12)$$

CO_2 absorption into aqueous ammonia in a falling film can be considered as mass transfer in stagnant element. Besides, this model is only interested in 1 dimension, i.e., no dispersion is assumed.

$$\frac{\delta C_A}{\delta t} = D_A \frac{\delta^2 C_A}{\delta x^2} + R_A \quad (13)$$

The boundary conditions are shown below:

When x = 0, t > 0; $C_A = C_{Ai}$;
When x > 0, t = 0; $C_A = 0$;
When x = α, t > 0; $C_A = 0$. \quad (14)

The first condition in Eq. (14) shows that CO_2 is contacted with liquid after certain time. This occurs at the vapour-liquid interface. Therefore, the concentration of CO_2 is expressed as C_{Ai}. While CO_2 diffuses into liquid layer, which is beyond the liquid-vapour interface, it will react immediately with the solvent. Consequently, it approaches to zero CO_2 after an extent of thickness. Third condition discusses no solute is found in infinite liquid layer on account to significant reduce of CO_2 concentration in liquid film. This shows that solvents must be sufficient and able to react continuously. A concentration profile of CO_2 is drawn and shown in Fig.2 below.
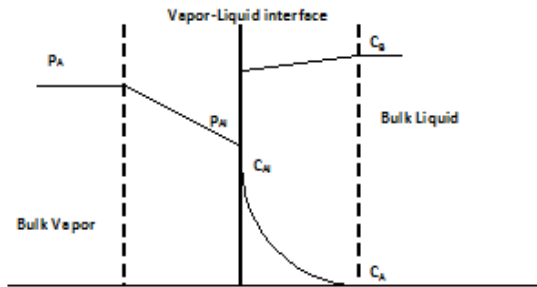

Fig.2: A concentration profile of carbon dioxide

As the enough solvent is assumed based on replenish principle, a pseudo-first-order reaction can be achieved. This has also been explained by Levenspiel (1999). If another reactant remains approximately constant at all times, the second order reaction will approach pseudo first-order reaction. Therefore, Eq. (13) can be re-written as:

$$\frac{\delta C_A}{\delta t} = D_A \frac{\delta^2 C_A}{\delta x^2} - k_1 C_A \quad (15)$$

This equation is difficult to be solved. Therefore, Laplace Transform is performed and after the re-arrangement,

$$\frac{d^2 C_A(s)}{dx^2} - \frac{(k_1 + s)}{D_A} C_A(s) = 0 \tag{16}$$

Integral of Eq. (16) gives

$$C_A(s) = A_1 e^{\sqrt{\frac{(s+k_1)}{D_A}}x} + A_2 e^{-\sqrt{\frac{(s+k_1)}{D_A}}x} \tag{17}$$

With the defined boundary conditions in Eq. (14), it can be simplified into:

$$C_A(s) = \frac{C_{Ai}}{s} e^{-\sqrt{\frac{(s+k_1)}{D_A}}x} \tag{18}$$

Inverse Laplace Transform is performed to Eq. (18) in order to return to t-domain:

$$C_A = \frac{C_{Ai}}{2} e^{-\sqrt{\frac{k_1}{D_A}}x} erfc(\frac{x}{2\sqrt{D_A t}} - \sqrt{k_1 t}) + \frac{C_{Ai}}{2} e^{\sqrt{\frac{k_1}{D_A}}x} erfc(\frac{x}{2\sqrt{D_A t}} + \sqrt{k_1 t}) \tag{19}$$

The flux of A at the interface at any time is obtained by differentiating Eq. (19), which is also indicated as Fick's law (Froment & Bischoff, 1979).

$$N_A(t) = C_{Ai} \sqrt{k_1 D_A} \left(erf(\sqrt{k_1 t}) + \frac{e^{-k_1 t}}{\sqrt{\pi k_1 t}} \right) \tag{20}$$

On the account of vertical wetted wall column position, smooth liquid flow is assumed. Hence, Higbie's uniform age is applied for the average rate of absorption at contact surface (Froment & Bischoff, 1979).

$$N_A = \sqrt{D_A(k_1 + s)} C_{Ai} \tag{21}$$

The parameter, s, can be either related to the transfer coefficient or diffusivity (Froment & Bischoff, 1979). Since CO_2 is in gas phase, it is more proper to express in term of partial pressure. Therefore, Henry law is suggested.

$$C_{Ai} = \frac{p_A}{H_A} \tag{22}$$

H_A refers to Henry constant of CO_2 at specific temperature (mol Pa m^{-3}) and p_A is the partial pressure of CO_2 (Pa). Substituting Eq. (22) back into Eq. (21) will give:

$$N_A = \sqrt{D_A k_1} \frac{p_A}{H_A} \tag{23}$$

This expression shows the relationship between the partial pressure and the CO_2 molar flux. The account of the equation shown above is based on the scenario of single pseudo-first-order reaction, thus, a modification of the equation regards on the real situation is necessary. Consequently, the concentration of aqueous ammonia (mol m^{-3}) is included in Eq. (24):

$$N_A = \sqrt{D_A k_1 \, [NH_3]} \; \frac{p_A}{H_A} \tag{24}$$

Also, the objective of this paper is to investigate the effect of temperature to CO_2 removal where diffusivity, Henry constant and kinetics are the function of temperature. These functions are also highlighted in other research (see Puxty et al., 2010; Qin et al., 2010; Cullinanae & Rochelle, 2004).

$$D_{CO_2\text{-}H_2O} = 2.35 \times 10^{-6} \, e^{-\frac{2199}{T}} \tag{25}$$

$$H_{CO_2\text{-}H_2O} = 2.82 \times 10^{-6} \, e^{-\frac{2044}{T}} \tag{26}$$

$$k = k_{ref} \, e^{-\frac{E}{R}(\frac{1}{T} - \frac{1}{T_o})} \tag{27}$$

Eq. (25) and Eq. (26) are established based on the relation between water and CO_2 by experimental constant. Although there are theoretical methods for estimating the diffusivity of the interested system, these equations are still acceptable since the diluted aqueous ammonia solution mainly consists of water. The reference kinetic, k_{ref} is 0.915 m^3 mol^{-1}s^{-1}, reference temperature, To, at 283K, activation energy, E is 61 kJ mol^{-1} and R, gas constant, 8.314 J mol^{-1} K^{-1} (Puxty et al., 2010; Qin et al., 2010). Lastly, by summarizing all the equations, it can be shortened as follow:

$$N_A = 0.2 \, 2 \times 10^{-3} \, \sqrt{[NH3]} \, P_A \, e^{-\frac{6822}{T}} \tag{28}$$

The molar flux of carbon dioxide can be also expressed as in molar rate, J_A (mol s^{-1}) over a contact area, A_c (m^2).

$$N_A = \frac{J_A}{A_C} \tag{29}$$

The contact area of vapour liquid can be defined as in Fig.1. It consists of semi-sphere at the pipe end side and the surrounding of the tubes. The equation is expressed in term of tube radius, r (m) and the tube height, h (m).

$$A_C = 2\pi \, r(r + h) \tag{30}$$

Height of the column is crucial after considering a real unit apply in a CO_2 captured power plant. This is because of the cost and investment into this project depends on column height and chemical solvents. Based on the rules of thumb, the ratio of height to diameter of a column should not exceed a certain designed figure due to safety purposes (Kister, 1992). Combining Eq. (30) into the previous equation, CO_2 molar rate can be expressed as below.

$$J_A = 0.22 \times 10^{-3} \sqrt{[NH_3]} \, P_A \, e^{-\frac{6822}{T}} \, 2\pi \, r(r+h) \tag{31}$$

On the other hand, pipe diameter is relatively small compared to the height of the column, while the term for the semi-sphere can be ignored.

$$J_A = 0.22 \times 10^{-3} \sqrt{[NH_3]} \, P_A \, e^{-\frac{6822}{T}} \, 2\pi \, rh \tag{32}$$

In general, it is crucial and essential to perform model checking on the account of validating the reliability of developed model. Moreover, a reliable model can assist on future work, especially on the predicting the influences and outcomes of alternating parameter via the investigation of the trend. The objectives of this paper are to study the effects of partial pressure and temperature to the CO_2 molar flux. Thus, model verification is based on the two parameters that are further discussed in the following subsection.

RESULTS AND DISCUSSION

Effects of Partial Pressure

Some previous investigators had worked on the kinetic of CO_2 absorption into aqueous ammonia experimentally under various conditions. These results are referred in this paper to determine the reliability of the developed mathematical model. Liu and co-workers (2009) conducted experiments which were conducted twice at different temperatures, 293K and 313K, respectively. According to Eq. (25) – Eq. (27), diffusivity, Henry constant and kinetic rate constant have been calculated at different temperatures. The findings are listed in Table 1.

TABLE 1: Parameters at different temperature

Parameter	Temperature (K)	
	293	313
D_{co2} (m² s⁻¹)	1.3×10^{-9}	2.1×10^{-9}
H_{co2} (Pa m³ mol⁻¹)	2633.68	4112.95
k (m³ mol⁻¹ s⁻¹)	2.217	10.980

Two sets of CO_2 molar flux, $N_{CO2,model,inlet}$ and $N_{CO2,model,lm}$ based on the inlet partial pressure and log mean partial pressure, respectively, were calculated from the model using aqueous ammonia concentration of 10 vol% and reported in Table 2. The molar carbon dioxide flux from the model is plotted as a function of CO_2 partial pressure at the temperatures 293K and 313K and reported in Fig.3 and Fig.4, respectively. The literature data (Liu *et al*., 2009) are also included in Fig.3 and Fig.4. It can be seen from both Fig.3 and Fig.4 that the molar flux of CO_2 increases as the partial pressure of CO_2 increases. The calculated flux from the model follows the same trend as that of the experimental data.

TABLE 2: CO_2 molar flux at different partial pressures

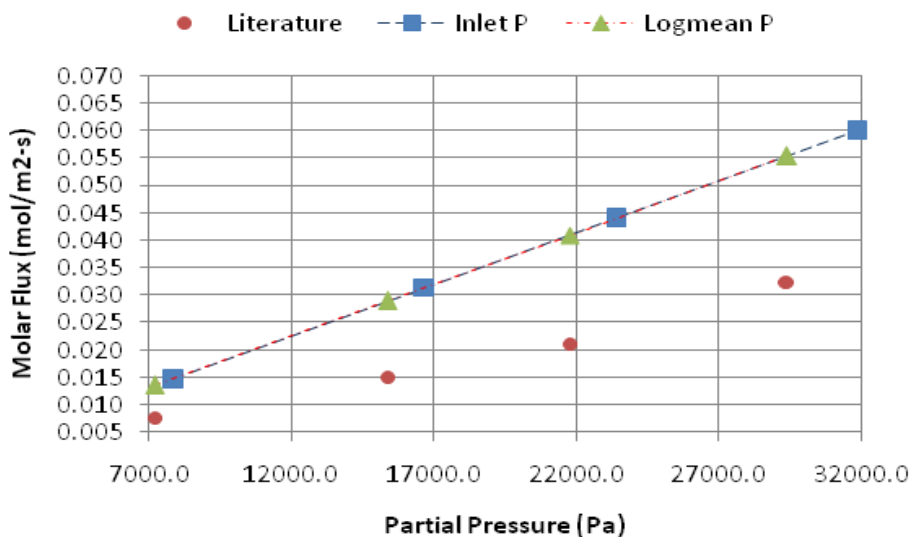| Temp (K)	P_{CO2},in (Pa)	P_{CO2},out (Pa)	P_{CO2},lm (Pa)	N_{CO2}, literature (mol m^{-2}s^{-1})	N_{CO2}, model, inlet (mol m^{-2} s^{-1})	N_{CO2}, model, lm (mol m^{-2} s^{-1})	Ratio of literature data over model
	7840	6580	7191.6	0.008	0.015	0.014	0.56
293	16640	14120	15345.5	0.015	0.031	0.029	0.52
	23390	20170	21740.3	0.021	0.044	0.041	0.52
	31840	27040	29374.7	0.032	0.060	0.055	0.59
	7740	5840	6745.5	0.012	0.025	0.022	0.54
313	15400	11930	13591.3	0.022	0.050	0.044	0.51
	22830	18270	20465.4	0.031	0.074	0.066	0.46
	31310	24800	27928.7	0.045	0.102	0.091	0.50

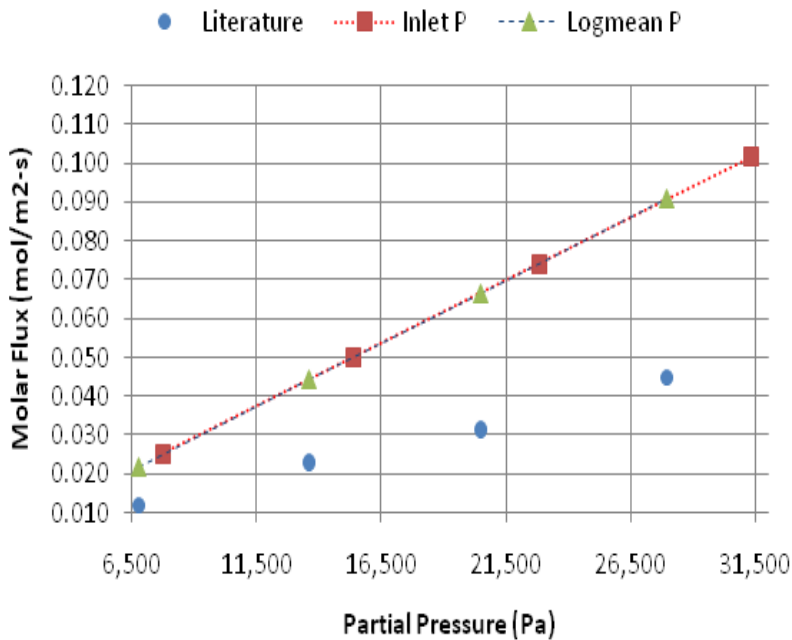Fig.3: Molar flux as a function of partial pressure of CO_2 at 293K

Fig.4: Molar flux as a function of partial pressure of CO_2 at 313K

Pressure has strong relationship to the time exposure and mass transfer. In this paper, inlet partial pressure and log mean partial pressure were applied on the calculation of absorption flux. These values yield mostly the similar results in this scenario. However, when the pressure difference between the gas inlet and gas outlet are significant, the molar fluxes of CO_2 of each scenario are no longer in a compromised status.

$$t = 0, \, y = 0; \, P = Po$$
$$t > 0, \, y > 0, \, P = Py \qquad (33)$$

Boundary condition, as illustrated in Eq. (33), indicates that the pressure at distance of y does not return to initial value or inlet pressure. Moreover, the absorbed and reacted gas component into the liquid would decrease the fraction of those in rich gas. According to Dalton's law, partial pressure can be expressed by mole fraction of component in total mixture.

$$p_A = P_{total} y_A \qquad (34)$$

The log mean partial pressure was calculated to get the average value that could represent the system in a better way. Based on the simulation results, it is reported that the model outcome is averagely twice of the literature result.
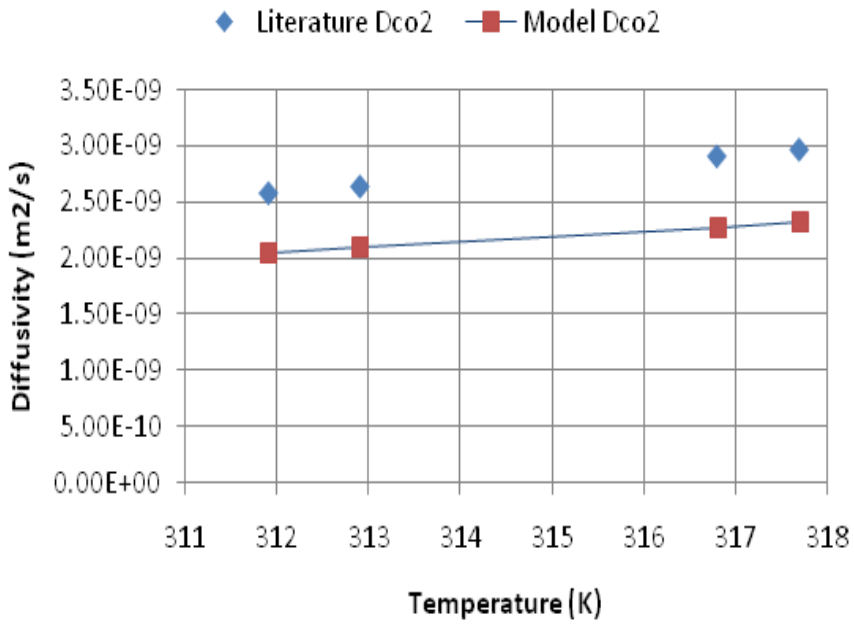
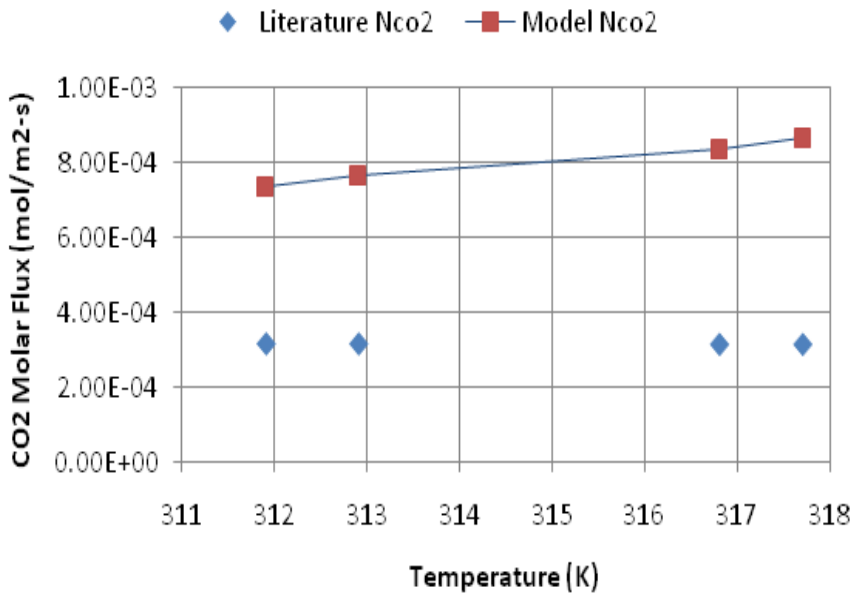Fig.5: CO_2 Diffusivity as a function of temperature

Fig.6: CO_2 molar flux as a function of temperature

Effects of Temperature

Temperature has a strong relationship with vapour-liquid equilibrium. According to the results from some previous researchers, increases of temperature within a scope will contribute on better absorption (Qin *et al*., 2010). Carbon dioxide diffusivity calculated from Eq. (25) is plotted in Fig.5 as a function of temperature. Molar carbon dioxide flux from the model as a function of temperature is shown in Fig.6. It can be seen from Fig.6 that the molar carbon dioxide flux increases as the temperature increases. The increase of temperature increases the diffusivity and kinetic rate constant and thereby increasing the molar flux of CO_2. It can be seen from Fig.5 and Fig.6 that CO_2 diffusivity and flux calculated from the model equation follow the same trend as that of the experimental data.

Aqueous ammonia has a low boiling point. As a result of being high vapour pressure, aqueous ammonia will boil up and undergo vaporization more easily with the lower boiling point. Therefore, it is predicted that the carbon dioxide removal rate will increase until an extent just before the solvent starts boiling off. It will have a significant reduction beyond that temperature. Besides, the account of lowering down the heat of absorption of carbon dioxide, cool or chilled ammonia, which is at low temperature, has mainly been studied (Darde *et al*., 2009).
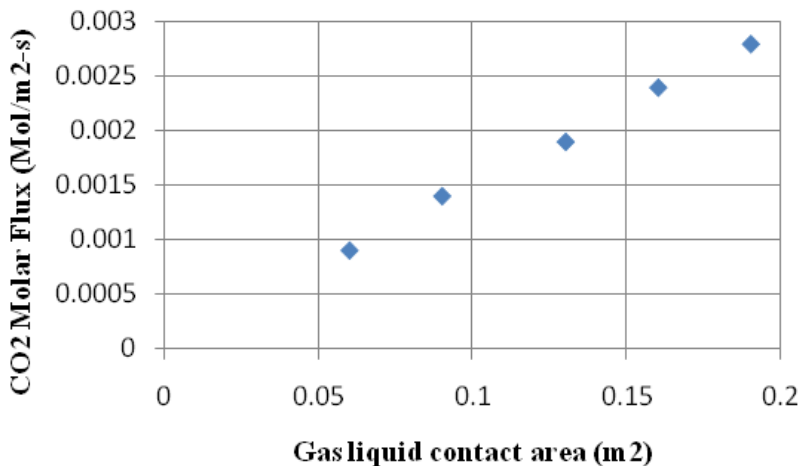

Fig.7: CO2 molar flux as a function of gas-liquid contact area

Effects of Contact Area

While the height of the column is increasing, the area of contact will become larger. As a result, it enhances the diffusion of components. Moreover, this result gives a linear expression as shown in Fig.7. Since there has been no current available literature result for the comparison, this relationship is merely based on model prediction. Radius, which is another dimension of area, is kept at constant during the simulation on the account of varying of radius will not give significant effect to the system. Furthermore, the layer that is formed by the falling liquid is negligible. This assumption is made based on the thin film assumption and slow liquid rate which cause a smooth flow.

However, the changes in height will contribute to the pressure loss of solution simultaneously. This is due to the fact that the distance of flow has been extended. As a consequence, the physical properties of the interested solvent such as the density will be varied significantly. Also, higher pressure at the lower stage will induce the phase change and increase the plant cost.

CONCLUSION

In this paper, a mathematical model is developed based on mass and momentum balance for CO_2 absorption into aqueous ammonia in a wetted wall column. The model is simplified based on the assumption that the CO_2 absorption into aqueous ammonia is a pseudo-first-order reaction. Laplace transform method is applied in order to solve the partial differential model equation. Finally, the CO_2 molar flux is expressed as a function of partial pressure of CO_2, concentration of aqueous ammonia, temperature and gas-liquid contact area. The molar flux of CO_2 increases as the partial pressure of CO_2 increases. The calculated flux from the model follows the same trend as that of the experimental data. Carbon dioxide flux increases as the temperature increases. CO_2 diffusivity and flux calculated from model equation follow the same trend as that of the experimental data. CO_2 molar flux is also found to increase with increase in gas-liquid contact area. The developed mathematical model is very useful to predict the CO_2 molar flux as a function of the concentration of aqueous ammonia, partial pressure of CO_2, temperature and gas-liquid contact area.

ACKNOWLEDGEMENTS

REFERENCES

Cullinane, J. T. & Rochelle, G. T. (2004). Carbon dioxide absorption with aqueous potassium carbonate promoted by piperazine. *Chemical Engineering Science, 59*, 3619-3630.

Darde, V., Thomsen, K., van Well, W. J. M., & Stenby, E. H. (2009). Chilled ammonia process for CO_2 capture. *Energy Procedia, 1*, 1035-1042.

Darde, V., Thomsen, K., van Well, W. J. M., & Stenby, E. H. S. (2010). Chilled ammonia process for CO_2 capture. *International Journal of Greenhouse Gas Control, 4*, 131-136.

Dave, N., Do, T., Puxty, G., Rowland, R., Feron, P. H. M., & Attalla M. I. (2009). CO_2 capture by aqueous amines and aqueous ammonia. *Energy Procedia, 1*, 949-954.

Derks, P. W. J. & Versteeg, G. F. (2009). Kinetics of absorption of carbon dioxide in aqueous ammonia solutions. *Energy Procedia, 1*, 1139-1146.

Diao, Y. F., Zheng, X. Y., He, B. S., Chen, C. H., & Xu, X. C. (2004). Experimental study on capturing CO_2 greenhouse gas by ammonia scrubbing. *Energy Conversion and Management, 45*, 2283-2296.

Energy Information Administration (EIA). (2006a). *Annual Energy Outlook 2006*. Retrieved from http://www.eia.doe.gov/oiaf/aeo.

Energy Information Administration (EIA). (2006b). *International Energy Outlook 2006*. Retrieved from http://www.eia.doe.gov/oiaf/ieo/index.html.

Feng, Q., Wang, S. J., Hartono, A., Svendsen, H. F., & Chen, C. H. (2010). Kinetics of CO_2 absorption in aqueous ammonia solution. *International Journal of Greenhouse Gas Control, 4*(5), 729-738.

Froment, G.F. & Bischoff, K.B. (1979). Chemical reactor analysis and design. (2nd Ed.). New Jersey: John Wiley & Sons.

Ghosh, U. K., Kentish, S. E., & Stevens, G. W. (2009). Absorption of carbon dioxide into aqueous potassium carbonate promoted by boric acid, *Energy Procedia, 1*, 1075-1081.

Ghosh, U. K. & Yee, S. C. (2013). Modelling and simulation of reaction kinetics of carbon dioxide absorption into aqueous ammonia in a wetted wall column. *International Journal of Environmentand Pollution, 51*(1/2), 121-138.

IPCC (2005). *Carbon Dioxide Capture and Storage*.

Kim, J. Y., Han, K., & Chun, H. D. (2009). CO_2 absorption with low concentration ammonia liquor. *Energy Procedia, 1,* 757-762.

Kim, Y. J., You, J. K., & Hong, W. H. (2008). Characteristics of CO_2 absorption into aqueous ammonia. *Separation Science and Technology, 43*, 766-777.

Kister, H. Z. (1992). *Distillation Design*. New York: McGraw-Hill.

Kohl, A. L. & Nielsen, R. B. (1997). *Gas Purification* (5th Edn.). Houston: Gulf Publishing.

Levenspeil, O. (1999). *Chemical reaction engineering* (3rd Edn.). New York: John Wiley & Sons.

Liu, J., Wang, S., Zhao, B., Tong, H., & Chen C. (2009). Absorption of carbon dioxide in aqueous ammonia. *Energy Procedia., 1*, 933-940.

Liu, J., Wang, S., Qi, G., Zhao, B., & Chen, C. (2011). Kinetics and mass transfer of carbon dioxide absorption into aqueous ammonia. *Energy Procedia, 4*, 525-532.

Puxty, G., Rowland, R., & Attalla, M. (2010). Comparison of the rate of CO_2 absorption into aqueous ammonia and monoethanolamine. *Chemical Engineering Science, 65*, 915-922.

Qin, F., Wanga, S., Hartono, A., & Svendsen, H. F. (2010). Kinetics of CO_2 absorption in aqueous ammonia solution. *International Journal of Greenhouse Gas Control, 4*, 729-738.

Shen, S., Feng, S., Zhao, R., Ghosh, U.K., & Chen, A. (2013). Kinetic study of carbon dioxide absorption with aqueous potassium carbonate promoted by arginine. *Chemical Engineering Journal, 222*, 478-487.

Smith, K., Ghosh, U., Khan, A., Simioni, M., Endo, K., Zhao, X., Kentish, S., Qader, A., Hooper, B., & Stevens, G. (2009). Recent developments in solvent absorption technologies at the CO_2CRC in Australia. *Energy Procedia, 1*, 1549-1555.

Strube, R., Pellegrini, G., & Manfrida, G. (2011). The environment impact of post-combustion CO_2 capture with MEA, with aqueous Ammonia, and with an aqueous ammonia-ethanol mixture for a coal-fired power plant. *Energy, 36(*6), 3763-3770.

Suda, T., Lijima, M., Tanaka, H., Mitsuoka, S., & Iwaki, T. (1997). Countercurrent Absorption of CO_2 in a real flue gas into aqueous Alkanolamine Solutions in a Wetted Wall Column. *Environmental Progress, 16*(3), 200-207.

Yeh, A. C. & Bai, H. (1999). Comparison of ammonia and monoethanolamine solvents to reduce CO_2 greenhouse gas emissions. *The Science of the Total Environment, 22*8, 121-133.

Yeh, J. T., Resnik, K. P., Rygle, K., & Pennline, H. W. (2005). Semi-batch absorption and regeneration studies for CO_2 capture by aqueous ammonia. *Fuel Processing Technology, 86*, 1533-1546.

Zeng, Q., Guo, Y., & Niu, Z. (2011). Experimental studies on removal capacity of carbon dioxide by a packed reactor and a spray column using aqueous ammonia. *Energy Procedia, 4*, 519-524.

NOMENCLATURE

A_c contact area (m^2)

C_A concentration of carbon dioxide (mol m^{-3})

C_{Ai} concentration of carbon dioxide at gas-liquid interface (mol m^{-3})

D_A diffusivity of carbon dioxide (m^2 s^{-1})

E   activation energy for carbon dioxide absorption (kJ mol^{-1})

H_A Henry's law constant (mol Pa m^{-3})

h   height of wetted wall column (m)

J_A carbon dioxide absorption rate (mol s^{-1})

k_1 pseudo-first-order rate constant of carbon dioxide absorption (m^3 mol^{-1} s^{-1})

m_A mass rate of carbon dioxide (kg s^{-1})

M_A molecular weight of carbon dioxide (g mol^{-1})

N_A carbon dioxide molar flux (mol m^{-2} s^{-1})

p_A partial pressure of carbon dioxide at the bulk gas (Pa)

p_{Ai} partial pressure of carbon dioxide at gas-liquid interface (Pa)

R   gas constant (J mol^{-1} K^{-1})

R_A reaction rate of carbon dioxide (mol $m^{-3}s^{-1}$)

r   radius of wetted wall column (m)

s   coefficient of Laplace transform

t   time (s)

v_x velocity of gas in x-direction, (m s^{-1})