GHGT-11

Modeling and Simulation of CO_2 Capture Process for Coal-based Power Plant using Amine Solvent in South Korea

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Abstract

The interest in carbon capture technology is continuously rising since worldwide climate-change problems have intensified the concern regarding efficient removal of carbon dioxide. Amine-based capture technology is a conventional technology to remove carbon dioxide in natural gas processing, and also can be used for carbon dioxide removal from flue gas in coal-based power plants. In particular, monoethanolamine is a conventional commercial absorbent to remove carbon dioxide and considered as a standard amine absorbent. Due to the high non-ideality of amine, rate-based models have been suggested to describe absorption and desorption of amine absorbent. However, most suggested models were validated against large-scale pilot plant results, and there were few models to consider both absorber and stripper with rate-based model. In this study, we applied two rate-based models introduced by previous literature to the actual pilot plant operation data in 0.1MW-scale Boryeong pilot plant, South Korea and developed a modified model with increased accuracy. The developed model showed good agreements with pilot plant results for both absorber and stripper. However, under low liquid-to-vapor ratio operation with high rich loading value, all model showed worse estimations.

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1. Introduction

Increasing concerns about worldwide climate change has demanded the reduction of carbon dioxide more importantly. The worldwide climate change has strongly influenced the global environment and life activities, and it is becoming highly significant problem for the whole world. As a cause to trigger climate change, greenhouse gases are pointed out by many research groups. In particular, carbon dioxide has been illuminated as the most significant greenhouse gas, which demands its reduction more progressively.

Among various carbon capture technologies, amine-based absorption technologies have been considered as strong candidates for carbon capture. Amine-based carbon capture, which uses amine-based absorbent to remove carbon dioxide from gas mixture, is a proven technology to be used to remove acid gas from natural gas for decades. This amine-based capture also can be applied to remove carbon dioxide from flue gas of a coal-based power plant, which is one of the largest carbon dioxide emission sources in the world. MEA (monoethanolamine) is a representative amine-based absorbent, and have been used industrially and commercially. For that reason, many researchers have referred MEA as a standard absorbent for amine-based carbon capture processes. [1-12]

In other to optimize and improve process economics when applying amine-based carbon capture process to existing industrial large-scale power plants, rigorous modeling and simulation is required. The amine absorption process is highly non-ideal due to interactions between molecules-molecules, ions-ions and ions-molecules. To increase model accuracy and precision, rate-based modeling approach with considering reaction kinetics has been introduced. Rate-based modeling offers rigorous and accurate estimation results comparing to traditional equilibrium stage modeling using Maxwell-Stefan diffusivities, process hydrodynamics, and mass transfer between vapor-liquid interfaces.

Many researchers reported rigorous modeling and simulation for the amine-based carbon capture validated against pilot plant data. Kucka et al. [1] developed a rate-based absorber model for MEA using Aspen custom modeler. The model based on vapor–liquid equilibrium by Austgen et al.[2] and kinetics by Kucka et al.[3], and validated their results by comparison with experimental data[4, 5]. Tobiesen et al.[6, 7] developed rate-based models for the absorber and stripper for MEA implemented in FORTRAN90. The model was validated by comparison with laboratory pilot plant operation results. Zhang et al.[8] developed a rate-based absorber model for MEA using Aspen Plus®. The model based on vapor-liquid equilibrium by Hilliard et al.[9] and experimental data by Aboudheir et al.[10]. The results were validated against pilot plant data[11]. Plaza et al.[12] developed a rate-based model for MEA and PZ using Aspen Plus®. The model based on vapor-liquid equilibrium by Hillard et al.[9] and validated with pilot plant data.
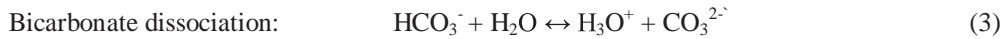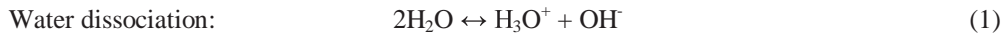
However, in most developed models by previous researchers, only a few studies considered both absorber and stripper in the model. Even fewer showed validation against pilot plant data with good agreement. In this study, two rate-based models which were developed by previous researchers were applied to validate against 0.1MW-scale pilot plant operation data located in Boryeong pilot plant in South Korea, and modified model was developed to validate the pilot plant operation results.

2. Process Models

In this study, two process models were developed for the validation against pilot plant operation at Boryeong, South Korea. Model 1 was based on the model suggested by Aspen Plus®[13], and Model 2 was by Zhang et al.[8]. Both two models were based on electrolyte NRTL property methods and used pilot plant operation data from University at Texas Austin.[11] Model 3 was a modified version of Model 1 with changing partial model and parameters.
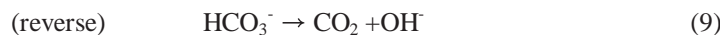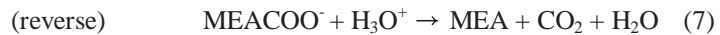
2.1. +Thermodynamic models

Electrolyte NRTL activity coefficient model was used to describe non-ideal activity and interactions between molecules and ions. To account for CO_2-water-MEA system, the following solution chemistries were considered.

Water dissociation:	$2H_2O \leftrightarrow H_3O^+ + OH^-$	(1)
CO2 hydrolysis:	$CO_2 + 2H_2O \leftrightarrow H_3O^+ + HCO_3^-$	(2)
Bicarbonate dissociation:	$HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^{2-`}$	(3)
Carbamate hydrolysis:	$MEACOO^- + H_2O \leftrightarrow MEA + H_3O^+$	(4)
MEA protonation:	$MEA + H_3O^+ \leftrightarrow MEAH^+ + H_2O$	(5)

Interaction parameters and equilibrium parameters for Model 1 were obtained from the works of Austgen et al.[2] and other literatures.[13] In Model 2, Hilllard[9] representation was used.

2.2. Kinetic models

In Model 1, reaction kinetics was presented with following two reactions.

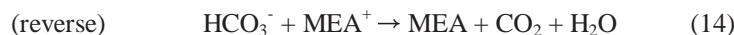|			
Carbamate formation:	(forward)	$MEA + CO_2 + H_2O \rightarrow MEACOO^- + H_3O^+$	(6)
	(reverse)	$MEACOO^- + H_3O^+ \rightarrow MEA + CO_2 + H_2O$	(7)
Bicarbonate formation:	(forward)	$CO_2 + OH^- \rightarrow HCO_3^-$	(8)
	(reverse)	$HCO_3^- \rightarrow CO_2 + OH^-$	(9)

The reduced power law expression with n=0 in equation 10 was used with concentration basis of molarity. The kinetic parameters for the reactions were obtained from the work of Hikita et al. and Pinsent et al., as shown Table 1.[13]

$$r_j = k_j T^n \, exp(-E_j/RT) \prod C_i^{ai} \tag{10}$$

Table1. Constants for power law expressions for Model 2

Reaction	Reaction direction	k_j	E_j (cal/mol)
Carbamate formation	forward	$9.77 \cdot 10^{10}$	9855.8
	reverse	$3.23 \cdot 10^{19}$	15655
Bicarbonate formation	forward	$4.32 \cdot 10^{13}$	13249
	reverse	$2.38 \cdot 10^{17}$	29451

In Model 2, reaction kinetics was presented with two reactions as follows. Power raw expression with n=0 as shown in equation 15 was used and the concentration basis was activity. Table 2 shows constants for power law expressions for Model 2.

Carbamate formation:	(forward)	$2\,MEA + CO_2 \rightarrow MEA^+ + MEACOO^-$	(11)
	(reverse)	$MEA^+ + MEACOO^- \rightarrow 2\,MEA + CO_2$	(12)
Bicarbonate formation:	(forward)	$MEA + CO_2 + H_2O \rightarrow HCO_3^- + MEA^+$	(13)
	(reverse)	$HCO_3^- + MEA^+ \rightarrow MEA + CO_2 + H_2O$	(14)

$$r_j = k_j T^n \prod a_i^{\alpha} \qquad k_j = k_j^o \, exp((-E_j/R)/(1/T-1/298.15)) \tag{15}$$

Table 2. Kinetic rate expressions and constants for power law expressions for Model 2

Reaction	Reaction direction	Kinetic expression	k_j^o(kmol/m^{3}s)	E_j(kJ/gmol)
Carbamate formation	forward	$r_1=k_1\,a_{MEA}{}^2\,a_{CO2}$	$4.73\cdot10^9$	19.34
	reverse	$r_2=(k_1/K_{MEACOO-})\,a_{MEACOO-}\,a_{MEA+}$	$4.23\cdot10^5$	107.47
Bicarbonate formation	forward	$r_3=k_3\,a_{MEA}\,a_{CO2}$	9025.5	49.00
	reverse	$r_4=(k_3/K_{HCO3-})(a_{HCO3-}\,a_{MEA+})/a_{H2O}$	3312.6	112.74

2.3. Property models

For liquid molar volume, Clarke density model was used. Jones-Dole viscosity model was used to calculate liquid viscosity. Onsager-Samaras surface tension model was used for the liquid mixture surface tension. For thermal conductivity, Riedel model was used. For CO_2 diffusivity, Nernst-Hartley model and Wilke-Chang model was used in Model 1 and 2, respectively.

3. Pilot Plant Operations

In South Korea, 0.1 MW scale (2 ton of CO_2/day) pilot plant was built in November 2011 and scale-up project to 10MW is under construction. Figure 1 shows a picture and process diagram of 0.1MW scale pilot plant.
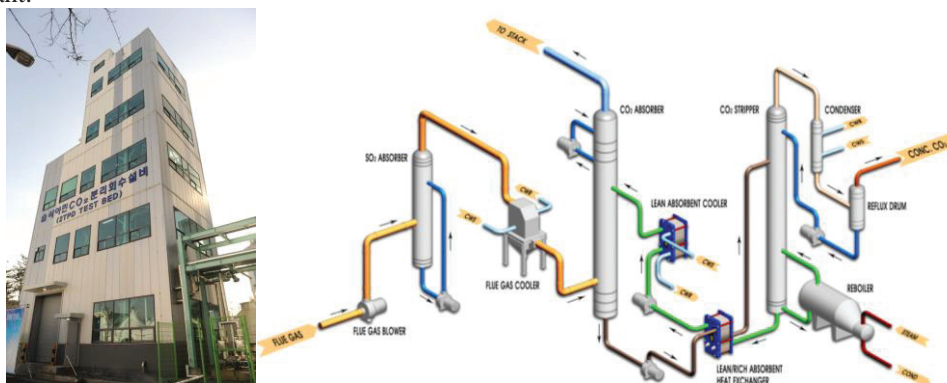

Fig. 1. (a) a picture of 0.1MW scale pilot plant; (b) a process diagram

0.1 MW scale pilot plant has been operated using MEA and KOSOL, developed by KEPCO. 34 and 35 runs were operated with MEA and KoSol, respectively. Table 3 shows specification and operating condition for MEA operations in pilot plant.

Table 3.Specification and operating conditions for pilot plant

Specification	Absorber	Stripper	Operating conditions	
Column Diameter (m)	4	3.5	MEA concentration (%)	29.8-31.2
Packing Height (m)	8.4, 12.6, 16.8	11.75	L/G ratio (kmol/kmol)	2.7, 3.8, 4.8
Packing Type	IMTP25	IMTP25	Stripper Pressure (kg/cm^2)	1.36, 1.51, 1.81
			CO2 removal (%)	89-92
			Stripper inlet Temp.(C)	93

4. Simulation

Pilot plant was modeled with simulation flowsheet as shown in Figure 2. Simulation specifications for the absorber and stripper for each model are shown in Table 4. 18 runs of MEA operation in pilot plant were used for validation.
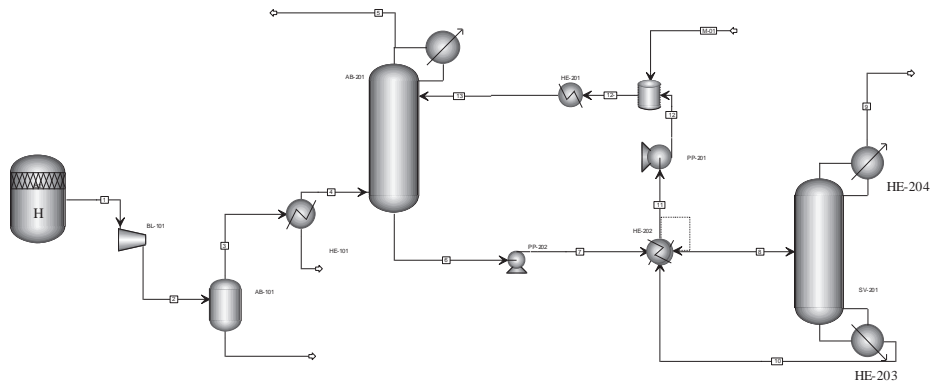

Fig. 2. Simulation flowsheet for pilot plant

Table 4.Specifications for simulation models

	Model 1		Model 2		Model 3	
	Absorber	Stripper	Absorber	Stripper	Absorber	Stripper
Unit model	Radfrac Rate-based calculation					
Stages	20	20	20	20	h_p=0.15-0.30	
Pressure and Pressure drop	Actual operating value					
Flow model	Mixed	Mixed	Mixed	Mixed	Countercurrent	VPlug
Reaction condition factor	0.9					
Film discretization ratio	5					
Additional discretization points	5					
Mass transfer coefficient model	Onda[14]	Onda	Onda	Onda	Hanley[15]	Hanley
Interfacial area method	Onda	Onda	Onda	Onda	Hanley	Hanley
Interfacial area factor	1.2	1.2	1.8	1.8	1	1
Heat transfer coefficient method	Chilton and Colburn					
Holdup correlation	Stichlmair					
Film resistance	Discrxn for liquid film, Film for vapor film					

In Model 3, flow model was changed to countercurrent model because it was reported that the counter-current model gave more accurate results[8]. However, counter-current model is more computationally intensive and sometimes unstable, as reported by Zhang et al.[8]. To decide the reasonable segment size, the following equation 17 was used[12].

$$N_m = h_s \, / \, h_p \tag{17}$$

Where N_m is the number of stages to represent a packing section, h_s is the height of packing for a section, h_p is the characteristic element height of the installed packing.

Proper packing element height for the packing type of IMTP25 was estimated to 0.15-0.3, but cannot be fixed yet due to the gap between absorber and stripper and further study is required. Because it was reported that Onda correlation[14] could underestimate interfacial area, Hanley correlation[15] for random packing type of IMTP was used in Model 3.

5. Results and Discussion

Figure 3 shows the simulation and operation results of lean loading, rich loading, and regeneration energy in the stripper in model 1-3. The Model 3 shows the best agreement between simulation and operation results.
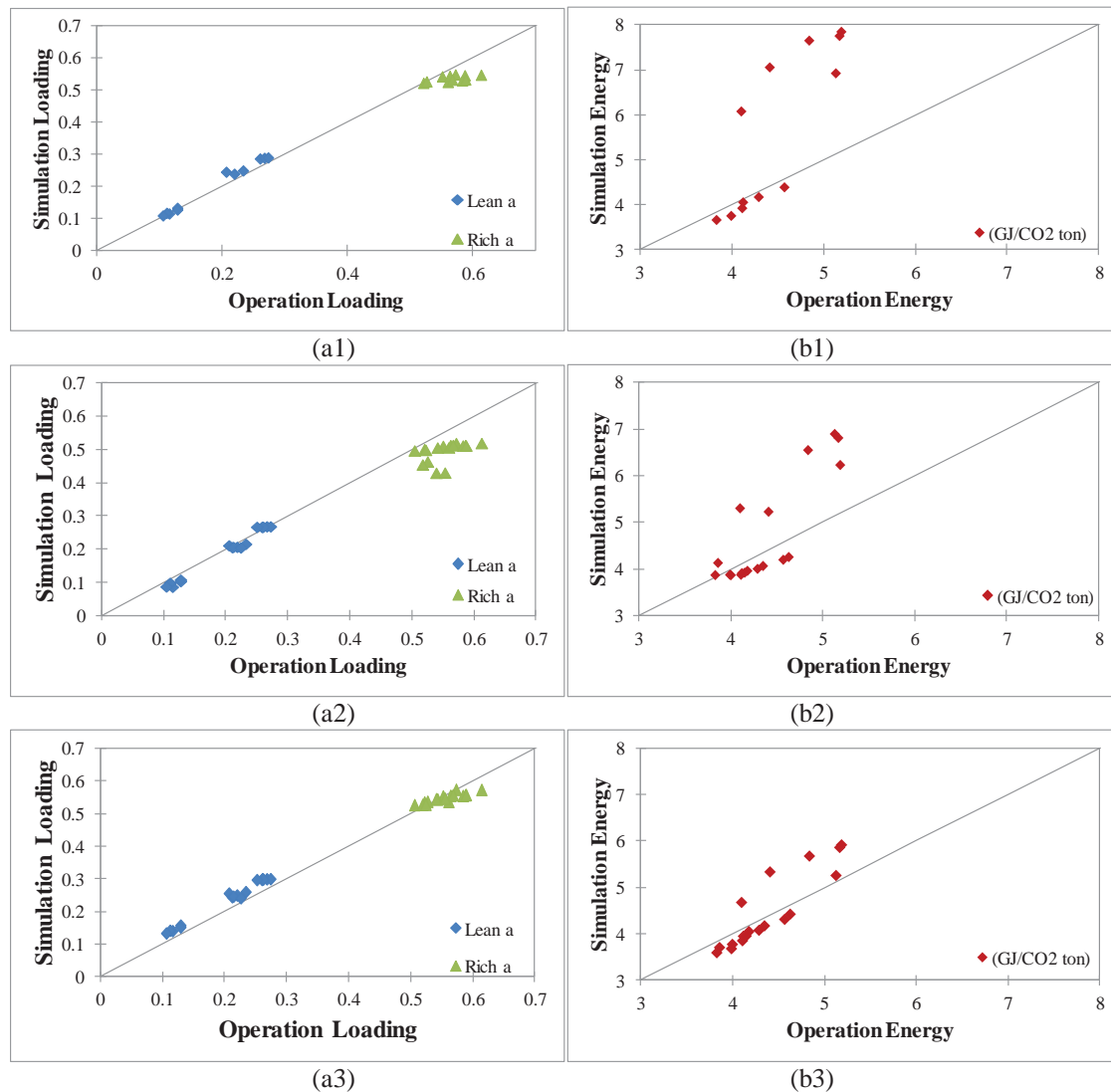
Fig. 3. (a1-a3) Simulation and operation results of loading in model 1-3; (b1-b3) Simulation and operation results of regeneration energy required in the stripper in model 1-3

In every model, under the low liquid-to-vapor ratio operation shows overestimated heat duty. The low L/G ratio operation causes lower lean loading of near 0.1 and higher rich loading of above 0.55. Because the developed models are based on the regressed properties through whole range of the loading value, estimated properties near the boundary could have greater error. In cases with low L/G ratio operation, the estimated top temperature of the stripper was higher than operating results and reflux feed was increased. This caused higher heat duty required in the stripper in the simulation.

Figure 4 shows the temperature profile calculated by simulation and the temperature at the pilot plant of representative operation cases. For the absorber, Model 1 shows the best agreement with pilot plant operation results, but for the stripper, Model 3 shows the best agreement.
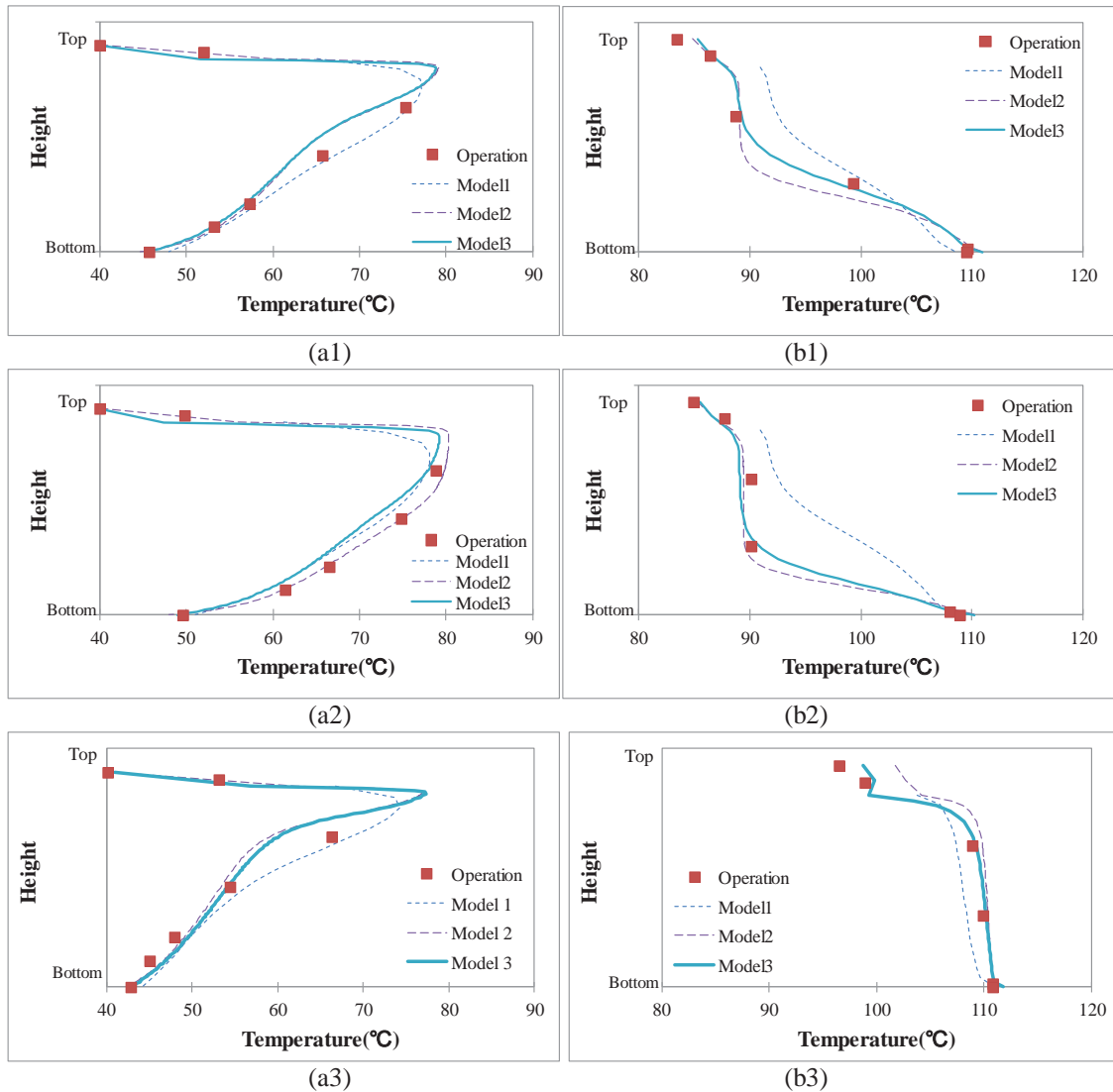

Fig.43. (a1-a3) Temperature profile calculated by each model and observed temperature in the absorber; (b1-b3) Temperature profile calculated by each model and observed temperature in the stripper

6. Conclusion

A modified model was developed based on the rate-based models introduced by previous literature, and validated against the pilot plant operation results in 0.1MW-scale Boryeong pilot plant, South Korea. The developed model showed good agreements with pilot plant results for estimation of loading, heat duty, and temperature in the stripper. Under low L/G ratio operation, all model showed worse estimations due to low lean loading and high rich loading value.

Acknowledgements

References

[1] Kucka, L, Muller, I, Kenig, EY and Gorak, A. On the modelling and simulation of sour gas absorption by aqueous amine solutions. Chemical engineering science 2003; 58: 3571.

[2] Austgen, DM, Rochelle, GT, Xiao, P and Chen, CC. Model of vapor-liquid equilibria for aqueous acid gas-alkanolamine systems using the electrolyte-nrtl equation. Industrials and Engineering Chemistry Research 1989; 28: 1060.

[3] Kucka, L, Kenig, EY and Gorak, A. Kinetics of the gas-liquid reaction between carbon dioxide and hydroxide ions. Industrial & engineering chemistry research 2002; 41: 5952.

[4] Tontiwachwuthikul, P, Meisen, A and Lim, CJ. Co 2 absorption by naoh, monoethanolamine and 2-amino-2-methyl-1-propanol solutions in a packed column. Chemical engineering science 1992; 47: 381.

[5] Pintola, T, Tontiwachwuthikul, P and Meisen, A. Simulation of pilot plant and industrial co2-mea absorbers. Gas Separation and Purification 1993; 7: 47.

[6] Tobiesen, FA, Svendsen, HF and Juliussen, O. Experimental validation of a rigorous absorber model for co2 postcombustion capture. AIChE journal 2007; 53: 846.

[7] Tobiesen, FA, Juliussen, O and Svendsen, HF. Experimental validation of a rigorous desorber model for co2 post-combustion capture. Chemical engineering science 2008; 63: 2641.

[8] Zhang, Y, Chen, H, Chen, CC, Plaza, JM, Dugas, R and Rochelle, GT. Rate-based process modeling study of co2 capture with aqueous monoethanolamine solution. Industrial & engineering chemistry research 2009; 48: 9233.

[9] Hilliard, MD. A predictive thermodynamic model for an aqueous blend of potassium carbonate, piperazine, and monoethanolamine for carbon dioxide capture from flue gas. 2008.

[10] Aboudheir, A. Kinetics, modeling and simulation of co2 absorption into highly concentrated and loaded mea solutions. University of Regina. Ph. D. thesis; 2002.

[11] Dugas, RE. Pilot plant study of carbon dioxide capture by aqueous monoethanolamine. University of Texas at Austin. Master thesis; 2006.

[12] Plaza, JM. Modeling of carbon dioxide absorption using aqueous monoethanolamine, piperazine and promoted potassium carbonate. University at Texas Austin. Ph. D. Dissertation; 2011.

[13] AspenPlus, Rate-based model of the co2 capture process by mea using aspen plus;2011, p.^pp.

[14] Onda, K, Takeuchi, H and Okumoto, Y. Mass transfer coefficients between gas and liquid phases in packed columns. Journal of Chemical Engineering of Japan 1968; 1: 56.

[15] Hanley, B and Chen, CC. New mass-transfer correlations for packed towers. AIChE journal 2012; 58: 132.