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APPENDICES

Appendix A Amine Solution Preparation Calculations

The solution concentration for the experimental analysis of the ternary AMP-PZ-MEA blend is discussed in this subsection. The properties of each solvent stock solution as provided in the material safety data sheet (MSDS) is highlighted in Table A1 below;

Table A1 Properties of AMP, PZ and MEA

	AMP	PZ	MEA
Molecular Weight (g/mol)	89.14	86.14	61.08
Purity (wt%)	99	99	99
Density (g/L)	930		1012
Calculated Molar Concentration (mole/L, M)	10.3		16.5

The molarity (molar concentration) of the stock solution of each solvent (available in liquid form: AMP and MEA) was calculated using the general formula seen in Equation A1.

$$\text{Molarity (mol/L)} = \frac{\text{purity (wt\%)} \times \text{density (g/L)}}{\text{molecular weight (g/mol)} \times 100} \qquad A1$$

The ternary blend solution was prepared based on molarity basis (moles/L or kmol/m^3 or M). The preparation followed the correlation described in Equation A2.

$$Mass\ of\ Solv.(g) = Solv.Conc.\left(\frac{mole}{L}\right) \times Solution\ Vol.(L) \times MW\left(\frac{g}{mole}\right) \qquad A2$$

$$MW = Molecular\ Weight\ of\ solvent,\left(\frac{g}{mole}\right)$$

Example A1:

Preparing 500 mL of 2 M AMP – 0.5 M PZ – 3 M MEA solution.

Calculation:

From Equation A2 it is noticed that the unit of the sample solution is in liters (L) and moreso the concentration is based on 'how many moles of the solvent is present in the sample solution'. Therefore, 500 mL will be converted to 'L' which gives 0.5 L. The

AMP;

$$Mass\ of\ PZ\ (g) = 2\ \left(\frac{mole}{L}\right) \times 0.5\ (L)\ \times 89.14\ \left(\frac{g}{mole}\right)$$

$$Mass\ of\ PZ\ = 89.14\ g$$

PZ;

$$Mass\ of\ PZ\ (g) = 0.5\ \left(\frac{mole}{L}\right) \times 0.5\ (L)\ \times 86.14\ \left(\frac{g}{mole}\right)$$

$$Mass\ of\ PZ\ = 21.53\ g$$

MEA;

$$Mass\ of\ PZ\ (g) = 3\ \left(\frac{mole}{L}\right) \times 0.5\ (L)\ \times 61.08\ \left(\frac{g}{mole}\right)$$

$$Mass\ of\ PZ\ = 91.62\ g$$

Its very important to note that all the mass of each individual solvent should be weighed out separately, and when mixing them do not add 500 mL of water. First add all the solvents, then add about 250 mL of water and allow a homogenous mixture to occur. Then fill the volumetric flask with water to the 500 mL mark. This will guarantee the exact concentration of each solvent. In this case one of the solvents (PZ) is in solid form, and this will add some volume to the blended solution. If 500 mL of water is added with

the mass of all solvents, the final solution volume will exceed 500 mL and as such give a different concentration of each solvent.

Appendix B Hydrochloric (HCl) Acid Preparation and Standardization

Hydrochloric acid (HCl) is integral in the experimental analysis because its used as a titrant to determine amine solution concentration and for the CO_2 loading analysis. The Table B1 shows the properties of the HCl stock solution as indicated in the MSDS (Material Safety Data Sheet);

Table B1 Required properties of HCl and Na_2CO_3

	HCl	Na_2CO_3
Molecular Weight (g/mol)	36.46	105.99
Purity (%)	37	
Density (g/L)	1190	
Calculated Molar Concentration (mole/L, M)	12.1	

HCl Preparation;

The simple dilution formula (Equation B1) is used to dilute the stock solution to the desired final concentration. In this case 1 M of HCl is prepared.

$$V_1 = \frac{C_2 \times V_2}{C_1}$$

$B1$

$V_1 = Volume\ of\ Stock\ Solution\ required, mL$

$C_1 = Concentration\ of\ Stock\ Solution, M$

$V_2 = Volume\ of\ Final\ Solution, mL$

$c_2 = Concentration\ of\ Final\ Solution, M$

The molar concentration of HCl was calculated using the informations on Table B1 and the Equation A1.

$V_1 =?\ mL$

$C_1 = 12.1\ M$

$$V_2 = 1000, mL$$

$$c_2 = 1\ M$$

$$V_1 = \frac{1 \times 1000}{12.9} = 82.6\ mL \approx 83\ mL$$

Therefore, to prepare 1000 mL (1 L) of 1 M HCl, 83 mL of the HCl stock solution will be mixed with 917 mL of distilled water.

HCl Standardization:

This prepared 1 M HCl must be standardized before its used during the experimental analysis. This will confirm the exact concentration in 2 decimal places. In practice, and most often, the prepared HCl will not be exactly 1 M. It could be within the accepted accuracy of ± 0.05 M.

The standardization is done using sodium carbonate (Na_2CO_3) according to the reaction in Equation B2 below;

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O \qquad\qquad B2$$
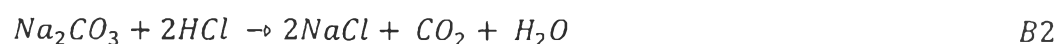
Datas from a simple titration using a known mass of Na_2CO_3 is used to standardize the HCl using Equation B3.

$$\text{HCl Conc.} = \left(\frac{g_{Na_2CO_3} \times 1000}{\frac{MW_{Na_2CO_3}}{2} \times V_{HCL\_Endpoint}} \right) \qquad\qquad B3$$

$$g_{Na_2CO_3} = Mass\ of\ weighed\ Na_2CO_3, \text{g}$$

$$MW_{Na_2CO_3} = Molecular\ weight\ of\ Na_2CO_3, \text{g/mol}$$

$$V_{HCl\_Endpoint} = Volume\ of\ HCl\ at\ endpoint, mL$$

Considering the 1.05 g of Na_2CO_3 was weighed out and the volume of HCl at endpoint is 19.4 mL, then the actual concentration of the HCl is;

$$HCl\ Conc. = \left| \frac{1.05 \times 1000}{\left(\frac{105.99}{2}\right) \times 19.4} \right| = 1.02\ M$$

Note: This standardized HCl concentration (1.02 M) is to be used for calculation during the experimental analysis. This standardization should be done atleast twice to confirm the concentration. If in any case the concentration of the 2 standardization differs by ± 0.05, the average of the 2 concentrations should be used for calculations.

Appendix C Amine Solution Concentration Calculation

Once the desired concentration of the ternary blend is prepared as described in Appendix A, a simple titration using standardized HCl as described in Appendix B is used to confirm the actual concentration of the blend. Methyl orange is used as the indicator. Citing the complexity of the blend, a derived correlation below is used to calculate the ternary blend concentration;

Use only when:

1). Solvent sample size to titrate is 1 mL

2). HCl concentration is 1 M

3). Amine solution concentration is 2 M AMP – 0.5 M PZ – 3 M MEA

$$A + D = Salt \qquad\qquad C1$$

$$B + D = Salt \qquad\qquad C2$$

$$C + D = Salt \qquad\qquad C3$$

AMP (amine with 1 N so it is 1:1 ratio)

$$M_A \times V = M_D \times V_{D1} \qquad\qquad C4$$

MEA (amine with 1 N so it is 1:1 ratio)

$$M_B \times V = M_D \times V_{D2} \qquad\qquad C5$$

PZ (amine with 2 N so it is 1:2 ratio)

$$M_C \times V = (M_D \times V_{D3})/2 \qquad\qquad C6$$

$$2\,M_C \times V = M_D \times V_{D3} \qquad\qquad C7$$

$$(C4) + (C5) + (C6), \qquad V = 1\,mL \text{ and } M_D = 1\,M$$

$$M_A + M_B + 2\,M_C = V_{D1} + V_{D2} + V_{D3} = V_{HCl\_Endpoint} \qquad\qquad C8$$

Molar ratio; $\dfrac{M_A}{M_B} = \dfrac{2}{3}$ and $\dfrac{M_A}{M_C} = \dfrac{2}{0.5}$ $\qquad$ C9

$$M_A + \left(\frac{3\,M_A}{2}\right) + 2\,\left(\frac{0.5\,M_A}{2}\right) = V_{HCl\_Endpoint} \times M_D \qquad C10$$

$$M_A + \left(\frac{3\,M_A}{2}\right) + 0.5\,M_A = V_{HCl\_Endpoint} \times M_D \qquad C11$$

$$1.5\,M_A + \left(\frac{3\,M_A}{2}\right) = V_{HCl\_Endpoint} \times M_D \qquad C12$$

$$3\,M_A + 3\,M_A = 2\,(V_{HCl\_Endpoint} \times M_D) \qquad C13$$

$$6\,M_A = 2\,(V_{HCl\_Endpoint} \times M_D) \qquad C14$$

$$3\,M_A = V_{HCl\_Endpoint} \times M_D \qquad C15$$

$$M_A = \frac{V_{HCl\_Endpoint} \times M_D}{3} \qquad C16$$

$$M_B = \frac{3 \times V_{HCl\_Endpoint} \times M_D}{6} \qquad C17$$

$$M_C = \frac{0.5 \times V_{HCl\_Endpoint} \times M_D}{6} \qquad C18$$

$$M_{A+B+C} = M_A + M_B + M_C \qquad C19$$

$M_A =$ Molar concentration of AMP, (M or moles/L)

$M_B =$ Molar concentration of MEA, (M or moles/L)

$M_C =$ Molar concentration of PZ, (M or moles/L)

$M_D =$ Molar concentration of HCl, (M or moles/L)

$V =$ Amine solution sample volume, (mL)

$V_{HCl\_Endpoint} = V_{D1} + V_{D2} + V_{D3}$, (mL)

$M_{A+B+C} =$ Total Amine solution concentration, (M or moles/L)

Note: Since PZ contains 2 amino groups it was accounted for in the correlation (C6 and C7). This procedure can be used to derive new correlations for sample volume more than 1 mL, other polyamines (2, 3 or more amino groups) and different blends (binary, ternary, quartenary).

Example C1;

Data's collected during the titration of the amine solution to determine its concentration is presented below;

$M_A = ? \, M$

$M_B = ? \, M$

$M_C = ? \, M$

$M_{A+B+C} = ? \, M$

$M_D = 1 \, M$

$V = 1 \, mL$

$V_{HCl\_Endpoint} = 6.05 \, mL$

Using Equations C16-19;

$$M_A = \frac{V_{HCl\_Endpoint} \times M_D}{3} = \frac{6.05 \times 1}{3} = 2.02 \, M$$

$$M_B = \frac{3 \times V_{HCl\_Endpoint} \times M_D}{6} = \frac{3 \times 6.05 \times 1}{6} = 3.03 \, M$$

$$M_C = \frac{0.5 \times V_{HCl\_Endpoint} \times M_D}{6} = \frac{0.5 \times 6.05 \times 1}{6} = 0.50 \, M$$

$$M_{A+B+C} = M_A + M_B + M_C = 2.02 + 3.03 + 0.5 = 5.55 \, M$$

Note: To limit the sources of error during and after the experimental analysis, it is imperative to keep the deviation (absolute average deviation, %AAD) of the amine solution concentration to ± 2.5 %.

The %AAD of the desired and measured concentration for each solvent was calculated. The general formula (Equation 20) for calculating standard deviation;

$$(\%AAD) = \left(\frac{C_{measured} - C_{desired}}{C_{measured}} \right) \times 100 \qquad\qquad C20$$

$C_{measured}$ = Measured solvent concentration, M

$C_{desired}$ = Desired solvent concentration, M

For the analyzed concentration above, the %AAD for the solvents are below;

AMP

$$(\%AAD) = \left(\frac{2.02 - 2}{2.02}\right) \times 100 = 0.99\,\%$$

MEA

$$(\%AAD) = \left(\frac{3.03 - 3}{3.03}\right) \times 100 = 0.99\,\%$$

PZ

$$(\%AAD) = \left(\frac{0.5 - 0.5}{0.5}\right) \times 100 = 0.0\,\%$$

Appendix D Carbon Dioxide (CO_2) Loading Calculation

The procedure to determine CO_2 loading of each solubility run is described in Section 3.2.5 and the correlation for its calculation is highlighted in the Equation D1.

$$\alpha CO_2 = \frac{\left[\frac{(V_{CO2}-V_{HCl})(P)(273\ K)}{(760\ mmHg)(T)}\right]}{C_1 V_1 A} \qquad\qquad D1$$

$\alpha CO_2 = $ amine solution CO_2 loading, mol CO_2/mol amine

$T = $ room temperature (K)

$P = $ barometric pressure $(mmHg)$

$C_1 = $ rich amine solution concentration (M)

$V_1 = $ amine solution sample volume (mL)

$A = $ conversion constant $(22.41\ L/mole)$

$V_{CO2} = $ volume of CO_2 collected in gas burette (mL)

$V_{HCl} = $ volume of acid titrant at end point (mL)

Note: The rich amine concentration is calculated using the correlation (M_{A+B-C}) as described in Appendix C.

Sample Calculation:

The data below are from CO_2 solubility in 2 M AMP -0.5 M PZ – 3 M MEA at 25 °C and 100 % CO_2 (93.93 kPa CO_2 partial pressure).

$\alpha CO_2 = ?$ mol CO_2/mol amine

$T = 297K$

$P = 760\ mmHg$

$C_1 = ?\ M$

$V_1 = 1\ mL$

$A = 22.41\ L/mole$

$$V_{CO2} = 98 \, mL$$

$$V_{HCl} = 6.05 \, mL$$

Using the datas gotten from the titration analysis (Chittick Apparatus), the concentration of the rich amine solution is first calculated;

$$M_D = HCl \; concentration = 1.02 \, M$$

$$M_A(AMP) = \frac{V_{HCl\_Endpoint} \times M_D}{3} = \frac{6.05 \times 1.02}{3} = 2.05 \, M$$

$$M_B(MEA) = \frac{3 \times V_{HCl\_Endpoint} \times M_D}{6} = \frac{3 \times 6.05 \times 1.02}{6} = 3.08 \, M$$

$$M_C(PZ) = \frac{0.5 \times V_{HCl\_Endpoint} \times M_D}{6} = \frac{0.5 \times 6.05 \times 1.02}{6} = 0.51 \, M$$

$$C_1 = M_A + M_B + M_C = 2.05 + 3.08 + 0.51 = 5.64 \, M$$

Note: The amine concentration to use for this calculation must be the rich amine solution concentration and not the lean amine solution concentration.

$$\alpha CO_2 = \frac{\left[\frac{(98-6.05)(760)(273)}{(760)(297)} \right]}{(5.64)(1)(22.41)} = 0.668 = \mathbf{0.67} \; mol \, CO_2/mol \; amine$$

Note: For more précised accuracy, the CO_2 loading should be approximated to 2 decimal places.

Appendix E Carbon Dioxide (CO_2) Partial Pressure Calculation

The experimental set-up consists of a saturation chamber to complete the flue gas simulation ($CO_2 + N_2 + H_2O$). Therefore, the CO_2 composition upstream of the saturator would not be the same at the saturator downstream. The presence of water vapor will be accounted for and hence determine the actual CO_2 partial pressure of the flue gas going to the absorption reactor (Equation E1).

$$P_{CO_2} = N_{CO_2} \left(P_{Total} - P_{H_2O} \right) \qquad\qquad E1$$

$P_{CO_2} = CO_2\ Partial\ Pressure, kPa$

$N_{CO_2} = CO_2\ Mole\ Fraction$

$P_{Total} = Total\ Pressure\ of\ System, kPa$

$P_{H_2O} = H_2O\ Vapor\ Pressure, kPa$

The water vapor pressure is dependent of temperature and not dependent on the pressure or volume of water. The water vapor pressures at different temperatures are listed below;

$P_{CO_2} @\ 25^oC = 3.16\ kPa$

$P_{CO_2} @\ 40^oC = 7.37\ kPa$

$P_{CO_2} @\ 60^oC = 19.91\ kPa$

$P_{CO_2} @\ 100^oC = 101.3\ kPa$

The correlation shown in Equation E1 was used to determine the CO_2 partial pressures at different temperatures during the experimental analysis.

Sample Calculation at 25 ^{o}C:

$P_{CO_2} = ?\ kPa$

$N_{CO_2} = 1.0\ (100\ \%)$

$$P_{Total} = 101.3 \; kPa$$

$$P_{H_2O} = 3.16 \; kPa$$

$$P_{CO_2} = 1 \, (101.3 - 3.16) = 98.14 \; kPa$$

Appendix F H_2O/PZ Molar Ratio Calculation

Citing Section 4.4.2.1.1, when PZ is part of the amine blends, it's important that all the crystals of PZ dissolves in the amine solution without stirring or heating. According to the study of Bishnoi (2000) the solubility of PZ concentration in water was 1.64 M and 1.88 M at 20 °C and 25 °C respectively. The water concentrations (Equation F1) of 1.64 M PZ and 1.88 M PZ was calculated and used to determine their H_2O/PZ molar ratios. The calculated H_2O/PZ molar ratios was then used as a benchmark for the bi-solvent and tri-solvent blends.

$$H_2O\ Conc.in\ amine\ solution = \frac{H_2O\ Vol.\ (mL) \times H_2O\ Conc.(M)}{Amine\ Soln.Vol.\ (mL)} \qquad F1$$

Preparing 20 mL of 1.88 M PZ

$1\ M\ PZ = 1.88 \times 0.02 \times 86.14 = 3.24\ g$

Using a mass balance, 3.24 g of PZ was added in a calibrated beaker and mixed some volume of water until all the PZ crystals to dissolve. Extra was was then added to make up the final volume to 20 mL. In this case, the volume of water added to the 3.24 g of PZ was 17 mL. To confirm that 17 mL of water can dissolve all the PZ crystals (3.24 g) without stirring, 17 mL of water was added in separate calibrated beaker containing 3.24 g of PZ crystals. It was confirmed that all the PZ crystals completely dissolved. The concentration of the aqueous PZ solution was also confirmed using the titration technique as described in Appendix B. Using Equation F1, the water concentration in 1.8 M PZ was calculated as seen below;

$$H_2O\ Conc.in\ PZ\ solution = \frac{17 \times 55.5}{20} = 47.2\ M$$

The next step is to correlate the H_2O/PZ molar ratio which was determined using Equation F2.

$$\frac{H_2O\ Molar\ Concentration\ in\ Amine\ Solution}{PZ\ Molar\ Concentration\ in\ Amine\ Solution} \qquad F2$$

Therefore, the H_2O/PZ molar ratio is;

$$\frac{H_2O\ molar\ conc.}{PZ\ molar\ conc.} = \frac{47.2}{1.88} = 25.1$$

The same procedure was used in calculating the H_2O/PZ molar ratio of 1.64 M PZ which was 29.5. A sample calculation for the tri-solvent blends is shown below;

Preparing 20 mL of 2 M AMP – 1 M PZ – 3 M MEA

2 M AMP $= 2 \times 0.02 \times 89.14 = 3.56\ g = 4\ mL$

1 M PZ $= 1 \times 0.02 \times 86.14 = 1.72\ g$

3 M MEA $= 3 \times 0.02 \times 61.08 = 3.66\ g = 3.7\ mL$

The same procedure used in preparing the 1.88 M PZ was used for all the tri-solvent blends. For this particular amine blend 10.7 mL of water was the final volume of water added. The water concentration in the blended amine solution is calculated using Equation F1.

$$H_2O\ Conc.\ in\ amine\ solution = \frac{10.7\ \times 55.5}{20} = 29.7\ M$$

The H_2O/PZ molar ratio for 2 M AMP – 1 M PZ – 3 M MEA was calculated below;.

$$\frac{H_2O \text{ molar conc.}}{PZ \text{ molar conc.}} = \frac{29.7}{1} = 29.7$$

Note: Since PZ is in crystal form, the additional volume it adds in the amine solution was studied. This is necessary because all solids add a certain volume when preparing solutions. It was seen that on preparing 20 mL of 1 M PZ, the equivalent mass of PZ was 1.72 g and the required volume of distilled water was 18.4 mL. This means that 1.72 g of PZ exerted about 1.6 mL to the solution. On the other hand, when 20 mL of 1.5 M PZ was prepared, the equivalent mass of PZ was 2.58 g and the required volume of distilled water was 17.6 mL. This also means that 2.58 g of PZ added 2.4 mL to the solution. This was integral in understanding the equivalent volume of water required when preparing the ternary solutions, since AMP and MEA can be added to the amine solution as liquids. With this information about the volume exerted by PZ, the H_2O/PZ molar ratios of the aqueous amines solutions can be predicted prior to preparing the amine solutions. This was als confirmed when preparing PZ concentrations of 1.64 M and 1.88 M.

Appendix G Process Simulation Result Datas of Base Case (5 M MEA) and the Ternary Blends

The simulation results for the base case (5 M MEA) and all the ternary blends are presented below (Figures G1 – G10). For the base case MEA all the results are presented, but for the ternary blends only the major datas are presented.

<u>5 M MEA</u>

Name Absorber

| Connections | Process Data | Stage Data | Specifications | Convergence | Analyses | Plots | Streams | Notes |

Number of Stages	17
Degrees of Freedom	0
Column Type	TSWEET Kinetics
Flash Type	VLE
Column Add-ons	None
Calculate Column Hydraulics	☑
Efficiency Phase	Light Liquid
Thermal Efficiency	☑
Main Liquid Phase	Light Liquid
Number Column Top Down	☑
Phase Threshold	0.5 %

Figure G1 Absorber process data informations for the simulation.

Name   Absorber

| Connections | Process Data | Stage Data | Specifications | Convergence | Analyses | Plots | Streams | Notes |

Grouping

Summary

Hardware

Efficiencies

Recoveries

Vapor

Light Liquid

Heavy Liquid

Phase Properties

K-Values

Specify Pressure Change below, or specify at least the top and bottom stage pressures in the Stage Summary table.

| Pressure Change | 10 | kPa |
| Bottoms Head | 0 | psi |

Stage	Show Stage	3 Phases	Temperature	Pressure	Vapor	Light Liquid	Heavy Liquid
						Molar Flow	
			°C	kPa		kmol/h	
1		☐	57.9958	110	50781.2	334192	
2	☑	☐	70.7859	110.625	59538.9	342069	
3	☑	☐	76.6706	111.25	67415.7	345563	
4	☑	☐	78.2258	111.875	70910.3	346140	
5	☑	☐	77.9793	112.5	71486.8	345514	
6	☐	☐	77.0402	113.125	70861.5	344476	
7	☐	☐	75.8331	113.75	69823.1	343327	
8	☐	☐	74.5267	114.375	68673.8	342178	
9	☐	☐	73.1862	115	67525	341064	
10	☐	☐	71.8265	115.625	66410.8	339983	
11	☐	☐	70.4322	116.25	65330.1	338916	
12	☐	☐	68.9536	116.875	64263.4	337831	
13	☑	☐	67.3524	117.5	63178.3	336680	
14	☑	☐	65.4824	118.125	62026.7	335388	
15	☑	☐	63.1397	118.75	60734.8	333829	
16	☑	☐	59.8678	119.375	59175.9	331752	
17		☐	54.4312	120	57098.9	328629	

Figure G2a Absorber stage data summary and results for the base case simulation.

Name   Absorber

Connections | Process Data | Stage Data | Specifications | Convergence | Analyses | Plots | Streams | Notes

Grouping

Summary

Hardware

Efficiencies

Recoveries

Vapor

Light Liquid

Heavy Liquid

Phase Properties

K-Values

General | Tray | Random | Structured

Stage	Hardware	Diameter	Fraction Flooding	Residence Time	Real/Ideal Stage Ratio	System Factor	Liquid Load	System Limit Flood	Flow Parameter	Cs Factor	Fs Factor
		m	%	s			m^3/(m^2·h)	%		m/s	Pa^0.5
1	Structured	17.4411	80	1.5	1	0.8	30.9069	32.271	0.15774	0.0544517	1.79061
2	Structured	18.1804	80	1.5	1	0.8	28.577	33.7337	0.140598	0.0564888	1.85331
3	Structured	18.5875	80	1.5	1	0.8	27.9197	34.0357	0.136696	0.0567605	1.86134
4	Structured	18.6672	80	1.5	1	0.8	27.8977	34.091	0.13668	0.0567228	1.8624
5	Structured	18.6067	80	1.5	1	0.8	28.0729	34.0673	0.137841	0.0565987	1.86187
6	Structured	18.4946	80	1.5	1	0.8	28.3189	34.0129	0.139426	0.0564462	1.86065
7	Structured	18.3659	80	1.5	1	0.8	28.5946	33.9426	0.141192	0.0562833	1.85887
8	Structured	18.2337	80	1.5	1	0.8	28.8837	33.8627	0.143043	0.0561172	1.8566
9	Structured	18.1026	80	1.5	1	0.8	29.1801	33.7759	0.144943	0.0559503	1.8539
10	Structured	17.5949	80	1.5	1	0.8	30.7657	31.8576	0.146897	0.0582062	1.93124
11	Structured	17.4798	80	1.5	1	0.8	31.0539	31.6885	0.148937	0.0579474	1.92498
12	Structured	17.3623	80	1.5	1	0.8	31.3594	31.5121	0.151125	0.0576707	1.91793
13	Structured	17.2376	80	1.5	1	0.8	31.6985	31.3205	0.15357	0.0573634	1.90975
14	Structured	17.0978	80	1.5	1	0.8	32.0905	31.1002	0.156464	0.0570026	1.89978
15	Structured	16.9288	80	1.5	1	0.8	32.5909	30.8256	0.160195	0.056544	1.88664
16	Structured	16.6992	80	1.5	1	0.8	33.3156	30.4401	0.166691	0.0558852	1.86709
17	Structured	16.3191	80	1.5	1	0.8	34.6371	29.7783	0.175938	0.0547205	1.8312

Figure G2b Absorber stage data hardware general results for the base case simulation.

Name Absorber

Connections | Process Data | Stage Data | Specifications | Convergence | Analyses | Plots | Streams | Notes

Grouping

General | Tray | Random | Structured

Summary

Hardware

Efficiencies

Recoveries

Vapor

Light Liquid

Heavy Liquid

Phase Properties

K-Values

Stage	Structured Packing Types	Flood Model	Stage Pressure Drop	Holdup	Linear Holdup Time	Surface Area	Void Fraction	Billet Cfl	Billet Cp	Billet Ch	Billet CL	Billet Cv
			mbar/m	%	s/m	1/ft	%					
1	Sulzer Melapak® 250.Y metal	Sulzer	1.3012	6.5092	7.58183	76.2	98.3	2.464	0.292	0.554	1.068	0.405
2	Sulzer Melapak® 250.Y metal	Sulzer	1.36735	5.89592	7.42742	76.2	98.3	2.464	0.292	0.554	1.068	0.406
3	Sulzer Melapak® 250.Y metal	Sulzer	1.37382	5.65668	7.29381	76.2	98.3	2.464	0.292	0.554	1.068	0.405
4	Sulzer Melapak® 250.Y metal	Sulzer	1.37562	5.61335	7.24364	76.2	98.3	2.464	0.292	0.554	1.068	0.406
5	Sulzer Melapak® 250.Y metal	Sulzer	1.37672	5.6441	7.23736	76.2	98.3	2.464	0.292	0.554	1.068	0.405
6	Sulzer Melapak® 250.Y metal	Sulzer	1.37736	5.70322	7.25014	76.2	98.3	2.464	0.292	0.554	1.068	0.406
7	Sulzer Melapak® 250.Y metal	Sulzer	1.37741	5.7737	7.26396	76.2	98.3	2.464	0.292	0.554	1.068	0.406
8	Sulzer Melapak® 250.Y metal	Sulzer	1.37686	5.84865	7.28964	76.2	98.3	2.464	0.292	0.554	1.068	0.406
9	Sulzer Melapak® 250.Y metal	Sulzer	1.37576	5.92547	7.31035	76.2	98.3	2.464	0.292	0.554	1.068	0.406
10	Sulzer Melapak® 250.Y metal	Sulzer	1.4682	6.12476	7.1668	76.2	98.3	2.464	0.292	0.554	1.068	0.406
11	Sulzer Melapak® 250.Y metal	Sulzer	1.48226	6.20354	7.19161	76.2	98.3	2.464	0.292	0.554	1.068	0.405
12	Sulzer Melapak® 250.Y metal	Sulzer	1.47536	6.28699	7.21735	76.2	98.3	2.464	0.292	0.554	1.068	0.406
13	Sulzer Melapak® 250.Y metal	Sulzer	1.46716	6.37921	7.24532	76.2	98.3	2.464	0.292	0.554	1.068	0.406
14	Sulzer Melapak® 250.Y metal	Sulzer	1.45651	6.48725	7.27758	76.2	98.3	2.464	0.292	0.554	1.068	0.406
15	Sulzer Melapak® 250.Y metal	Sulzer	1.44112	6.62471	7.31768	76.2	98.3	2.464	0.292	0.554	1.068	0.406
16	Sulzer Melapak® 250.Y metal	Sulzer	1.41806	6.82273	7.37248	76.2	98.3	2.464	0.292	0.554	1.068	0.406
17	Sulzer Melapak® 250.Y metal	Sulzer	1.3749	7.17476	7.45707	76.2	98.3	2.464	0.292	0.554	1.068	0.406

Figure G2c Absorber stage data structured hardware results for the base case simulation.

Name Absorber

| | Connections | Process Data | Stage Data | Specifications | Convergence | Analyses | Plots | Streams | Notes |

Grouping		
Parameters	Outer Loop Iterations	
	Enthalpy Model	Composition-Dependent
Variables	Inner Loop model	Boston-Sullivan Nonideal
Solver	K Damping	0
	Boston-Sullivan Kb	☑
	Maximum Initial Iterations	50
	Use Last Solution	☑

Figure G3 Absorber convergence specification.

Name Stripper

| Connections | Process Data | Stage Data | Specifications | Convergence | Analyses | Plots | Streams | Notes |

Number of Stages	17
Degrees of Freedom	0
Column Type	TSWEET Alternate Stripper
Flash Type	VLE
Column Add-ons	Partial Condenser w/Reboiler
Calculate Column Hydraulics	☑
Efficiency Phase	Light Liquid
Thermal Efficiency	☐
Main Liquid Phase	Light Liquid
Number Column Top Down	☑
Phase Threshold	0.5 %

Figure G4 Stripper process data informations for the simulation.

Name   Stripper

Grouping

Summary

Hardware

Efficiencies

Recoveries

Vapor

Light Liquid

Heavy Liquid

Phase Properties

K-Values

Specify Pressure Change below, or specify at least the top and bottom stage pressures in the Stage Summary table.

Pressure Change		20	kPa
Bottoms Head		0	psi

Stage	Show Stage	3 Phases	Temperature	Pressure	Vapor	Light Liquid	Heavy Liquid
						Molar Flow	
			°C	kPa		kmol/h	
Condenser		☐	29.9997	180	7716.32	10289.1	
1		☐	100.8	130	18005.5	11599.2	
2	☑	☐	104.734	181.25	19315.6	334383	
3	☑	☐	104.689	182.5	13470.3	334326	
4	☑	☐	104.65	183.75	13413	334273	
5	☑	☐	104.613	185	13360.2	334222	
6	☐	☐	104.578	186.25	13309.6	334174	
7	☐	☐	104.547	187.5	13261.7	334130	
8	☐	☐	104.523	188.75	13217.7	334093	
9	☐	☐	104.515	190	13180.7	334070	
10	☐	☐	104.542	191.25	13157.5	334076	
11	☐	☐	104.643	192.5	13163.5	334146	
12	☐	☐	104.908	193.75	13233.1	334356	
13	☑	☐	105.524	195	13442.9	334365	
14	☑	☐	106.817	196.25	13952.7	335968	
15	☑	☐	109.164	197.5	15054.9	338045	
16	☑	☐	112.585	198.75	17132.9	341265	
17		☐	116.422	200	20352.4	345267	
Reboiler		☐	120	200	24354.7	320913	

Figure G5a Stripper stage data summary and results for the base case simulation.

Name   Stripper

| Connections | Process Data | Stage Data | Specifications | Convergence | Analyses | Plots | Streams | Notes |

Grouping

General | Tray | Random | Structured

Summary

Hardware

Efficiencies

Recoveries

Vapor

Light Liquid

Heavy Liquid

Phase Properties

K-Values

Stage	Hardware	Diameter	Fraction Flooding	Residence Time	Real/Ideal Stage Ratio	System Factor	Liquid Load	System Limit Flood	Flow Parameter	Cs Factor	Fs Factor
		m	%	s			m^3/(m^2·h)	%		m/s	Pa^0.5
1	Structured	6.70987	30	1.5	1	0.35	5.47641	62.9007	0.0141083	0.107918	3.33819
2	Structured	9.60565	30	1.5	1	0.35	102.782	19.0785	0.830985	0.0343836	1.13463
3	Structured	9.53976	30	1.5	1	0.35	103.086	19.0378	0.835327	0.0343064	1.13213
4	Structured	9.57445	30	1.5	1	0.35	103.389	18.9977	0.839595	0.0342326	1.12933
5	Structured	9.55951	30	1.5	1	0.35	103.636	18.9584	0.8438	0.0341602	1.12759
6	Structured	9.54502	30	1.5	1	0.35	103.976	18.9203	0.847913	0.0340899	1.1254
7	Structured	9.5312	30	1.5	1	0.35	104.254	18.8838	0.851858	0.0340226	1.12331
8	Structured	9.51852	30	1.5	1	0.35	104.51	18.8505	0.855518	0.0339608	1.1214
9	Structured	9.50807	30	1.5	1	0.35	104.721	18.8234	0.858532	0.0339102	1.11984
10	Structured	9.50227	30	1.5	1	0.35	104.836	18.8094	0.860168	0.0338831	1.11903
11	Structured	9.50656	30	1.5	1	0.35	104.742	18.824	0.858782	0.0339076	1.11938
12	Structured	9.53273	30	1.5	1	0.35	104.198	18.9006	0.850902	0.0340437	1.12432
13	Structured	9.60466	30	1.5	1	0.35	102.735	19.1051	0.830027	0.0344094	1.13613
14	Structured	9.7626	30	1.5	1	0.35	99.6541	19.5425	0.787242	0.0351904	1.16116
15	Structured	10.0496	30	1.5	1	0.35	94.4779	20.3034	0.71878	0.0365382	1.20392
16	Structured	10.7301	30	1.5	1	0.35	83.5756	22.6881	0.637632	0.036433	1.19724
17	Structured	11.2125	30	1.5	1	0.35	77.5295	23.7718	0.563909	0.0332133	1.25039

Figure G5b Stripper stage data hardware general results for the base case simulation.

Name Stripper

Connectons | Process Data | Stage Data | Speations | Convergence | Analyses | Plots | Streams | Notes

Grouping
Summary
Hardware
Efficiences
Recoveries
Vapor
Light Liquid
Heavy Liquid
Phase Properties
K-Values

General | Tray | Random | Structured

Stage	Structured Packing Types	Flood Model	Stage Pressure Drop	Holdup	Linear Holdup Time	Surface Area	Void Fraction	Billet Cfl	Billet Cp	Billet Ch	Billet CL	Billet Cv
			mbar/m	%	s/m	1/ft	%					
1	Sulzer Mellapak® 250.Y metal	Sulzer	3.27093	2.35169	15.4592	76.2	98.8	2.464	0.292	0.554	1.068	0.406
2	Sulzer Mellapak® 250.Y metal	Sulzer	1.3181	9.43589	3.30498	76.2	98.8	2.464	0.292	0.554	1.068	0.406
3	Sulzer Mellapak® 250.Y metal	Sulzer	1.3266	9.45332	3.30132	76.2	98.8	2.464	0.292	0.554	1.068	0.406
4	Sulzer Mellapak® 250.Y metal	Sulzer	1.33501	9.47101	3.29781	76.2	98.8	2.464	0.292	0.554	1.068	0.406
5	Sulzer Mellapak® 250.Y metal	Sulzer	1.34331	9.48833	3.29436	76.2	98.8	2.464	0.292	0.554	1.068	0.406
6	Sulzer Mellapak® 250.Y metal	Sulzer	1.35144	9.50517	3.29101	76.2	98.8	2.464	0.292	0.554	1.068	0.406
7	Sulzer Mellapak® 250.Y metal	Sulzer	1.35928	9.52123	3.28778	76.2	98.8	2.464	0.292	0.554	1.068	0.406
8	Sulzer Mellapak® 250.Y metal	Sulzer	1.36655	9.53569	3.28478	76.2	98.8	2.464	0.292	0.554	1.068	0.406
9	Sulzer Mellapak® 250.Y metal	Sulzer	1.37267	9.5477	3.26223	76.2	98.8	2.464	0.292	0.554	1.068	0.406
10	Sulzer Mellapak® 250.Y metal	Sulzer	1.37628	9.55346	3.2806	76.2	98.8	2.464	0.292	0.554	1.068	0.406
11	Sulzer Mellapak® 250.Y metal	Sulzer	1.37439	9.54607	3.28099	76.2	98.8	2.464	0.292	0.554	1.068	0.406
12	Sulzer Mellapak® 250.Y metal	Sulzer	1.36564	9.51011	3.28571	76.2	98.8	2.464	0.292	0.554	1.068	0.406
13	Sulzer Mellapak® 250.Y metal	Sulzer	1.32306	9.41558	3.29937	76.2	98.8	2.464	0.292	0.554	1.068	0.406
14	Sulzer Mellapak® 250.Y metal	Sulzer	1.24466	9.21539	3.32924	76.2	98.8	2.464	0.292	0.554	1.068	0.406
15	Sulzer Mellapak® 250.Y metal	Sulzer	1.11808	8.87401	3.38137	76.2	98.8	2.464	0.292	0.554	1.068	0.406
16	Sulzer Mellapak® 250.Y metal	Sulzer	1.05355	8.22665	3.54361	76.2	98.8	2.464	0.292	0.554	1.068	0.406
17	Sulzer Mellapak® 250.Y metal	Sulzer	0.89723	7.7824	3.61368	76.2	98.8	2.464	0.292	0.554	1.068	0.406

Figure G5c Stripper stage data structured hardware results for the base case simulation.

Name Stripper

| Connections | Process Data | Stage Data | Specifications | Convergence | Analyses | Plots | Streams | Notes |

Degrees of Freedom 0

Name		Target	Value	Active	Estimate
Reflux Ratio 1		1	1.33343	☐	☐
Boilup Ratio 1		0.0412886	0.0758919	☐	☐
Condenser Temperature	°C	30	29.9997	☑	☐
Reboiler Temperature	°C	120	120	☑	☐

Figure G6 Stripper specifications for the simulations.

Name Stripper

| Connections | Process Data | Stage Data | Specifications | Convergence | Analyses | Plots | Streams | Notes |

Grouping

Parameters

Variables

Solver

Outer Loop Iterations	
Enthalpy Model	Composition-Dependent
Inner Loop model	Boston-Sullivan Nonideal
K Damping	0
Boston-Sullivan Kb	☐
Maximum Initial Iterations	50
Use Last Solution	☑

Figure G7 Stripper convergence specification for the simulations.

Names	Units	Flue Gas	FG to CO2 Plant	Treated Gas	H2O
Temperature	°C	40*	40	57.996	40
Pressure	kPa	120*	120	110	120
Mass Flow	t/h	1685.7	1625.1	1372.3	60.575
CO2(Mass Flow)	t/h	368.17*	368.15	36.813	0.011514
CO2(Mole Fraction)	%	14.59*	15.498	1.6472	0.0077818
N2(Mole Fraction)	%	69.97*	74.328	79	0.00087854
O2(Mole Fraction)	%	2.85*	3.0275	3.2177	6.8793e-005
H2O(Mole Fraction)	%	11.69*	6.1899	15.1	99.991
Ar(Mole Fraction)	%	0.9*	0.95606	1.0161	2.3032e-005
Molar Flow	kmol/h	57338*	53976	50781	3362

Names	Units	R-Amine	L-Amine
Temperature	°C	54.431	43*
Pressure	kPa	120	120*
Std Liquid Volumetric Flow	sgpm	36214	34773
CO2 Loading Mole/Mole Amine		0.5	0.3
MEA(Mass Fraction)	%	29.1	30
Mass Flow	t/h	8074.4	7821.5

Names	Units	CO2	Steam	Q-2	1	Reflux
Mass Flow	t/h	334.74	530.55		503	185.61
CO2(Mass Fraction)	%	99	0*		20.7	0.221
CO2(Mole Fraction)	%	97.6	0*		9.73	0.0907
Energy Rate	MW	-835	-1.95e+003	323	-1.71e+003	-816
Energy Rate	GJ/h	-3.01e+003	-7.03e+003	1.16e+003	-6.17e+003	-2.94e+003
Temperature	°C	30	124*		120	30
Pressure	kPa	180	224.73		200	180

Reboiler Ratio	3.8#	GJ/t
Steam Ratio	1.6#	ton/ton
Cyclic Capacity	0.196#	mol CO2/mol Amine
LG Ratio	4.6#	%
CO2 Recovery2	90#	%

Figure G8 Simulation results for the base case 5 M MEA.

2 M AMP – 0.5 M PZ – 2.5 M MEA

Names	Units	Flue Gas	FG to CO2 Plant	Treated Gas	H2O
Temperature	°C	40*	40	49.709	40
Pressure	kPa	120*	120	110	120
Mass Flow	t/h	1685.7	1625.1	1318.1	60.575
CO2(Mass Flow)	t/h	368.17*	368.15	36.814	0.011514
CO2(Mole Fraction)	%	14.59*	15.498	1.7518	0.0077818
N2(Mole Fraction)	%	69.97*	74.328	84.014	0.00087854
O2(Mole Fraction)	%	2.85*	3.0275	3.4219	6.8793e-005
H2O(Mole Fraction)	%	11.69*	6.1899	9.7054	99.991
Ar(Mole Fraction)	%	0.9*	0.95606	1.0806	2.3032e-005
Molar Flow	kmol/h	57338*	53976	47751	3362

Names	Units	R-Amine	L-Amine
Temperature	°C	59.425	43*
Pressure	kPa	120	120*
Std Liquid Volumetric Flow	sgpm	38549	36870
CO2 Loading Mole/Mole Amine		0.45	0.27
Mass Flow	t/h	8322.1	8015.1
AMP(Mass Fraction)	%	18.29	19
PZ(Mass Fraction)	%	4.5257	4.7
MEA(Mass Fraction)	%	14.444	15

Names	Units	CO2	Steam	Q-2	1	Reflux
Mass Flow	t/h	334.74	554.08		538.37	212.82
CO2(Mass Fraction)	%	99	0*		26	0.237
CO2(Mole Fraction)	%	97.6	0*		12.8	0.0972
Energy Rate	MW	-835	-2.04e+003	337	-1.78e+003	-936
Energy Rate	GJ/h	-3.01e+003	-7.34e+003	1.21e+003	-6.4e+003	-3.37e+003
Temperature	°C	30	124*		120	30
Pressure	kPa	180	224.73		200	180

Reboiler Ratio	4#	GJ/t
Steam Ratio	1.7#	ton/ton
Cyclic Capacity	0.183#	mol CO2/mol Amine
LG Ratio	4.8#	%
CO2 Recovery2	90#	%

Figure G9 Simulation results for 2 M AMP – 0.5 M PZ – 2.5 M MEA.

2 M AMP – 0.5 M PZ – 3 M MEA

Names	Units	Flue Gas	FG to CO2 Plant	Treated Gas	H2O
Temperature	°C	40*	40	56.531	40
Pressure	kPa	120*	120	110	120
Mass Flow	t/h	1685.7	1625.1	1354.5	60.575
CO2(Mass Flow)	t/h	368.17*	368.15	36.817	0.011514
CO2(Mole Fraction)	%	14.59*	15.498	1.6816	0.0077818
N2(Mole Fraction)	%	69.97*	74.328	80.642	0.00087854
O2(Mole Fraction)	%	2.85*	3.0275	3.2845	6.8793e-005
H2O(Mole Fraction)	%	11.69*	6.1899	13.314	99.991
Ar(Mole Fraction)	%	0.9*	0.95606	1.0372	2.3032e-005
Molar Flow	kmol/h	57338*	53976	49748	3362

Names	Units	R-Amine	L-Amine
Temperature	°C	57.698	43*
Pressure	kPa	120	120*
Std Liquid Volumetric Flow	sgpm	33466	31947
CO2 Loading Mole/Mole Amine		0.48	0.29
Mass Flow	t/h	7203.5	6932.9
AMP(Mass Fraction)	%	18.27	19
PZ(Mass Fraction)	%	4.5218	4.7
MEA(Mass Fraction)	%	17.319	18

Names	Units	CO2	Steam	Q-2	1	Reflux
Mass Flow	t/h	334.72	498.34		483.97	179.39
CO2(Mass Fraction)	%	99	0*		28.5	0.234
CO2(Mole Fraction)	%	97.6	0*		14.3	0.0959
Energy Rate	MW	-835	-1.83e+003	303	-1.58e+003	-789
Energy Rate	GJ/h	-3.01e+003	-6.6e+003	1.09e+003	-5.7e+003	-2.84e+003
Temperature	°C	30	124*		120	30
Pressure	kPa	180	224.73		200	180

Reboiler Ratio	3.6#	GJ/t
Steam Ratio	1.5#	ton/ton
Cyclic Capacity	0.193#	mol CO2/mol Amine
LG Ratio	4.1#	%
CO2 Recovery2	90#	%

Figure G10 Simulation results for 2 M AMP – 0.5 M PZ – 3 M MEA.

2 M AMP – 1 M PZ – 2 M MEA

Names	Units	Flue Gas	FG to CO2 Plant	Treated Gas	H2O
Temperature	°C	40*	40	54.608	40
Pressure	kPa	120*	120	110	120
Mass Flow	t/h	1685.7	1625.1	1343.3	60.575
CO2(Mass Flow)	t/h	368.17*	368.15	36.817	0.011514
CO2(Mole Fraction)	%	14.59*	15.498	1.7029	0.0077818
N2(Mole Fraction)	%	69.97*	74.328	81.662	0.00087854
O2(Mole Fraction)	%	2.85*	3.0275	3.3261	6.8793e-005
H2O(Mole Fraction)	%	11.69*	6.1899	12.221	99.991
Ar(Mole Fraction)	%	0.9*	0.95606	1.0503	2.3032e-005
Molar Flow	kmol/h	57338*	53976	49127	3362

Names	Units	R-Amine	L-Amine
Temperature	°C	58.454	43*
Pressure	kPa	120	120*
Std Liquid Volumetric Flow	sgpm	35079	33511
CO2 Loading Mole/Mole Amine		0.49	0.29
Mass Flow	t/h	7428.1	7146.2
AMP(Mass Fraction)	%	18.264	19
PZ(Mass Fraction)	%	9.1366	9.5
MEA(Mass Fraction)	%	11.542	12

Names	Units	CO2	Steam	Q-2	1	Reflux
Mass Flow	t/h	334.72	527.39		521.95	206.09
CO2(Mass Fraction)	%	99	0*		27.3	0.237
CO2(Mole Fraction)	%	97.6	0*		13.6	0.0971
Energy Rate	MW	-835	-1.94e+003	321	-1.71e+003	-906
Energy Rate	GJ/h	-3.01e+003	-6.98e+003	1.16e+003	-6.16e+003	-3.26e+003
Temperature	°C	30	124*		120	30
Pressure	kPa	180	224.73		200	180

Reboiler Ratio	3.8#	GJ/t
Steam Ratio	1.6#	ton/ton
Cyclic Capacity	0.203#	mol CO2/mol Amine
LG Ratio	4.2#	%
CO2 Recovery2	90#	%

Figure G11 Simulation results for 2 M AMP – 1 M PZ – 2 M MEA.

2 M AMP – 1 M PZ – 2.5 M MEA

Names	Units	Flue Gas	FG to CO2 Plant	Treated Gas	H2O
Temperature	°C	40*	40	59.35	40
Pressure	kPa	120*	120	110	120
Mass Flow	t/h	1685.7	1625.1	1373.1	60.575
CO2(Mass Flow)	t/h	368.17*	368.15	36.816	0.011514
CO2(Mole Fraction)	%	14.59*	15.498	1.648	0.0077818
N2(Mole Fraction)	%	69.97*	74.328	79.033	0.00087854
O2(Mole Fraction)	%	2.85*	3.0275	3.2191	6.8793e-005
H2O(Mole Fraction)	%	11.69*	6.1899	15.033	99.991
Ar(Mole Fraction)	%	0.9*	0.95606	1.0165	2.3032e-005
Molar Flow	kmol/h	57338*	53976	50761	3362

Names	Units	R-Amine	L-Amine
Temperature	°C	56.531	43*
Pressure	kPa	120	120*
Std Liquid Volumetric Flow	sgpm	30360	28924
CO2 Loading Mole/Mole Amine		0.52	0.31
Mass Flow	t/h	6408.3	6156.3
AMP(Mass Fraction)	%	18.23	19
PZ(Mass Fraction)	%	9.122	9.5
MEA(Mass Fraction)	%	14.405	15

Names	Units	CO2	Steam	Q-2	1	Reflux
Mass Flow	t/h	334.71	471.79		467.77	173.17
CO2(Mass Fraction)	%	99	0*		30	0.233
CO2(Mole Fraction)	%	97.6	0*		15.2	0.0954
Energy Rate	MW	-835	-1.74e+003	287	-1.52e+003	-761
Energy Rate	GJ/h	-3.01e+003	-6.25e+003	1.03e+003	-5.46e+003	-2.74e+003
Temperature	°C	30	124*		120	30
Pressure	kPa	180	224.73		200	180

Reboiler Ratio	3.4#	GJ/t
Steam Ratio	1.4#	ton/ton
Cyclic Capacity	0.215#	mol CO2/mol Amine
LG Ratio	3.7#	%
CO2 Recovery2	90#	%

Figure G12 Simulation results for 2 M AMP – 1 M PZ – 2.5 M MEA.

2 M AMP – 1 M PZ – 3 M MEA

Names	Units	Flue Gas	FG to CO2 Plant	Treated Gas	H2O
Temperature	°C	40*	40	61.534	40
Pressure	kPa	120*	120	110	120
Mass Flow	t/h	1685.7	1625.1	1387.5	60.575
CO2(Mass Flow)	t/h	368.17*	368.15	36.817	0.011514
CO2(Mole Fraction)	%	14.59*	15.498	1.6229	0.0077818
N2(Mole Fraction)	%	69.97*	74.328	77.83	0.00087854
O2(Mole Fraction)	%	2.85*	3.0275	3.1701	6.8793e-005
H2O(Mole Fraction)	%	11.69*	6.1899	16.319	99.991
Ar(Mole Fraction)	%	0.9*	0.95606	1.0011	2.3032e-005
Molar Flow	kmol/h	57338*	53976	51546	3362

Names	Units	R-Amine	L-Amine
Temperature	°C	54.967	43*
Pressure	kPa	120	120*
Std Liquid Volumetric Flow	sgpm	27046	25673
CO2 Loading Mole/Mole Amine		0.55	0.33
Mass Flow	t/h	5690.8	5453.2
AMP(Mass Fraction)	%	18.177	19
PZ(Mass Fraction)	%	9.0979	9.5
MEA(Mass Fraction)	%	17.241	18

Names	Units	CO2	Steam	Q-2	1	Reflux
Mass Flow	t/h	334.71	433.63		431.93	155.43
CO2(Mass Fraction)	%	99	0*		32.6	0.23
CO2(Mole Fraction)	%	97.6	0*		16.9	0.0944
Energy Rate	MW	-835	-1.6e+003	264	-1.39e+003	-683
Energy Rate	GJ/h	-3.01e+003	-5.74e+003	950	-5e+003	-2.46e+003
Temperature	°C	30	124*		120	30
Pressure	kPa	180	224.73		200	180

Reboiler Ratio	3.1#	GJ/t
Steam Ratio	1.3#	ton/ton
Cyclic Capacity	0.224#	mol CO2/mol Amine
LG Ratio	3.2#	%
CO2 Recovery2	90#	%

Figure G13 Simulation results for 2 M AMP – 1 M PZ – 3 M MEA.

2 M AMP – 1 M PZ – 4 M MEA

Names	Units	Flue Gas	FG to CO2 Plant	Treated Gas	H2O
Temperature	°C	40*	40	63.071	40
Pressure	kPa	120*	120	110	120
Mass Flow	t/h	1685.7	1625.1	1393.2	60.575
CO2(Mass Flow)	t/h	368.17*	368.15	36.817	0.011514
CO2(Mole Fraction)	%	14.59*	15.498	1.6132	0.0077818
N2(Mole Fraction)	%	69.97*	74.328	77.362	0.00087854
O2(Mole Fraction)	%	2.85*	3.0275	3.151	6.8793e-005
H2O(Mole Fraction)	%	11.69*	6.1899	16.821	99.991
Ar(Mole Fraction)	%	0.9*	0.95606	0.99507	2.3032e-005
Molar Flow	kmol/h	57338*	53976	51859	3362

Names	Units	R-Amine	L-Amine
Temperature	°C	51.753	43*
Pressure	kPa	120	120*
Std Liquid Volumetric Flow	sgpm	16539	15191
CO2 Loading Mole/Mole Amine		0.71	0.38
Mass Flow	t/h	3441.9	3209.9
AMP(Mass Fraction)	%	17.67	19
PZ(Mass Fraction)	%	8.8521	9.5
MEA(Mass Fraction)	%	22.369	24

Names	Units	CO2	Steam	Q-2	1	Reflux
Mass Flow	t/h	334.68	384.21		410.56	165.63
CO2(Mass Fraction)	%	99	0*		37	0.223
CO2(Mole Fraction)	%	97.6	0*		19.8	0.0913
Energy Rate	MW	-835	-1.41e+003	234	-1.3e+003	-728
Energy Rate	GJ/h	-3.01e+003	-5.09e+003	842	-4.67e+003	-2.62e+003
Temperature	°C	30	124*		120	30
Pressure	kPa	180	224.73		200	180

Reboiler Ratio	2.8#	GJ/t
Steam Ratio	1.1#	ton/ton
Cyclic Capacity	0.328#	mol CO2/mol Amine
LG Ratio	1.9#	%
CO2 Recovery2	90#	%

Figure G14 Simulation results for 2 M AMP – 1 M PZ – 4 M MEA.

Appendix H Equilibrium Curve and Reproducibility of Experimental Results

As outlined in Section 3.2, the CO_2 solubility was kept at constant operation for 4 – 14 hours to confirm that equilibrium was reached. During the initial analysis of each amine solution (ternary blend), the CO_2 solubility run was kept in constant operation up to 24 hours. This helped to ascertain the average time to hit equilibrium and hence reduce experimental analysis time period. Figure H 1 highlights the CO_2 equilibrium graph of 2 M AMP – 0.5 M PZ – 3 M MEA at 25 – 60 °C at 100 % CO_2. Taking reference from Appendix E (calculation of CO_2 partial pressure), the CO_2 partial pressure of 100 % CO_2 at the different temperatures are listed below;

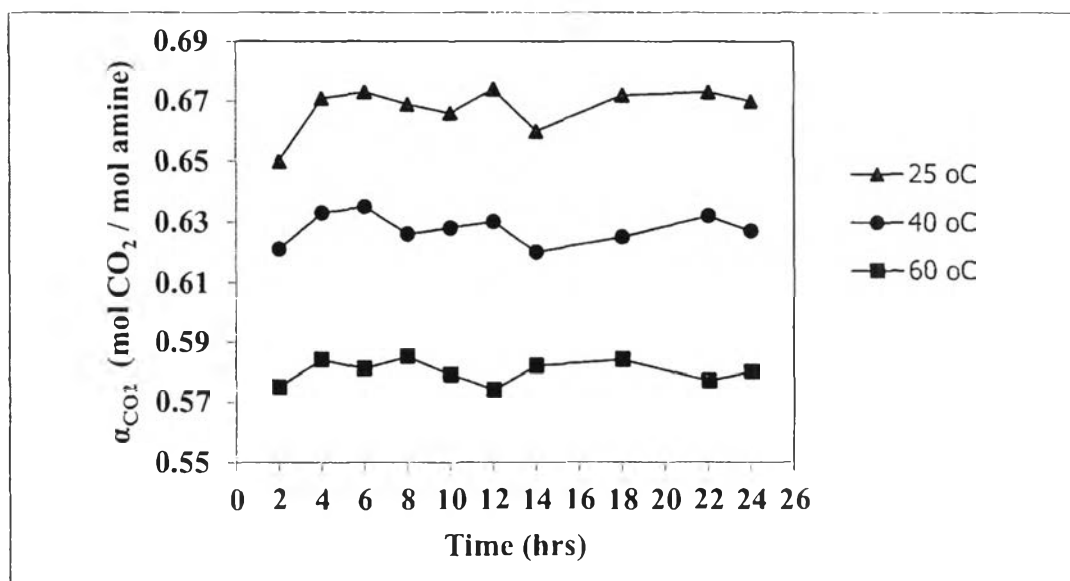25 °C = 98.13 kPa

40 °C = 93.93 kPa

60 °C = 81.39 kPa

Figure H1 CO_2 Equilibrium graph for 2 M AMP – 0.5 M PZ – 3 M MEA at 25 – 60 °C and 100 % CO_2.

From Figure H1, it can be noticed that equilibrium is usually reached between 4 – 8 hours of constant operation. The reported results in this case are the equilibrium datas between 4 – 8 hours. The fluctuations in the CO_2 loading even after equilibrium is attained can be attributed to the slight changes in the amine solution concentration during the CO_2 solubility run. The minor fluctuation does not have a huge impact in the CO_2 loading. It's also important to note that at lower CO_2 partial pressure more time will be required to hit equilibrium. In those cases, the experiment is extended to 14 hours.

It's also important to note that the absorption rate of the amine solution can be deduced from plotting CO_2 loading vs time as seen in Figure H1. The absorption rate is also an important parameter in confirming potential amine solutions for CO_2 capture.

For the reproducibility of the experimental results, each data point was repeated 3 times to further confirm the level of accuracy and reliability of the experimental results. Figure H2 shows reproducibility results of 2 M AMP – 0.5 M PZ – 3 M MEA at 25 – 60 °C and 100 % CO_2.
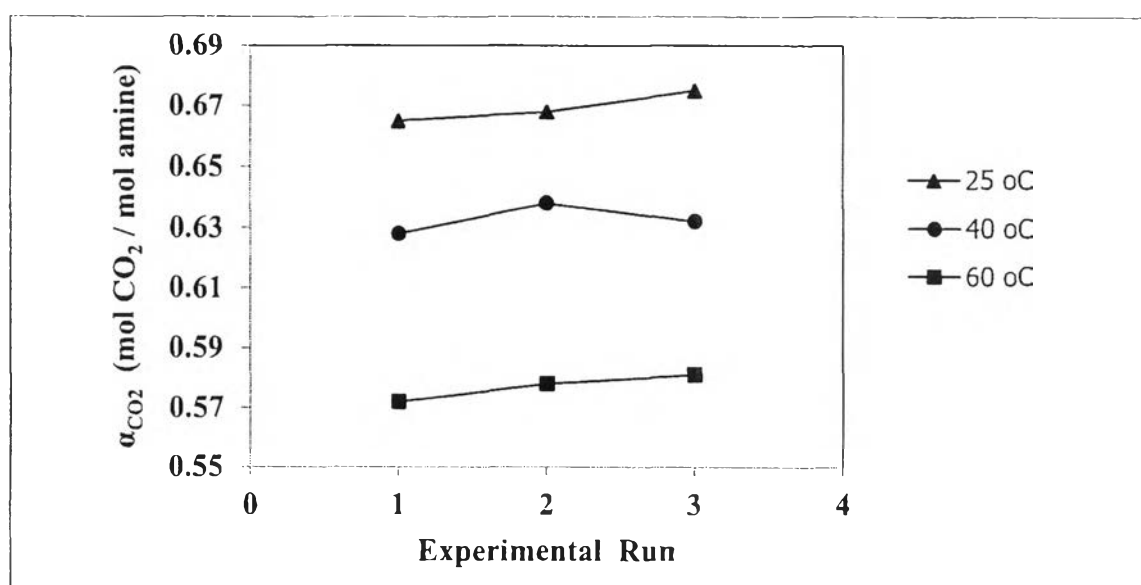

Figure H2 Reproducibility results of 2 M AMP – 0.5 M PZ – 3 M MEA at 25 – 60 °C and 100 % CO_2.

The %AAD from the reproduced results was between 0.5-3 % deviation. This confirmed the reliability of the experimental results. The final CO_2 loading reported in this research project is the average of both the equilibrium data points and the reproduced data points.

Appendix I Reducing Sources of Error during Experimental Analysis

Ability to minimize the possible sources of error will increase the reliability of the experimental results. Figure I1 depicts various areas by which errors can arise during experimental analysis (CO_2 solubility run).
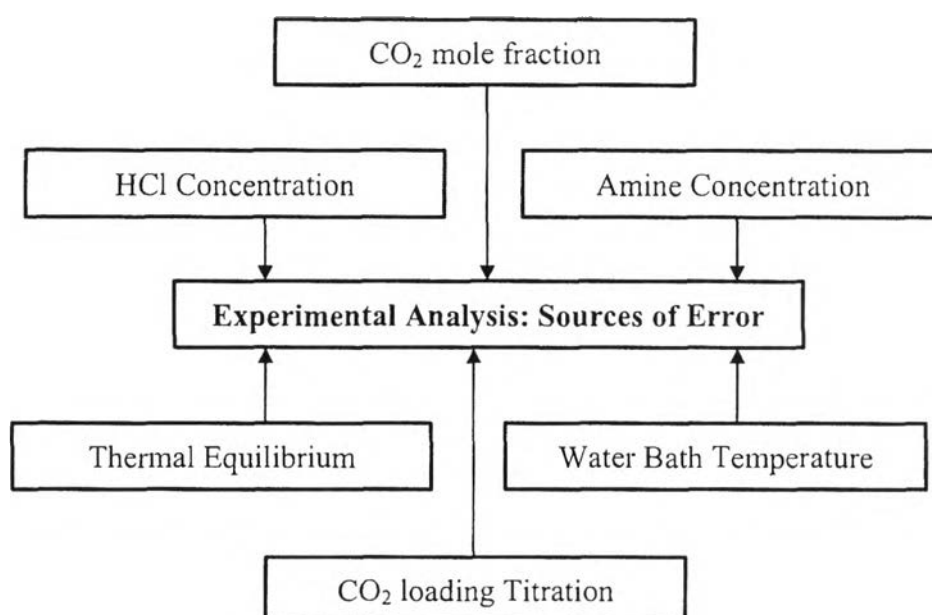

Figure I1 Sources of error during experimental analysis.

For some of the mentioned sources above, its minimal error cannot be controlled. For instance, the water temperature and CO_2 mole fraction indicated by the water bath ($\pm$ 0.1 $^{\circ}$C) and CO_2 analyzer ($\pm$ 0.1 %) already have an existing precision and accuracy as provided by the manufacturer. Therefore, more focus should be directed towards minimizing errors from the amine solution concentration, HCl concentration, thermal equilibrium and CO_2 loading titration. Below are some procedures to limit errors from these sources;

Amine Concentration

During experimental analysis (CO_2 solubility run) for any amine solution concentration at more than 1 data point, it is recommended that the amine solution concentration prepared at once instead of in parts. In another scenario where reproducibility experiment will be conducted, it is also important to prepare the amine solution all at once. For instance, if the desired amine solution volume for each CO_2 solubility run is 20 mL and the 2 data points will be analyzed, then the errors will be reduced if 40 mL of the amine solution is prepared at once instead of preparing 20 mL for 2 different data points (Figure I2). Also, if 1 data point will be conducted but a second experiment (for reproducibility) will be conducted then 40 mL amine solution should be prepared. This will ensure constant amine solution concentration during the entire experimental analysis. Apart from reduced error other merits are listed below;

- Less titration to confirm the amine solution concentration (prior to the CO_2 solubility run). Also a reduced amine solution volume to confirm concentration.
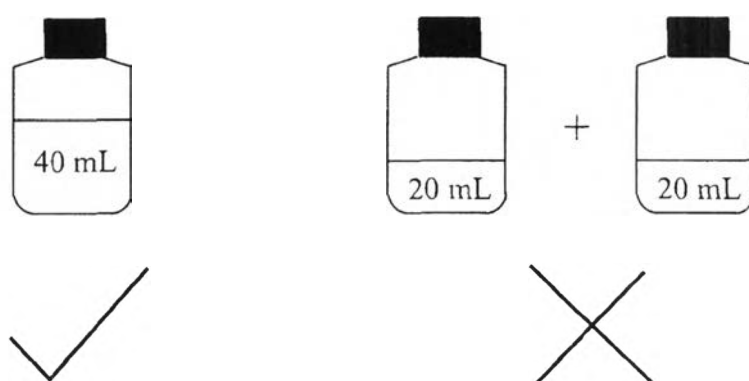- Less HCl volume consumed during the confirmation of the amine solution concentration.

Figure 12 Preparing desired amine solution volume to correspond the proposed experimental data points.

Note: The other source of error in amine concentration is during its preparation. This has been discussed in Appendix A.

HCl Concentration

The correlation for calculating HCl concentration and its standardization was described in Appendix B. It's good to note that most times the concentration of the prepared HCl differs by ± 0.05 M compared to the desired concentration. For instance, if the desired concentration is 1 M, the prepared concentration might be between 0.95 – 1.05 M. This was the case during this research project. In such cases, all calculations involving HCl must be done with the exact concentration and not 1 M. To limit possible errors arising from HCl concentration, it's better to prepare a large volume of HCl to be used almost throughout the proposed experimental analysis (experimental data points). As high as 5 L of 1 M HCl can be prepared and kept for use. This is similar to the idea in Figure I 2.

In addition, if another HCl concentration is prepared (during the experimental time frame) and its concentration is slightly different from the previously prepared HCl, it might be useful to check the concentration an amine solution that has been confirmed by the previous HCl concentration. The 2 different amine solution concentrations (from the previous and current HCl concentrations) can be compared, as it can also show the accuracy of the newly prepared HCl.

Thermal Equilibrium

This has a huge influence in the equilibrium CO_2 loading of any data point. In the absence of reaching thermal equilibrium before starting the CO_2 solubility run, the eventual CO_2 loading will be higher than the actual loading. For instance, if CO_2 partial pressure is 81.39 kPa and the desired temperature is 60 °C, without reaching thermal equilibrium before commencing the CO_2 solubility run the loading will be higher than 0.58 mol CO_2/mol amine. Below are few recommendations;

- The saturation cell and absorption reactor should be submerged in the water bath before switching on the water bath. This will allow water in the saturator and amine solution in the absorption reactor to heat up as the water bath reaches the desired set temperature. In this case, extra minutes must be allowed for the water and amine solution in the saturator and amine reactor to reach the desired temperature.

- If the water bath is already at the desired set temperature before submerging the saturator and absorption reactor, then it is important to allow the water and amine solution to heat from $24 - 25$ °C to the desired temperature. If the desired temperature is 40 or 60 °C, then it will take about 20 to 35 minutes respectively.

For both recommendations, the final temperature must be confirmed by a thermometer before commencing the CO_2 solubility run.

CO_2 Loading Titration

The standard procedure for determining the CO_2 loading in a CO_2 loaded amine solution is described in detail in Section 3.2.5 and must be strictly adhered to if high accuracy is of paramount importance. Appendix D also detailed the correlation for calculating the CO_2 loading. Since this is the final procedure during any CO_2 solubility run, high accuracy in the other sources of error (previously discussed) must precede this.

Appendix J CO$_2$ Solubility in AMP – PZ – DETA – MEA Quartenary (Quad-Solvent) Blends

The potential success of ternary solvent blends showed that quartenary solvent (quad-solvent) blends might offer better qualities like high equilibrium CO$_2$ loading, high net cyclic capacity, no precipitation and much reduced energy of regeneration. The already researched AMP – PZ – MEA ternary blend was further promoted with a polyamine (diethylenetriamine, DETA). Table J1 shows the skeletal structure of DETA. DETA, a triamine contains three amino groups consisting of two primary and one secondary amino groups (Hartono *et al.*, 2011). The addition of DETA allowed much lower concentration of each amine solvent to be utilized thereby limiting any possibility of forming solid precipitates. The polyamine, DETA have been previously studied which indicated higher CO$_2$ absorption capacity and reaction rate than MEA (Yu *et al.*, 2012b). Yu *et al.* (2012b) stated that the higher boiling point and the vapor pressure of DETA will lead to a reduced energy required and reduced absorbent losses in stripper compared with MEA. The reduced heat duty for DETA was also recently expressed by Zhang *et al.* (2014). DETA as a single solvent for CO$_2$ capture have been studied by Hartono *et al.* (2011); Hartono *et al.* (2009).

Table J1 Skeletal Structure of other DETA

	Acronym	Chemical/Skeletal Structure
Diethylenetriamine	DETA	

The concentrations of the quartenary blends analyzed are 2 M AMP – 0.5 M PZ – 1 M DETA – 1.5 M MEA and 1.5 M AMP – 0.5 M PZ – 1.5 M DETA – 1.5 M MEA keeping their total concentration at 5 M. These two quartenary solutions showed a much higher equilibrium CO_2 loading (39.8 – 45.7 %) and absorption working capacity (36.6 – 43.3 %) compared to 5 M MEA (Figure J1). They also possessed slightly higher equilibrium CO_2 loading (0 – 4.8 %) and higher absorption working capacity (10.8 – 16.2 %) than the binary 3 M AMP – 1.5 M PZ (Figure J1). From Figure J1, when AMP – PZ – DETA – MEA is compared to the already studied AMP – PZ – MEA ternary blend of same total concentration (5 M), the quartenary blends exhibited superior equilibrium CO_2 loading (24.6 – 32.3 %) and absorption working capacity (22.8 – 30.3 %).

Based on this success, it can be suggested that the application of quartenary solvent blends might out-perform single, binary and ternary blends for capture of CO_2.
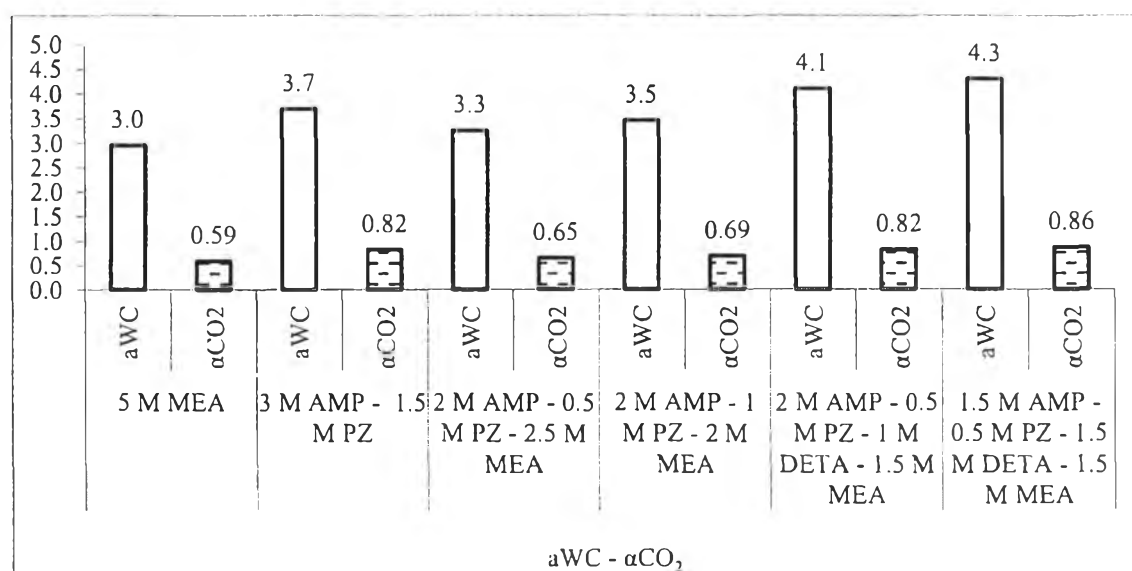

Figure J1 CO_2 Solubility (mol CO_2/mol amine) and absorption working capacity (aWC, mol CO_2/L amine solution) of different concentrations of quartenary AMP-PZ-DETA-MEA Blends at 40 °C and 93.93 kPa CO_2 partial pressure compared to 5 M MEA, 3 M AMP – 1.5 M PZ and AMP-PZ-MEA ternary blends.

The rich solution of the quartenary blends was also cooled at 20 °C for over 400 hours without forming any solid precipitate.

It is also important to note that during the CO_2 solubility run of the quartenary blend, color change was noticed (from colorless to redish-brown) as shown in Figure J2 and 3. It is yet to be ascertained why there was color change, but it can be said to be the introduction of DETA into the blend. This color change might not be related to degradation.

Figure J2 Rich Solution of 2 M AMP – 0.5 M PZ – 1 M DETA – 1.5 M MEA showing the color change.
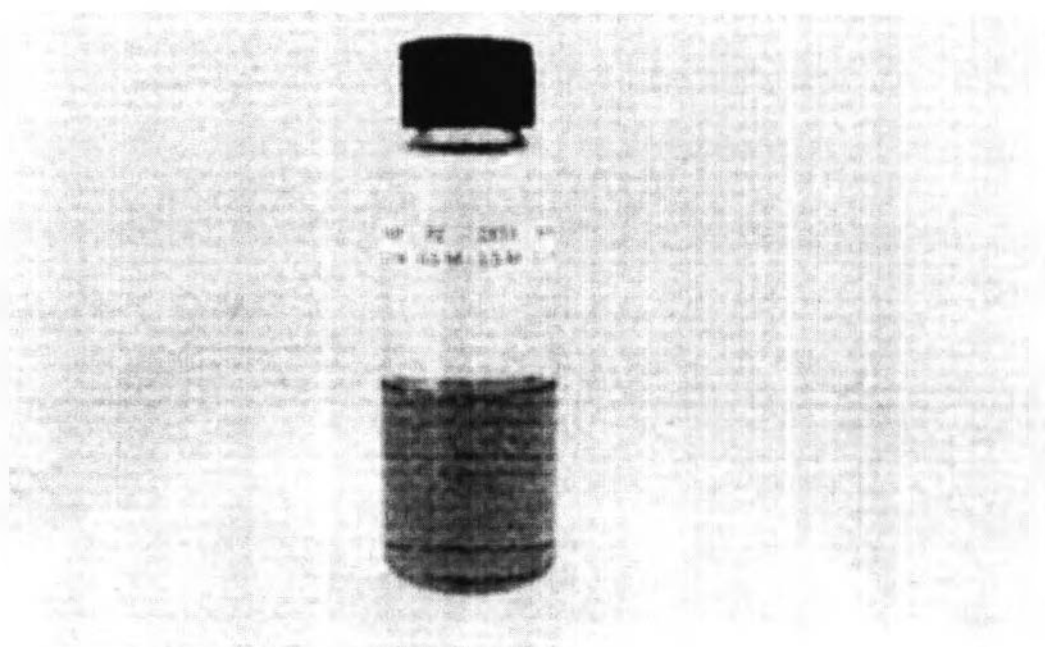
Figure J3 Rich Solution of 1.5 M AMP – 0.5 M PZ – 1.5 M DETA – 1.5 M MEA showing the color change.

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Publication:

1. Nwaoha, C.; Saiwan, C.; Tontiwachwuthikul, P.; and Supap, T. (2015) Solubility of carbon dioxide (CO_2) in solutions of aqueous 2-amino-2-methyl-1-propanol (AMP) solvent promoted by piperazine (PZ) and monoethanolamine (MEA) blends. International Journal of Greenhouse Gas Control, (submitted).

Proceedings:

1. Nwaoha, C.; Saiwan, C.; Tontiwachwuthikul, P.; and Supap, T. (2015, April 21) CO_2 absorption: Solubility of CO_2 in 2-amino-2-methyl-1-propanol solvent promoted by piperazine and monoethanolamine. Proceedings of the 21st PPC Symposium on Petroleum, Petrochemicals, and Polymers, Bangkok, Thailand. (Oral Presentation)

Presentation:

1. Nwaoha, C.; Saiwan, C.; Tontiwachwuthikul, P.; and Supap, T. (2015, May 17 – 21) Equilibrium solubility of CO_2 in 2-amino-2-methyl-1-propanol solvent promoted by piperazine and monoethanolamine blends. Paper accepted at The IEA Seventh International Conference on Clean Coal Technologies (CCT2015), Krakow, Poland.

2. Nwaoha, C.; Saiwan, C.; Tontiwachwuthikul, P.; and Supap, T. (2015, September 8 – 11) Solubility of carbon dioxide (CO_2) in highly concentrated aqueous ternary blend of 2-amino-2-methyl-1-propanol (AMP), piperazine (PZ), and monoethanolamine (MEA). Paper presented at IEAGHG 3rd Post Combustion Capture Conference (PCCC3), Regina, Canada. (Oral Presentation)