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Multicriterial Analysis of Simulated Process of Post-Combustion Capture of Pure H_2S and Mixtures of H_2S and CO_2 Using Single and Blended Aqueous Alkanolamines

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The paper evaluates the performance of the nine selected alkanolamines, namely, monoethanolamine (MEA), diethanolamine (DEA), monomethylethanolamine (MMEA), aminoethylethanolamine (AEEA), diisopropanolamine (DIPA), triethanolamine (TEA), dimethylethanolamine (DMEA), N-methyldiethanolamine (MDEA), and piperazine (PZ) for post-combustion capture of pure hydrogen sulfide (H_2S) and mixtures of hydrogen sulfide and carbon dioxide (CO_2) at different solvent mass flows: 500, 750, and 1000 kg/h using Aspen Plus® Version 7.2. The objective of the paper is to select the best chemical absorbent for each different criterion: percent H_2S removal, percent H_2S solvent carrying capacity, percent H_2S retained in the lean solvent, percent CO_2 and H_2S removal, percent CO_2 and H_2S solvent carrying capacity, percent CO_2 and H_2S retained in the lean solvent. Based from the obtained results, piperazine is an absorbent that has a good potential for use as a single amine or in mixtures with other amines for capture of pure H_2S and mixtures of H_2S and CO_2.

Keywords: Absorption, Alkanolamine, Carbon Dioxide, Post-Combustion Capture, Hydrogen Sulfide, Simulation.

INTRODUCTION

The amount of increase of greenhouse gases in the atmosphere has accelerated and the world is warming more quickly in response. Among these greenhouse gases are carbon dioxide (CO_2) and hydrogen sulfide (H_2S). CO_2 contributes about 80 percent of greenhouse gases. The main reason of global environmental issues is the CO_2 produced in the energy utilization and emitted directly by human beings

(Peng *et al.*, 2012). It is reported that half of the CO_2 emissions are produced by industry and power plants using fossil fuels. Another gas produced in industrial and domestic processes is H_2S. It is an extremely hazardous gas and can result from many industries, primarily from the extraction and refining of oil and natural gas, and from paper and pulp manufacturing. The gas is also present at sewage treatment plants, manure-handling plants, tanneries, and coke oven plants. It is very toxic and highly corrosive gas. Furthermore, the combustion of H_2S produces sulphur dioxide (SO_2) which can react with water in the atmosphere leading to acid rain which is one of the major environmental problems (Rongwong *et al.*, 2012). Usually natural gas refinery streams contain H_2S and CO_2 as major impurities (Faiz and Al-Marzouqi, 2009).

The simultaneous absorption of CO_2 and H_2S is a very significant operation in industrial processing. Some examples of these are purification of ammonia and methanol synthesis gas, sweetening of natural gas, waste water treatment, and hydrogen purifying (Keshavarz *et al.*, 2008). Qi and Cussler (1985) studied membrane absorption of acid gases for the first time. Since then most of studies have been done on the removal of CO_2, particularly from combustion gases which are the major sources of greenhouse gas emissions. Few experimental studies on simultaneous absorption of H_2S and CO_2 by membrane contactors have been reported (Hedayat *et al.*, 2011). Usually absorption into a solvent using conventional gas – liquid contactors such as packed or plate absorption towers are widely used for removal of CO_2 and H_2S. Simultaneous absorption of H_2S and CO_2 using packed towers has been extensively studied, both experimentally and theoretically. Using alkaline solution as the absorption medium, H_2S selectivity was reported to be in the range of 10 to 30 (Faiz and Al-Marzouqi, 2009). However, these conventional chemical absorption processes are not easy to operate because of many disadvantages and operational limitations such as flooding, foaming, entraining, channeling, high capital and operating costs (Rongwong *et al.*, 2012). Additionally, monoethanolamine (MEA) and diethanolamine (DEA) are usually used today for total acid gas CO_2 and H_2S removal (Mandal and Bandyopadhyay 2005). Yet, in spite of the immense commercial significance of single amines or aqueous blended amine solvents for simultaneous removal of CO_2 and H_2S from sour natural gas streams, studies on simultaneous removal of CO_2 and H_2S using different alkanolamines that would be an ideal chemical absorbent with minimal capital investment for capture process have not been reported in the literature so far. Therefore, there is the need for more investigations in finding out the best alkanolamine for pure H_2S and simultaneous H_2S and CO_2 capture using a multicriterial analysis.

This paper evaluated the performances of the nine selected alkanolamines, namely, monoethanolamine (MEA), diethanolamine (DEA), monomethylethanolamine (MMEA), aminoethylethanolamine (AEEA), diisopropanolamine (DIPA), triethanolamine (TEA), dimethylethanolamine (DMEA), N-methyldiethanolamine (MDEA), and piperazine (PZ), and among them choose the best chemical absorbent for each different criterion as follows::

1. Percent H_2S removal
2. Percent H_2S solvent carrying capacity
3. Percent H_2S retained in the lean solvent
4. Percent CO_2 and H_2S removal
5. Percent CO_2 and H_2S solvent carrying capacity
6. Percent CO_2 and H_2S retained in the lean solvent

Aspen Plus® Version 7.2 was used for simulation in the overall performance of the capture process. Also, this study determined the effect of mixing the selected alkanolamines by varying the mass fractions of every solvent – water mixtures. The above assessment was also considered for pure H_2S capture.

METHODS

Selection of Aqueous Single and Blended Alkanolamine Solutions

Aqueous solutions of alkanolamines and amino acid salts are frequently used for the removal of acid gases, such as CO_2 and H_2S, from a variety of gas streams. The dissociation constant is one of the important factors in the selection of an alkanolamine for acid gas removal. It can measure the basic strength of the alkanolamine at a specific temperature and interprets the interaction between the solvent and CO_2 and H_2S molecules (Hamborg and Versteeg, 2009). Hence, the nine selected alkanolamines are presented in Table 1 with their corresponding dissociation constants at a given temperature.

Table 1. Dissociation constant of the studied alkanolamines

Division	Alkanolamine	T (K)	ln (*K*)	Reference
Primary	MEA	298.24	-21.73	Hamborg & Versteeg, 2009
Secondary	DEA	298.15	-8.883	Bower *et al.*, 1962
Secondary	MMEA	298.15	-22.65	Hamborg & Versteeg, 2009
Secondary	AEEA	298.15	-21.43	Hamborg & Versteeg, 2009
Secondary	DIPA	298.09	-20.42	Hamborg & Versteeg, 2009
Tertiary	TEA	298.24	-17.77	Hamborg & Versteeg, 2009
Tertiary	DMEA	293.15	-9.23	Littel *et al.*, 1990
Tertiary	MDEA	298.15	-11.56	Hamborg & Versteeg, 2009
Activated	PZ	298.15	-19.78	Hamborg & Versteeg, 2009

Nine mixtures of selected alkanolamines was simulated with a solvent – water mixture having a constant mass of 30 to 70 mass ratios, respectively, considering the solutions' viscosity and the solvents' economic viability. For varied results, a mass ratio of 10:20 and 20:10 for the two blended alkanolamines will be considered. A total of 81 cases of single and blended aqueous alkanolamine solutions presented in Table 2 were ran into the simulation process (Leron *et al.*,

Table 2. Single and blended aqueous alkanolamine compositions considered in this study

Alkanolamine	Mass%	Alkanolamine	Mass%
MEA^{1*}	30	MMEA + TEA^{42*}	10 – 20
DEA^{2*}	30	MMEA + DMEA^{43*}	10 – 20
MMEA^{3*}	30	MMEA + MDEA^{44*}	10 – 20
AEEA^{4*}	30	MMEA + PZ^{45*}	10 – 20
DIPA^{5*}	30	MMEA + AEEA^{46*}	20 – 10
TEA^{6*}	30	MMEA + DIPA^{47*}	20 – 10
DMEA^{7*}	30	MMEA + TEA^{48*}	20 – 10
MDEA^{8*}	30	MMEA + DMEA^{49*}	20 – 10
PZ^{9*}	30	MMEA + MDEA^{50*}	20 – 10
MEA + DEA^{10*}	10 – 20	MMEA + PZ^{51*}	20 – 10
MEA + MMEA^{11*}	10 – 20	AEEA + DIPA^{52*}	10 – 20
MEA + AEEA^{12*}	10 – 20	AEEA + TEA^{53*}	10 – 20
MEA + DIPA^{13*}	10 – 20	AEEA + DMEA^{54*}	10 – 20
MEA + TEA^{14*}	10 – 20	AEEA + MDEA^{55*}	10 – 20
MEA + DMEA^{15*}	10 – 20	AEEA + PZ^{56*}	10 – 20
MEA + MDEA^{16*}	10 – 20	AEEA + DIPA^{57*}	20 – 10
MEA + PZ^{17*}	10 – 20	AEEA + TEA^{58*}	20 - 10
MEA + DEA^{18*}	20 – 10	AEEA + DMEA^{59*}	20 – 10
MEA + MMEA^{19*}	20 – 10	AEEA + MDEA^{60*}	20 – 10
MEA + AEEA^{20*}	20 – 10	AEEA + PZ^{61*}	20 – 10
MEA + DIPA^{21*}	20 – 10	DIPA + TEA^{62*}	10 – 20
MEA + TEA^{22*}	20 – 10	DIPA + DMEA^{63*}	10 – 20
MEA + DMEA^{23*}	20 – 10	DIPA + MDEA^{64*}	10 – 20
MEA + MDEA^{24*}	20 – 10	DIPA + PZ^{65*}	10 – 20
MEA + PZ^{25*}	20 – 10	DIPA + TEA^{66*}	20 – 10
DEA + MMEA^{26*}	10 – 20	DIPA + DMEA^{67*}	20 – 10
DEA + AEEA^{27*}	10 – 20	DIPA + MDEA^{68*}	20 – 10
DEA + DIPA^{28*}	10 – 20	DIPA + PZ^{69*}	20 – 10
DEA + TEA^{29*}	10 – 20	TEA + DMEA^{70*}	10 – 20
DEA + DMEA^{30*}	10 – 20	TEA + MDEA^{71*}	10 – 20
DEA + MDEA^{31*}	10 – 20	TEA + PZ^{72*}	10 – 20
DEA + PZ^{32*}	10 – 20	TEA + DMEA^{73*}	20 – 10
DEA + MMEA^{33*}	20 – 10	TEA + MDEA^{74*}	20 – 10
DEA + AEEA^{34*}	20 – 10	TEA + PZ^{75*}	20 – 10
DEA + DIPA^{35*}	20 – 10	DMEA + MDEA^{76*}	10 – 20
DEA + TEA^{36*}	20 – 10	DMEA + PZ^{77*}	10 – 20
DEA + DMEA^{37*}	20 – 10	DMEA + MDEA^{78*}	20 – 10
DEA + MDEA^{38*}	20 – 10	DMEA + PZ^{79*}	20 – 10
DEA + PZ^{39*}	20 – 10	MDEA + PZ^{80*}	10 – 20
MMEA + AEEA^{40*}	10 – 20	MDEA + PZ^{81*}	20 – 10
MMEA + DIPA^{41*}	10 – 20		

**Superscript represents the solvent's entry number.*

2014).

Simulation and Modeling

The software Aspen Plus® Version 7.2 developed by Aspen Technology Incorporated was used in all the simulation processes. The Rate-Based Model (RBM) design approach was used in all simulations that considered a reactive and real system for amine towers. It was more applicable than the Equilibrium-Based Method (EBM) by giving more accurate qualitative analyses. While, Non-Random Two Liquid model with Redlich-Kwong equation of state (NRTL-RK) was used as the property method and Henry's Law as the activity coefficient to simulate aqueous electrolyte systems and mixed solvent electrolyte systems with the presence of water. The brief details of the calculations along with the governing equations used were discussed in Appendices A and B. Additionally, the rigorous various type of multistage vapour-liquid fractionation operations model RadFrac was applied both in the design of the absorber and desorber columns (Leron *et al.*, 2014).

Throughout the simulations, the following process parameters were considered:

1. The flue gas feed to the simultaneous capture process simulation of CO_2 and H_2s was composed of the following: 8.4357 mol% CO_2, 0.5668 mol% H_2S, 15.05401 mol% H_2O, 3.8222 mol% O_2, 71.2704 mol% N_2, and 0.8559 mol% Ar (Leron *et al.*, 2014).
2. The flue gas feed to the capture process simulation of pure H_2S was composed of the following: 0.6190 mol% H_2S, 16.4257 mol% H_2O, 4.1723 mol% O_2, 77.8462 mol% N_2, and 0.9348 mol% Ar (Leron *et al.*, 2014).
3. To set real systems, compositions from existing power plants and pilot plants (Al Baghli *et al.*, 2001; Gabrielsen *et al.*, 2007; Oexmann *et al.*, 2008) were used as boundary conditions upon simulation.

The first set of simulations had solvent-water mixture mass flow rate of 1000 kg/h, followed by 750, and lastly 500 kg/h. The inlet temperature and pressure of the solvent mixture was set to 25°C and 5 atm, respectively, based on the previous work of Leron *et al.* (2014).

Details of the Absorption-Desorption Process

The process of absorption and desorption was performed separately to simplify the design of each column. The four streams included in the model of the absorber column, presented in Figure 1, provided the needed information as follows:

1. FLUEGAS – contains the components of the industrial flue gas.
2. LSOLVENT – refers to lean solvent; input of single or blended fresh solvent-water mixtures.
3. RSOLVENT – refers to rich solvent; output of single or blended solvent-water mixtures that have undergone the process of CO_2 and H_2S capture, and pure H_2S capture.
4. GASOUT – gas released to the atmosphere after the capture process.

Normally, according to the study of

Padurean *et al.* (2011), flue gas from industrial plants having extremely high temperatures is cooled with cooling water to around 40 to 50°C prior feeding to the acid gases capture unit. As stated from the study of Oexmann *et al.*, (2008), as no flue gas cooler is applied; the temperature profile in the absorber is dominated mostly by the hot inlet temperature of the flue gas rather than by the exothermic absorption reaction. Therefore, there is a continuous decrease in the absorber temperature from the bottom to the top of the column and does not show a pronounced bulge over the absorber height. There is a further increase in theoretical equilibrium stages that will lead to a change in the results in terms of rich loading and specific reboiler duty of less than 5%. Hence, the typical inlet temperature of flue gas for amine-acid gas absorber at 40°C was suggested to be used and pressure of 5 atmospheres for the study (Al Baghli *et al.*, 2001; Gabrielsen *et al.*, 2007; Oexmann *et al.*, 2008).

The configurations of the absorption column that was used were specified in Table 3. The vendor and material of the packing characteristics were both based from the basic design of an absorption column provided by Aspen Plus® (Leron *et al.*, 2014). All solvent mixtures were simulated using the same configurations.

After the absorption process, the rich solvent mixtures that contain CO_2 and H_2S will be the input in the desorption column, also known as stripping column. This measured and verified the amount of CO_2 and H_2S remained in the alkanolamines. Figure 2 represents the designed desorption column which composed of three material streams and the following are the needed information:

1. RSOLVENT – refers to rich solvent; input of single or blended solvent-water mixtures that have undergone the process of CO_2 and H_2S capture and pure H_2S capture.
2. GASOUT –gas released to the atmosphere after the desorption process.
3. LSOLVENT – refers to lean solvent; output of regenerated single or

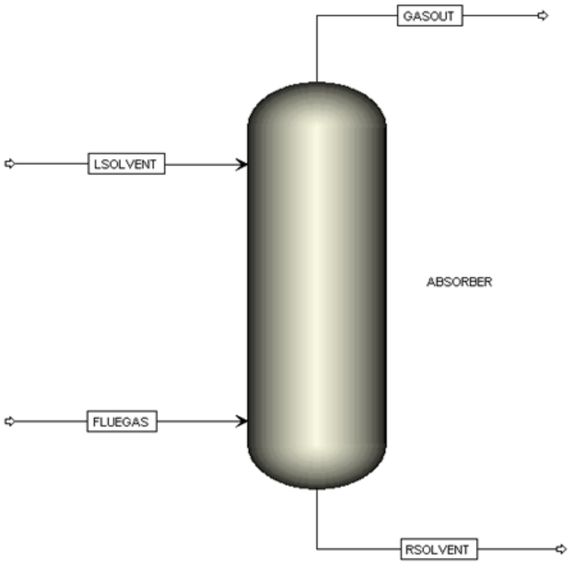

Fig. 1: Absorption column with material streams.

Table 3. Details of the absorption column used in this study

Parameter	SI Unit	Assessment
Calculation Type	---	Rate Based
Number of stages	---	10
Condenser	---	None
Reboiler	---	None
Packing Characteristics		
Vendor	---	Norton
Material	---	Metal
Section diameter	M	0.427
Section packed height	M	6.1
Dimension	Mm	0.38

*Reference: Adornado *et al.*, 2012.

blended solvent-water mixtures that have undergone the desorption process.

Since the simulations were performed separately, the composition of the rich solvent mixtures obtained from the absorption process was manually entered as the composition values of the rich solvent stream of the desorption column The value of the temperature considered was the same temperature obtained after the absorption process, while the pressure was set constant (Leron *et al.*, 2014). Then, the specifications of the desorption column were specified as presented in Table 4. Same with the absorber, the vendor and material of the packing characteristics used were based on the basic design of a desorption column provided by Aspen Plus®. All rich solvent mixtures were simulated using the same configurations.

After the absorption and desorption process simulations, the percent CO_2 and H_2S removal, percent CO_2 and H_2S solvent carrying capacity, and percent CO_2 and H_2S retained in the lean solvent of each solvent-water mixtures, from solvent entry number 1 to 81 with three different mass flow rates, were calculated using Eqns. (1) to (3) for CO_2, correspondingly and (4) to (6) for H_2S.

$$\%\ \mathrm{CO_2\ removal} = \frac{\text{Absorbed } \mathrm{CO_2} \text{ mass flow in the rich solvent (RS)}}{\text{Inlet } \mathrm{CO_2} \text{ mass flow in effluent gas (EG)}}\ x\ 100 \quad (1)$$

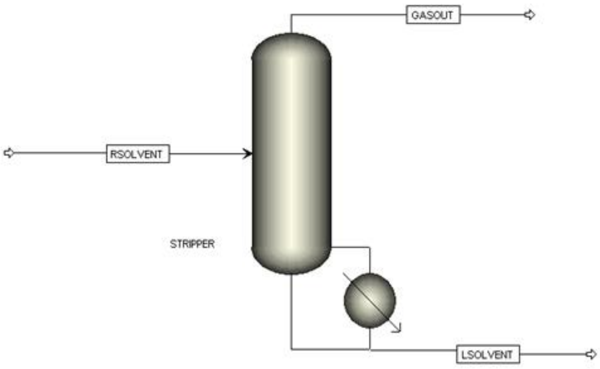

Fig. 2: Desorption column with material streams.

Table 4. Details of the desorption column used in this study

Parameter	SI Unit	Assessment
Calculation Type	---	Rate Based
Number of stages	---	10
Condenser	---	None
Reboiler	---	Kettle
Packing Characteristics		
Vendor	---	Norton
Material	---	Metal
Section diameter	M	0.427
Section packed height	M	10
Dimension	Mm	0.38

*Reference: Adornado *et al.,* 2012.

$$\%\ \mathrm{CO_2}\ \text{solvent carrying capacity}= \frac{\text{Absorbed } \mathrm{CO_2} \text{ in RS}}{\text{Solvent mass flow rate in RS}}\ x\ 100 \qquad (2)$$

$$\%\ \mathrm{CO_2}\text{retained in lean solvent}= \frac{\text{Absorbed } \mathrm{CO_2} \text{ in lean solvent (LS)}}{\text{Absorbed } \mathrm{CO_2} \text{ in RS}}\ x\ 100 \qquad (3)$$

$$\%\ \mathrm{H_2S}\ \text{removal}= \frac{\text{Absorbed } \mathrm{H_2S} \text{ mass flow in the rich solvent (RS)}}{\text{Inlet } \mathrm{H_2S} \text{ mass flow in effluent gas (EG)}}\ x\ 100 \qquad (4)$$

$$\%\ \mathrm{H_2S}\ \text{solvent carrying capacity} = \frac{\text{Absorbed } \mathrm{H_2S} \text{ in RS}}{\text{Solvent mass flow rate in RS}}\ x\ 100 \qquad (5)$$

$$\%\ \mathrm{H_2S}\ \text{retained in lean solvent}= \frac{\text{Absorbed } \mathrm{H_2S} \text{ in lean solvent (LS)}}{\text{Absorbed } \mathrm{H_2S} \text{ in RS}}\ x\ 100 \qquad (6)$$

RESULTS AND DISCUSSION

Pressure Optimization for Absorption-Desorption Process

The original methodology proposed was supposed to use a pressure close to atmospheric pressure which is 1.2 atm based on the previous study done by Leron *et al.* (2014). However, it was observed that 1.2 atm is not effective in the system especially for simultaneous capture of CO_2 and H_2S when simulated. Therefore, different pressures were used at different run to optimize the pressure that will yield to a high effective absorption. Table 5 presented the percent removal of the top ten aqueous alkanolamine solutions at 1.2 atm and was compared to the following pressures: 2 atm, 3 atm, 4 atm, and 5 atm at 1000 kg/h solvent flow rate. As seen in this table, there was a substantial increase in percentage removal of H_2S from 1.2 atm up to 5 atm. Primarily, this is due to the composition of the flue gas where there is a small amount of H_2S and needs to be pressurized to obtain the desired percentage capture. In addition, according to the previous work of Leron *et al.* (2014) the increase in column pressure, rich loading increases and hence, the

Table 5. Comparison of percent H_2S removal at different pressures*

Solvent	% H_2S Removal				
	1.2 atm	2 atm	3 atm	4 atm	5 atm
30% PZ[9]	81.393	96.522	99.316	99.782	99.906
10% MEA + 20% PZ[17]	81.372	96.368	99.260	99.761	99.896
20% MEA + 10% PZ[25]	81.273	96.181	99.194	99.735	99.884
10% MMEA + 20% PZ[45]	81.208	96.369	99.268	99.764	99.898
10% DMEA + 20% PZ[77]	81.208	96.426	99.288	99.772	99.901
30% MEA[1]	81.091	95.959	99.117	99.706	99.870
20% MEA + 10% DMEA[23]	81.054	96.066	99.160	99.723	99.878
20% DMEA + 10% PZ [79]	81.018	96.327	99.259	99.762	99.897
20% MMEA + 10% PZ[51]	80.990	96.198	99.215	99.745	99.889
20% MEA + 10% MMEA [19]	80.984	95.979	99.130	99.712	99.874

**Ten highest solvent system in terms of percent H_2S removal at 1000 kg/h solvent and 1.2 atm.*

percent acid gases capture also increases. Pressures at 3 atm to 5 atm have almost the same percentage removal of pure H_2S.

Table 6 showed a minimal difference of percent removal of simultaneous CO_2 and H_2S at different pressures. As seen in this table, 5 atm pressure gave the highest effective removal of the acid gases. To compare the results of pure capture and simultaneous capture, this paper opted to use the same conditions all throughout. Thus, 5 atm was considered for both pure and simultaneous capture in absorption-desorption process here after.

Simulation Results for Absorption Process

For the absorption process, two criteria were evaluated to verify the performance of the alkanolamine solutions used in the simulation. These were percent acid gas removal and percent solvent carrying capacity. Both should be significantly high to consider a solvent to be a good chemical absorbent.

H_2S Removal

Figure 3 illustrated the percent removal of 81 cases of single and blended alkanolamine mixtures at three different flow rates. When the flue gas and fresh solvent entered the process, it was observed that the alkanolamine mixture was effective since it captured 98-99% of H_2S for 500, 750, and 1000 kg/h solvent flow rate. These three flow rates were considered to evaluate the significance of varying the solvent mass flow rate. The plot showed the increase in percent removal of H_2S as the flow rate of solvent increases since more H_2S were allowed to absorb (Cheng and Tan, 2009) due to many solvent allowing more capture of gases. Furthermore, at 1:10 ratio was

Table 6. Comparison of percent CO_2 and H_2S removal at different pressures*

Solvent	%CO2 and H2S Removal				
	1.2 atm	2 atm	3 atm	4 atm	5 atm
30% PZ [9]	45.059	71.031	90.167	96.756	98.754
10% DMEA + 20% PZ [77]	45.002	70.891	90.005	90.005	98.711
10% MMEA + 20% PZ [45]	45.181	71.018	89.976	89.976	98.685
20% DMEA + 10% PZ [79]	44.944	70.750	89.843	89.843	98.667
10% MEA + 20% PZ [17]	45.472	71.292	90.066	96.633	98.682
30% DMEA [7]	44.886	70.609	89.681	96.484	98.622
10% MDEA + 20% PZ [80]	44.681	70.364	89.544	89.544	98.604
10% AEEA + 20% PZ [56]	44.785	70.447	89.547	89.547	98.594
20% MMEA + 10% PZ [51]	45.290	70.964	89.762	89.762	98.609
10% MMEA + 20% DMEA [43]	45.058	70.714	89.637	89.637	98.591

**Ten highest solvent system in terms of percent CO_2 and H_2S removal at 1000 kg/h solvent and 5 atm.*

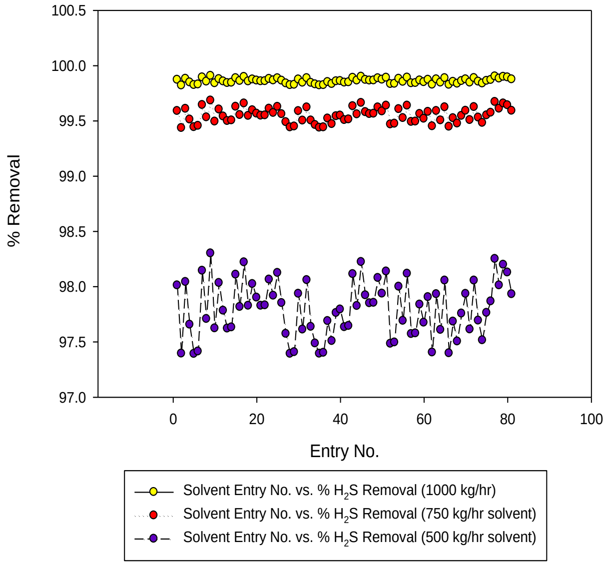

Fig.3: Plot of the percent removal of pure H_2S using the considered solvent systems.

identified as the most effective ratio of flue gas and lean solvent since it removed almost 100 percent of H_2S in the flue gas. Hence, the percentage H_2S removal of aqueous solutions of alkanolamine for the three flow rates are acceptable having the range of 98 to almost 100 % removal because in considering the good chemical absorbent, it must be evidently high.

The top five most promising aqueous solutions of alkanolamines for H_2S removal were presented in the Table 7. These alkanolamine mixtures were based on the 500 kg/h solvent mass flow rate since they captured as high as the two other flow rates (750 and 1000 kg/hr). Among the nine selected alkanolamines, Piperazine (PZ) which is an activated amine was the most effective alkanolamine in capturing H_2S. It has a promising performance for

Table 7. Top five alkanolamine mixtures for H_2S removal*

Solvent Entry No.	Solvent	Type of Amine System	% Hydrogen Sulfide Removal
9	30% PZ	Activated amine	98.299
77	10% DMEA + 20% PZ	Tertiary amine and activated amine	98.249
45	10% MMEA + 20% PZ	Tertiary amine and activated amine	98.222
17	10% MEA + 20% PZ	Secondary amine and activated amine	98.219
79	20% DMEA + 10% PZ	Tertiary amine and activated amine	98.197

**In decreasing order at 500kg/h solvent flow.*

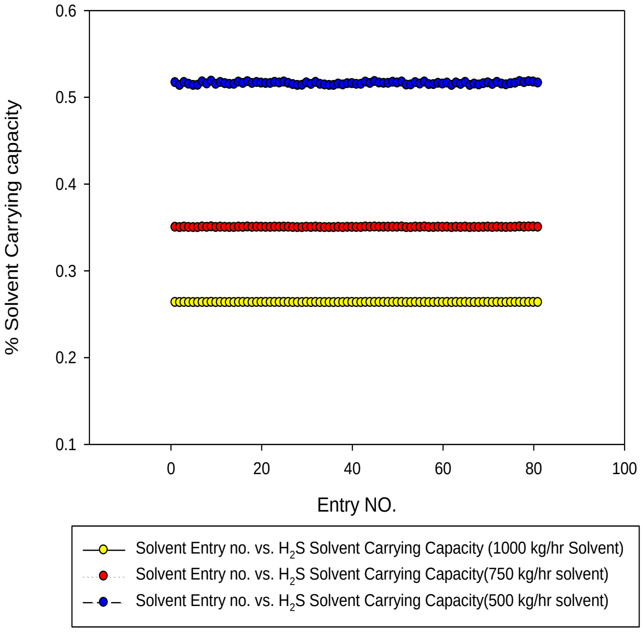

Fig.4: Plot of the solvent carrying capacity of pure H_2S using the considered solvent systems.

both single and blended alkanolamine solvent.

PZ is a novel solvent for carbon dioxide capture by absorption or stripping. New studies illustrated that concentrated PZ gives fast kinetics rate, high absorption capacity and beneficial solvent properties (Freeman *et al.*, 2010). Furthermore, PZ consists of a six-membered ring containing two opposing nitrogen atoms that made it reach very high loadings. It also absorbed acid gas rapidly.

Solvent Carrying Capacity

This is the amount of H_2S that can be carried by an alkanolamine mixture. Figure 4 shows the H_2S carrying capacity of the single and blended alkanolamine

Table 8. Comparison of H_2S solvent carrying capacity at 500 and 1000 kg/h solvent flow

Solvent	Solvent Carrying Capacity	
	500 kg/h Solvent	1000 kg/h Solvent
30% PZ [9]	0.5182	0.2633
10% DMEA + 20% PZ 7[7]	0.5178	0.2632
10% MMEA + 20% PZ [45]	0.5177	0.2632
10% MEA + 20% PZ [17]	0.5177	0.2633
20% DMEA + 10% PZ [79]	0.5176	0.2632

Table 9. Top five alkanolamine mixture for H_2S solvent carrying capacity*

Solvent Entry No.	Solvent	Division	Solvent Carrying Capacity
9	30% PZ	Activated amine	0.5182
77	10% DMEA + 20% PZ	Tertiary amine and activated amine	0.5178
45	10% MMEA + 20% PZ	Tertiary amine and activated amine	0.5177
17	10% MEA + 20% PZ	Secondary amine and activated amine	0.5177
79	20% DMEA + 10% PZ	Tertiary amine and activated amine	0.5176

**In decreasing order; 500 kg/h solvent flow rate.*

solutions at three different flow rates. As seen in this figure, 500 kg/h solvent flow rate gave a better solvent carrying capacity of H_2S than the other two flow rates. It implies that the smaller the amount of solvent entering the absorber, the higher H_2S was carried by the solvent. This is due to the high absorbed amount of H_2S molecules over the small quantity of inlet solvent. Also, it is established on the study of Lu *et al.* (2006) that with the increase of H_2S loading of lean-solution, H_2S removal efficiency decreases. Therefore, it is better to have a smaller flow rate to achieve a good result for the evaluation of the solvent carrying capacity. Comparison of H_2S solvent carrying capacity at 1000 kg/h solvent flow and 500 kg/h solvent flow were given in Table 8.

The five most promising aqueous solution of alkanolamines for carrying capacity was presented in Table 9. The same set of top five from the removal of H_2S from pure H_2S removal appeared to have the highest values for carrying capacity. Likewise, PZ performed better among the evaluated selected alkanolamines. It is anticipated since it gave a good performance on H_2S removal therefore, it should give the same performance on the carrying capacity.

Simultaneous CO_2 and H_2S Removal

The removal of simultaneous H_2S and CO_2 using 81 solvent systems of single and blended aqueous solution of alkanolamines at three different flow rates was shown in Figure 5. As depicted in the figure, as the solvent flow rate decreases, the percent removal of both CO_2 and H_2S decreases. The 1:10 ratio of flue gas and fresh solvent is the highly effective ratio for removing the desired gases which gave almost 100 % removal. However, there is a high difference between the removal of 500 and 1000 kg/h solvent flow. This is due to the amount of CO_2 and H_2S entering the absorber. The composition of the gases in the flue gas is high. Hence,

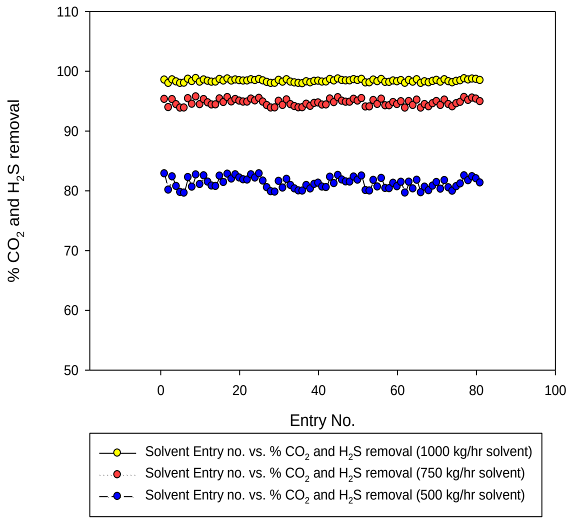

Fig.5: Plot of the percent CO_2 and H_2S removal using the considered solvent systems.

Table 10. Top five alkanolamine mixture for CO_2 and H_2S percent removal*

Solvent Entry No.	Solvent	Division	CO_2 and H_2S Percent Removal
9	30% PZ	Activated amine	98.754
77	10% DMEA + 20% PZ	Tertiary amine and activated amine	98.711
45	10% MMEA + 20% PZ	Tertiary amine and activated amine	98.685
17	10% MEA + 20% PZ	Secondary amine and activated amine	98.682
79	20% DMEA + 10% PZ	Tertiary amine and activated amine	98.667

**In decreasing order; 1000 kg/h solvent flow rate.*

high rate of solvent must be considered as well. The removal of 500 kg/h is acceptable since it gives more than 80 % removal of CO_2 and H_2S.

The top five promising aqueous alkanolamine solution for 1000 kg/h were shown in Table 10. As observed in the table, the top five aqueous alkanolamine solutions in removing pure H_2S are the same set of aqueous alkanolamines in CO_2 and H_2S removal. Still, PZ is the best among the nine selected alkanolamines in terms of removing the acid gases. Based from obtained results, higher amount of PZ in the solution resulted to higher percent removal of CO_2 and H_2S. Not only as a single solvent compromising 30% of the alkanolamine-water solution, PZ can perform satisfactorily in removing acid gases even if it is blended with other alkanolamines specifically in tertiary amine and secondary amine. As presented by Bishnoi and Rochelle (2000, 2002), PZ has been used in gas treating as an additive, primarily with methyldiethanolamine (MDEA) which has been commercialized by BASF Corporation, as well as with diethanolamine (DEA) and together with monomethylmethanolamine (MMEA) for over 20 years. Also, PZ is almost 10 times more reactive with CO_2 than any of the other common amines. This makes it as an excellent promoter for the reactions that occur when CO_2 absorbs.

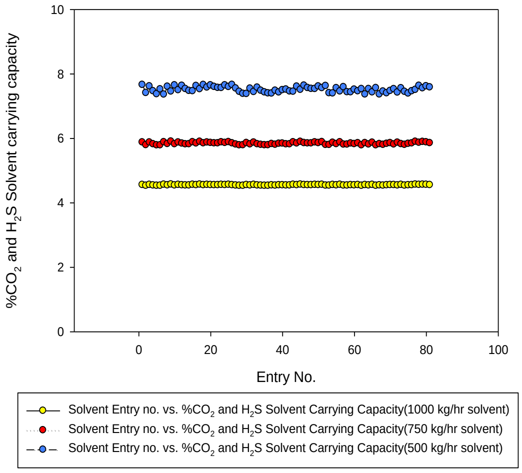

Fig. 6:Plot of the solvent carrying capacity of CO_2 and H_2S using the considered solvent

Table 11. Top five alkanolamine mixture for CO_2 and H_2S solvent carrying capacity*

Solvent Entry No.	Solvent	Division	Solvent Carrying Capacity
9	30% PZ	Activated amine	4.567
77	10% DMEA + 20% PZ	Tertiary amine and activated amine	4.565
45	10% MMEA + 20% PZ	Tertiary amine and activated amine	4.564
17	10% MEA + 20% PZ	Secondary amine and activated amine	4.564
79	20% DMEA + 10% PZ	Tertiary amine and activated amine	4.563

In decreasing order; 1000 kg/h solvent flow rate.

Simultaneous Solvent Carrying Capacity

Figure 6 shows the capacity of the aqueous alkanolamine solutions to carry CO_2 and H_2S under the absorption process. As can be seen in the figure, when the solvent flow rate was lowered, there was an increase in solvent carrying capacity. This is also true and the same compared to the results obtained in the absorption of pure H_2S. Thus, it implied the consistency of the results. If there is a great removal in flue gas and small quantity of the inlet solvent it will yield to better solvent carrying capacity.

Table 11 shows the same set of top five aqueous alkanolamine solutions for both percent removal and percent carrying capacity from the simultaneous capture of CO_2 and H_2S. PZ is highly effective for both removal and solvent carrying capacity for the acid gases being the top solvent among 81 systems. Therefore, it follows that aqueous solution of alkanolamines with high effectiveness in removing the undesired gases in the flue gas would have a high carrying capacity.

Simulation Results for Desorption Process

Another criterion for choosing an affective solvent is based from the amount of gas retained in the solvent. High attraction between the gas molecules and the solvent can give an undesirable effect since the gas cannot easily desorbs from the solvent due to high affinity to the molecules and thus, results low regeneration of the alkanolamines. The

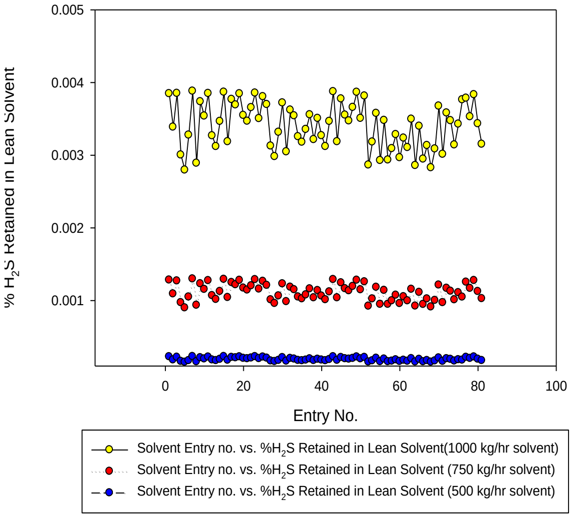

Fig. 7: Plot of the percent H_2S retained in the lean solvent

Table 12. Percent H_2S retained in 30% DIPA and 30% PZ*

Solvent Entry No.	Solvent	Division	H_2S Retained
5	30% DIPA	Secondary Amine	0.0001484
9	30% PZ	Activated amine	0.0002115

In decreasing order; 500 kg/h solvent flow rate.

higher the amount of acid gas in the solvent, the more difficult it is to remove these gases from the solvent. Thus, more fresh solvent is needed for absorption of gases due to less solvent that is regenerated. Consequently, this may result to high increase of cost for the whole method since more fresh solvent is needed when less recycled solvent is attained.

H_2S Removal

Figure 7 shows the percent H_2S retained in lean solvent. Based on the figure, there was a small difference between the desorption capability of 500 kg/h and 1000 kg/h. Among the collected results, entry number 5 (30% DIPA) for both flow rate of 500 kg/h and 1000 kg/h of solvent has the lowest attraction to H_2S molecules. This value is true since 30% DIPA is one of the alkanolamine mixtures which capture the least amount of H_2S.

Considering 30% PZ in desorbing gas, Table 12 shows the performance of 30% PZ as it is compared with 30% DIPA. As it is observed, there is just a small difference between their percent H_2S retained hence, 30% PZ can also be considered for this criterion.

Simultaneous CO_2 and H_2S Removal

Figure 8 shows the simulation results during the desorption process of simultaneous CO_2 and H_2S. As expected,

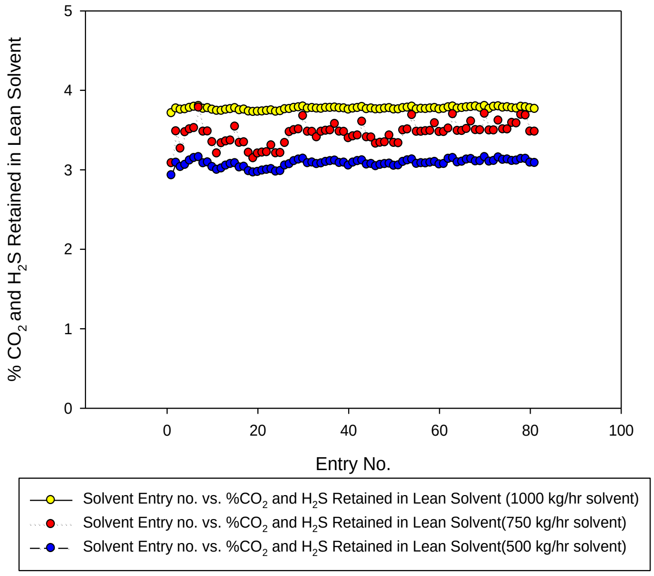

Fig. 8: Plot of the percent CO_2 and H_2S retained in lean solvent.

solvent with mass flow rate of 500 kg/h consists of lowest percentage of CO_2 and H_2S after desorption process based from its absorption capability. From top alkanolamine mixtures that contain low percentage of CO_2 and H_2S after desorption process, entry number 1 (30% MEA) contains the least number of CO_2 and H_2S for all solvent mass flow rate (500, 750, and 1000 kg/h). For simultaneous desorption of CO_2 and H_2S, a small difference was observed on gas retained between 30% MEA and 30% PZ having 2.928% and 3.090% respectively as presented in Table 12, thus, PZ can again considered for this criterion.

CONCLUSION

CO_2 capture using aqueous alkanolamine solution by absorption-desorption process was proven to be effective in removing CO_2 gas from flue gas of various industries. However, this paper not only proved that only CO_2 capture can be applied on the same process but also pure H_2S and simultaneous capture of CO_2 and H_2S. On the other hand, there should be a thorough investigation in selecting the appropriate alkanolamines that will be used to remove the gases because not all alkanolamines have high potential. Thus, the following conclusions were drawn from the study:

1. Thirty percent (30%) of PZ (solvent entry number 9) is the most promising alkanolamine solution or absorption of pure H_2S and simultaneous capture of CO_2 and H_2S since it captured almost 100% at three different mass flow rates of 500, 750, and 1000 kg/h. Also, the CO_2 and H_2S retained in the mixture are found to be relatively low.
2. Piperazine (PZ) which is an activated amine when blended with secondary amine like monoethanolamine (MEA) or tertiary amine such as dimethylethanolamine (DMEA) and

monomethyethaolamine (MMEA) can still be effective in absorption process.

3. Solvent flow rate affects the removal and carrying capacity. The higher the amount of solvent the higher the percent removal during the absorption process. Meanwhile, the minimum flow rate is highly effective in carrying CO_2 and H_2S molecules.
4. PZ which removed almost all the gases also got low possibility to strip out or desorb the CO_2 and H_2S that it carried. In other words, alkanolamine mixtures that have high attractions on these gases would yield to low amount of stripping.

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APPENDIX A

Electrolyte NRTL Activity Coefficient Model

The ENRTL equation (Chen & Evan, 1986; Mock *et al.*, 1986; Augsten *et al.*, 1989) used in this work to calculate excess Gibbs free energy is given by Eq. (1):

$$g^{ex^*} = g^{ex^*}{}_{PDH} + g^{ex^*,Born} + g^{ex^*,local} \tag{A.1}$$

$$g^{ex^*}{}_{PDH} = -RT\left(\sum_k x_k\right)\left(\frac{1000}{M_s}\right)^{1/2}\left(\frac{4A_\emptyset I_x}{\rho}\right) \ln\left(1+\rho {I_x}^{1/2}\right) \tag{A.2}$$

where Pitzer–Debye–Hückel (Pitzer, 2002) parameter, $A_\emptyset$, and ionic strength of solvent, I_x, are given by Eqs. (3) and (4), respectively.

$$A_\emptyset = \frac{1}{3}\left(\frac{2\pi N_o d}{1000}\right)^{1/2}\left(\frac{e^2}{D_w k_B T}\right)^{1.5} \tag{A.3}$$

$$I_x = 0.5\sum_k x_k {z_k}^2 \tag{A.4}$$

The Born correction term (Robinson & Stokes, 1970) for the excess Gibbs free energy is given by:

$$g^{ex^*,Born} = RT\left(\frac{e^2}{2k_B T}\right)\left(\frac{1}{D_s}-\frac{1}{D_w}\right) \left(\sum_k \frac{x_k {z_k}^2}{r_k}\right) 10^{-2} \tag{A.5}$$

The NRTL expression for the short range interactions is given as:

$$g^{ex^*,local} = \left(\sum_m X_m \frac{\sum_j X_j G_{jm}\tau_{jm}}{\sum_k X_k G_{km}}\right) +$$

$$\sum_c X_c \sum_{a'} \frac{X_{a'} \sum_j G_{jc,a'c}\tau_{jc,a'c}}{\left(\sum_{a''} X_{a''}\right)\left(\sum_k X_k G_{kc,a'c}\right)} + \cdots +$$

$$+ \sum_a X_a \sum_{c'} \frac{X_{c'} \sum_j G_{ja,c'a}\tau_{ja,c'a}}{\left(\sum_{c''} X_{c''}\right)\left(\sum_k X_k G_{ka,c'a}\right)} \tag{A.6}$$

where *j* and *k* can be any species. The definitions of all terms in Eq. (6) were given earlier by Augsten *et al.*, 1989 and Renon & Prausnitz, 1968.

$$G_{jc,a'c} = e^{\left(-\alpha_{jc,a'c}\tau_{jc,a'c}\right)} \tag{A.7}$$

$$G_{ja,c'a} = e^{\left(-\alpha_{ja,c'a}\tau_{ja,c'a}\right)} \tag{A.8}$$

$$\tau_{ca,m} = -\frac{\ln G_{ca.m}}{\alpha_{ca,m}} \tag{A.9}$$

$$\tau_{im} = -\frac{\ln G_{im}}{\alpha_{im}} \tag{A.10}$$

where $X_j = x_j C_j$ ($C_j = z_j$ for ions, and 1 for molecules), α_{ij} is the non-randomness factor and τ_{ij} is the binary energy interaction parameter. The activity coefficient for any species (ionic or molecular, solute or solvent) is calculated from the partial derivative of the excess Gibbs energy with respect to mole number as follows:

$$\ln\gamma_i = \frac{1}{RT}\left[\frac{\partial\left(n_t G^{*E}\right)}{\partial n_i}\right]_{T,P,n_{j\neq i}} \quad i,j = m,c,a \tag{A.11}$$

APPENDIX B

Kinetic Modeling

The power law kinetic expressions are used for the rate controlled reactions where the rate is the product of kinetic factor and driving force. The general power law expression is:

$$r = k\left(\frac{T}{T_o}\right)^n \exp\left[\left(\frac{-E}{R}\right)\left(\frac{1}{T}-\frac{1}{T_o}\right)\right]\prod_{i=1}^{N} {C_i}^{a_i} \tag{B.1}$$

To account for the highly non-ideal nature of the solvent, the kinetics are modeled with activities as shown in Eq. (B.2)

$$r = k\prod_i a_i \tag{B.2}$$

Table B.1. Reaction Set for the Studied CO_2 – H_2S – Amine – H_2O System

Type	Reaction	Stoichiometry
Equilibrium	1	$2H_2O \leftrightarrow H_3O^+ + OH^-$
Equilibrium	2	$CO_2 + 2H_2O \leftrightarrow H_3O^+ + HCO_3{}^-$
Equilibrium	3	$HCO_3{}^- + H_2O \leftrightarrow H_3O^+ + CO_3{}^{2-}$
Equilibrium	4	$H_2O + H_2S \leftrightarrow HS^- + H_3O^+$
Equilibrium	5	$H_2O + HS^- \leftrightarrow S^{2-} + H_3O^+$
Equilibrium	6	$MEAH^+ + H_2O \leftrightarrow MEA + H_3O^+$
Equilibrium	7	$MEACOO^- + H_2O \leftrightarrow MEA + HCO_3{}^-$
Equilibrium	8	$DEAH^+ + H_2O \leftrightarrow DEA + H_3O^+$
Equilibrium	9	$DEACOO^- + H_2O \leftrightarrow DEA + HCO_3{}^-$
Equilibrium	10	$MMEAH^+ + H_2O \leftrightarrow MMEA + H_3O^+$
Equilibrium	11	$MMEACOO^- + H_2O \leftrightarrow MMEA + HCO_3{}^-$
Equilibrium	12	$AEEAH^+ + H_2O \leftrightarrow AEEA + H_3O^+$
Equilibrium	13	$AEEACOO^- + H_2O \leftrightarrow AEEA + HCO_3{}^-$
Equilibrium	14	$DIPAH^+ + H_2O \leftrightarrow DIPA + H_3O^+$
Equilibrium	15	$DIPACOO^- + H_2O \leftrightarrow DIPA + HCO_3{}^-$
Equilibrium	16	$TEAH^+ + H_2O \leftrightarrow TEA + H_3O^+$
Equilibrium	17	$DMEAH^+ + H_2O \leftrightarrow DMEA + H_3O^+$
Equilibrium	18	$MDEAH^+ + H_2O \leftrightarrow MDEA + H_3O^+$
Equilibrium	19	$PZH^+ + H_2O \leftrightarrow PZ + H_3O^+$
Equilibrium	20	$PZ + HCO_3{}^- \leftrightarrow PZCOO^- + H_2O$
Equilibrium	21	$HPZCOO + H_2O \leftrightarrow PZCOO^- + H_3O^+$
Equilibrium	22	$PZCOO^- + HCO_3{}^- \leftrightarrow PZ(COO^-)_2 + H_2O$
Kinetic	23	$CO_2 + OH^- \leftrightarrow HCO_3{}^-$
Kinetic	24	$MEA + CO_2 + H_2O \leftrightarrow MEACOO^- + H_3O^+$
Kinetic	25	$DEA + CO_2 + H_2O \leftrightarrow DEACOO^- + H_3O^+$
Kinetic	26	$MMEA + CO_2 + H_2O \leftrightarrow MMEACOO^- + H_3O^+$
Kinetic	27	$AEEA + CO_2 + H_2O \leftrightarrow AEEACOO^- + H_3O^+$
Kinetic	28	$DIPA + CO_2 + H_2O \leftrightarrow DIPACOO^- + H_3O^+$
Kinetic	29	$TEA + CO_2 + H_2O \leftrightarrow TEAH^+ + HCO_3{}^-$
Kinetic	30	$DMEA + CO_2 + H_2O \leftrightarrow DMEAH^+ + HCO_3{}^-$
Kinetic	31	$MDEA + CO_2 + H_2O \leftrightarrow MDEAH^+ + HCO_3{}^-$
Kinetic	32	$PZ + CO_2 + H_2O \leftrightarrow PZCOO^- + H_3O^+$
Kinetic	33	$PZCOO^- + CO_2 + H_2O \leftrightarrow PZ(COO^-)_2 + H_3O^+$

k is the reaction constant and a_i is the activity of component i. k can be computed using Eq. (B.3)

$$k = k_o \exp\left[\left(\frac{-E_A}{R}\right)\left(\frac{1}{T}-\frac{1}{T_{ref}}\right)\right] \tag{B.3}$$

Here k_o is the reaction pre-exponential, E_A is the activation energy, R is the universal gas constant, and T_{ref} is the reference temperature.

The reaction set in Table B.1 has two types of reactions: kinetic and equilibrium. Equilibrium reactions are handled by the thermodynamic model calculating the excess Gibbs free energy. Kinetic reactions are a pair of forward and reverse reactions, where each reaction rate can be calculated by Eq. (B.2). The reaction pre-exponential and the activation energy in Eq. (B.3) can be regressed for the forward reactions, while the reverse rate can be back calculated from the reaction equilibrium

Table B.2. Reaction Parameters for Kinetic Reactions

Stoichiometry	k_o (in SI units)		E (cal/mol)	
	Forward	Reverse	Forward	Reverse
$\mathrm{CO_2 + OH^- \leftrightarrow HCO_3{}^-}$	4.32E+13	2.38E+17	13,249	29,451
$\mathrm{MEA + CO_2 + H_2O \leftrightarrow MEACOO^- + H_3O^+}$	9.77E+10	3.23E+19	9,856	15,655
$\mathrm{DEA + CO_2 + H_2O \leftrightarrow DEACOO^- + H_3O^+}$	6.48E+06	1.34E+17	5,072	11,497
$\mathrm{MMEA + CO_2 + H_2O \leftrightarrow MMEACOO^- + H_3O^+}$	-	-	-	-
$\mathrm{AEEA + CO_2 + H_2O \leftrightarrow AEEACOO^- + H_3O^+}$	-	-	-	-
$\mathrm{DIPA + CO_2 + H_2O \leftrightarrow DIPACOO^- + H_3O^+}$	4.09E+09	2.16E+19	9,563	15,021
$\mathrm{TEA + CO_2 + H_2O \leftrightarrow TEAH^+ + HCO_3{}^-}$	3.01E+09	4.63E+11	12,291	18,576
$\mathrm{DMEA + CO_2 + H_2O \leftrightarrow DMEAH^+ + HCO_3{}^-}$	-	-	-	-
$\mathrm{MDEA + CO_2 + H_2O \leftrightarrow MDEAH^+ + HCO_3{}^-}$	2.22E+07	1.06E+16	9,029	25,424
$\mathrm{PZ + CO_2 + H_2O \leftrightarrow PZCOO^- + H_3O^+}$	4.14E+10	9.47E+20	8,038	15,333
$\mathrm{PZCOO^- + CO_2 + H_2O \leftrightarrow PZ(COO^-)_2 + H_3O^+}$	3.62E+10	3.46E+20	8,038	17,958

constant from the thermodynamic model. This will ensures consistency with the thermodynamic model. The reaction parameters are shown in Table B.2. They are grouped by the CO_2 product.