# CHAPTER III

# EXPERIMENTAL

## 3.1 Materials and Equipment

### 3.1.1 Materials

#### 3.1.1.1 Gases

- Nitrogen ($N_2$, 99.99 % purity)
- Carbon dioxide ($CO_2$, 99.99 % purity)

#### 3.1.1.2 Chemicals

- Piperazine, PZ ($\geq$ 99 % purity), ACROS ORGANICS, New Jersey, USA.

- Monoethanolamine, MEA ($\geq$ 99 % purity), Merck KGaA, Darmstadt, Germany.

- 2-Amino-2-Methyl-1-Propanol, AMP (99 % purity), ACROS ORGANICS, New Jersey, USA.

- Diethylenetriamine, DETA ($\geq$ 98 % purity), MERCK, Schuchardt OHG, Hohenbrunn, Germany.

- Methyl orange (0.10 % concentration).

- Hydrochloric acid solution, HCl (37 % purity), RCI Lab-scan Limited, Thailand.

### 3.1.2 Equipment

- Portable infrared (IR) $CO_2$ gas analyzer, Model: 906 ranging from 0.0 % to 100 % $CO_2$ with 0.1 % accuracy, Quantek Instruments, Inc., Grafton, MA, USA.

- Electronic AALBORG Mass Flow Controller for $CO_2$, Model: GFC-17 with range of 0 – 200 mL/min.

- Electronic AALBORG Mass Flow Controller for $N_2$, Model: GFC-17 with range of 0 – 200 mL/min.

- Memmert Water Bath (GmbH + Co. KG Schwabach FRG, Germany), with temperature range of 10 °C to 95 °C and precision of 0.1 °C.

- Cooling circulator (Peter Huber Kältemaschinenbau GmbH, Germany, model CC – K6 with temperature range between - 25 °C to 200 °C and temperature stability of ± 0.02 °C)

- Mass Balance (Sartorius AG Gottingen Germany, model TE214S) with maximum measuring range of 210 g and accuracy of ± 0.1 mg.

### 3.1.3 Software
- ProMax® version 3.2 (licensed by Bryan Research and Engineering, USA).

## 3.2 Experimental Procedures

### 3.2.1 Experimental Set-up
The step wise procedure during the experimental run for each data point is described below;

- Prior to the $CO_2$ solubility run, the concentration of each amine solution was confirmed by acidification technique using 1 M of HCl solution to the end point of 0.10 wt% methyl orange indicator.

- A desired $CO_2$ concentration in the feed gas mixture ($CO_2$ and $N_2$) will be fed to the system through a mass flow controller. The $CO_2$ analyzer is used to determine the actual $CO_2$ concentration in the gas mixture before sending it to the saturation cell.

- The simulated flue gas is first saturated in the saturation cell containing 15 mL of distilled water to achieve the $CO_2 + N_2 + H_2O$ mixture.

- The wet flue gas is then sent to the absorption reactor (50 mL capacity) which contains 20 mL of a desired concentration ratio of amine blend.

- The absorption reactor and saturation cell respectively containing the amine solution and distilled water (DI water) are immersed in the water bath and allowed to reach thermal equilibrium at the desired temperature.

- A condenser located downstream of the absorption reactor recovers all condensable species back to the reactor. The condenser was continuously supplied with cold water at 10 – 15 °C to maintain a minimum amine solution loss.

- The $CO_2$ solubility system is kept in constant operation for 4 - 14 hours. This is to confirm that equilibrium has been reached.

- At 2 hours intervals (within the expected equilibrium time frame), liquid samples was taken to analyze for $CO_2$ loading.

- For each liquid sample taken every one or two hours, $CO_2$ will be evaluated 3 times until $CO_2$ loading is constant, or until two consecutive readings show only slight difference of ± 2 %.

- The $CO_2$ loading that is reported is the average of the three equilibrium data points.

The experimental procedure stated above and the set-up shown in Figure 3.1 below used for determining the equilibrium solubility of $CO_2$ were similar to those reported in the work of Tontiwachwuthikul *et al.* (2008). Reproducibility of experimental results indicates the level of accuracy and reliability of the results. The accuracy is also a factor of the minor uncertainties of both the temperature of the water bath (± 0.1 °C), amine solution concentration (± 0.05 M), and mole fraction of $CO_2$ in the simulated flue gas (± 0.1 %). The experimental data points were repeated three times and the estimated average uncertainty (standard deviation) in the measured $CO_2$ loading was between 0.5–3 %. All the reported experimental results are the average of the repeated experiments.
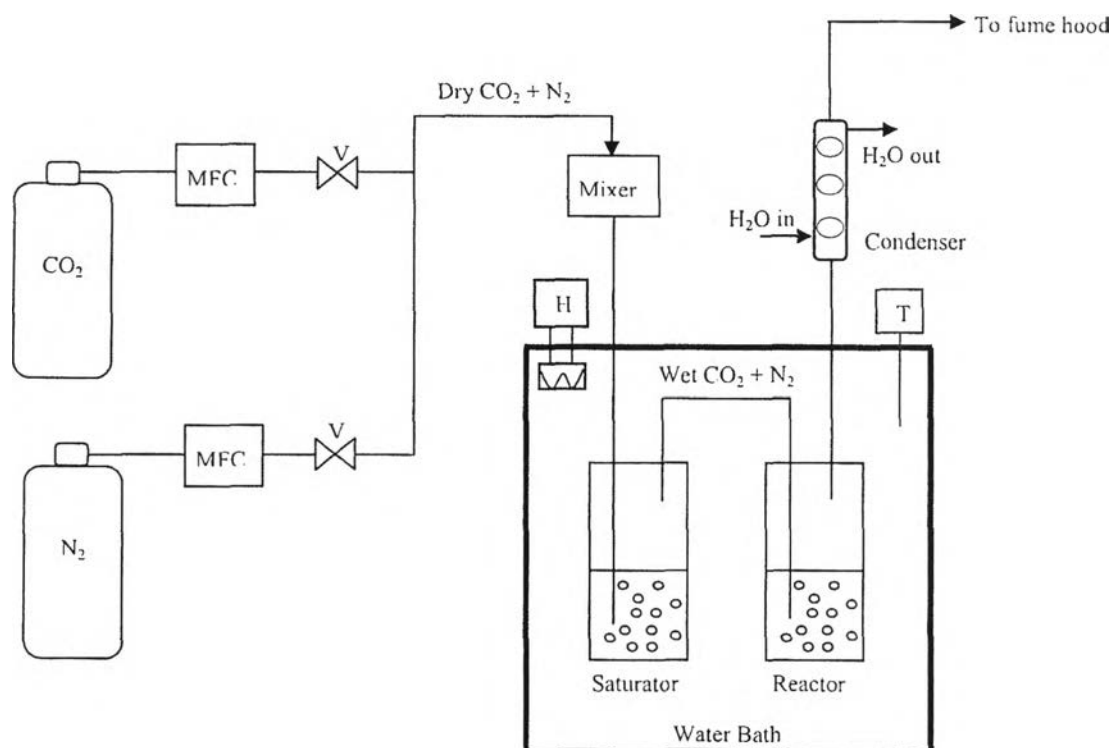
Nomenclature: V = valve, T = temperature gauge, H = heating coil, MFC = mass flow controller.

**Figure 3.1** Diagram of the experimental set-up (Tontiwachwuthikul *et al.*, 2008).

### 3.2.2 Solution Preparation Analysis

The calculation for the preparation of the blended amine solution for the experimental analysis is discussed in Appendix A. The properties of each solvent stock solution as provided in the material safety data sheet (MSDS) is highlighted in Table 3.1 below;

**Table 3.1** Properties of AMP, PZ and MEA

|  | AMP | PZ | MEA |
|---|---|---|---|
| Molecular Weight (g/mol) | 89.14 | 86.14 | 61.08 |
| Purity (%) | 99 | 99 | 99 |
| Density (g/L) | 930 |  | 1015 |
| Calculated Molar Concentration (mole/L, M) | 10.3 |  | 16.5 |

The ternary blend solution was prepared based on molarity basis (moles/L) instead of volumetric basis (vol/vol %). This was chosen first considering that PZ was provided in crystal form. Secondly, AMP (a viscous solvent) is almost pure and hence was in an almost solid form and cannot be taken with the pipette (Figure 3.2). Though it could be melted in the water bath prior to pipetting the desired volume, but the error might be high. This is because some of the AMP will stick in the inner walls of the pipette. Therefore, a mass balance was used to determine the weight of the solvent that corresponds to the desired concentration. This was also done for MEA solvent, though it's pure liquid. The weight of substances are same, irrespective of being in liquid, gaseous or solid form. For every substance, the number of grams in one mole is known (molecular weight). This is very important especially when dealing with substances that their density is unknown, but their molecular weight is known. This limits the error level.

**Figure 3.2** Pure 2-amino-2-methyl-1-propanol, AMP (99 wt%).

### 3.2.3 Solvent Concentration Analysis

The concentration of each solvent in the blend as prepared in the previous section (prior to the $CO_2$ solubility run) were determined by titration technique using 1 M HCl and 0.10 % methyl orange as indicator.

*Procedure*

• The calibrated acid dispensing burette was filled with 1 M HCl to the zero mark. Some of the HCl was released from the burette to remove all trapped air bubbles in the burette.

• 1 mL of the ternary amine solution was added in a decomposition flask.

• Two drops of the methyl orange indicator was injected into the decomposition flask containing 1 mL of the amine sample solution.

- The HCl is gradually dropped into the sample solution and mixed with the aid of a magnetic stirrer.

- The endpoint is reached when the color of the solution changes from orange to red.

- At endpoint, the volume of HCl consumed is measured and noted.

- Knowing the HCl concentration and volume at endpoint, amine sample volume, then the concentration of the sample solution can be calculated using a derived correlation. This correlation used to calculate the concentration of each solvent in the ternary blend is described in Appendix C.

### 3.2.4 Hydrochloric Acid Preparation and Standardization

The concentration of the HCl used during experimental analysis was prepared to 1 M. Methyl red was used for the standardization of the prepared HCl. Prior to using this HCl for analysis, it must be standardized using sodium carbonate ($Na_2CO_3$). This low HCl concentration was used to avoid any physical damage in any case of spillage. Appendix B explained the calculations involved in the preparation and standardization. The stepwise procedure for preparing and standardizing the HCl is described below;

*HCl Preparation Procedure*

- A volumetric flask equaling the desired 1 M HCl volume to be prepared is kept in place. For instance 250 mL volumetric flask.

- First add some DI water into the volumetric flask and then gently add the required HCl volume which corresponds to the desired concentration. Then shake the volumetric flask slowly for proper mixing.

- Then fill the volumetric flask with DI water to the 250 mL mark.

This ordinarily would represent the desired concentration of the prepared HCl, but it must be standardized before using it during experimental analysis.

*HCl Standardization Procedure*

- Add a desired gram of $Na_2CO_3$ into a conical flask or beaker and completely dissolve it with DI water.

- Add two drops of methyl red in the conical flask or beaker containing the dissolved $Na_2CO_3$. The solution will be colorless upon adding 2 drops of methyl red.

- Then gently drop the prepared HCl into the $Na_2CO_3$ solution. End point is reached when the colorless solution turns red.

- Then use the correlation as described in Appendix B to calculated for the actual HCl concentration.

- This standardization procedure should be done at least two times for proper confirmation. The final HCl concentration to be used during the $CO_2$ solubility run will be the average of the 2 or more procedures.

### 3.2.5 $CO_2$ Loading Analysis (αCO2)

The $CO_2$ loading was analyzed using the acidification technique known as "Chittick Apparatus" as stated by the Association of Official Analytical Chemists, AOAC (Horwitz, 1975). This is an analytical method to determine the amount of $CO_2$ that is absorbed in any given amine solution. It is also used to determine the concentration of the rich amine solution. The schematic is shown on Figure 3.2. This chittick apparatus is made up of a decomposition flask (A), a graduated acid addition burette (B), three-way stopcock (C), a graduated gas measuring burette (D), a leveling bulb (E), and a magnetic plate (F). In addition, a thermometer and barometer are required.

*Procedure*

- Connect the chittick apparatus as shown in Figure 3.3, which will contain both the magnetic bar (stirrer) and the amine solution sample (with 2 drops of methyl orange) in the decomposition flask (A) and the pink displacement solution in both the gas measuring burette (D) and the leveling bulb (E).

- Open the three-way stop cock (C), to the atmosphere and adjust the liquid level in the gas measuring burette (D) to precisely 0 mL by regulating the height of the leveling bulb (E).

- Then, with the three-way stop cock (C) close the system to the atmosphere.

- Switch on the magnetic plate (F) to stir the amine solution sample using the magnetic bar in the decomposition flask.

- Once the magnetic bar is stirring the amine solution, simultaneously drop the HCl solution from the graduated acid addition burette (B) and start lowering the leveling bulb. At all times during the liberation of $CO_2$ from the amine solution sample, the level of the displacement solution in the leveling bulb (E) should be kept a bit lower (1 – 2 cm) than the liquid level in the gas measuring burette (D).

- Once the color of the amine solution sample changes from orange to red, this indicates the end point, then record the volume of dispensed HCl. Extra drops of the HCl from the graduated acid addition burette (B) is added to confirm any possible change in the level of the displacement solution in the leveling bulb (E). The volume of this extra HCl dispensed should also be recorded. If there's no net change in the level, this confirms that all the $CO_2$ in the amine sample solution have been liberated.

- Allow the system stand for 2 – 3 minutes to confirm equilibrium.

- Then equalize the level of the displacement solution in the leveling bulb (E) with the level in the gas measuring burette (D), and record the volume of $CO_2$ liberated.

- Record the temperature (K) of the air and barometric pressure (mmHg) of the surrounding near the apparatus. The temperature and pressure is used in converting the volume of $CO_2$ to standard conditions. The calculation sequence and procedure is detailed in Appendix D.
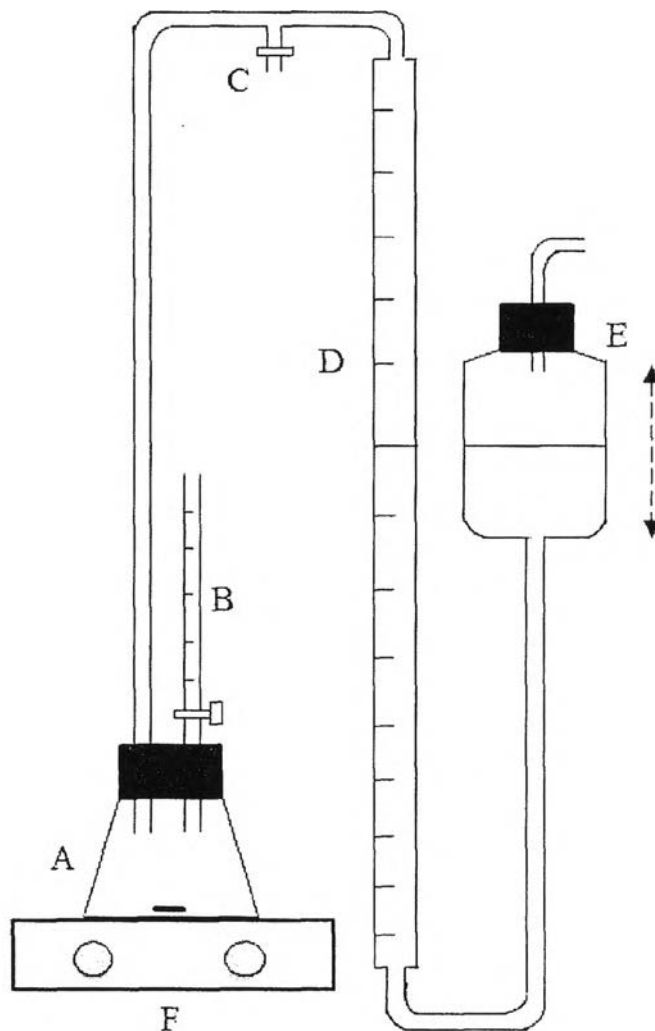
**Figure 3.3** Schematic of chittick apparatus (Horwitz, 1975).

The Appendix D shows the correlation for calculating the $CO_2$ loading using datas gotten from the chittick apparatus.

### 3.2.6 Displacement Solution Preparation

The displacement solution in the gas burette and leveling bulb (pink colored in the laboratory) as shown in Figure 3.3 during $CO_2$ loading analysis is not deionized water or colored water. This is an acidic solution prepared to avoid any possibility of $CO_2$ dissolution. Therefore, this acidic solution was prepared as stated by official and tentative methods of analysis of the Association of Official Agricul-

tural Chemists (1945). The step wise procedure for the preparation of the displace-
ment solution is highlighted below;

*Procedure*

- Prepared diluted sulfuric acid by diluting 1 part of concentrated sul-
furic acid with 5 parts of distilled water.

- Dissolve 100 g of sodium chloride in 350 mL in distilled water and
add about 1 g of sodium bicarbonate and 2 mL of methyl orange indicator.

- When the sodium bicarbonate fully dissolves, sufficient quantity of
the prepared diluted sulfuric acid is then added. This makes the solution
acidic and will then assume a pink color.

- Keep stirring until all free carbon is removed. The gas burette and
leveling bulb is filled with the displacement solution.