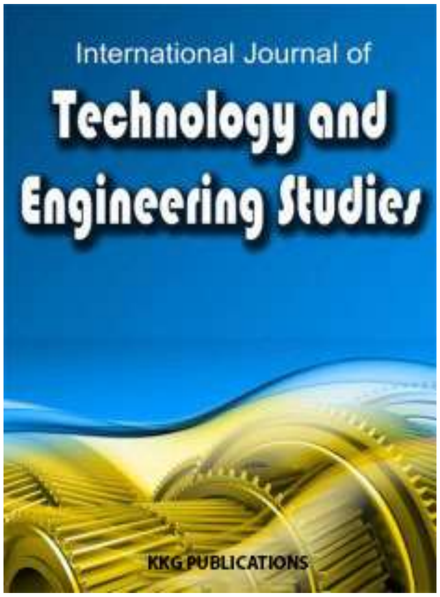

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Kinetic Study of Carbon Dioxide Absorption into Glycine Promoted Methyl di Ethanolamine (Mdea)

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KINETIC STUDY OF CARBON DIOXIDE ABSORPTION INTO GLYCINE PROMOTED METHYL DI ETHANOLAMINE (MDEA)

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Abstract. The main purpose of this study is to provide reaction kinetics data of CO^2 absorption into glycine-promoted methyl diethanolamine (MDEA) by using laboratory-scale wetted wall column equipment at atmospheric pressure. By varying temperature from 303.15 to 328.15 and glycine concentration from 1% to 3%, and the carbon dioxide absorption rate is measured by titration of liquid effluent. Based on the result of this study, we observed that by increasing the temperature and concentration of glycine, the absorption rate of carbon dioxide in the MDEA solution would increase. In addition, the reaction rate constant was affected by the temperature and the concentration of the promoter. The correlation of reaction rate constant k glycine is k glycine =8.113E+18exp (-5137.6/T) with activation energy for glycine promoter is 42.714 kJ/mol.

INTRODUCTION

Global warming and climate change refer to an increase in average global temperatures. Natural events and human activities are believed to be contributing to an increase in average global temperatures. This is caused primarily by increases in “greenhouse” gases such as Carbon Dioxide and trace gases It is widely accepted that increasing carbon dioxide emissions to our atmosphere is the major contributor to global climate change, which pollutes environment, and concentration of a large number of trace gases could exceed that the increasing concentration of CO_2 [1]. A warming planet thus leads to a change in climate which can affect weather in various ways. Environmental solutions are necessary to reduce the emissions mainly responsible of anthropogenic greenhouse effect. This study focused on one of the solutions. Since absorption has such advantages as large capacity, high efficiency and good industrial performance, it always has been favored by researchers. The selective chemical absorption of by a solvent is the most well-established method of capture in power plants and from the gas sources. High product yields and purities can be obtained with this method. Because the alkanolamines solution is one of the most effective solvents, it have been widely used in capturing from natural gas sources and refinery gases or fossil fuel combustion [2], we observe that many researchers used MDEA solvent as the absorbent with a several promoter for example PZEA [3], because it has several advantages such as: A low vapor pressure, it is not easy degradation, low corrosive, low reaction heat, high selectivity to remove CO_2, and more attractive [4]. However it has low reaction rate that is why we added a glycine promoters to the conventional solvent to enhance the reaction rate. The kinetics of absorption into glycine promoted methyl di ethanolamine (MDEA) solution hasn’t been investigated by previous studies.

LITERATURE REVIEW

The Method of Carbon Dioxide Removal

Several processes have been proposed and studied for the removal of carbon dioxide from sour gas. The most important gas purification techniques is absorption. It involves the transfer of carbon dioxide from the gaseous to the liquid phase through the phase boundary. At the process of absorption of gas into liquid, gas principally is absorbed through mechanism of diffusion (molecular & turbulent) and convection into liquid through interface. Carbon dioxide absorption may be physical when merely dissolved in the absorbing solvent such as water, or it may be chemical when carbon dioxide reacts with the absorbing solution such MDEA solutions, so there are two types of absorption, physical absorption and chemical absorption.

Carbon Capture and Storage (CCS) refers to the set of technologies developed to capture carbon dioxide gas from the exhausts of power stations and from other industrial sources, the infrastructure for handling and transporting to use as an energy source. There are several technologies that could be used for captures, such as absorption, adsorption, cryogenic recovery, membrane separation and chemical looping combustion. Chemical absorption has been regarded as one of the most promising method to capture CO_2 from flue gas.

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Reaction Kinetic of Carbon Dioxide Absorption

When the carbon dioxide is absorbed in the MDEA solution there are several reactions occurring [5] as follows:

$$CO_2 + R1R2R3 + H_2O \xleftrightarrow{k_{MDEA}} R1R2R3NH^+ + HCO_3^- \quad (1)$$

$$H_2NCH_2COO^- + CO_2 \xrightarrow{Kglycine} -OOCNHCH_2COO^- + H^+ \quad (2)$$

$$-OOCNHCH_2COO^- + H_2O \xrightarrow{kglycine} H_2NCH_2COO^- + HCO_3^- \quad (3)$$

$$H_2O \overset{k_w}{\leftrightarrow} H^+ + OH^- \quad (4)$$

$$CO_2 + H_2O \overset{k_1}{\leftrightarrow} HCO_3^- + H^+ \quad (5)$$

$$HCO_3^- \overset{k_2}{\leftrightarrow} CO_3^{-2} + H^+ \quad (6)$$

Where $K_w = [H^+][OH^-]$, $K_1 = \frac{[HCO_3^-][H^+]}{[CO_2]}$ and $K_2 = \frac{[CO_3^{-2}][H^+]}{[HCO_3^-]}$

This study was conducted to determine the reaction kinetics data of carbon dioxide absorption gas into glycine promoted (MDEA) using a laboratory scale wetted wall column as used by [6] and shown in Fig 1 and 2 at atmospheric pressure and the temperature in the interval of 303.15 K (30° C) - 328.15 K (55 ° C).

The inlet gas contains 20% CO2 and 80% N2, The absorbent used is Glycine promoted MDEA containing 30 % MDEA and 1-3% Glycine, The gas flow rate is 6 L/min, and the liquid flow rate is 200 mL/min .The carbonate and bicarbonate concentration in liquid effluent was determined using titration method. The wetted wall column has diameter of 0.013 m and 0.093 m high:

METHOD AND MATERIALS

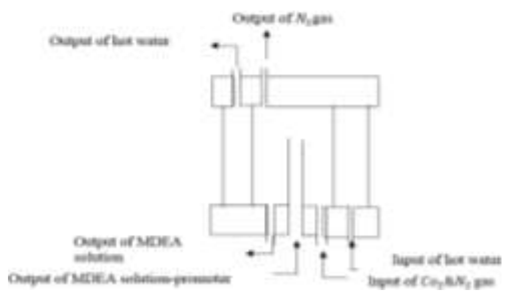

Fig. 1. Absorption column wetted wall column type

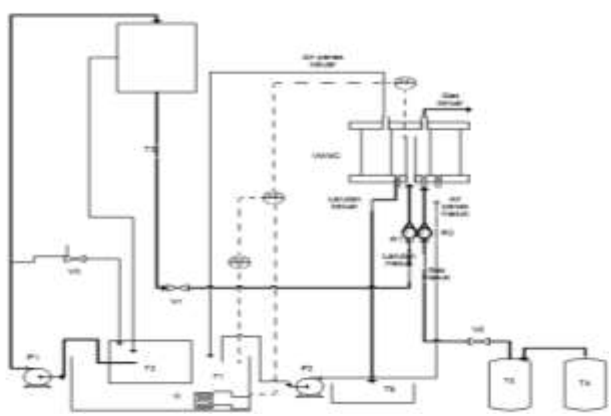

Fig. 2. Equipment scheme wetted wall column

C: coil of heater, P1 : Pump of MDEA solution with promoter, P2: Water Pump, R1: Rotameters of liquid, R2: Rotameters of gas, T1: Water bath,T2 : Tank reservoir (MDEA solution tank with promoter), T3: Tank of overflow, T4: Feed tank of gas (CO_2), T5: Tube saturator, T6 : Tank of samples, TT: Thermo transmitter, TC: Thermo control, V1 : Gate valve solution,V2: Gate valve CO_2, V3: Gate valve (bypass), WWC: wetted wall column.

Data Evaluation

Based on data from experimental results and some of the literature, the reaction rate constants of promoter can be calculated as follows,

1. Calculation of gas - liquid contact time [7]

$$t = \frac{h}{U_s} = \frac{2h}{3}\left[\frac{3\mu}{g\rho}\right]^{1/3}\left[\frac{\pi d}{\nu}\right]^{2/3} \quad (7)$$

2. The calculation of the amount of gas absorbed per unit surface area for contact time (t) , and the average rate of absorption during t [7]:

$$\frac{Q(t)}{t} = \frac{q}{\pi dh} \quad (8)$$

Where

$$q = v \times ([CO_3^{2-}] + [HCO_3^-])$$

3. Calculation of $[OH^-]$ and $[CO_2]_e$ of the equilibrium reaction using equation [8]:

$$[OH^-] = \frac{K_W}{K_2}\frac{[CO_3^{2-}]}{[HCO_3^-]} \quad (9)$$

$$[CO_2]_e = \frac{K_c K_2}{K_{eq} K_1}\frac{[HCO_3^{2-}]^2}{[CO_3^{2-}]} \quad (10)$$

The value of K_W , K_1 and K_2 obtained from the following equation :

$$K_W = exp\left(39{,}555 - \frac{9{,}879\,x10^4}{T} + \frac{5{,}6883\,x10^7}{T^2} - \frac{1{,}465\,x10^{10}}{T^3} + \frac{1{,}3615\,x10^{12}}{T^4}\right) \quad (11)\ [8]$$

$$\log K_1 = -\frac{3404{,}7}{T} + 14{,}843 - 0{,}03279T \quad (12)\ [8]$$

$$K_2 = exp\left(-294{,}74 + \frac{3{,}6439\,x10^5}{T} - \frac{1{,}8416\,x10^8}{T^2} + \frac{4{,}1579\,x10^{10}}{T^3} - \frac{3{,}5429\,x10^{12}}{T^4}\right) \quad (13)\ [8]$$

$$K_{MDEA} = 2x10^9 \exp\left(\frac{-5797.8}{T}\right) \quad (14)$$

4. The calculation of the value of C_{Ai} obtained by trial kov , using equation (15)

$$C_{Ai} = \frac{k_g P_A + C_{Ae}\sqrt{D_{AL} k_{ov}}}{k_g H_e + \sqrt{D_{AL} k_{ov}}} \quad (15)$$

5. After C_{Ai} values obtained from equation (15) , then the value kov can be determined from equation [7]

$$\frac{Q}{t} = \bar{R} = (C_{Ai} - C_{Ae})\sqrt{D_{AL} x k_{ov}} \quad (16)$$

6. Determining the k_{app} value from the following equation:

$k_{app} = k_{ov} - k_{OH^-}[OH^-] - k_{MDEA}[MDEA]$ (17)

Where

$k_{app} = k_{glycine}[glycine]$ (18)

The value of k_{OH^-} can get from following equation [13]:

$$log_{10} k_{OH^-} = 13{,}635 - \frac{2895}{T} \quad (19)$$

7. The reaction rate constant of glycine($k_{glycine}$) is a function of temperature represented by the Arrhenius equation:

$$k_{glycine} = A_{glycine} e^{\frac{-E}{RT}} \quad (20)$$

Mass transfer and solubility data needed for data evaluation were obtained from the correlation in literatures [9], [10], [11] and [12].

$$k_g = \frac{Sh D_{AG}}{RTd} \quad (21)$$

Where

$$Sc = \frac{\mu_g}{\rho_g D_{AG}} \quad (22)$$

$$Re = \frac{\rho_g v d}{\mu_g} \quad (23)$$

$$Sh = 1.075\,(ReSc\frac{d}{h})^{0.85} \quad (24)$$

$$k_L = 0.422\sqrt{\frac{D_{AL} x \Gamma}{\rho\,(B_F{}^2)}} \quad (25)$$

$$D_A^L = 1{,}173\,x10^{-16}\sqrt{(\varphi M_W)}\frac{T}{\mu_W V_A^{0,6}} \quad (26)$$

$$\left(\frac{D_{A,T}^G}{D_{A,T0}^G}\right) = (\frac{T}{T_o})^{1,75} \quad (27)$$

$$H_{e\,T}^0 = H_{e\,298}^0 \exp\left(\frac{-d \ln kH}{d(1/T)} x \left(\frac{1}{T} - \frac{1}{298}\right)\right) \quad (28)$$

RESULTS

The results of this study can be depicted in Figure 3, 4, 5 and 6. Figure 3 shows the effect of temperature and promoter concentration on CO_2 absorption rate. The carbon dioxide absorption rate tends to increase with increasing temperature and the increase is slower for the higher promoter concentration. This phenomena can be explained that the kinetic energy of reactant molecule increase with increasing temperature. Moreover, the diffusivity of substance in gas and liquid phase increase with increasing temperature [13]. The absorption process is affected by mass transfer (diffusion) and chemical reaction phenomena. At low promoter concentration, the effect of chemical reaction is higher than the effect of diffusion. While at higher promoter concentration, the effect of diffusion is more significant. Increasing promoter concentration from 1% to 3 % will increase the absorption rate significantly.

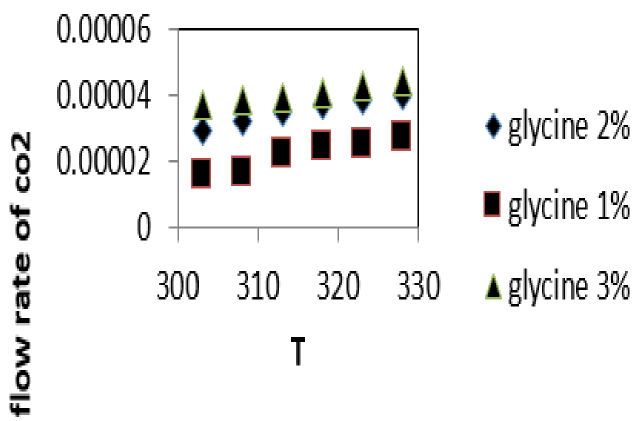

Fig. 3. The effect of the temperature and the concentration of promoter on the carbon dioxide absorption rate.

Reaction Rate Constant

The equation of reaction rate constant obtained from the results of this research is featured in two model that is glycine promoter reaction rate constant (k glycine) and apparent reaction constant rate (kapp). Fig. 4 shows the effect of temperature on overall reaction rate constant. This Figure shows that the reaction rate constant increase significantly with increasing temperature for promoter concentration of 2 and 3 %. The overall reaction rate constant consists of CO2 reaction with Glycine, hydroxyl ion and MDEA. The reaction rate constant for CO_2-OH^- and CO_2-MDEA system was determined from literature [14,16,17]. So, the reaction rate constant for promoter glycine can be calculated and shown in Fig. 5.

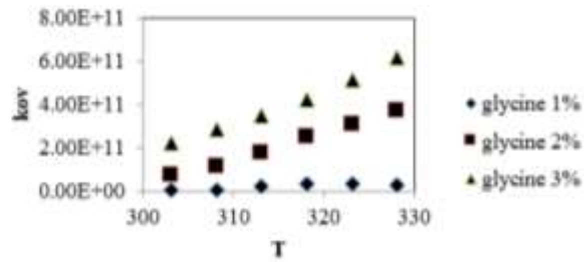

Fig. 4. The effect of the temperature and the concentration of promoter on overall constant rate reaction.

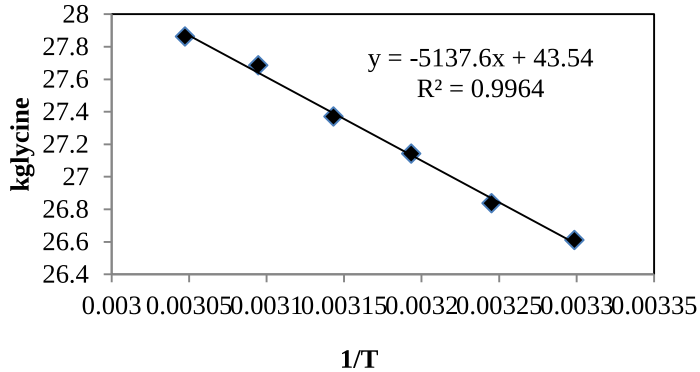

Fig. 5. The effect of the temperature and the concentration of promoter on promoter constant rate reaction

Reactivity of glycine as a promoter in the absorption of carbon dioxide can be determined from the reaction rate constants expressed by Arrhenius equation k =A*exp (-E/RT). In Figure 5, we obtained intercept for glycine that is in A = 43.54 and slope (-E/R) = -5137.6, so the equation kglycine = 8.113E+18exp (-5137.6 / T). From above equation obtained the regression value 0.9964 for glycine promoter and the activation energy is 42.714 kJ/kmol.

Reaction Rate Constant Apparent (KAPP)

From experiment calculation, the correlation of reaction rate constant apparent equation can be obtained (reaction rate constant of glycine promoter) function of temperature by used equation (18). The relation between temperature and ln kapp can be shown in fig (6)

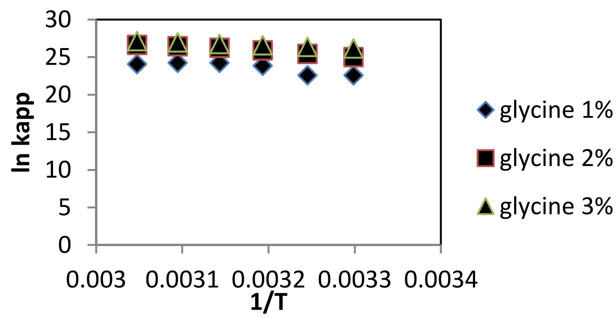

Fig. 6. The effect of the temperature and the concentration of promoter on ln kapp reaction rate constant apparent

The reaction rate constant apparent as function of temperature is expressed by Arrhenius equation, kapp=A*exp (-E/RT) where $A = 6.8234E + 15[glycine]^{-7.1956}$ and

$E = 24940203.91[glycine]^{-0.5158}$

Comparison between k glycine and rate constant for other promoters**:**

The reaction rate constant for CO_2 absorption using Glycine obtained from this study was compared with other solvent obtained from literature and shown in Table 1 and Figure 7.

Observed that glycine reaction rate constant is too bigger than mono ethanolamine and methyl di ethanolamine constant rate at the deference temperatures.

TABLE 1
COMPARISON OF REACTION RATE CONSTANT FOR CARBON DIOXIDE ABSORPTION WITH SEVERAL

Promoter	Value of k (L/mol.s)	References
Glycine	$8.113\ x\ 10^{18}\exp(\frac{-5137.6}{T})$	This study
MEA	$9{,}56\ x\ 10^{8}\exp(\frac{-3802{,}4}{T})$	[15]
MDEA	$2{,}58\ x\ 10^{8}\exp(\frac{-3736{,}5}{T})$	[15]

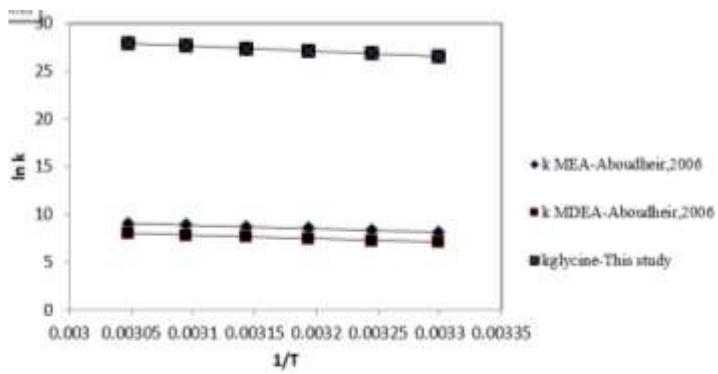

Fig. 7. Comparison of k glycine with the rate constant for other promoter

CONCLUSION AND RECOMMENDATIONS

Based on the result of this study, we observed that by increasing temperature and concentration of glycine, the absorption rate of carbon dioxide in MDEA solution will increase, In addition the reaction rate constant was affected by the temperature and the concentration of promoter. The correlation of reaction rate constant k glycine is: k glycine =8.113E+18exp(-5137.6/T) with activation energy for glycine promoter is 42.714 kJ/kmol, and the correlation of reaction rate constant apparent for reaction of CO2 with glycine depending of concentration of the glycine is the correlation kapp=A*exp (-ER/T) where:

$$A = 7.49894E + 13[\text{glycine}]^{-0.2266}$$

$$E = 28853599.55[\text{glycine}]^{-0.0979}$$

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