Available online at www.sciencedirect.com
ScienceDirect
Energy Reports 9 (2023) 1–7
www.elsevier.com/locate/egyr

TMREES23-Fr, EURACA 06–08 February 2023, Metz-Grand Est, France

Comparative mass transfer performance of CO_2 absorption using highly-concentrated AMP-PZ-MEA ternary amines solvent

Sukanya Nakrak[a], Benjapon Chalermsinsuwan[a,b], Paitoon Tontiwachwuthikul[c], Hongxia Gao[d], Zhiwu Liang[d], Teerawat Sema[a,b,*]

[a] *Department of Chemical Technology, Faculty of Science, Chulalongkorn University, Pathumwan, Bangkok, 10330, Thailand*
[b] *Center of Excellence on Petrochemical and Materials Technology, Chulalongkorn University, Pathumwan, Bangkok, 10330, Thailand*
[c] *Clean Energy Technologies Research Institute, Faculty of Engineering and Applied Science, University of Regina, SK, S4S 0A2, Canada*
[d] *Joint International Center for CO_2, Capture and Storage (iCCS), Provincial Hunan Key Laboratory for Cost-effective Utilization of Fossil Fuel Aimed at Reducing CO_2 Emissions, College of Chemistry and Chemical Engineering, Hunan University, Changsha, 410082, PR China*

Received 15 May 2023; accepted 21 May 2023
Available online 7 June 2023

Abstract

Mass transfer performance of CO_2 absorption is based on selecting an effective amine solvent, hence, an examination of the overall mass transfer coefficient (K_Ga_v) and CO_2 removal efficiency, is significant for obtaining the most favorable CO_2 capture performance. This study compared K_Ga_v and CO_2 removal efficiency of the highly concentrated ternary amines solvent at various concentrations with the benchmark monoethanolamine (MEA) in a laboratory scale CO_2 absorption packed-column. The six blends of 2-amino-2-methyl-1-propanol (AMP), piperazine (PZ), and MEA are formulated as ternary solvents at high PZ/AMP molar ratio (1.25–3.75) and total amine concentration (6M and 7M). Be noted that the solvent precipitation was not observed in this study. The absorption experiment was operated at 303 K temperature, 12% CO_2 by volume, and CO_2 loading of 0.25 mol CO_2/mol amine. The experimental results showed that K_Ga_v and CO_2 removal efficiency for AMP-PZ-MEA and MEA solvents increased as total amine concentration increased. Also, K_Ga_v and CO_2 removal efficiency of the PZ-AMP-MEA solvent are greater than those of 5M MEA. An increase of PZ/AMP molar ratio had a positive influence on the absorption performance for ternary amines. In comparison with the benchmark 5M MEA, all the studied AMP-PZ-MEA solvents showed an outperformance. The two suggested formulae, which are 0.95:3.55:1.5 (6M) and 0.95:3.55:2.5 (7M), possessed approximately 1.5 and 2.5 times higher K_Ga_v and 17.34% and 17.63% greater CO_2 removal efficiency compared with the benchmark 5M MEA.

Peer-review under responsibility of the scientific committee of the TMREES23-Fr, EURACA, 2023.

Keywords: Mass transfer; CO_2 absorption; Amine; Ternary solvent; Packed column

* Corresponding author at: Department of Chemical Technology, Faculty of Science, Chulalongkorn University, Pathumwan, Bangkok, 10330, Thailand.
E-mail address: teerawat.se@chula.ac.th (T. Sema).

https://doi.org/10.1016/j.egyr.2023.05.219

Peer-review under responsibility of the scientific committee of the TMREES23-Fr, EURACA, 2023.

Nomenclature

G_I	Inert gas flow rate (kmol/m^2 h)
k_G	Gas phase mass transfer coefficient (m/s)
K_G	Overall interfacial area gas phase mass transfer coefficient (kmol/m^2 h kPa)
$K_G a_v$	Overall volumetric mass transfer coefficient (kmol/m^3 h kPa)
P	Total pressure of the system (kPa)
y_A^*	Mole fraction of solute A in gas phase that is in equilibrium with bulk liquid (mol/mol)
$y_{A,G}$	Mole fraction of solute A in bulk gas phase (mol/mol)
$Y_{A,G}$	Mole ratio of solute A in gas phase (mol/mol)
Z	Height of absorption column (m)

1. Introduction

A continuously accumulation of emitted anthropogenic carbon dioxide (CO_2) creates an extreme global warming due to a retained heat from the greenhouse effect. Hence, an increase of the atmospheric CO_2 concentration is a key problem of climate change, raise of global temperature, and air pollution. It negatively impacts human health and environment. The combustion of fossil fuels, which produce heating energy, is a principal cause of CO_2 emission. Since the economic expansion, an increase trend of the CO_2 emission has been continuously observed [1]. Therefore, carbon capture and storage (CCS) technology is currently being considered as the most importance way to decrease the CO_2 emission. Up to date, many carbon capture methods have been suggested: absorption, adsorption, cryogenics, and membrane technology. Chemical absorption process has been commonly used in a gas treating application due to its highly CO_2 removal effectiveness [2]. Different conventional amine solvents are wildly used for CO_2 absorption. For example, monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), 2-amino-2-methyl-1-propanol (AMP), and piperazine (PZ).

Development of novel amine solvent is one of the essential profits for an effective absorption CO_2 process (i.e., lower regeneration heat duty, improve absorption capacity, and enhance reaction and mass transfer rate) [3]. MEA is a benchmark amine solvent, which rapidly reacts with CO_2 but requires high heat duty for CO_2 regeneration and has a limited of CO_2 absorption loading. The sterically hindered amine (AMP) reacts directly with CO_2 to generate bicarbonate and free AMP in the solution. As a result, it has low regeneration energy and high CO_2 absorption capacity. PZ is a cyclic diamine absorbent with high CO_2 capture capacity and rapid reaction with CO_2. The disadvantage of this amine is limited workable concentration due to the solvent precipitation at high concentration and CO_2 loading.

In previous studies [4,5], the first-generation AMP-PZ-MEA was found to have higher CO_2 absorption and regeneration performance than the single MEA. To improve the performance of the AMP-PZ-MEA, Apaiyakul et al. [6] suggested that PZ/AMP molar ratio should be maximized while MEA concentration of MEA should be minimized. Accordingly, six highly concentrated AMP-PZ-MEA blends (i.e., 2:2.5:1.5, 1.3:3.2:1.5, 0.95:3.55:1.5, 2:2.5:2.5, 1.3:3.2:2.5, and 0.95:3.55:2.5) were proposed. Their reported data include the precipitation behavior, density, viscosity, and CO_2 absorption capacity. However, their studied performance of the six proposed AMP-PZ-MEA blends still lacks of the mass transfer data that signified rate of transfer CO_2 gas in absorption column to complete extensive absorbed evaluation. Additionally, these data are essential for designing the high of the absorption column.

This studied aims to investigate the mass transfer performance of CO_2 absorption in a laboratory-scale Sulzer DX packed column using the sixed newly proposed AMP-PZ-MEA solvents in terms of overall mass transfer coefficient ($K_G a_v$) and CO_2 removal efficiency. The six highly-concentrated 6M and 7M solvents will be comparatively investigated with the benchmark MEA and the formerly studied AMP-PZ-MEA.

2. Determination of $K_G a_v$ and CO_2 removal efficiency in packed column

For capturing CO_2 by amine, a chemical absorption process happens when one component (CO_2) moves from the gas phase through the gas–liquid interface and into the opposite liquid phase based on the two-film theory. It is

well accepted that the driving force for mass transfer is the CO_2 concentration gradient ($y_{A,G} - y_A^*$). In the packed column, a gas phase mass transfer coefficient (k_G) varies according to the specific interfacial contact area (a_v), which is difficult to measure. Therefore, the overall mass transfer coefficient ($K_G a_v$) based on the volume of absorption column is more favorable to be used instead of the overall interfacial area gas phase mass transfer coefficient (K_G). $K_G a_v$ can be given as follow [7]:

$$K_G a_v = \left(\frac{G_I}{P(y_{A,G} - y_A^*)}\right)\left(-\frac{dY_{A,G}}{dZ}\right) \tag{1}$$

where G_I represents the inert gas flow rate, P is the pressure of system, Z is the height of absorption column, $Y_{A,G}$ is the mole ratio of component A in gas phase, $y_{A,G}$ and y_A^* are the mole fraction of component A in the gas phase and equilibrium at interface, respectively.

The term $y_{A,G}$ can be obtained by a measurement of CO_2 concentration in gas phase along the packed column height. Correspondingly, the mole ratio $Y_{A,G}$ can be calculated. The mole ratio concentration gradient ($dY_{A,G}/dZ$) is a slope of the plot between mole ratio against the height of the column. The mole fraction of CO_2 at interface (y_A^*) can be calculated by Henry's constant. In comparison with $y_{A,G}$, y_A^* was found to be very small and can be ignored [7].

The CO_2 removal efficiency can be calculated by concentration of CO_2 in gas phase at the inlet and outlet of the absorption column as follow:

$$CO_2 \textit{ removal efficiency} = \left|\frac{y_{CO_2,inlet} - y_{CO_2,outlet}}{y_{CO_2,inlet}}\right| \times 100\% \tag{2}$$

where $y_{CO_2,inlet}$ and $y_{CO_2,outlet}$ are mole fractions of CO_2 at the inlet and outlet to the absorption column, respectively

3. Methodology

3.1. Chemical

AMP with a purity of 98% and PZ with a purity of 99% were purchased from Sigma-Aldrich, Switzerland. MEA at purity of 98% was supplied by Chemipan Corporation Co., Ltd., Thailand. A premixed gas of 12% by volume of CO_2 balanced with nitrogen (N_2) was obtained from Thai-Japan Gas Co., Ltd., Thailand. Standard 1.0 M HCl solution was purchased from Kemaus, Australia. All materials were used as received without further purification.

3.2. Solvent formulation

Absorption for CO_2 capture mostly uses an aqueous alkanolamine solvent as a liquid absorbent. The solvent should not be precipitated in aqueous solution because the solid precipitation blocks fluid flow in the column. As a result, the operation cannot be proceeded and needs a shut down for cleaning. Since both AMP and PZ can precipitate at high concentration and CO_2 loading, the use of them should be carefully considered. Additionally, the formulated solvent (with AMP and PZ) should be done at appropriate blended ratio. Apaiyakul et al. [6] investigated the possible precipitation of AMP-PZ-MEA at high total amine concentrations of 6M and 7M. It was found that an increase of PZ/AMP molar ratio and an elevation of total amine concentration induced the solvent precipitation. Based on the six high potential blends (i.e., 2:2.5:1.5, 1.3:3.2:1.5, 0.95:3.55:1.5, 2:2.5:2.5, 1.3:3.2:2.5, and 0.95:3.55:2.5) proposed by Apaiyakul et al. [6], (i) the first-generation AMP-PZ-MEA blend (1.5:1.5:3) and (ii) the industrially used benchmark 5 M MEA were also included in the present work for the mass transfer analysis. Table 1 shows the ten formulae of single MEA and blended AMP-PZ-MEA solvents used in this work.

3.3. Experimental CO_2 absorption in packed column

For each experiment, a determination of the CO_2 absorption performance was conducted in laboratory-scale packed column (1.6 m height and 3.0×10^{-2} m internal diameter), in which the diagram and picture are shown in Fig. 1(a) and Fig. 1(b), respectively. Sulzer DX structural packing (900 m^2/m^3 surface area and 1.5 m total packing height) was loaded into a glass vessel absorption column. In addition, ten thermocouples and twelve gas sampling ports were installed along the height of column to collect temperature and CO_2 concentration in the gas phase. The

Table 1. Formulae and mass balance errors of single MEA and ternary AMP-PZ-MEA solvents used in this study.

Amine solvent	Amine concentration (M)			Total concentration (M)	PZ/AMP molar ratio	Mass balance error (%)
	AMP	PZ	MEA			
Single MEA	0	0	5	5	–	4.45
	0	0	6	6	–	4.01
	0	0	7	7	–	4.68
First generation blend	1.5	1.5	3	6	1	4.75
High potential blends proposed by Apaiyakul et al. [6]	2	2.5	1.5	6	1.25	4.12
	1.3	3.2	1.5	6	2.5	4.24
	0.95	3.55	1.5	6	3.75	4.59
	2	2.5	2.5	7	1.25	3.69
	1.3	3.2	2.5	7	2.5	4.89
	0.95	3.55	2.5	7	3.75	4.22

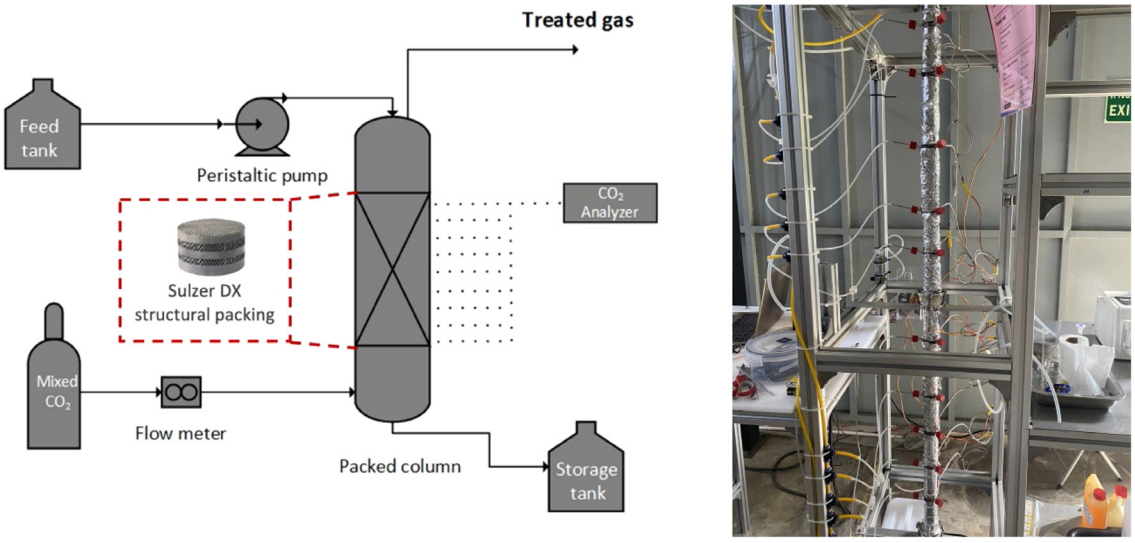

Fig. 1. Absorption packed column (a) experimental diagram and (b) picture of the facility.

infrared CO_2 analyzer (SprintIR–6S100%, CO_2 METER, Canada) was used to record the concentration of gaseous CO_2 with accuracy of $\pm$ 0.3%. The laboratory CO_2 absorption experiment was set-up and operated according to a procedure described in our previous studied [8]. Both $K_G a_v$ and CO_2 removal efficiency for the CO_2 absorption performance was calculated from Eqs. (1) and (2), respectively. Mass balance error was calculated in order to ensure an accuracy for each experimental investigation. Detailed description on the calculation can be found in our previous work [5]. The error (see Table 1) was found to be below 10%, which is in the same range with that reported in the literature [7]. It should be noted that the operating condition used in this work is the suggested condition reported in our previous works [5,8] as follows: liquid flow rate 3.67 $m^3/m^2 \cdot$ h, gas flow rate 509.30 $m^3/m^2 \cdot$ h, and CO_2 loading in lean solvent of 0.25 mol CO_2/mol amine at temperature of 303 K (room temperature) and atmospheric pressure. Be informed that effects of the operating conditions were not considered in this work. Such a detailed discussion was reported by Nakrak et al. [5].

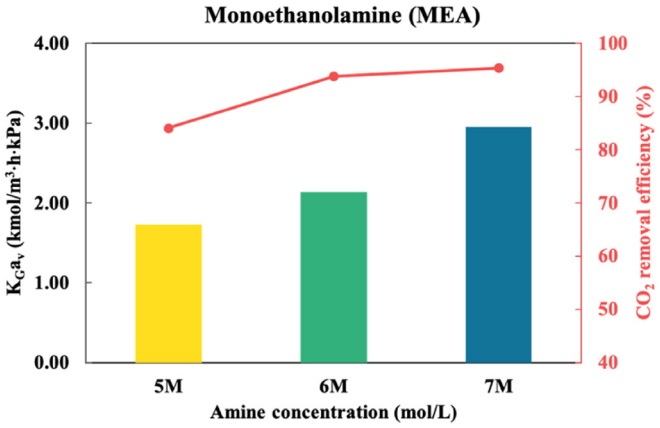

Fig. 2. Effect of amine concentration on K_Ga_v and CO_2 removal efficiency for MEA single amine solvent.

4. Results and discussion

4.1. Mass transfer performance of MEA

The absorption performance of high concentration solvent (5M-7M MEA) was compared in terms of K_Ga_v and CO_2 removal efficiency, as shown in Fig. 2. The results indicated that the amine concentration has a positive influence on the K_Ga_v and CO_2 removal efficiency. In other words, the mass transfer performance increased as the MEA concentration increased. This was because of an abundance of the free active amine molecules, which increase the reaction with CO_2 molecules [9]. For the comparative performance, K_Ga_v and CO_2 removal efficiency of 7M MEA is 71% and 13% higher than those of benchmark 5M MEA, respectively. Consequently, highly concentrated MEA solvent could be operated for capturing CO_2.

4.2. Mass transfer performance of AMP-PZ-MEA ternary amines

To maximize the mass transfer performance, it is necessary to adjust the blended ratio of each amine in the AMP-PZ-MEA solvent due to the different advantages and disadvantages of each amine component. The comparison of mass transfer performance in terms of K_Ga_v and CO_2 removal efficiency of the studied amine solvents (presented in Table 1) in the packed absorption column is presented in Fig. 3. As can be seen, K_Ga_v increased with an increase

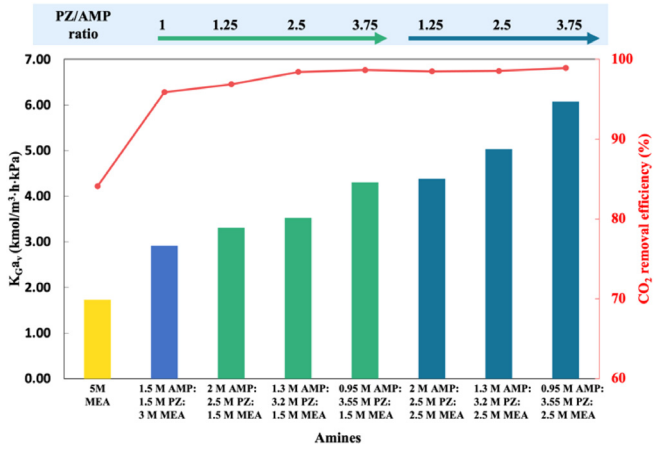

Fig. 3. Comparison K_Ga_v and CO_2 removal efficiency between 5M MEA versus blended AMP-PZ-MEA ternary amines solvent.

of PZ/AMP molar ratio (ranging of 1.25–3.75). The behavior of blending AMP-PZ could be related to an increase of the absorption performance since it refers to an increase of concentration of PZ, which is the highest reactivity with CO_2 among the three studied amine components [4]. In addition, the CO_2 removal efficiency increased with a rise of PZ/AMP molar ratio for both 6M and 7M total amine concentrations. However, an elevation of the CO_2 removal efficiency for 7M AMP-PZ-MEA was small because almost the maximum value of 100% removal efficiency was about to be reached. It can be inferred that an increase of PZ/AMP molar ratio increased the highly reactive amine component, and thereby improved CO_2 capture performance [4]. Interestingly, all the six proposed highly concentrated AMP-PZ-MEA solvents showed greater K_Ga_v and CO_2 removal efficiency than both the benchmark 5M MEA and the previous studied ternary amine (1.5:1.5:3). Based on the presented data, 0.95:3.55:1.5 and 0.95:3.55:2.5 blends were suggested for total amine concentrations of 6M and 7M, respectively. This is because of their highest K_Ga_v and CO_2 removal efficiency among the blends with the same total amine concentration. The two suggested solvents had 1.5 and 2.5 times higher K_Ga_v and 17.34% and 17.63% greater CO_2 removal efficiency than the benchmark 5 M MEA.

It is worth mentioning that the mass transfer data (i.e., K_Ga_v and CO_2 removal efficiency) obtained from the laboratory scale absorption column might not be able to fully represent the behavior in the industrial scale column. However, the data obtained from this work can (i) preliminary evaluate the mass transfer performance of the studied solvents and (ii) be used to calculate the column dimension regarding K_Ga_v, gas flux, and liquid flux. Additionally, an optimization of K_Ga_v and CO_2 removal efficiency by varying the PZ/AMP molar ratio and total amine concentration should be considered. However, the ranges of total amine concentration and PZ/AMP molar ratio used in this work are limited. Hence, it is suggested that the optimization of the mass transfer performance using an objective function should be further investigated.

In comparison with the benchmark 5 M MEA and the first generation AMP-PZ-MEA, the newly proposed second generation AMP-PZ-MEA showed more highly promising mass transfer performance (K_Ga_v and CO_2 removal efficiency), especially the 0.95:3.55:2.5 blends. It is expecting that the use of these high potential solvents will results in a much lower liquid to gas ratio for the existing absorption tower operation and a considerably shorter column height for the new tower construction. As a result, both operating and capital investment for CO_2 capture can be reduced.

5. Conclusion

The mass transfer performance of CO_2 absorption by the high potential AMP-PZ-MEA solvents was investigated regarding the overall mass transfer coefficient (K_Ga_v) and CO_2 removal efficiency in packed column. It was found that the total amine concentration and PZ/AMP molar ratio had positive impact on K_Ga_v and CO_2 removal efficiency within the operating concentration of 5M-7M and PZ/AMP molar ratio of 1.25–3.75. The six studied AMP-PZ-MEA blends had a considerably better mass transfer performance than the benchmark 5M MEA and the first-generation AMP-PZ-MEA. Two ternary AMP-PZ-MEA solvents, which are 0.95:3.55:1.5 (6M total amine concentration) and 0.95:3.55:2.5 (7M total amine concentration) were suggested as replacements of the benchmark 5M MEA. In addition to the mass transfer evaluation of the six suggested high potential AMP-PZ-MEA blends, the economic feasibility of replacing (i) the benchmark 5M MEA and (ii) 7M MEA with the proposed six blends should be investigated. This is to obtain both technical and economical perspective of the six proposed AMP-PZ-MEA blends to be used in substitution of 5-7M MEA.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request

Acknowledgments

This work is funded by National Research Council of Thailand (NRCT) and Chulalongkorn University, Thailand (Mid-Career Research Grant, N42A660521). The support from Thailand Science Research and Innovation Fund Chulalongkorn University, Thailand (DIS66230001) is also acknowledged.

References

[1] Jeon Hwayoung. CO_2 emissions, renewable energy and economic growth in the US. Electr J 2022;35:107170, 2022.

[2] Rochelle Gary T. Amine scrubbing for CO_2 capture. Science 2009;325(5948):1652–4, 2009.

[3] Sema Teerawat, Gao Hongkia, Liang Zhiwu, Tontiwachwuthikul Paitoon, Idem Raphael O. New insights and updated correlations for density, viscosity, refractive index, and associated properties of aqueous 4-dieythylamino-2-butanol solution. Fluid Phase Equilib 2022;562:113565, 2022.

[4] Nwaoha Chikezie, Saiwan Chintana, Tontiwachwuthikul Paitoon, Supap Teeradet, Rongwong Wichitpan, Idem Raphael, et al. Cabon dioxide (CO_2) capture: absorption-desorption capabilities of 2-amino-2methyl-1-propanol (AMP), piperazine (PZ) and monoethanolamine (MEA) tri-solvent blends. J Nat Gas Sci Eng 2016;33:742–50, 2016.

[5] Nakrak Sukanya, Tontiwachwuthikul Paitoon, Gao Hongxia, Liang Zhiwa, Sema Teerawat. Comprehensive mass transfer analysis of CO_2 absorption in high potential ternary AMP-PZ-MEA solvent using three-level factorial design. Environ Sci Pollut Res 2023;10001–23, 2023.

[6] Apaiyakul Rattanaporn, Nimmanterdwong Prathana, Kanchanakungvalkul Thitiya, Puapan Papitchaya, Gao Hongxia, Liang Zhiwu, et al. Precipitation behavior, density, viscosity, and CO_2 absorption capacity of highly concentrated ternary AMP-PZ-MEA solvents. Int J Greenh Gas Control 2022;120:103775, 2022.

[7] Naami Abdulaziz Mohamed Edali, Sema Teerawat, Idem Raphael, Tontiwachwuthikul Paitoon. Mass transfer performance of CO_2 absorption into aqueous solution of 4-diethylamino-2-butanol, monoethanolamine, and N-methyldiethanolamine. Ind Eng Chem Res 2012;51:6470–9, 2012.

[8] Nakrak Sukanya, Yurata Tarabodin, Chalermsinsuwan Benjapon, Tontiwachwuthikul Paitoon, Sema Teerawat. Preliminary mass transfer performance of CO_2 absorption into AMP-PZ-MEA ternary amines. 2021, Available at SSRN 3821405.

[9] Xu Bin, Gao Hongxia, Luo Xiao, Liao Huiying, Liang Zhiwu. Mass transfer performance of CO_2 absorption into aqueous DEEA in packed columns. Int J Greenh Gas Control 2016;51:11–7, 2016.