

Kinetics of CO₂ Absorption into Aqueous MDEA Solution Promoted by Mixture of Potassium Salt of *l*-Arginine and *l*-Glutamic Acid

Toto Iswanto[#], Ali Altway[#], Maya Shovitri⁺, Muhammad Haikal[#], Septiani Ayustiningrum[#], Tri Widjaja^{##}

[#]Department of Chemical Engineering, Faculty of Industrial Technology, Institut Teknologi Sepuluh Nopember, Surabaya, 60111, Indonesia
E-mail: *triw@chem-eng.its.ac.id

⁺Department of Biology, Faculty of Science, Institut Teknologi Sepuluh Nopember, Surabaya, 60111, Indonesia

Abstract—Amino acid salt can be a promising alternative as the promoter for increasing the absorption kinetics rate of MDEA toward CO₂. In this study, the absorption kinetics of carbon dioxide (CO₂) into an aqueous 40 wt% equivalent Methyldiethanolamine (MDEA) solution promoted by 1 and 5 wt% of mixed amino acid salt, potassium salt of *l*-arginine (*Arg*) and *l*-glutamic acid (*Glu*), was performed using a wetted wall column at temperatures from 303.15 to 323.15 K. Effect of various mixture ratios of those promoters on the reaction rate parameters and its physicochemical properties was investigated based on the fast pseudo-first-order regime. The reaction between CO₂ and amino acid was described with the zwitterionic mechanism. Aqueous MDEA without promoter was set as the control. The result revealed that the mixed promoter has affected to increase CO₂ absorption rate into the aqueous MDEA solution compared with the control and using the single promoter due to the interaction between *Arg* and *Glu*. In addition, the overall reaction rate constant, k_{ov} , significantly increased with the increase of mixed promoter concentration and temperature under the investigated range. The aqueous MDEA solution promoted by 5% of mixed *Arg* and *Glu* in 1:1 ratio was obtained as the best CO₂ absorbent.

Keywords— CO₂ absorption kinetics; *l*-arginine; *l*-glutamic acid; MDEA; mixed promoter; wetted wall column.

I. INTRODUCTION

Nowadays, biogas as renewable and sustainable energy receives significant attention due to its potential utilization innovations which can be used in the various commercially feasible methods such as electricity generation; transport fuel; and multigeneration of heat, steam, electricity, and cooling in industry. Moreover, biogas can be utilized for energy storage applications; to stabilize intermittently operated wind and solar renewable energy systems or in cooking and lighting applications in rural districts [1]. However, the presence of CO₂ as major gas products in biogas, besides methane (CH₄), has given disadvantages because of its corrosive nature that can destroy pipelines and equipment. CO₂ also reduces the heating value of biogas due to its role as an inert gas in terms of combustion [2], [3]. The biogas which contains 60 vol% of CH₄ and 40 vol% of CO₂ has a low heat value (LHV) of 17,717 (kJ kg⁻¹) or about 2.9 times lower than 100 vol% CH₄ gas which has the LHV of 50,200 (kJ kg⁻¹) [4]. Therefore, CO₂-capture technologies are so essential prior to that biogas utilization.

One of that technologies is based on the chemical absorption process which has widely employed due to its higher capture efficiencies even at low concentrations of CO₂, higher selectivity and lower cost than the other

processes [5]. In chemical absorption, a solvent with high CO₂ loading capacity and low regeneration energy is an interesting topic to be developed recently. In this case, MDEA was reported has a higher CO₂ loading capacity compared to commonly used alkanolamine such as monoethanolamine (MEA) and diethanolamine (DEA). In addition, it is not corrosive to carbon steel and has lower energy requirements for regeneration, lower solvent degradation rate compared to MEA and DEA, and high selectivity toward H₂S as the trace element in raw biogas [6], [7]. Unfortunately, its reaction rate to CO₂ is lower than MEA and DEA. Therefore, the suitable alternative promoters to improve its reaction rate are highly needed.

Amino acid salts have been investigated to obtain a promising alternative promoter due to their oxidative stability and negligible volatility [8]. Furthermore, it has favorable biodegradation properties which make it environmentally friendly [9]. Many kinds of amino acid salts such as potassium salt of *l*-arginine, *l*-glutamic acid, *l*-proline, *l*-ornithine, methionine, β -alanine, sarcosine, glycine, lysinate, taurine, and 6-Aminohexanoic acid have been used as a single promoter in the aqueous amine and alkanolamine solution to absorb CO₂ [9]–[11]. To the best of our

knowledge, one of which was never used with others as a mixed promoter in MDEA solution.

In this study, the potassium salt of *Arg* and *Glu* were selected as a mixed promoter in aqueous 40 wt% equivalent MDEA solution to capture CO₂ under the biogas circumstance. *Arg* is an expensive amino acid which has a higher CO₂ absorption kinetics rate and apparent rate constant than *Glu*. In contrast, *Glu* has a relatively low pKa value and high overall rate constant which is potentially good for minimizing energy requirements during the regeneration or desorption process. Therefore, their combination was hypothesized to give a better CO₂ absorption process at a lower cost. Therefore, this study aims to investigate the effect of utilization of mixed *Arg* and *Glu* as promoter at various ratio and temperature on the kinetics of CO₂ absorption into the MDEA solution and to determine the reaction rate constant of each promoter in aqueous MDEA/*Arg*/*Glu* solution system to evaluate its performance as a mixed promoter.

II. MATERIALS AND METHOD

A. Chemical

L-arginine (≥99% purity) and l-glutamic acid (≥99% purity) were purchased from Sigma Aldrich. MDEA was received with a given purity of ≥98%. A mixed gas of CO₂ and N₂ have been used with the fixed volumetric concentration ratio of CO₂ to N₂ at 40:60. The high concentration of CO₂ in the gas feed was adapted to typical biogas characteristic. Nitrogen has been used to substitute methane gas, which is acceptable due to the same characteristic as inert gas toward the absorbent solution. Potassium hydroxide (KOH), sodium hydroxide, hydrogen chloride, barium chloride, sodium borate, oxalic acid, and other chemicals used for titration analysis were purchased from Merck.

B. Experimental section

The experiment was conducted at 303.15, 313.15, 323.15, and 333.15 K using a wetted wall column (WWC) under modified design from the previous work of [12]. WWC's dimension and other supporting apparatus in the present study are presented in Fig. 1. The absorbent solution was made by mixing an aqueous 40 wt% equivalent MDEA solution supplemented by 1 or 5 wt% of mixed *Arg* and *Glu*

with the ratio of 1:0, 0:1, 1:1 and 1:2. Aqueous MDEA solution without promoter was set as a control. *Arg* and *Glu* have been deprotonated using equimolar of KOH, forming the amino acid salt solution which is more reactive toward CO₂. The temperature of the absorbent solution was adjusted using a hot water bath. After reaching out the operating temperature, it was pumped to overflow tank and prepared to enter the WWC. Mixed gas from the mixed gas tank was firstly saturated with water vapor in a saturator tank to easily maintain the balance CO₂ mass during CO₂ absorption. That absorbent solution and mixed gas were set in 200 mL min⁻¹ and 6 L min⁻¹, respectively using mass flow controller before introducing to the WWC. The process phenomenon in WWC has been explained in detail by [13]. For short, it can allow counter-current contact between a falling thin liquid film and a flowing gas stream with a measurable surface area of the column for accurate measurements of CO₂ flux into the solution.

C. Analysis

To determine the absorption rate of CO₂ (*q*) into the absorbent solution, CO₂ concentration in liquid samples before and after contacting process in the WWC has been analyzed and calculated by equation (1). The liquid sample was drawn from the WWC outlet when the system reached steady state condition. The concentration of free dissolved CO₂ and RNHCOO⁻ in the liquid sample was analyzed using the method as described by [14] which allowed converting those species to HCO₃⁻, then to CO₃²⁻ using excess NaOH. An excess amount of 0.5M barium chloride (BaCl₂) solution was added into the sample to precipitate all carbonate in form of BaCO₃. Then, that precipitation was filtered using vacuum filtration through a 0.45 Millipore filter and dissolved with a known volume of 0.1M HCl in excess. The remaining excess amount of HCl was calculated using titration with NaOH in the presence of methyl orange as an endpoint indicator.

$$q = v ([CO_2]_{\text{final}} - [CO_2]_{\text{initial}}) \quad (1)$$

The pH of the liquid sample was determined by pH-meter from Laqua (HORIBA Advanced Techno Co. Ltd). Its density and viscosity were measured using pycnometer and Ostwald viscometer, respectively, to estimate the liquid-film thickness and the contact time in the WWC [15].

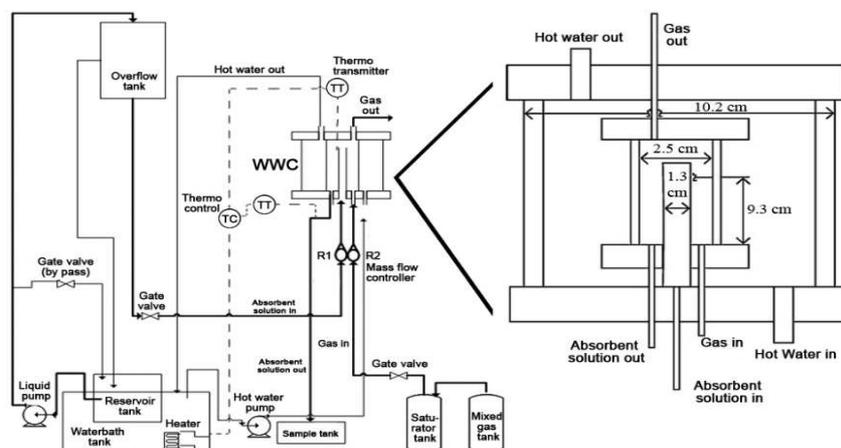


Fig. 1 WWC dimension and its other supporting apparatus.

D. Reaction Kinetic Measurements

MDEA is a tertiary amine group while *l*-arginine and *l*-glutamic acid are amino acids which more reactive toward CO₂. The molecular structure of MDEA, *Arg*, and *Glu* are presented in Table I.

TABLE I
MOLECULAR STRUCTURE OF THE SPECIES IN ABSORBENT SOLUTION

Name of species	Molecular Structure	pKa	Ref.
MDEA		8.62	[16]
<i>l</i> -Arginine		2.01 (-COOH) 9.04 (-NH3 ⁺) 13.8 ± 0.1 (R group)	[13] [17]
<i>l</i> -Glutamic acid		9.98	[11]

If these amino acid are dissolved in water, the amino group will be completely protonated. The ionic equilibrium of the amino acids is shown in equation (2) [11].



In aqueous solutions, the reaction of CO₂ with amino acid, *Arg* and *Glu* (denoted by RNH₂), is similar with primary and secondary alkanolamines because they have the same functional groups [11], as written below:



where k_{RNH_2} is k_{promoter} as described in the equation (44).

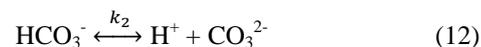
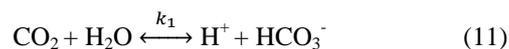
The direct reaction between CO₂ with *Arg* and *Glu* results in the zwitterion intermediate as shown in equation (4). Then, the zwitterion is deprotonated by the bases (B) in the solution such as OH⁻, guanidinium group in the side chain of arginine (see Table I), H₂O, and MDEA.



Furthermore, a reaction of carbamate reversion could be occurred during the process, to form bicarbonate. Its overall reaction is written in equation (8) which is not possibly resulted by direct reaction with water. It is suggested that reaction has resulted from the competing mechanisms of carbamate formation and the bicarbonate formation. Reference [18] described that the sum of the reverse carbamate formation and the bicarbonate formation in equation (6) and (7), respectively, gives the explanation for that carbamate reversion.



CO₂ gas was absorbed into aqueous MDEA solution and the stoichiometry and equilibrium reaction are described as the following equations;



Where,

$$K_{\text{MDEA}} = \frac{C_{\text{MDEAH}^+} \cdot C_{\text{HCO}_3^-}}{C_{\text{CO}_2} \cdot C_{\text{MDEA}}} \quad (14)$$

$$K_w = C_{\text{H}^+} \cdot C_{\text{OH}^-} \quad (15)$$

$$K_1 = \frac{C_{\text{HCO}_3^-} \cdot C_{\text{H}^+}}{C_{\text{CO}_2}} \quad (16)$$

$$K_2 = \frac{C_{\text{CO}_3^{2-}} \cdot C_{\text{H}^+}}{C_{\text{HCO}_3^-}} \quad (17)$$

$$K_3 = \frac{C_{\text{MDEAH}^+}}{C_{\text{MDEA}} \cdot C_{\text{H}^+}} \quad (18)$$

In the present study, there were several assumptions to measure the kinetic reaction value.

1. The concentration of formed bicarbonate that became carbonate was very small. Hence its concentration was equal to MDEAH⁺ concentration.
2. Promoter concentration is constant.

By rearranging the equations (14)-(18), C_{OH^-} and $C_{\text{CO}_2,e}$ could be determined as the equation (19) and (20), respectively:

$$C_{\text{OH}^-} = \frac{K_w \cdot C_{\text{CO}_3^{2-}}}{K_2 \cdot C_{\text{HCO}_3^-}} \quad (19)$$

$$C_{\text{CO}_2,e} = \frac{K_2 K_3 \cdot (C_{\text{HCO}_3^-})^2}{K_{\text{MDEA}} \cdot C_{\text{CO}_3^{2-}}} \quad (20)$$

Then K_w was determined as below [19]:

$$K_w = \exp(140.932 - \frac{13445.9}{T} - 22.4773) \quad (21)$$

K_1 and K_2 were obtained from equation (22) and (23), respectively [20]. K_3 was determined by equation (24), as described by [10, 11]

$$K_1 = \exp(235.482 - \frac{12092.1}{T} - 36.7816 \ln T) \quad (22)$$

$$K_2 = \exp(220.067 - \frac{12431.7}{T} - 35.4819 \ln T) \quad (23)$$

$$K_3 = \frac{1}{10^{(-14.01+0.0184T)}} \quad (24)$$

$$K_{\text{MDEA}} = K_1 K_3 \quad (25)$$

The following reaction mechanisms have also occurred in the solution:



For Solution pH > 8, the reaction (26) could be ignored, and the reaction (27) is predominant and a limiting reaction rate.

The forward reaction is pseudo first order, and the reverse reaction rate is constant. Hence, its reaction rate is

$$r_{CO_2-OH^-} = k_{OH^-} C_{OH^-} (C_{CO_2} - C_{CO_2,e}) \quad (28)$$

which k_{OH^-} have been explained by [22] as:

$$\log_{10} k_{OH^-} = 13.635 - \frac{2895}{T(K)} \quad (29)$$

Diffusivity coefficient in the gas and liquid phase was defined by the following equation (30) [23] and (31), respectively:

$$D_{AG} = \left(\frac{T}{298,15 K} \right)^{1,75} \times 0,167 \times 10^{-4} \quad (30)$$

$$D_{AL/BL} = 1,173 \times 10^{-16} \sqrt{(\varphi M_B)} \frac{T}{\mu_B V_A^{0,6}} \quad (31)$$

Mass transfer coefficient at the gas side (k_g) was measured by equation (32) [24]:

$$k_g = \frac{Sh D_{AG}}{R T h} \quad (32)$$

where,

$$Sc = \frac{\mu_g}{\rho_g D_{AG}} \quad (33)$$

$$V = \frac{4 \times Q_G}{\pi \times d^2} \quad (34)$$

$$Re = \frac{\rho_g v h}{\mu_g} \quad (35)$$

$$Sh = 1.075 (Re Sc \frac{d}{h})^{0,85} \quad (36)$$

Solubility data were obtained from Henry's equation below [25]:

$$\log \left(\frac{He}{He^0} \right) = h_1 I_1 + h_2 I_2 \quad (37)$$

$$H_{eT}^0 = H_e^0 298 \exp \left(\frac{-d \ln kH}{d(\frac{1}{T})} \times \left(\frac{1}{T} - \frac{1}{298} \right) \right) \quad (38)$$

where $\left(\frac{-d \ln kH}{d(\frac{1}{T})} \right)$ for CO₂ was 2400 K [26].

The concentration of carbon dioxide in the solution interface, $C_{CO_2,i}$, was determined by the trial of k_{ov} using equation (39):

$$C_{CO_2,i} = \frac{k_g P_A + C_{CO_2,e} \sqrt{D_{AL} k_{ov}}}{k_g H_e + \sqrt{D_{AL} k_{ov}}} \quad (39)$$

After determining the value of $C_{CO_2,i}$, k_{ov} has been determined using the following equations [22]:

$$\varphi = \left(\frac{\frac{Q}{T} \times k_g \times H_e}{k_g P_A - C_{Ae} k_g H_e - \frac{Q}{T}} \right) \quad (40)$$

$$\varphi = \sqrt{D_{AL} \times k_{ov}} \quad (41)$$

From previous research by [27], k_{MDEA} was determined by equation (9) where $k_{MDEA} = 4,01 \times 10^8 \exp(-5400/T)$. The overall reaction (r_{ov}) could be defined as the equation (42), as reported by [13]:

$$r_{ov} = k_{ov} (C_{CO_2} - C_{CO_2,e}) \quad (42)$$

Where k_{ov} is the constants of reaction rate for overall pseudo first order:

$$k_{ov} = k_{OH^-} C_{OH^-} + k_{app} C_{promoter} + k_{MDEA} C_{MDEA} \quad (43)$$

$$k_{app} C_{promoter} = k_{ov} - k_{OH^-} C_{OH^-} - k_{MDEA} C_{MDEA} \quad (44)$$

where,

$$k_{app} C_{promoter} = k_{Arg} C_{Arg} + k_{Glu} C_{Glu} \quad (45)$$

The individual reaction rate constants of k_{Arg} and k_{Glu} were expressed by the Arrhenius equation:

$$Y = B + m X_1 \quad (46)$$

where,

$$k_{promoter} = A_{promoter} e^{\frac{-E}{RT}} \quad (47)$$

Equation (46) was modified to be equation (48):

$$\ln k_{promoter} = \ln A_{promoter} - \frac{E}{RT} \quad (48)$$

thus,

$$Y = \ln k_{promoter}; B = \ln A_{promoter}; m = \frac{E}{R} \text{ and } X_1 = \frac{1}{T} \quad (49)$$

III. RESULTS AND DISCUSSION

A. Effect of the mixed promoter on density, viscosity, and CO₂ absorption rate

Density, viscosity, and CO₂ absorption rate have been investigated for aqueous 40 wt% equivalent MDEA solution promoted by 1 wt% and 5 wt% of mixed *Arg* and *Glu* with different ratios at the temperature of 303.15, 313.15, and 323.15 K, as listed in Table II. pH of the sample during the steady-state condition was in the range of 10.6-11.03.

The results revealed that the promoter concentration and temperature certainly influence the density, viscosity, and CO₂ absorption rate. At the same mixed promoter's concentration and ratio, density and viscosity decreased as temperature increase. In contrast, CO₂ absorption rates increased as temperature and promoter concentration increase (see Fig. 2). That was occurred due to the increase of molecular kinetic energy that took effects on the acceleration of reacted molecular substances [28], and therefore caused the faster absorption reaction of CO₂ into the absorbent solution.

In addition, it was caused by the presence of amine group in the chain of *Arg* and *Glu* which allow to react quickly with CO₂ to form zwitterions and transfer protons to MDEA [29]. Hence, the absorption rate of CO₂ was increased greatly, compared with the aqueous MDEA (only) solution. The zwitterionic mechanism was presented in equation (4).

The contact time (t_c), has been derived from the WWC hydrodynamics, Equation (50) [22]. It showed the time needed to contact between the gas and absorbent solution in the WWC. The measured t_c are presented in Table II.

$$t_c = \frac{h}{U_s} = \frac{2h}{3} \left(\frac{3\mu}{g\rho} \right)^{1/3} \left(\frac{\pi d}{v} \right)^{2/3} \quad (50)$$

TABLE II
DENSITY AND VISCOSITY OF 40 WT% EQUIVALENT MDEA WITH MIX PROMOTER

Properties	T(K)	Arg:Glu ratio for 1 wt%				Arg:Glu ratio for 5 wt%			
		1:0	0:1	1:1	1:2	1:0	0:1	1:1	1:2
Density (kg m ⁻³)	303.15	1040.3	1039.0	1039.4	1040.9	1049.6	1055.8	1049.5	1052.2
	313.15	1039.2	1038.5	1038.7	1040.7	1049.3	1054.8	1048.8	1052.0
	323.15	1038.1	1036.8	1037.8	1038.1	1048.8	1054.0	1046.4	1047.2
Viscosity (mPa s)	303.15	5.813	4.405	4.984	4.634	4.903	4.907	4.908	5.680
	313.15	5.187	3.833	4.216	4.052	4.316	4.338	4.320	5.126
	323.15	4.988	3.644	4.016	3.857	4.120	4.144	4.130	4.941
t _c (s)	303.15	0.39	0.36	0.37	0.37	0.37	0.37	0.37	0.39
	313.15	0.38	0.34	0.35	0.35	0.36	0.36	0.36	0.38
	323.15	0.37	0.34	0.35	0.34	0.35	0.35	0.35	0.37

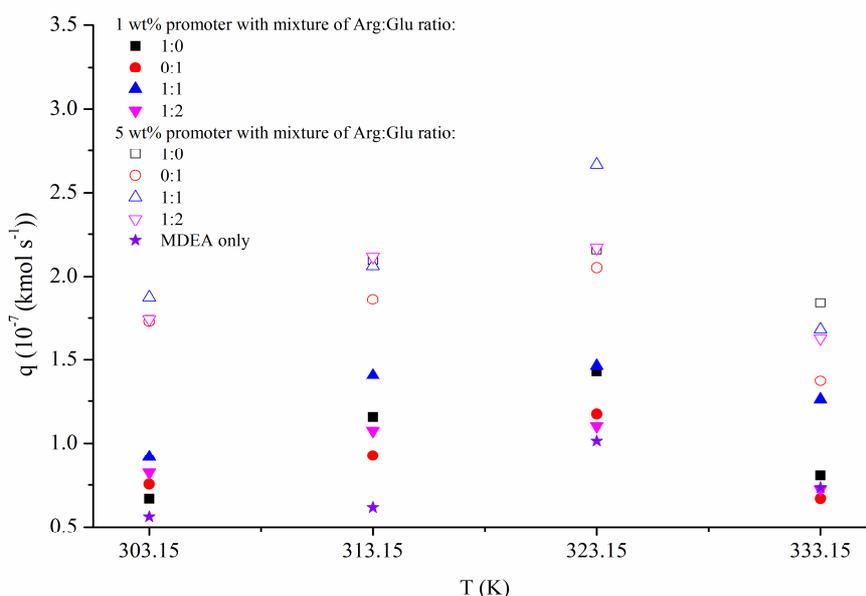


Fig. 2 CO₂ Absorption rate in 40 wt.% equivalent MDEA with different of Arg:Glu ratio for 1 wt% and 5 wt% of mixed promoter

The CO₂ absorption rate was calculated using equation (1) and shown in Fig. 2 which demonstrates the obvious effect on absorption behavior. The addition 1 wt% of single promoter presented in Arg:Glu (1:0 ratio) has a better CO₂ absorption rate than Arg:Glu (0:1 ratio) in along with the rise of temperature. Arg shows a high absorption rate because it has the primary amino group and a guanidinium group in its side chain, causing a pKa value higher than Glu. The basicity of an amine (pKa) can affect the CO₂ reaction rate of the amine to form a carbamate, catalyzes the hydration of CO₂, and promotes the amine to accept a proton. Where the higher pKa value will lead to an increase of k_{app} value and maximise the initial CO₂ absorption rates [9]. The conjugation of double bonded nitrogen and nitrogen lone pairs in the guanidinium group is able to delocalize positive charge to participate in multiple hydrogen bonds with water, which would be helpful to form the carbamate and promote the CO₂ absorption [13]. However, another study has also stated that the high pKa would probably require larger energy input in the desorption process [11]. This is a consideration for further applications of Arg. Therefore, using a cheaper promoter with a relatively low pKa such as Glu in their mixture would come as a good strategy because

their CO₂ absorption rate was higher than those as a single promoter.

In this investigation, the mixture of Arg and Glu with 1:1 ratio has resulted in the highest CO₂ absorption rate in both of addition 1 wt% and 5 wt% of a mixed promoter. For 1 wt% of the mixed promoter with 1:1 ratio, CO₂ absorption rate showed a satisfied performance than the addition of 1 wt% of Arg as a single promoter. However, its value was not a significant difference in CO₂ absorption at 323.15 K. in contrast with the addition 5 wt% of the mixed promoter which obtained a higher CO₂ absorption rate with the promoter ratio of 1:1 at 323.15K.

The mixed promoter ratio of 1:1 has given close CO₂ absorption rate with Arg as a single promoter, which means that Arg substitution by Glu has given a saving of cost. In this experiment, the CO₂ absorption rate for aqueous MDEA without promoter was obtained 0.6159 x 10⁻⁷ kmol s⁻¹ at 313.15K. In the same temperature, the addition of 1 and 5 wt% of mixed promoter with 1:1 ratio has been increasing the CO₂ absorption rate to 1.404 x 10⁻⁷ kmol s⁻¹ (~2.3 times higher) and 2.0622 x 10⁻⁷ kmol s⁻¹ (3.35 times higher), respectively than 40% equivalent aqueous MDEA without promoter. This result was in accordance with the experiment proven by [30]. Amino acid has the same function with a

primary amine which was the most reacted amine towards CO₂ because it has more hydrogen cluster to be protonated.

The Reaction between CO₂ and amino acid was stable and faster than the reaction between CO₂ and alkanolamine [11].

TABLE III
FAST PSEUDO-FIRST ORDER EVALUATION ON 40 WT% EQUIVALENT MDEA WITH MIX PROMOTER

Properties	T(K)	Arg:Glu ratio for 1 wt%				Arg:Glu ratio for 5 wt%			
		1:0	0:1	1:1	1:2	1:0	0:1	1:1	1:2
k_L ($\times 10^{-5} \text{ m.s}^{-1}$)	303.15	8.64	9.05	8.87	8.98	8.91	8.91	8.91	8.69
	313.15	9.89	10.4	10.24	10.31	10.22	10.22	10.21	9.93
	323.15	11.05	11.64	11.46	11.53	11.43	11.43	11.42	11.08
Hatta Number	303.15	20.1	22.1	28.6	24.8	67.5	67	76.2	69.4
	313.15	44.5	31.9	56	38.9	105	85.9	101.7	109.4
	323.15	68.2	49.3	68.1	45.9	128.1	116.7	196.4	109.4
$\frac{1}{2} E_i$	303.15	105.4	107.6	111.7	109.3	144	143.1	150.2	109.4
	313.15	153.7	144.9	164.5	150.4	211.8	194.6	208.6	109.4
	323.15	212	197.1	214.1	193.2	279.5	267.3	345.4	109.4

However, the CO₂ absorption rate sharply decreased at the temperature of 333.15 K. This phenomena was also found in the study of [30]. They reported that when the lean amine temperature reaches about 330.15 to 333.15 K, the solubility of CO₂ in the amine solution will decrease and usually become the overriding factor, and the net CO₂ pickup will begin to decrease. In that condition, the solubility will take over in the determination of absorption rate, not reaction kinetic anymore. Moreover, that was probably caused by MDEA degradation which can be occurred at that temperature range.

B. Fast Pseudo-first Order Evaluation

The reaction of CO₂ absorption into MDEA solution with a mixture of Arg/Glu promoter was investigated based on the fast pseudo-first order reaction regime. The regime must be satisfied with this condition, $3 < Ha$ (Hatta number) $\ll \frac{1}{2} E_i$, where the Hatta number was calculated by the following equation:

$$Ha = \frac{\sqrt{D_{CO_2} k_{ov}}}{k_L} \quad (51)$$

Where k_L has been determined using equations below:

$$k_L = \sqrt{\frac{4 \times D_{AB} \times V_{max}}{\pi h}} \quad (52)$$

$$V_{max} = \frac{\rho g \delta^2}{2\pi} \quad (53)$$

$$\delta = \left(\frac{3\mu\theta}{\rho g \pi D} \right)^{1/3} \quad (54)$$

E_i is an infinite enhancement factor. It is dimensionless and formulated as follow :

$$E_i = \sqrt{\frac{D_{AL}}{D_{BL}} + \frac{C_{R_3N}}{z \cdot C_{CO_2,i}} \sqrt{\frac{D_{BL}}{D_{AL}}}} \quad (55)$$

All Hatta numbers of the absorbent have satisfied the required condition of fast pseudo-first order reaction regime (see Table III), which those numbers have more than 3 and much less than $\frac{1}{2} E_i$.

C. Kinetic Data

In the previous chapter, a higher CO₂ absorption rate was obtained in 40 wt% equivalent MDEA with addition 5 wt% of the promoter. The value of r_{ov} , k_{ov} , and k_{app} for this promoter concentration were calculated using equation (42), (43), and (44), respectively at 303.15, 313.15, and 323.15 K. The value of r_{ov} and k_{app} are listed in Table IV. While the overall absorption kinetics constant (k_{ov}) is displayed in Fig. 3. It reveals that the highest r_{ov} , k_{ov} , and k_{app} value were obtained from the ratio 1:1 which this composition could be used as recommended consideration for further applications.

TABLE IV
KINETICS DATA IN 40 WT% EQUIVALENT MDEA WITH VARIOUS MIXED PROMOTER RATIOS

Properties	T (K)	Arg:Glu ratio for 5 wt%			
		1:0	0:1	1:1	1:2
r_{ov}	303.15	753	669	724	644
	313.15	2474	1357	1670	2234
	323.15	4162	3043	9331	3720
k_{app} (s^{-1})	303.15	15610	15390	19926	15739
	313.15	39422	26372	36964	40485
	323.15	59640	49410	139985	60305

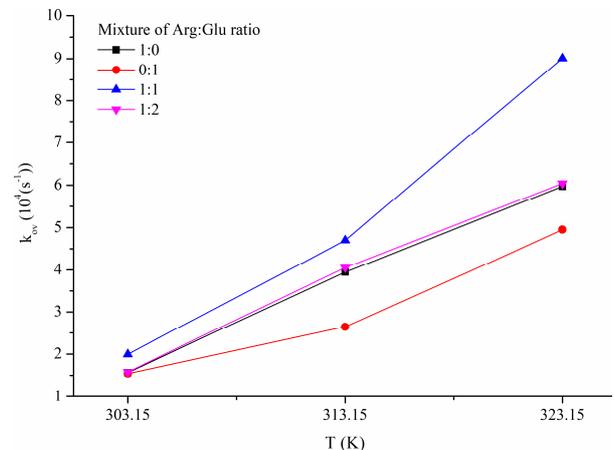


Fig. 3 k_{ov} values in 40 wt% equivalent MDEA with 5 wt% of the mixed promoter at the different ratio as a function of temperature.

The value of reaction rate constant of *Arg* and *Glu* as a mixed promoter in CO₂ absorption can be evaluated from measured k_{app} at all variables of promoter concentration and mixture ratio under the investigated temperature, as shown in the equation (45). First, k_{Arg} and k_{Glu} in the absorbent solution and the same temperature was calculated using multiple linear regression which evaluate the effect of one or some variables to other variables, as presented in equation (56) and (57). Then, the predicted k_{app} (k_{app}') can be formulated as equation (58) and compared with measured k_{app} to find out the calculation error.

$$\sum k_{app} C_{Arg} = k_{Arg} \sum C_{Arg}^2 + k_{Glu} \sum C_{Arg} C_{Glu} \quad (56)$$

$$\sum k_{app} C_{Glu} = k_{Arg} \sum C_{Arg} C_{Glu} + k_{Glu} \sum C_{Glu}^2 \quad (57)$$

$$k_{app}' = k_{Arg} C_{Arg} + k_{Glu} C_{Glu} \quad (58)$$

To determine the value of reaction rate constant of *Arg* and *Glu* as a single promoter (k_{Arg}' or k_{Glu}') in the absorbent solution, the general linear model was used with the variable data of 1 and 5 wt% from the ratio 1:0 for *Arg* and 0:1 for *Glu*.

$$k_{promoter}' = \frac{\sum C_{promoter} k_{app}}{\sum C_{promoter}^2} \quad (59)$$

$$k_{app}' = k_{promoter}' C_{promoter} \quad (60)$$

Finally, the k value of each promoter either as a mixed promoter or single promoter has been obtained.

In this study, $k_{promoter}$ as a function of temperature over the investigated range were correlated using Arrhenius equation as shown in Fig. 4 with R^2 value for k_{Arg} , k_{Glu} , k_{Arg}' , and k_{Glu}' are 0.983, 0.997, 0.999, and 0.996, respectively. The results are listed in Table V and Fig. 5.

TABLE V
REACTION RATE CONSTANT OF THE SPECIES FROM THIS STUDY AND OTHER REFERENCES

Name of Species (solution system)	k ($m^3 kmol^{-1} s^{-1}$)	References
MDEA (MDEA/MEA solution)	$2.58 \times 10^8 \exp(-3736.5/T)$	[31]
MDEA (MDEA solution)	$1.146 \times 10^{16} \exp(-9567.053/T)$	This study
<i>Arg</i> (K_2CO_3/Arg solution)	$2.58 \times 10^{16} \exp(-8645/T)$	[13]
<i>Arg</i> (MDEA/Arg/ <i>Glu</i> solution)	$2.041 \times 10^{15} \exp(-7396/T)$	This study
<i>Glu</i> (MDEA/Arg/ <i>Glu</i> solution)	$6.48 \times 10^{13} \exp(-6378.3/T)$	This study
<i>Arg'</i> (MDEA- <i>Arg</i> solution)	$2.22 \times 10^{14} \exp(-6725.7/T)$	This study
<i>Glu'</i> (MDEA- <i>Glu</i> solution)	$8.10 \times 10^{12} \exp(-5774.4/T)$	This study

Fig. 5 shows k_{Arg} in the aqueous MDEA/Arg/*Glu* solution system has the highest reaction rate constant in CO₂ absorption than the other solution systems. It also exhibits that *Arg* and *Glu* as a mixed promoter have a higher reaction

rate constant of CO₂ absorption compared to theirs as a single promoter.

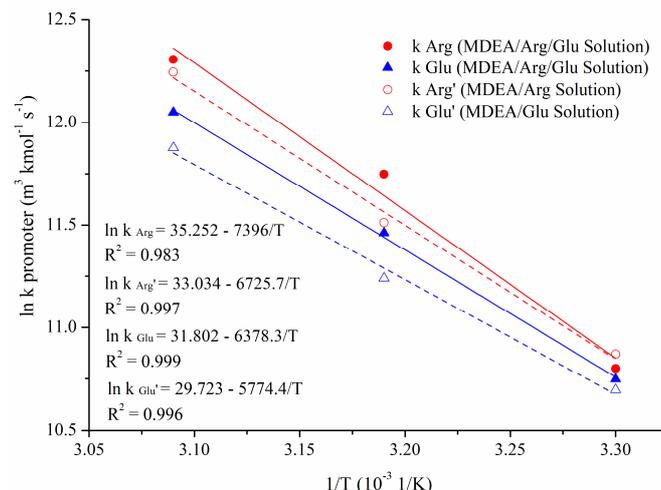


Fig. 4 Arrhenius plot of k_{Arg} , k_{Glu} , k_{Arg}' , and k_{Glu}' for 40% equivalent MDEA promoted by a mixture and single promoter.

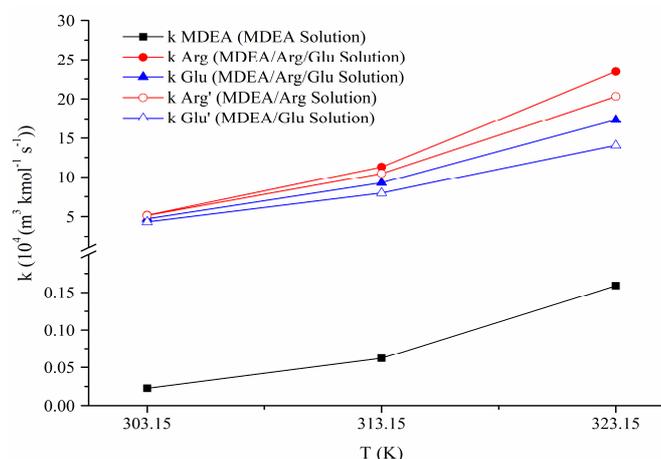


Fig. 5 Plot reaction rate constant of CO₂ absorption (k) as a function of temperature.

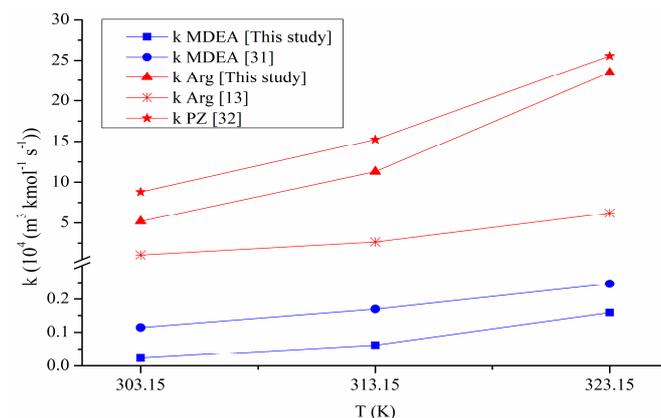


Fig. 6 Correlation between the temperature and k value of MDEA and other promoters resulted from this study and the literature

Correlation between temperature and k value in various absorbent and promoter resulted from the present study and the literature were shown in Fig. 6. It reveals that k_{MDEA} obtained in the present study has slightly the same value with the previous work of [31]. The value of k_{Arg} in MDEA/Arg/*Glu* solution was higher compared to k_{Arg} in

K₂CO₃/Arg solution system, investigated by [13], but still lower compared to k_{PZ} in MDEA/Piperazine (PZ) system, investigated by [32]. In spite of that fact, Arg was environmentally friendly and less toxic than PZ [13]. Therefore, it can be considered as a good candidate promoter.

IV. CONCLUSION

The overall absorption rate constant, k_{ov}, significantly increased with the increase of mixed promoter concentration (1 to 5 wt %) and temperatures from 303.15 to 323.15 K. The absorbent solution with 5 wt% mixed promoter with mixture ratio of 1:1 has given the highest CO₂ absorption rate and resulted in a higher reaction rate constant than Arg as a single promoter at the same concentration in 40% of aqueous MDEA solution. The results exhibited that mixed promoter could significantly increase the kinetics of CO₂ absorption compared with using a single promoter that was probably caused by the presence of the interaction between Arg and Glu in the aqueous MDEA solution. The reaction rate constant of MDEA, Arg, and Glu during CO₂ absorption into aqueous 40% equivalent MDEA promoted by mixed amino acid salt of Arg and Glu was described as the following equation:

$$k_{\text{MDEA}} = 1.146 \times 10^{16} \exp(-9567.053/T);$$

$$k_{\text{Arg}} = 2.041 \times 10^{15} \exp(-7396/T); \text{ and}$$

$$k_{\text{Glu}} = 6.48 \times 10^{13} \exp(-6378.3/T).$$

ACKNOWLEDGMENT

The authors would like to thank LPPM ITS and all members of Biochemical Technology Laboratory and Heat and Mass Transport Laboratory, Department of Chemical Engineering for the help and support. This research was founded by PMDSU scholarship program from The Ministry of Research, Technology, and Higher Education of the Republic of Indonesia [grant number 482/PKS/ITS/2017, 2017].

NOMENCLATURE

D_{AL}	diffusivity of CO ₂ in water	m ² s ⁻¹
D_{BL}	diffusivity of MDEA in water	m ² s ⁻¹
D_{CO_2}	diffusivity of a CO ₂ in the solvent	m ² s ⁻¹
d	pipe diameter	m
E	enhancement factor	dimensionless
g	enhancement factor	dimensionless
Ha	Hatta number	dimensionless
He	Henry constant	Pa m ³ kmol ⁻¹
He^0	Henry constant for gas-liquid phase	Pa m ³ kmol ⁻¹
h	ionic strength of total solvent	m ³ kmol ⁻¹
I	ionic strength	kmol m ⁻³
h	height of the column	m
K	reaction equilibrium constant	kmol m ⁻³
k	reaction rate constant	s ⁻¹
k_{app}	apparence kinetic reaction	s ⁻¹
k_L	liquid phase mass transfer coefficient	m s ⁻¹
k_{OH^-}	reaction rate constant with hydroxide ion	L mol ⁻¹ s ⁻¹
K_w	dissociation constant for water	kmol ² m ⁻⁶
M_B	molecular weight of solvent	kg mol ⁻¹
q	absorption rate of CO ₂	kmol s ⁻¹
R	universal gas constant (8.314)	J mol ⁻¹ K ⁻¹
r	rate of reaction	kmol m ⁻³ s ⁻¹

Re	Reynolds number	
Sc	Schmidt number	
Sh	Sherwood number	
T	temperature	K
t_c	contact time	s
V	molal volume of solute at normal boiling point	cc g ⁻¹ mole ⁻¹
wt	total weight	%

Greek letters

v	velocity of absorbent solution	m ³ s ⁻¹
ρ	density	kg m ⁻³
μ	viscosity	mPa s
φ	solvent association parameter	
δ	film thickness in two film theory	m

Subscripts

A	in water
B	in MDEA
Arg	<i>l</i> -Arginine
CO ₂	carbon dioxide
e	equilibrium
g	gas
Glu	<i>l</i> -Glutamic Acid
H ⁺	ion hydrogen
H ₂ O	water
i	gas-liquid interface, infinite
MDEA	methyldiethanolamine
OH ⁻	ion hydroxide
ov	overall

REFERENCES

- [1] W. M. Budzianowski, "A review of potential innovations for production, conditioning and utilization of biogas with multiple-criteria assessment," *Renew. Sustain. Energy Rev.*, vol. 54, pp. 1148–1171, 2015.
- [2] M. Safari, A. Ghanizadeh, and M. M. Montazer-Rahmati, "Optimization of membrane-based CO₂-removal from natural gas using simple models considering both pressure and temperature effects," *Int. J. Greenh. Gas Control*, vol. 3, no. 1, pp. 3–10, 2009.
- [3] F. R. H. Abdeen, M. Mel, M. S. Jami, S. I. Ihsan, and A. F. Ismail, "A review of chemical absorption of carbon dioxide for biogas upgrading," *Chinese J. Chem. Eng.*, vol. 24, no. 6, pp. 693–702, 2016.
- [4] J. Arroyo, F. Moreno, M. Muñoz, C. Monné, and N. Bernal, "Combustion behavior of a spark ignition engine fueled with synthetic gases derived from biogas," *Fuel*, vol. 117, pp. 50–58, 2014.
- [5] B. Sreenivasulu, D. V. Gayatri, I. Sreedhar, and K. V. Raghavan, "A journey into the process and engineering aspects of carbon capture technologies," *Renew. Sustain. Energy Rev.*, vol. 41, pp. 1324–1350, 2014.
- [6] L. S. Tan, A. M. Shariff, K. K. Lau, and M. A. Bustam, "Factors affecting CO₂ absorption efficiency in packed column: A review," *J. Ind. Eng. Chem.*, vol. 18, no. 6, pp. 1874–1883, 2012.
- [7] M. Scholz, M. Alders, J. Lölsberg, and M. Wessling, "Dynamic process simulation and process control of biogas permeation processes," *J. Memb. Sci.*, vol. 484, pp. 107–118, 2015.
- [8] J. V. Holst, S. R. A. Kersten, and K. J. A. Hogendoorn, "Physicochemical properties of several aqueous potassium amino acid salts," *J. Chem. Eng. Data*, vol. 53, no. 6, pp. 1286–1291, 2008.
- [9] S. Yan, Q. He, S. Zhao, H. Zhai, M. Cao, and P. Ai, "CO₂ removal from biogas by using green amino acid salts: Performance evaluation," *Fuel Process. Technol.*, vol. 129, pp. 203–212, 2015.
- [10] R. Ramazani, S. Mazinani, A. Jahanmiri, S. Darvishmanesh, and B. V. D. Bruggen, "Investigation of different additives to monoethanolamine (MEA) as a solvent for CO₂ capture," *J. Taiwan Inst. Chem. Eng.*, vol. 65, pp. 341–349, 2016.

- [11] J. V. Holst, G. F. Versteeg, D. W. F. Brillman, and J. A. Hogendoorn, "Kinetic study of CO₂ with various amino acid salts in aqueous solution," *Chem. Eng. Sci.*, vol. 64, pp. 59–68, 2009.
- [12] H. Thee, K. H. Smith, G. da Silva, S. E. Kentish, and G. W. Stevens, "Carbon dioxide absorption into unpromoted and borate-catalyzed potassium carbonate solutions," *Chem. Eng. J.*, vol. 181–182, pp. 694–701, 2012.
- [13] S. Shen, X. Feng, R. Zhao, U. K. Ghosh, and A. Chen, "Kinetic study of carbon dioxide absorption with aqueous potassium carbonate promoted by arginine," *Chem. Eng. J.*, vol. 222, pp. 478–487, 2013.
- [14] B. Prasad, "Experimental investigation of CO₂ absorption capacity in amine blend of 2-Amino-2-methyl-1-propanol (AMP) and Tetraethylenepentamine (TEPA)," Master thesis, Thapar University, India, 2013.
- [15] S. Paul and K. Thomsen, "Kinetics of absorption of carbon dioxide into aqueous potassium salt of proline," *Int. J. Greenh. Gas Control*, vol. 8, pp. 169–179, 2012.
- [16] M. Gupta, F. Eirik, and H. F. Svendsen, "Computational study of equilibrium constants for amines and amino acids for CO₂ capture solvents," *Energy Procedia*, vol. 37, pp. 1720–1727, 2013.
- [17] C. A. Fitch, G. Platzer, M. Okon, B. G. E, and L. P. McIntosh, "Arginine: Its pKa value revisited," *Proteine Sci.*, vol. 24, no. 5, pp. 752–761, 2015.
- [18] K. A. Hoff, "Modeling and experimental study of carbon dioxide absorption in a membrane contactor," Doctoral thesis, Norwegian University of Science and Technology, Norway, 2003.
- [19] T. J. Edwards, G. Maurer, J. Newman, and J. M. Prausnitz, "Vapor-liquid equilibria in multicomponent aqueous solutions of volatile weak electrolytes," *AIChE J.*, vol. 24, no. 6, pp. 900–976, 1978.
- [20] G. Xu, C. Zhang, S. Qin, W. Gao, and H. Liu, "Gas-liquid equilibrium in a CO₂-MDEA-H₂O system and the effect of piperazine on it," *Ind. Eng. Chem. Res.*, vol. 37, pp. 1473–1477, 1998.
- [21] D. Barth, C. Tondre, and J. J. Delpuech, "Kinetics and mechanism of the reactions of carbon dioxide with alkanolamines: A discussion concerning the cases of MDEA and DEA," *Chem. Eng. Sci.*, vol. 39, no. 12, pp. 1753–1757, 1984.
- [22] P. V. Danckwerts, *Gas liquid reactions*. New York: McGraw-Hill, 1970.
- [23] C. J. Geankoplis, *Transport processes and unit operations*, 3rd editio. New Delhi: Prentice-Hall of India, 1997.
- [24] J. T. Cullinane and G. T. Rochelle, "Carbon dioxide absorption with aqueous potassium carbonate promoted by piperazine," *Chem. Eng. Sci.*, vol. 59, pp. 3619–3630, 2004.
- [25] F. Yi, H.-K. Zou, G.-W. Chu, L. Shao, and J.-F. Chen, "Modeling and experimental studies on absorption of CO₂ by Benfield solution in rotating packed bed," *Chem. Eng. J.*, vol. 145, no. 3, pp. 377–384, 2009.
- [26] C. R. Sander, "Compilation of Henry's law constants for inorganic and organic species of potential importance in environmental chemistry," *Max Planck Inst. Chem. J.*, vol. 3, p. 57, 1999.
- [27] H. Kierzkowska-pawlak, M. Siemieniec, and A. Chacuk, "Reaction kinetics of CO₂ in aqueous methyldiethanolamine solutions using the stopped-flow technique," *Chem. Process Eng.*, vol. 33, no. 1, pp. 7–18, 2011.
- [28] M. P. Gimeno, M. C. Mayoral, and J. M. Andrés, "Influence of temperature on CO₂ absorption rate and capacity in ionic liquids," *Energy & Fuels*, vol. 27, no. 7, pp. 3928–3935, 2013.
- [29] Z. Feng, F. Cheng-Gang, W. You-Ting, W. Yuan-Tao, L. Ai-Min, and Z. Zhi-Bang, "Absorption of CO₂ in the aqueous solutions of functionalized ionic liquids and MDEA," *Chem. Eng. J.*, vol. 160, no. 2, pp. 691–697, 2010.
- [30] J. A. Bullin, J. C. Polasek, and S. T. Donnelly, "The use of MDEA and mixtures of amines for bulk CO₂ removal," in *Proceedings of the Sixty-Ninth GPA Annual Convention*, 1990, pp. 1–9.
- [31] N. Ramachandran, A. Aboudheir, R. Idem, and P. Tontiwachwuthikul, "Kinetics of the absorption of CO₂ into mixed aqueous loaded solutions of monoethanolamine and methyldiethanolamine," *Ind. Eng. Chem. Res.*, vol. 45, no. 8, pp. 2608–2616, 2006.
- [32] M. Edali, R. Idem, and A. Aboudheir, "1D and 2D absorption-rate/kinetic modeling and simulation of carbon dioxide absorption into mixed aqueous solutions of MDEA and PZ in a laminar jet apparatus," *Int. J. Greenh. Gas Control*, vol. 4, pp. 143–151, 2010.