CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Liquid-Liquid Extraction

A liquid-liquid extraction is one of many separation methods that normally uses 1 or 2 diluents to extract a wanted component from unwanted components. A solute identified as the wanted component, is often dissolved in a mixture (e.g. aqueous solution), which must be separated from the other components due to many reasons, such as some of solute might exceed an environmental standard; wanted product is dissolved in a mixture of by-products; and un-reacted reactant etc. A diluent is often an organic liquid that can extract solute contained in an aqueous solution based on its solubility in the diluent and its selectivity of solute. Good diluents must possess a higher solubility of solute than the mixture, where the solute originally is dissolved; a high selectivity of solute to the diluent, which is an important factor taken into account in the selection process. The diluents must selectively interact to the solute of interest not the others.

The diluents can be classified into two major groups: polar and non polar diluents. Good diluents should be chemically stable, non-toxic, inexpensive, commercially available, easy to recover, and relatively immiscible with solute. Also, it should have a different density from the dissolving phase; thus, a new phase formed should be clearly seen.

The liquid-liquid extraction done at lower temperature (e.g. room temperature), has an advantage over a distillation reclaiming method, which the higher temperature is normally operated. The thermally sensitive solutes, potentially degraded during the distillation, should be separated by liquid-liquid extraction at an ambient temperature without a serious chemical decomposition. The diluents should also be recyclable for repeated extraction, thus, easy to recover solutes during regeneration is also a key in boosting up the extraction efficiency of the process (Seader *et al.*, 2006).

Extraction is preferred to distillation for the following application:

1.) Dissolved or complexed solute in organic or aqueous solutions.

2.) Removal of a component present in low concentrations.

3.) A high-boiling component is present in relatively small quantities waste stream. Extraction becomes competitive with distillation because of the expense of evaporating large quantities of water solution that very high heat of vaporization makes it consume more energy.

4.) Recovery of heat sensitive material, thus extraction may be cheaper than vacuum distillation.

5.) Separation of a mixture according to chemical type rather than relative volatility

6.) Separation of close-melting or close-boiling liquids, where solubility differences can be exploited.

7.) Mixtures that form azeotropes.

(Seader *et al.*,2006)

According to an efficiency of extraction, it measured by a distribution coefficient, K_D (Eq 2.1) defined as a ratio between concentrations of solute in solution 1 divided by concentration of solute in solution 2, where the two solutions are immiscible.

$$K_D = \frac{\text{concentration of solute in solution 1}}{\text{concentration of solute in solution 2}} \qquad (2.1)$$

The best way to roughly select the diluents is based on the distribution coefficient, which should be more than 1. If the solution 1 and 2 are immiscible, many solutes such as alcohol, amine, and carboxylic acid can be dissolved in both solutions due to polar and non-polar functional groups in their molecules, which mean the diluents must be strictly selected based on distribution coefficient (Seader *et al.*, 2006).

Thermodynamics of the extraction processes is an important parameter, which is needed to be determined when the liquid-liquid equilibrium occurs spontaneously for the two immiscible liquids in a single system. Specifically, an activity coefficient must be used in a non-ideal solution calculation, instead of

concentration and partial pressure of mixture, which normally applied to an ideal solution to represent the thermodynamic values. From thermodynamics point of view, if a ratio between two activity coefficients has a greatly different value, it would give a high value of distribution coefficient, which means the solute is easily extracted (Smith *et a.,* 2005).

Equation 2.2 shows the relation between distribution coefficient (K_D) and thermodynamics properties of two liquid phases. Where x_i^j is a liquid mole fraction of component, γ_{iL}^j is an activity coefficient in liquid phase, f_{iL}^{0j} is standard fugacity in liquid phase, and i and j represent component and liquid phase respectively.

$$K_D = \frac{x_i^{(1)}}{x_i^{(2)}} = \frac{\gamma_{iL}^{(2)} f_{iL}^{0(2)}}{\gamma_{iL}^{(1)} f_{iL}^{0(1)}} = \frac{\gamma_{iL}^{(2)}}{\gamma_{iL}^{(1)}} \tag{2.2}$$

From equation 2.2, standard fugacity of each liquid phase is equal and can be canceled out.

2.2 Absorption Process

In the past decades, acid gas treating processes have been extensively developed for environmental purposes (Seader *et al.,* 2006). One of the most effective methods to treat CO_2 is an absorption using reactive liquid solvent. A simplified diagram for CO_2 capture process using an aqueous amine solution is presented in Figure 2.1.
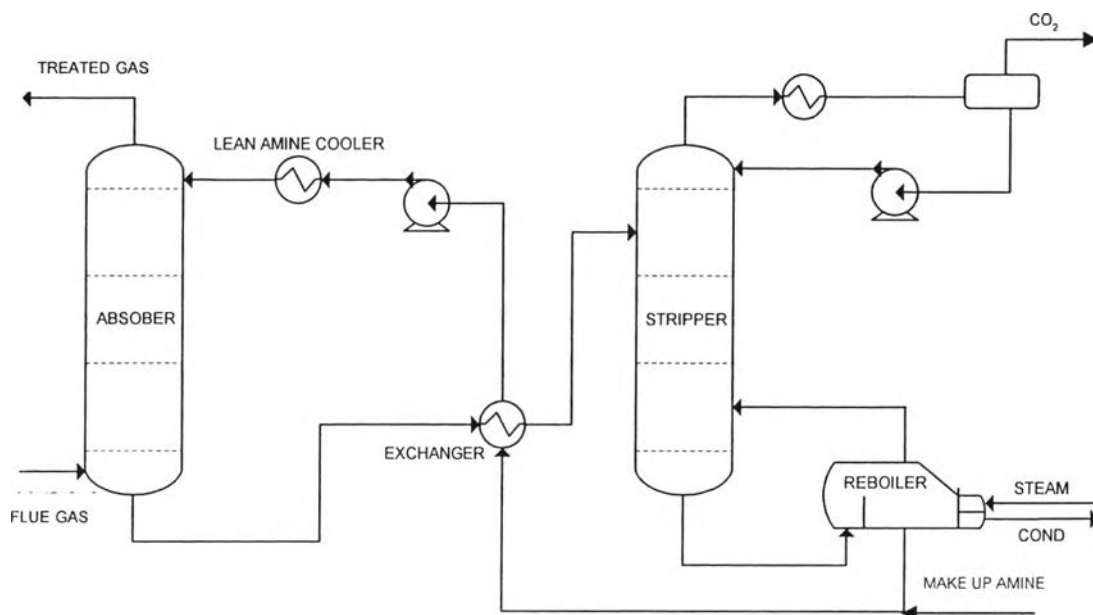
Figure 2.1 Simple process flow diagram of amine gas treating unit.

In Figure 2.1, an acid gas (sour gas), in this case CO_2 gas stream is flown in the absorption column at the bottom, counter-currently to the liquid solvent (alkanolamine), which is fed at the top of the column. The acid gas is chemically absorbed by the lean amine (low or no acid gas concentration). The effluent gas has become a sweet gas (no acid gas) and the lean amine solution becomes rich amine (high acid gas concentration). Due to exothermic reaction of amine and acid gas, an increase of temperature decreases the CO_2 absorption, which is due to a decrease in physical solubility of gases. The rich amine solution is flown to a regeneration zone for recycling of used amine. The regeneration zone or a stripping requires thermal energy to separate CO_2 out of amine. The stripping is similar to the distillation, which steam is used to strip off CO_2, and it is also comprised of a condenser, a reflux drum, and a reboiler, thus this section needs higher temperature than the absorption zone. To save an energy supplied to the regeneration zone, the rich amine is preheated in a heat exchanger, where there is exchanging heat from the lean amine flowing from the bottom of the stripping tower, and the rich amine entering the stripping column where the acid gas is stripped off, and the rich amine becomes lean

amine back to the absorption section again. A recovered gas is carried by steam out at the top section of column, where the phase separation of CO_2 occurs.

Paul *et al.* (2008) have proposed a new CO_2 separation method using a flat sheet membrane with an amine solution. A membrane separation was introduced with a goal set to reduce energy and operational problems related to flooding, foaming, channeling, and entrainment, which is normally found in the conventional amine absorption process. A micro-porous membrane contactor can overcome these problems and also provide a much larger gas-liquid interfacial contract area than that of the conventional amine process. However, this technique still suffers from an additional diffusion resistance through the glass filled membrane pores, which presented in a greater pressure loss. The advantage of this membrane contactor over others is that any type of the membrane can be formed into a flat sheet membrane module. In addition, the fabrication of the flat sheet membrane is easier compared to the other membrane. A flux in flat sheet membrane is also higher than the other membranes, such as hollow fiber and tubular membrane. The important factors affecting separation efficiency of the membrane are module geometry and membrane properties such as membrane material, pore size, porosity, and specific surface area. Process operating parameters including, gas and liquid flow rates, initial solvent and gas phase CO_2 concentrations, and pressure drop can also affect the membrane efficiency.

Saiwan *et al.* (2011) have reviewed corrosions as a major drawback in amine gas treating process for CO_2 capture. The corrosions often prevent amine from achieving its highest possible efficiency for separation of CO_2. The review identified the concentrations of amine, CO_2, oxygen (O_2), other impurities in gas stream (e.g. H_2S and CS_2), and temperature increased corrosion rate of carbon steel equipments during absorption operation. Corrosion in amine process cannot be avoided because a cathode and an anode always appear in the system, due to the cation and anion salts, which are dissolved in aqueous solution. Anodic and cathodic inhibitors are recommended to be added into the amine solution, which are changing oxidative and reductive reaction behavior that come from potential corrosive species.

2.3 Alkanolamine

The chemical absorption using, alkanolamines has been a popular method used in many gas sweetening processes due to its high efficiency, being shortly feasible and commercial applicability (Epp *et al.*, 2011). Examples of commonly commercial alkanolamines are monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), triethanolamine (TEA), digycolamine (DGA), diisopropanolamine (DIPA) and triisopropanolamine (TIPA) , which operating conditions are shown in Table 2.1 (Polasek, 2006). Other commercially available solvents having the ability in treating the acid gas include 2-amino-2-methyl-1-propanol (AMP), potassium sarcosinate and potassium glycinate (Epp *et al.*, 2011).

Table 2.1 Typical operating conditions for each amine (Polasek, 2006)

Amine:	MEA	DEA	DGA	MDEA
Solution strength, wt%	15-20	25-35	50-70	20-50
Acid gas loading, mole/mole (Carbon steel)	0.3-0.35	0.3-0.35	0.3-0.35	Unlimited
Ability to selectively absorb H_2S	No	Under Limited Condition	No	Under Most Conditions

2.3.1 Monoethanolamine (MEA)

In case of carbon steel equipments, the MEA concentration used is only limited to 10 – 30 wt% in aqueous solution to avoid corrosion. Loading of acid gas in the MEA solution for carbon steel equipments is limited to 0.3 – 0.5 mole acid gas/ mole MEA. However, in case of stainless steel equipments, it could be used up to 0.7 – 0.9 mole acid gas/ mole MEA without any corrosion. Actually, MEA is not considered as a corrosive chemical, but its oxidative degradation products are corrosive. MEA is a primary amine, the lightest molecule compared to the other amines, and high pH, which make MEA high efficient to capture the acid gas. MEA chemically absorb CO_2 with exothermic reaction (Polasek, 2006).

In Supap *et al.* (2011) review, they conclude works previously done by other researchers that the degradation of MEA induced by CO_2 and sulfur compound, such as COS and CS_2. MEA was easily degraded by these compounds to form various degradation products. In their research, when the rate of degradation of MEA was compared with DEA and MDEA, MEA was degraded faster than MDEA but slower than DEA. In the presence of COS, there was an exception that MEA was faster degraded than DEA. COS degrades MEA faster than CO_2. In this study of the oxidative degradation, MEA was compared to TEA and diaminoisopropanol for resistance to the oxidation, and result showed that MEA has the most resistibility, followed by TEA and diaminoisopropanol.

In 2008, Paul *et al.* reported that MEA was the most suitable for the absorption of CO_2 if considered on average flux of CO_2 in amine only. According to the same study, MEA has the highest CO_2 absorption flux followed by AMP, DEA and MDEA in sequence. Reaction rate is a function of amine concentration and it is dominating factor over the other physic-chemical properties.

2.3.2 Diethanolamine (DEA)

Polasek, (2006) has reported that 25 – 35 wt% of DEA in aqueous solution is a suitable range of concentration for CO_2 capture application. To prevent the corrosion, DEA used in carbon steel equipment can load acid gas only 0.3 – 0.35 mole of acid gas/mole of DEA as opposed to 1 mole of acid gas/mole of DEA in stainless steel absorption equipment. Some of corrosion inhibitors can also be added to the solution, thus DEA's capacity can be as high as 1 mole of acid gas/mole of DEA without any corrosion problem. Generally, DEA is not thermally reclaimable, due to its decomposition in atmospheric pressure. DEA is a secondary amine and less reactive to H_2S and CO_2 than MEA. Also, heat of reaction between the DEA and acid gases is 25% less than that of MEA, thus regeneration becomes less energy demanding. Compared to MEA, DEA can be more selective to H_2S than CO_2, if contact time between the solution and acid gases is more than 2 seconds. The H_2S selectively allows DEA to be used effectively, but H_2S must be treated isolatedly from the rest of the feed gas component (e.g. Natural gas treating process).

In Supap *et al.* (2011) study, they summarized works previously done by other researchers that DEA is the easiest amine to be degraded by CO_2 and sulfur compound as compared to MEA and MDEA. There were two possible pathways that DEA could be degraded. The first proposed was degradation of DEA convert to N,N,N'-tris(2-hydroxyetOhyl)ethyldiamine (THEED), N,N'-bis(2-hydroxyethyl)piperazine (BHEP) and finally to polymeric compound. The second was divided into three routes i.e. the fast molecular route was a formation of carbamate, the slower ionic route was carbamate degradation to THEED and subsequently to BHEP, and very slow thermal route was DEA thermally decomposed to THEED and BHEP.

2.3.3 Methyldiethanolamine (MDEA)

In 2006, Polasek has studied MDEA and suggested to use concentration range of 20 – 50 wt% in water. A lower concentration was even recommended to be used in very low pressure condition in the absorption process. Due to its lower corrosion than MEA and DEA, acid gas loading limit in carbon steel equipment is 0.7 – 0.8 mole of acid gas/ mole of MDEA. Structurally, MDEA has distinct advantages over both primary and secondary amines including lower vapor pressure, lower heat of reaction, higher resistance to degradation, fewer corrosion problems, and more selective toward H_2S in the presence of CO_2. MDEA does not have any hydrogen attached to nitrogen atom and cannot react directly with CO_2 to form the carbamate. The reaction is triggered by CO_2 dissolving in water to form a bicarbonate ion prior to undergoing an acid-base reaction with MDEA. In the acid gas mixture of H_2S and of CO_2, MDEA selectively removes H_2S by increasing temperature in absorber and also increasing liquid residence time to 1.5 – 3 seconds.

In 2011, Supap *et al.* have study works done from other researchers and conclude that MDEA could be degraded by CO_2 and there were many equilibriums of intermediates involved, where some were formed by parallel or series reactions depending on temperature and concentration. MDEA has the slowest rate of degradation compared to MEA and DEA, but seemed to be more susceptible to oxygen induced degradation than DEA and the formation of acid product.

2.3.4 Diglycolamine (DGA)

In 2006, Polasek reported that DGA is generally used in range of 50 – 70 wt% in water. To cope with the corrosion, acid gas loading of 0.35 mole of acid gas/mole of DGA could be used. DGA has a tendency to absorb CO_2 more than H_2S and has higher pH than MEA. DGA has significant advantages over the other amines including, its allowable higher concentration in streamline, lower circulation rate and lower freezing point. Only disadvantage is its highly exothermic reaction with acid gas.

2.3.5 Triisopropanolamine (TIPA)

According to Daneshvar *et al.* (2003), TIPA has many advantages over MEA, DIPA and MDEA in terms of solvent loss by evaporation, corrosion, chemical degradation, and energy consumption in regeneration. Therefore it has been proposed to be a good alternative solvent for acid gas treating process. TIPA, a highly sterically hindered was two times cheaper than DIPA. A vapor pressure of TIPA is approximately 0.01 mmHg at 20°C, which relatively lower than those of the other industrially used alkanolamines. TIPA also has more solubility in water than DIPA. Similar to DEA, TIPA, a tertiary amine cannot react with CO_2 directly, thus it will not form any carbamate, but absorbs CO_2 by acid-base mechanism. Low heat of reaction also allows the amine to be regenerated more easily, thus consuming low regeneration energy. One downside is that TIPA has a low equilibrium CO_2 absorption capacity, partly due to its high molecular weight, and high viscosity which limit mass transfer of CO_2 within the solution. To deal with this, more reactive primary amines, such as MEA can be added to the solution to boost up the CO_2 absorbing power of TIPA.

Table 2.2 shows the concentration range of amine used and also acid gas loading range of each amine mentioned above.

Table 2.2 Summary of alkanolamines

Amine	Concentration range (wt%)	Loading limit for carbon steel (mole acid gas/mole amine)	Reference
MEA	10 – 20	0.3 – 0.35	Polasek *et al.*
DEA	25 – 35	0.3 – 0.35	Polasek *et al.*
MDEA	20 – 50	0.7 – 0.8	Polasek *et al.*
DGA	50 – 70	-	Polasek *et al.*
TIPA	-	-	Daneshvar *et al.*

2.4 Alkanolamine Degradation Products

Stability of solvent in a CO_2 absorption process is an important parameter that needs to be closely monitored since it affects performance of absorption operation. An alkanolamine is known to degrade after repeated use and long exposure to oxygen, heat, and other impurities during CO2 capture operation. Furthermore, the degradation products in the amine solution can cause corrosion, fouling and foaming. It also decreases CO_2 loading of the amine which results in off-specification of the treated gas. Not only is CO_2 involved in reactions with amine, but the other reactive species in flue gas, specifically O_2, SO_2, NO_x and inorganic oxide fly ash also competitively react with amine. Reactions of amine with these components can form an irreversible product called heat stable salt (HSS) (Supap *et al.*, 2011). Contaminants in make-up water used in the absorption process including chloride, nitrate and nitrite could react further with amine to form an undesired products (Verma *et al.*, 2009).

Epp *et al.* (2011) and Supap *et al.* (2011) have proposed major types of degradation products. A salt formation from SO_x and NO_x aqueous solution can form an inorganic acid (HA) and further form an amine salt by acid-base reaction,

$$RNH_2 + HA \rightarrow RNH_3^+ + A^- \tag{2.3}$$

Second type of product is derived from oxidative degradation due to O_2 in flue gas,

$$Amine + nO_2 \rightarrow NH_3 + \text{Degradation product} \tag{2.4}$$

Thermal degradation can potentially produce the products via 2 pathways. First route occurs mostly beyond 200°C. Second route could be triggered by

temperature higher than 200°C, initiating catalytic degradation reaction to form irreversible products. Finally, the carbamate polymerization can occur due to the presence of CO_2 at a high temperature.

2.4.1 CO_2 and Sulfur Compound Induced Amine Degradation

Supap *et al.* (2011) reviewed extensively on the amine degradation by CO_2 and sulfur compounds, such as carbonyl sulfide (COS), carbon disulfide (CS_2), and hydrogen sulfide H_2S, which were found mainly in CO_2 capture process of high pressure natural gas. Even sulfur being treated before entering CO_2 absorption unit, there is always a small concentration of sulfur left in the gas stream and can still degrade the amine. It was found that MEA could be easily decomposed to 1-(2-hydroxyehtyl) imidazolidone-2 and N-(2-hydroxyehtyl) ethylenediamine (HEED) by heating a carbonate salt of MEA at 40 – 120°C in the presence of CO_2 and sulfur compounds. DEA was also easily decomposed by CO_2 and sulfur compounds at high temperature and moderate pressure, which generates N,N'-bis(2-hydroxyethyl) piperazine (BHEP), and N,N,N'-tris(2-hydroxyethyl) ethylenediamine (THEED). In this review, there were two proposed pathways for CO_2 and sulfur compounds induced DEA degradation. Firstly, DEA was degraded to 3-(hydroxyehtyl)-2-oxazolidone, THEED, BHEP, and polymeric compounds in range of 100 – 120°C. Secondly, under temperature 90 – 175°C and in the presence of CO_2 solubility more than 0.2g/g DEA, there were three routes involved, i.e. a fast molecular route, where CO_2 reacted directly with DEA to form the carbamate; a slower ionic route, where the carbamate transformed to THEED and further converted to BHEP; and a very slow thermal route, where DEA was thermally decomposed to THEED and BHEP. For MDEA degradation by CO_2 and sulfur compounds, it was more complicated by involving in many parallel and series reactions; and dependents on temperature and its concentration. Rate of degradation in these amines can be generally given in the order of MDEA < MEA < DEA but the order was changed to MEA > DEA when COS was present, COS could degrade MEA in the same way but higher rate than CO_2.

Supap *et al.* (2011) also reviewed effect of H_2S in amine degradation. H_2S present in gas stream could be oxidized by O_2 to form elemental sulfur (S^0),

sulfite (SO_3^{2-}), thiosulfate ($S_2O_3^{2-}$), sulfate (SO_4^{2-}) along with dithionites ($S_2O_4^-$), and polythionates ($S_nO_6^-$). Some of these components form a HSS by reacting with the amine. It was concluded that H_2S, CO_2, and sulfur compounds reacted with the amine and formed HSS. When H_2S was presence, acetic acid was dominantly formed while glycolic and formic acids were mostly generated in the absence of H_2S.

In 1996, Dawodu *et al.* reported degradation of DEA by CS_2. It was concluded that CS_2 reacted with DEA to form DEA dithiocarbamate, which further reacted with DEA to become DEA dithiocarbamate salt. Further reactions involving the dithiocarbamate and/or the salt lead to a formation of solid product. Another pathway was hydrolysis of CS_2 to COS, CO_2 and H_2S. These hydrolyzed products dissolved in water to form an ion which reacted further with amine to form the amine carbamate.

2.4.2 Oxidative Amine Degradation

Supap *et al.* (2006) studied 2 different systems with and without CO_2 in $MEA-H_2O-O_2$ and found that in the presence of CO_2, it produced more stable products than oxidative products. Thus, the extent of MEA oxidative degradation in the presence of CO_2 was less than the system consisting of O_2 alone. Based on their analysis, CO_2 which could be used to minimize the degradation was found to reduce O_2 solubility in MEA solution, thus decreasing formation of anionic degradation products. The degradation products, which mainly detected in this study, were formic and acetic acids. These carboxylic acids also generated more degradation products with MEA such as HSS, which lead to the formation of HSS. The oxidative degradation mechanism attributed to Jefferson chemical was proposed as shown in Figure 2.2.
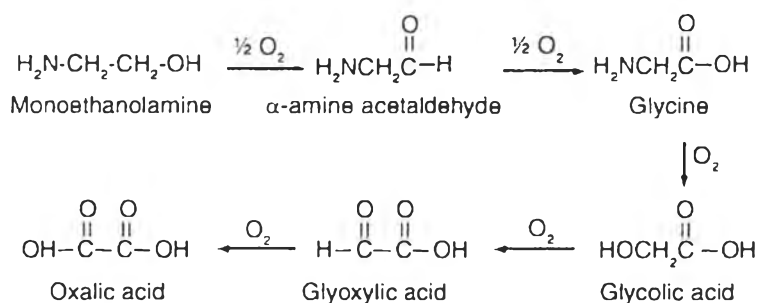

Figure 2.2 One of first MEA oxidative degradation mechanism (Supap *et al.*, 2011).

Supap *et al.* (2009) studied kinetics of the MEA degradation system in presence of O_2, SO_2 and CO_2. MEA showed a tendency to be degraded, if temperature and concentration of MEA, O_2, and SO_2 were increased. However, increases concentration of CO_2 showed the opposite effect. Even though SO_2 is present in a smaller amount than O_2, it was more contributed to the amine degradation than O_2. The degradation products were found to be the major component in the system with O_2 alone as compared to those of CO_2 alone, and combined O_2 and CO_2 systems. The higher temperature was also found to induce more degradation products.

According to Supap *et al.* (2011), blended MEA and MDEA, which degraded by presence of O_2, CO_2, and both O_2 and CO_2, showed similar trend that observed in MEA system. MDEA in the blending was found to induce a smaller number of CO_2 degradation products than MEA alone. In case of temperature higher than 373K, MDEA was more susceptible to oxidative degradation than MEA. The MDEA degradation protected MEA to degrades in the blended solvent, which reducing the extent of MEA degradation at higher temperature. In further investigation on the kinetics of the three different systems (i.e. O_2 presented, CO_2 presented, and O_2 and CO_2 presented), the system consisting of O_2 only showed the rate of degradation rate in the mixed MEA and MDEA increased with an increase of temperature and total concentration of amine. When lower MEA/MDEA concentration ratio was used, the degradation rate of MEA was reduced while that of MDEA was increased.

Supap *et al.* (2006) proposed three analysis methods for MEA degradation system in a presence of O_2, CO_2, and both combined. Three techniques were suggested for detection of the degradation products i.e. gas chromatograph-mass spectrometer (GC-MS), high performance liquid chromatography-refractive index detector (HPLC-RID) and capillary electrophoresisdiode array detector (CE-DAD). An Intermediate polarity column (e.g. HP-35MS) performed the best analysis and the most sensitive in GC-MS technique, which was showed the greatest number of the degradation products being detected. If analyzes only the degradation product, the intermediate polarity column is enough. A high polarity column (i.e. HP-Innowax) could be used in combination with the intermediate polarity column for

analysis of decreasing of MEA concentration. Anions of HSS were separated and could be simultaneously analyzed by HPLC-RID technique, using a cation-exchanger Nucleosil 100-5 SA column, and 0.05 kmol/m^3 KH$_2$PO$_4$ mobile phase. Similarly, CE-DAD could be used, but due to the high concentration of MEA, samples must be diluted to a lower concentration before analyzed.

Since SO$_2$ can trigger an additional degradation to MEA, its concentration must be kept as low as possible (<5 ppm), and should be removed before entering the absorption process (Supap *et al.*, 2006).

2.4.3 Oxidative and Thermal Degradation

In 2011, Supap *et al.* have reviewed about oxidative and thermal degradation of amine systems. The work summarized that reaction between dioxygen and substrate should occur at very low rate, except at elevated temperature or in presence of metal ions. The rate of NH$_3$ production in the gas phase was independent of iron concentration in the MEA and CO$_2$ loading system. Others metal ions such as Cu^{2+}, Cr^{3+}, Ni^{2+} and V^{5+} were found to catalyze the reaction of NH$_3$ production. From the study, amine autoxidation could occur through four pathways: high temperature reaction requiring a presence of the metal ions or fly ash in the reboiler, abstraction of hydrogen atoms by a hydroxyl radical, dioxygen reduction at lower temperature section of the absorber, and abstraction of hydrogen atoms by an organoperoxy radical. To avoid amine autoxidation taking place by the free redical mechanisms, it was suggested to use a good method to remove fly ash in order for amines to have high thermal stability and resist to CO$_2$ induced degradation. Four possible pathways was also proposed for MDEA degradation in the presence of air, i.e. oxidative disproportionation occurring at lower temperature, autoxidation of carbon based radical giving a final bicine product, autoxidation of carbonbased radical giving acetic, glycolic or formic acid degradation products, and initial oxidation of MDEA producing bicine and MDEA through a N-methyl-(N-hydroxyl)glycine intermediate.

In 2011, Supap *et al.* reviewed a degradation inhibitors formulated for amines used in CO$_2$ capture process. Sodium sulfite (Na$_2$SO$_3$), sodium potassium tartate tetrahydrate (KNaC$_4$H$_4$O$_6$.4H$_2$O), ethylenediaminetetraacetic acid (EDTA)

and hydroxylamine (NH_2OH) at optimum concentration of 0.05, 0.01, 0.0025, and 0.025 $kmol/m^3$, respectively were found to be the most effective in minimizing the degradation of MEA in the presence of O_2 and SO_2. When the inhibitors were used beyond these optimum concentrations, adverse effect increasing rate of degradation was seen. In the presence of O_2, SO_2, and CO_2; the blend of $Na_2SO_3/KNaC_4H_4O_6$ was more effective than the individual compounds. On the other hands, $Na_2SO_3/EDTA$ blend did not perform better than the individual Na_2SO_3 or EDTA. The power of inhibition of these inhibitors (i.e. $Na_2SO_3/KNaC_4H_4O_6$, $Na_2SO_3/EDTA$ and their individual compounds) decreased when CO_2 concentration was increased. In this study, $Na_2SO_3/KNaC_4H_4O_6$ was found to be the most effective inhibitor to prevent amine degradation.

2.5 Amine Oxidative Degradation Mechanism

Figure 2.3 shows the MEA oxidative degradation mechanism and the formation of carboxylic acids from modification of Jefferson chemical's mechanism as reviewed by Supap et al (2011).
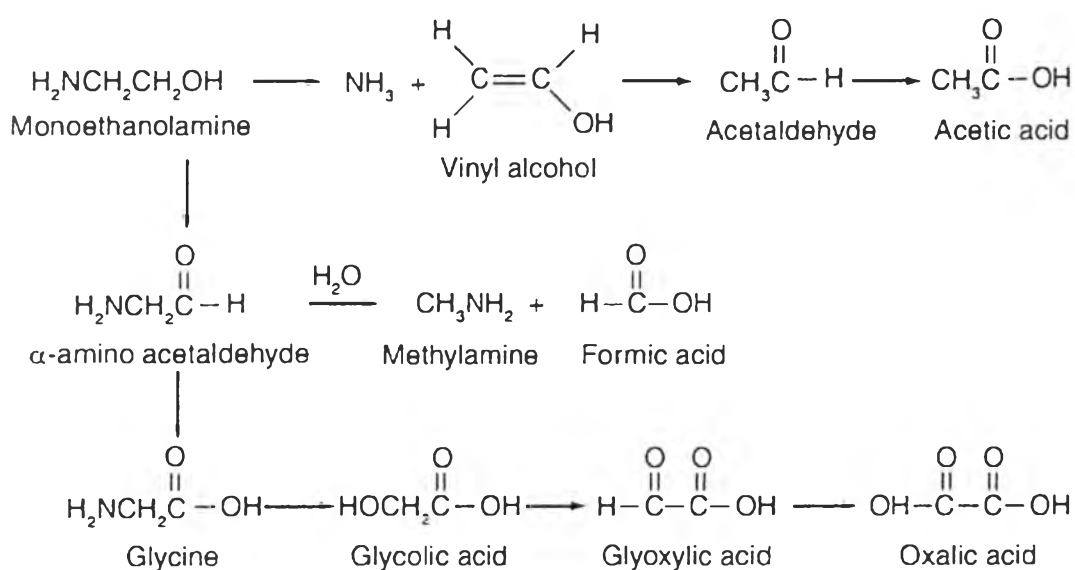
Figure 2.3 MEA oxidative degradation mechanisms (Rooney et al., 1998).

2.5.1 MEA-Formic Acid

According to study from Supap *et* al. (2011), further reaction of MEA with formic acid occurred instantly after the acid formation, which formed more degradation products, which existed in two forms in equilibrium (Figure 2.4). The first product was formate-HSS with MEA bonding by electrostatic force attraction; while N-(2-hydroxyethyl) formamide, the second compound occurred through covalent bonding between the amino group of MEA and the carboxyl group of formic acid.
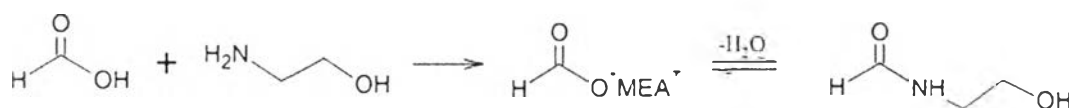
Figure 2.4 Role of formic acid in MEA oxidative degradation mechanism (Supap *et al.*, 2011).

2.5.2 MEA-Acetic Acid

In 2011, Supap *et* al. studied the reaction of MEA with acetic acid, which behaved similarly to formic acid as shown in Figure 2.5. Acetate-HSS of MEA and N-(2-hydroxyethyl) acetamide existed in the solution.
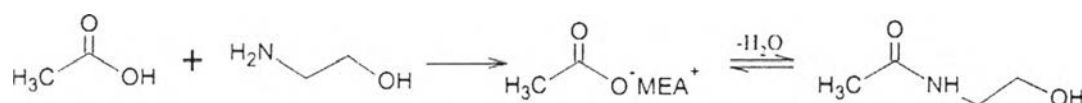
Figure 2.5 Role of acetic acid in MEA oxidative degradation mechanism (Supap *et al.*, 2011).

2.5.3 MEA-Glycolic Acid

Supap *et al.* (2011) studied the reaction of MEA with glycolic acid, which also produced an amide similar to those of formic and acetic acids. Figure 2.6 shows the mechanism that was believed to form an unstable N-(2-hydroxyethyl)

glycolamide, which readily decomposed to a more stable glycolate HSS. Moreover, glycolic acid could also decompose to formic acid through oxalic acid intermediate.
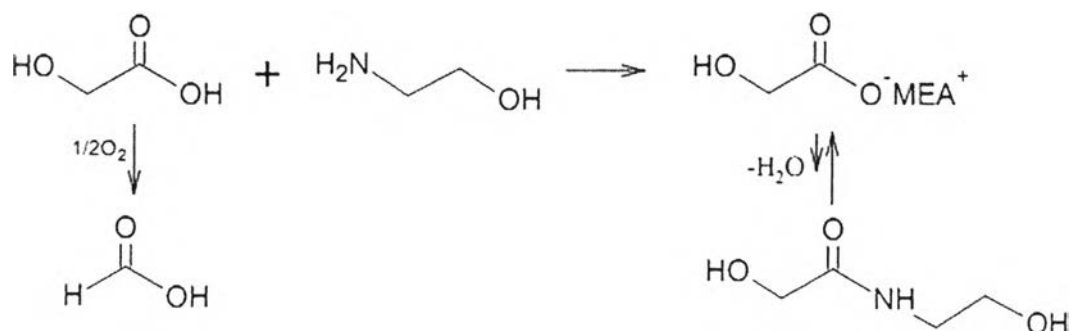

Figure 2.6 Role of glycolic acid in MEA oxidative degradation mechanism (Supap *et al.*, 2011).

2.5.4 MEA-Oxalic Acid

According to study from Supap *et* al. (2011), in Figure 2.7, oxalic acid once generated by in MEA degradation, it will instantly decomposed to formic acid which reacted further with MEA to give N-(2-hydroxyethyl) formamide. N, N'-Bis(2-hydroxyethyl) oxamide was also produced by oxalic acid with MEA reaction. However, the amide was unstable and readily decomposed to N'-Bis(2-hydroxyethyl) oxamide, which later also degrades to give oxalic acid and MEA. This indicated that oxalic acid was a highly reactive component, which could only be present as an intermediate in the oxidative degradation of MEA. Since oxalic acid quickly degraded to formic acid, N-(2-hydroxyethyl) formamide was always found instead of oxamide.
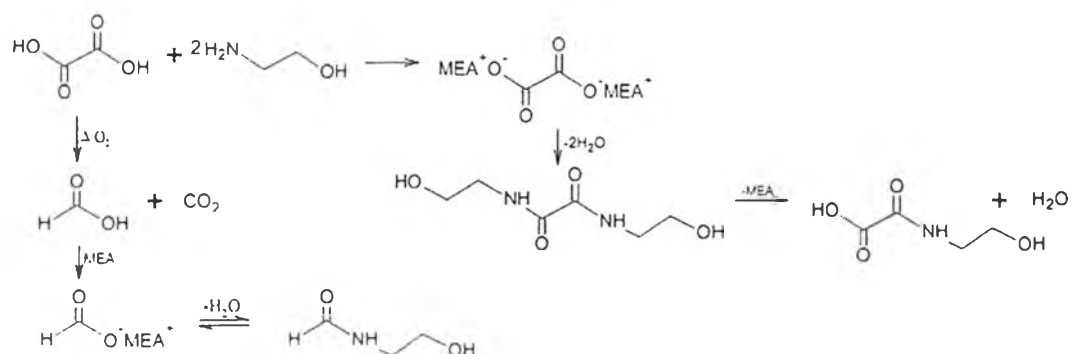
Figure 2.7 Role of oxalic acid in MEA oxidative degradation mechanism (Supap *et al.*, 2011).

2.5.5 MEA-Succinic Acid

Supap *et al.* (2011) studied the reaction between succinic acid with MEA, which was similar to all acids amine reaction described earlier. From the analysis, the detected product was N-(2-hydroxyethyl) succinimide, formed through N-(2-hydroxyethyl) succinamide intermediate. The reaction mechanism is shown in Figure 2.8.
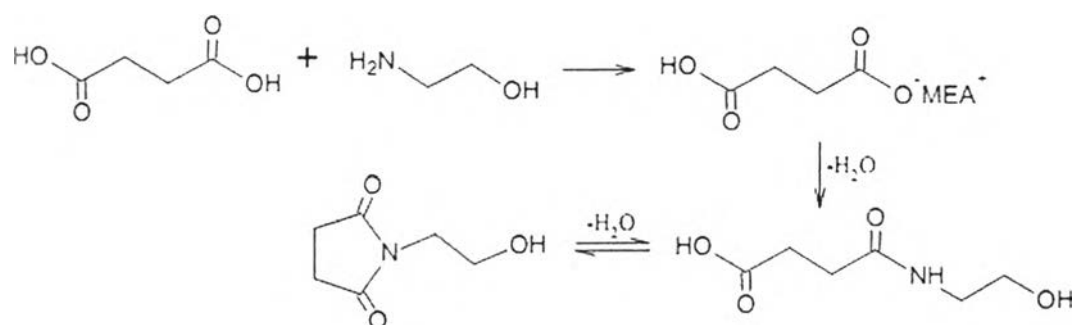

Figure 2.8 Role of succinic acid in MEA oxidative degradation mechanism (Supap *et al.*, 2011).

In 2011, Chanchey *et al.* studied an off-gas degradation products produced by reactions of MEA and O_2, CO_2, H_2SO_3 (representative of SO_2), and HNO_3 (representative of NO_2). NH_3 was found to be a major product in all conditions.

Possible pathways of a radical-induced oxidation were proposed as shown in Figure 2.9. First route occurred initially through a formation of α-hydroxyl acetamide, which quickly led (boxed mechanism) to a quick release of NH_3. The second route was less favorable where glycine was produced as an initial product. Further reaction of glycine and MEA gave the HSS equivalent compound, preventing NH_3 from being released

When H_2SO_3 (representative of SO_2), and HNO_3 (representative of NO_2) were present in the system; NH_3 still was the major VOC (Volatile Organic Compounds). Increases of either H_2SO_3 or HNO_3 concentration will decreased NH_3 concentration, but did not affect the other VOCs. The role of H_2SO_3 and HNO_3 were found to cut down the NH_3 route of formation but rather they induced the formation of formate and acetate HSS instead. The other significant information drawn from this study was the gaseous NH_3 from degradation, which was mostly trapped in liquid phase as NH_4^+ salt. Based on the analysis, concentration of NH_4^+ found in liquid phase was much higher than gaseous NH_3, which emitted to the gas phase of the system. The MEA degradation mechanism involving H_2SO_3 and HNO_3 is presented in Figure 2.10.
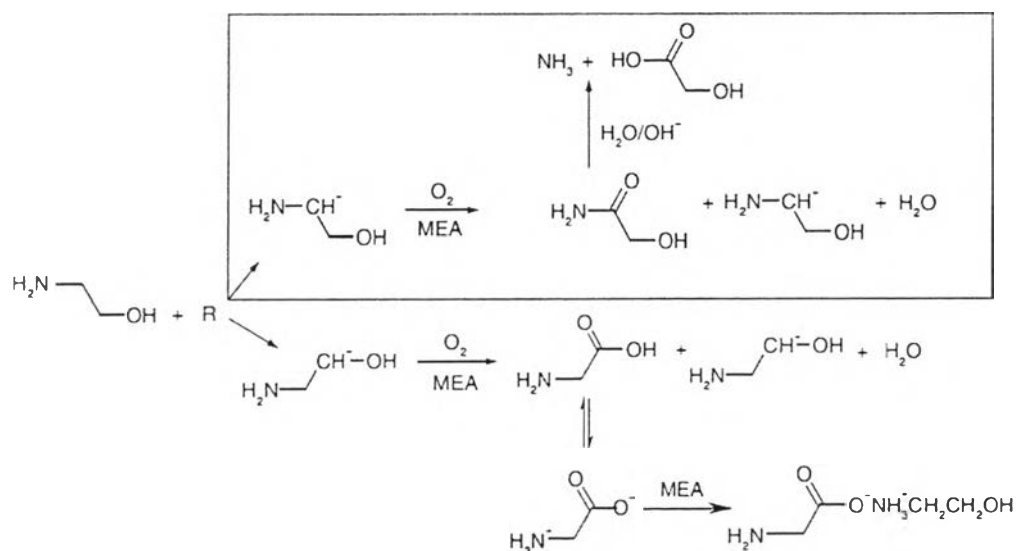

Figure 2.9 Two possible pathways of radical-induced oxidation of MEA responsible for NH_3 emission (Chanchey *et al.*, 2011).
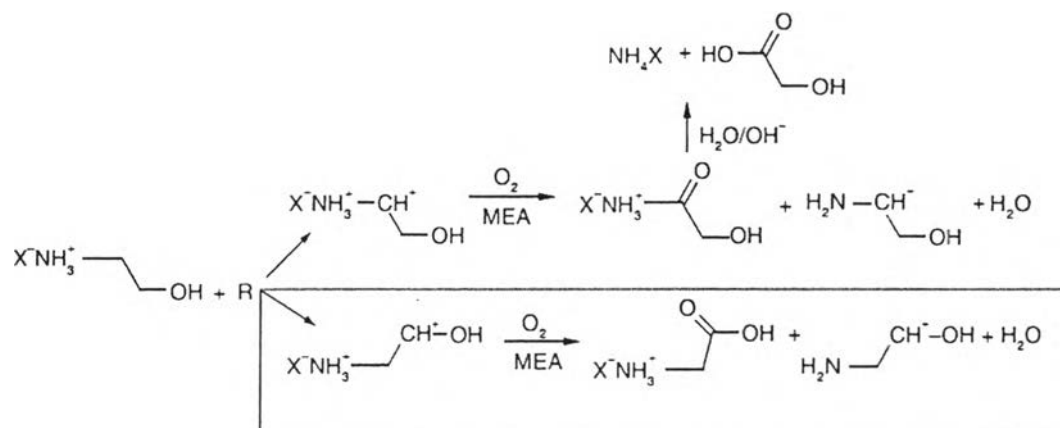
Figure 2.10   Two possible pathways of radical-induced oxidation of MEA responsible for H_2SO_3/HNO_3 (Supap *et al.*, 2011).

In 2011, Fostas *et al.* have studied an effect of NO_x present in the flue gas in MEA degradation. Based on their result, MEA was found to be degraded to secondary amine of DEA. DEA was nitrosated to a form of non volatile nitrosodiethanolamine (NDELA), which observed as only carcinogenic nitrosamine. Traces of the other volatile nitrosamine compounds detected were nitrosodimethylamine (NDMA) and nitrosomorpholine (NMOR). The volatile alkylamines, i.e. monomethylamine (MMA) and dimethylamine (DMA) also found in this study may come from nitrosamine and nitramines in the atmosphere at post emission.

2.6 Heat Stable Salts (HSS) Removal

Heat stable salts are anions of acids, such as carboxylic acids. These acids, which are stronger than the acid gases, can react with amines absorption solution, can be regenerated in the solvent regeneration condition, accumulate in the solvent, and thus present several problems. Operational problems triggered by a HSS formation in the amine solution can be categorized into four major issues which were amine foaming, leading to loss in solvent absorption efficiency; corrosion and erosion, increasing maintenance cost; amine loss; and off-specification of treated

gas. Industries normally manage the HSS problems by removal of them from the amine solution using methods, such as neutralization, solution purging, distillation, ion exchange, etc (Verma *et al.*, 2009).

2.6.1 Neutralization

Neutralization is a simple method, which involves in the addition of caustic soda into the amine solution to neutralize HSSs. This method is not effective because HSS still remains in solution but only in a different form.

During operation, a portion of amine solution is often bled out with its degradation products causing loss of active amine. As a result, the new amine has been fed to compensate from those lost in during the neutralization process. This method presents big disadvantages due to increases the cost of new amine and the disposal cost of old amine. In addition, HSS still contaminates the amine solution, thus this method is still not a good solution for the problems (Verma *et al.*, 2009).

2.6.2 Distillation

Distillation is a very energy demanding process when used to separate amine from its degradation products. In the amine solution, large volume of water and amine needs to be evaporated before HSS can be separated as the bottom residue in a reclaimer. Large energy input is needed to achieve this process (Verma *et al.*, 2009).

2.6.3 Ion-exchange

In this case, a cyclic process will selectively absorb the HSS anions from the amine solution with a suitable anion exchange resin bed. The used resin bed can be used again by regenerated with a caustic solution. However, the operational cost of this method is relatively high. Also, frequent regeneration of ion-exchange resin and disposal of waste containing acid and alkaline are needed, and become a major disadvantage of this technique (Verma *et al.*, 2009).

2.6.4 Electro Dialysis (ED)

Meng *et al.* (2008) have proposed method to remove HSS in MDEA solution using a specially designed three-compartment configuration of electrodialyzer. Electrodialysis (ED) is an electrochemical separation process, which uses an ion-exchange membrane with a difference in electrical potential. When applying the electrical potential, ionic components in the aqueous solution will move toward the electrode that has opposite charge [e.g. cation moves to cathode (negative charge) and anion moves to anode (positive charge)], thus they can be separated from the other uncharged components. Normally, the ED process consists of a selective membrane, which allows cation or anion to pass through between cathode and anode. Figure 2.11 shows three-compartment ED which sodium hydroxide (NaOH) is fed in section I and hydroxide anion (OH⁻) selectively passes through an anion-exchange membrane (AEM), on the right hand HSS in degraded MDEA, is fed in section II and HSS anions are allowed to move through AEM on the right, where they are compensated by OH⁻ from section I, due to a difference in anion concentration. The HSS anions selectively pass through section III which contain water, so HSSs can be removed from MDEA.
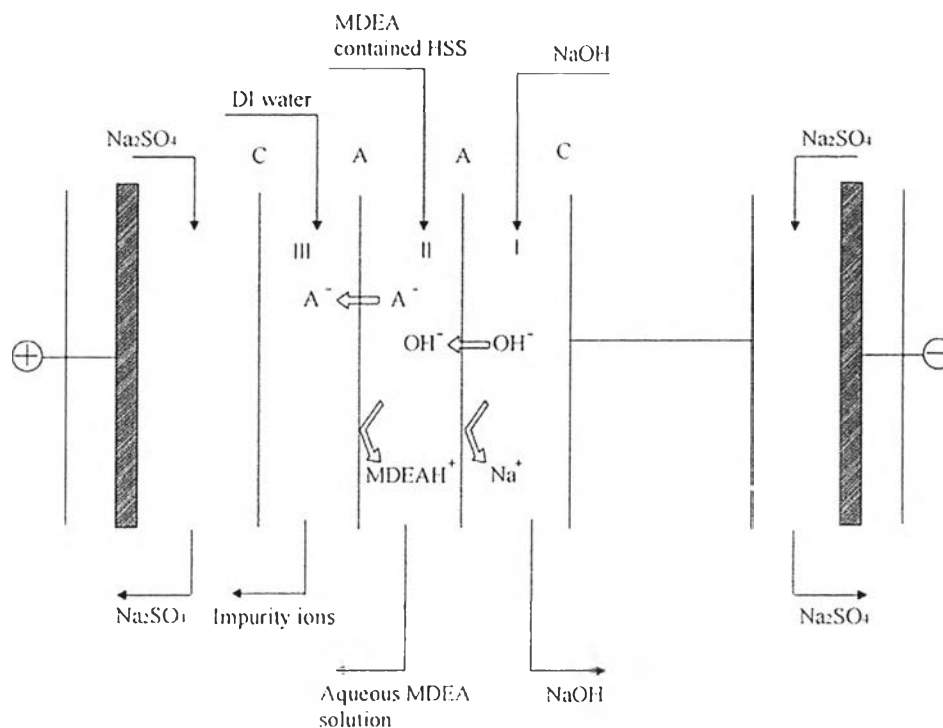
Figure 2.11 HSS removal from MDEA solution by three compartments electrodyalysis (Meng *et al.*, 2008).

The reaction in the section II, which OH⁻ reacted with H^+ from HSS and A⁻, represented as regenerated MDEA is shown in equation 2.5.

$$OH^- + MDEAH^+A^- \rightarrow A^- + MDEA + H_2O \qquad (2.5)$$

To summarize, the amine degradation can be classified in to two major pathways, which are the amine degradation from CO_2, H_2S, and in the presence of sulfur compound; and amine degradation from oxidative reaction. In the general point of view, industries do not concern the thermal degradation, because the operating condition in the absorption process does not exceed the degradation temperature (not higher than $150\,^{\circ}C$). In the presence of H_2S and sulfur compound, i.e. CS_2 and COS with O_2, it can generate inorganic salts such as SO_3^{2-}, $S_2O_3^{2-}$ and SO_4^{2-}, which can be reacted with amine to form the HSS products. When CO_2 and O_2 are present in the system, they can producing the degradation products, including 1-(2-hydroxyehtyl) imidazolidone-2, N-(2-hydroxyehtyl) ethylenediamine (HEED), N,N'-bis(2-hydroxyethyl) piperazine (BHEP) and N,N,N'-tris(2-hydroxyethyl)

ethylenediamine (THEED). Oxidation induced amine degradation comes from amine, which degraded by O_2 and transformed into carboxylic acids, which take an oxidation reaction with amine to form the carboxylate-HSS, i.e. acetate, formate, oxalate and glycolate. These carboxylate-HSS are mainly found and have a high concentration than inorganic anions as shown in a Table 2.3.

Table 2.3 Heat-Stable Salts concentration from common case found in Amine Gas Treating unit (Craig et al., 1996; Fan et al., 2000; Litchewski, 1996; Liu et al., 1995; Verma, 2009)

HSS	Source	Concentration (ppm)	Reference
Formate	DEA solution in refinery (vendor data)	0-35000	Fan et al.
	DEA solution in refinery (plant sample)	150000-170000	Fan et al.
	DEA solution in refinery (plant sample)	5000-7000	Fan et al.
	DEA solution in refinery (plant sample)	25000-30000	Fan et al.
	DEA solution in refinery (plant sample)	5000-15000	Fan et al.
	MDEA solution in refinery (plant sample)	500-11900	Litchewski
	MDEA solution in refinery (plant sample)	45000	Liu et al.
	MDEA solution in refinery (plant sample)	10474-57747	Liu et al.
	DEA solution in refinery (plant sample)	6000-21000	Craig et al.
	MDEA solution in refinery (vendor data)	500	Verma et al.
	MDEA solution in refinery (plant sample)	18814	Verma et al.
	MDEA solution in refinery (plant sample)	5620	Verma et al.
	MDEA solution in refinery (plant sample)	1900	Verma et al.
Acetate	DEA solution in refinery (vendor data)	0-1500	Fan et al.
	MDEA solution in refinery (plant sample)	5000	Liu et al.
	MDEA solution in refinery (plant sample)	2406-3789	Liu et al.
	DEA solution in refinery (plant sample)	750-1250	Craig et al.
	MDEA solution in refinery (vendor data)	1000	Verma et al.
	MDEA solution in refinery (plant sample)	2366	Verma et al.
	MDEA solution in refinery (plant sample)	1320	Verma et al.
	MDEA solution in refinery (plant sample)	60	Verma et al.
Glycolate	DEA solution in refinery (vendor data)	0-150	Fan et al.
Oxalate	MDEA solution in refinery (plant sample)	100	Liu et al.
	DEA solution in refinery (vendor data)	0-350	Fan et al.
	MDEA solution in refinery (vendor data)	250	Verma et al.
	MDEA solution in refinery (plant sample)	76	Verma et al.
	MDEA solution in refinery (plant sample)	5	Verma et al.
	MDEA solution in refinery (plant sample)	10	Verma et al.

2.7 Literature Review

Tamada *et al.* (1990a) researched on an extraction of carboxylic acids with an amine extractant. First part of their studies was focused on equilibriums, law of mass action, and extraction modeling. The extraction of acetic, lactic, succinic, malonic, fumaric, and maleic acids with Alamine 336, an aliphatic, tertiary amine exractants in various diluents (halogenated hydrocarbon, alcohol, ketone, aliphatic, and aromatic diluents) were carried out. The results have been interpreted using a chemical modeling approach to find exact stoichiometries of acid amine complexes and their corresponding equilibrium constants. The complex formation consisted of more than one acid per amine, which was a common behavior for monocarboxylic acids. The ratio of (1,1) to (2,1) (molecule of acid, molecule of amine) complex formation was depended on the diluents. Halogenated hydrocarbon and alcohol diluents will inhibit an overloading (more than one molecule of acid per one molecule of amine in the complex). In the contrary, ketone enhanced the overloading. Active diluents such as 1-octanol rarely showed the formation of (1,2) complex, which could be expected from dicarboxylic acids. The succinic acid did not show the (1,2) complex formation with Alamine 336 in chloroform, nitrobenzene, methyl isobutyl ketone (MIBK), but 1-octanol. While the fumaric acid in chloroform and MIBK were also formed the formation of (1,2) complex. In a nonideal behavior, active diluents are employed, which a loading of acid decreases with an increasing of amine concentration especially at high concentration. For a nonaggregate system in inert diluents including monocarboxylic acids in aliphatic or aromatic diluents, there is no effect of the amine concentration on the acid loading. For an aggregate system (acid-amine complexes are separated in third phase), for example, in dicarboxylic acids in the inert diluents, the loading increases with increasing the amine concentration. The acid-amine complexes from di- and tricarboxylic acids have a tendency to form the aggregate than monocarboxylic acid. A degree of extraction is generally the greater the ionizing acidity of the acid (pK_a value), the more it is extracted. For all of the acids, the strength of solvation of complex decreases in the order of alcohol $\geq$ nitrobenzene $\geq$ halogenated hydrocarbon > ketone > halogenated aromatic > benzene > alkyl aromatic > aliphatic hydrocarbon.

Tamada *et al.* (1990b) also reported chemical interactions involved in the complexation of carboxylic acid with Alamine 336 in various diluents. The (2,1) and (1,1) complex structures were proposed that the first acid interacted directly with the amine to form an ion pair of (1,1) structure, while the OH of a carboxyl group of the second acid molecule formed a hydrogen bond with conjugated CO of the carboxylate of the first formed acid, and finally became the (2,1) structure as shown in figure 2.12.
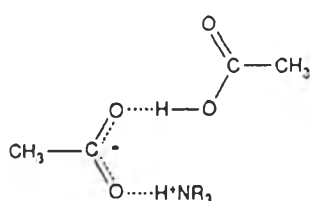
Figure 2.12 A structure of the (2,1) acid-amine complex (Tamada *et al.*, 1990b).

The authors also proposed an additional (3,1) complex. The addition of the third acid molecule by forming a hydrogen bonding with (2,1) complex to form a cyclic arrangement of the (3,1) structure around amine can also occur as shown Figure 2.13.
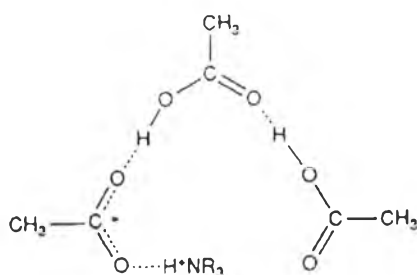

Figure 2.13 A structure of the (3,1) acid-amine complex (Tamada *et al.*, 1990b).

A ratio of interaction of first acid with amine equilibrium and that of the second acid with the complex equilibrium can be arranged in the order of acetic > succinic > lactic > malonic > maleic. The order was similar as their pK_a values. The (2,1) complex occurs by the hydrogen bond, which should be independent of the

ionizing acid strength as shown by the pK_a. On the other hands the (1,1) complex is controlled by an acid-base ion pairing reaction and depended greatly on the pK_a.

The diluents also affect a formation of the complex, which directly affects the stability of the (2,1) complex. Diluents capable of donating proton such as chloroform and 2-ethyl-hexanol can stabilize the (1,1) complex. Protonated diluents show a great tendency to decrease a formation of the (2,1) complex. An explanation of this phenomenon is due to a competition between the diluent and a carboxyl proton from the second acid molecule for a carboxylate binding site on the first acid molecule. This competition helps stabilize the (1,1) complex as shown in Figure 2.14.
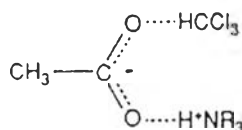

Figure 2.14 The competition of diluent, stabilized (1,1) complex (Tamada *et al.*, 1990b).

For the dicarboxylic acids, i.e. fumaric (*trans*-butenedioic), maleic (*cis*-butenedioic), and succinic (butanedioic) acids show opposite result from the previous monocarboxylic acid. For fumaric acid, the (1,2) formation complex shown in Figure 2.15 is favorable when the amine concentration is increased. Figure 2.16 shows the (1,1) complex of furmaic acid with amine.
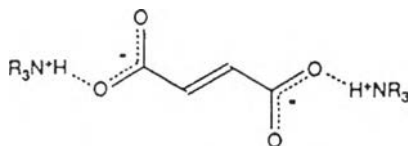

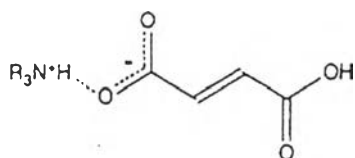**Figure 2.15** The formation of the (1,2) complex in fumaric acid (Tamada *et al.*, 1990b).

Figure 2.16 The ormation of the (1,1) complex with amine and dicarboxylic acid (Tamada *et al.*, 1990b).
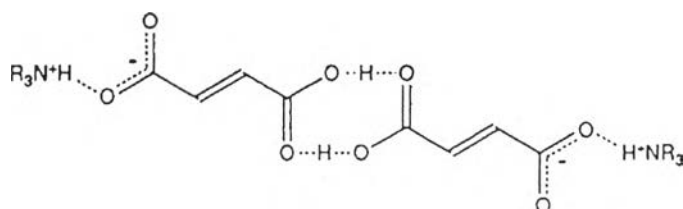

Figure 2.17 The formation of the (2,2) complex in fumaric acids (Tamada *et al.*, 1990).

The fumaric acid form the (2,2) complex (Figure 2.17) is more preferable than the (1,1) complex (Figure 2.16) because the two carboxyl groups not bonded to the amine formed inter-molecular hydrogen bond with another molecule.

For maleic and succinic acids, increase of amine to acid ratio does not increase carboxylate group but decrease carboxyl group, being predicted to be a formation of the (1,2) complexes. Two possible structures are suggested in Figure 2.18 and 2.19.
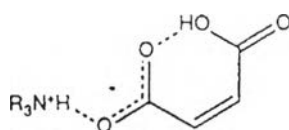

Figure 2.18 The formation of the (1,2) complex in maleic and succinic acid (Tamada *et al.*, 1990b).
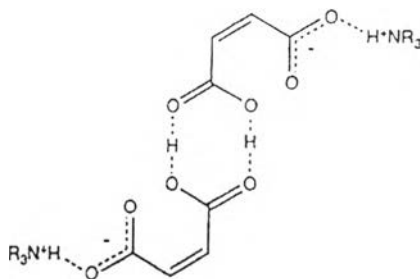
Figure 2.19 The formation of the (2,2) complex in maleic and succinic acids (Tamada *et al.*, 1990).

The structure in Figure 2.18 undergoes an intramolecular hydrogen bonding. In the other organic diluents, dicarboxylic acids undergo the internal hydrogen bonding between the carboxyl and carboxylate group. The (1,2) complex in Figure 2.18 is favorable for maleic and succinic acids. As opposed to the (1,1) complex in Figure 2.16 for fumaric acid. This is due to the intramolecular interaction, which can satisfy the carboxyl group not bonded to amine. For maleic or succinic acid, for the (2,2) complex formation is not favorable.

Di- and tricarboxylic acids show more tendencies to occur an aggregation and also form a third phase than the monocarboxylic acids because dicarboxylic acids containing two binding sites, which act as a linkage between the amines and the acid molecules to form a large aggregate. Monocarboxylic acids, having only one site cannot link the two amines together. The more inert the diluents, the more favorable for the polar complexes form the aggregate, shielding them from the nonpolar environment.

The effect of temperature, water coextraction and process considerations were also reported (Tamada *et al.*, 1990c). The coextraction of water during extraction of succinic acid by Almine 336 in the different diluents was measured. The coextraced water extent of acids had a similar trend to an acid solubility in water in the diluents without presence of amine. The coextracted water decreases in the order of fumaric > maloic > maleic = succinic > lactic > acetic acid. Water coextraction in the different diluents decreases in the order of 1-octanol > MIBK > nitrobenzene > methylenechloride > chloroform > heptanes, which had the same

order as for the solubility of the diluents in water. Study of the effect of temperature on extraction has showed that a distribution of acid into the diluent phase decreases sharply when increasing temperature.

Yang *et al.* (1991) studied the extraction of carboxylic acid with tertiary and quaternary amines. Amine extractants used in this research were Alamine 336, the aliphatic tertiary amine and Aliquat 336, the quaternary ammonium chloride. Aliquat 336 extracts both dissociated and undissociated acids and can be used under both acidic and basic conditions. However, the extractant regeneration by stripping HSS out may be difficult for Aliquat 336. When a concentration of Aliquat 336 in the diluents was greater than 25 % and pH of extracted liquid lower than 3, the third phase also known as an emulsion phase was observed. Although the third phase does not affect the equilibrium, it is hard to separate from the other two layers. 1-octanol was also found to have no effect on the extract efficiency of Aliquat 336. Alamine 336 extracted only the undissociated acid and must be used under an acidic condition only. However, Alamine 336 is more easier to regenerated, which can be separated by back-extraction with an alkaline solution than Aliquat 336. Alamine 336 could effectively extract propionic, lactic and butyric acids in a mixture, which cannot tolerate a pH value as low as 4.0.

Wisniewski *et al.* (2005) studied the carboxylic acid extraction with organophosphine oxide solvating extractants. The organophosphine oxides, such as Cyanex 921 and Cyanex 923 were used for an extraction of formic, acetic and propanoic acids from the aqueous solution. The stripping of monocarboxylic acid from the loaded extractant was also performed. Cyanex 921 had a slightly better extraction performance than Cyanex 923, although the (1,1) complexes were formed from both extractants. The extraction efficiency was dependent on temperature, acid concentration, where toluene found better than octane or Exxsol D 220/230. The extraction efficiency increases as acid concentration decreases, butthe efficiency decreases when temperature increases. A Salting-out effect from addition of NaCl increases the efficiency of the extraction, as well as the distribution ratio of acid loading. All loaded extractants were suggested to use acetic acid as a stripping agent.

Maurer (2005) made a modeling of liquid-liquid equilibrium for a carboxylic acid recovery from the aqueous solution. In this research, an extractant

was a tertiary amine of tri-n-octylamine (TOA). Carboxylic acids extracted with TOA form complexes that do not dissolve in water but in the organic phase. The organic diluent is essential for extraction because it prevents a precipitation of the complexes. Three diluents were used comprising of non-polar toluene, hydrogen accepting MIBK, and chloroform which were representing of hydrogen accepting and donating. The study found that the diluents might also form complexes with water, causing the precipitation from the aqueous solution. Typically, there were more complexes formed than just a single complex, which a complex stoichiometry depended on type of the organic diluent.

Rasrendra et al. (2011) recovered organic acids from an aqueous pyrolysis oil phase by a reactive extraction using tri-n-octylamine (TOA). The best results were obtained using 40wt% TOA in 2-ethyl-hexanol which 84% of acetic acid was recovered at equilibrium. Better results were obtained with polar diluents, such as 2-ethyl-hexanol. This was likely due to the diluent's higher solvating power, high boiling point, and low affinity for water. MIBK and ethyl acetate also gave a high efficiency, but they had a high affinity to water (i.e. more soluble in water). Other organic acids such as formic acid and glycolic acid were also co-extracted with 92% and 69% coextraction efficiency, respectively.

Vitasari et al. (2012) studied a reactive extraction of acetic acid with the tri-n-octylamine (TOA) in 2-ethyl-1-hexanol diluent from a wood-based pyrolysis oil-derived aqueous phase. The pure 2-ethyl-1-hexanol diluent provided the highest extraction yields. One step extraction used only for the 2-ethyl-1-hexanol system provided the best acetic acid extraction. In one step extraction, 40 wt% TOA provides the best acetic acid extraction performance. The extractant containing more than 50 wt% TOA in 2-ethyl-1-hexanol was preferred for a two-step extraction (acetic acid separation followed by glycolaldehyde co-extraction). When 2-ethyl-1-hexanol was only used without the amine extractant, a physical extraction only occurred, producing a very low distribution coefficient. The extraction process was also a temperature independent. Furthermore, water co-extraction also occurred. 2-Ethyl-1-hexanol is preferable to be used as diluents considering its low tendency to form esters, high boiling point and low water affinity. Acetic acid is regenerated from TOA-acid complex by distillation.

From the literature review, HSS accumulation in the amine solution presents many problems that needed to be taken care of. These problems are of a great concern as they often increase the operating cost of the CO_2 capture process. Although, distillation can be used to separate HSSs, the process requires a large energy input. Liquid-liquid extraction is becoming an interesting method, as low energy input. Also, the technique can be possibly applied to separate carboxylic acids in amines used for CO_2 capture due to its successful use in other applications shown in Table 2.4.

The selection of alcohol diluents such as 1-octanol, 2-ethyl-1-hexanol, 1-heptanol, 1-hexanol, and 1-pentanol in this research was based on the studies from Tamada et al. (1998) and Grzenia et al. (2008). The alcohols are immiscible with aqueous solution and have the polarity which increases extracting power of less-polar amine by providing additional solvating power that allows polar acid-amine complexes to stay in the organic phase. The alcohol diluents have the ability to donate proton to the carboxylic acid – amine complexes. The competition between alcohols, the proton donor, and the other molecules of carboxylic acid to form a hydrogen bond with oxygen atom in carboxyl group of the first carboxylic acid molecule in the complex results in alcohols to prevent the other carboxylic acids to form overloading complex formation (more than 1 acid molecule per 1 amine molecule). The alcohol diluents prevent the complex formations from overloading, which make the complexes more stabilized, easily to separate organic phase from aqueous solution, and increase extraction efficiency. Moreover, alcohol diluents help in increasing the physical properties of extractant, such as reduce viscosity which leads to higher mass transfer, reduce density which helps easier separation of organic and aqueous phase, and control pH of organic phase while extracting the carboxylic acid.

Yang et al. (1991) have conclusion of carboxylic acid extraction by aliphatic amine that extractant A in a chloride form can extract both forms of carboxylic acid. The pH below pK_a of the carboxylic acids indicates an undissociated form, which is extracted by protonated extraction by extractant. In the contrary, when the pH of solution above pK_a, the carboxylic acids are in dissociated forms, and the extraction is controlled by ion exchange with the extractant. Grzenia et al.

(2008) reviewed that there was no pH of solution change during extraction of extractant A (quaternary amine), which leads to high extraction capacity.

Table 2.4 Various extraction systems for carboxylic acid separation

Reference	Extractant	Diluents	Detected Component
Tamada *et al.* (1990)	Alamine 336	• MIBK • n-heptane • Methylene chloride • Nitrobenzene • Chloroform • 1-octanol • 2-ethyl-hexanol	Carboxylic acid
Yang *et al.* (1991)	• Alamine 336 • Aliquat 336	• Kerosene • 2-octanol	Carboxylic acid
Wisniewski *et al.* (2005)	• Cyanex 921 • Cyanex 923	• Toluene • Octane • Exxsol D 220/230	C1-C3 Carboxylic acid
Maurer (2005)	Tri-n-octylamine	• Toluene • MIBK • Chloroform	Carboxylic acid
Rasreda *et al.* (2011)	Tri-n-octylamine	• 2-ethyl-hexanol • 1-octanol • 1-decanol • MIBK • n-decane • n-octane	Acetic acid
Vitasari *et al.* (2012)	Tri-n-octylamine	• 2-ethyl-hexanol	Acetic acid