CHAPTER II

# THE ORETICAL BACKGROUND AND LITERATURE REVIEW

The energy information administration estimates that the primary source of energy consists of petroleum 36.0 %, coal 27.4 %, and natural gas 23.0 %, accounting for 86.4 %of primary energy consumption in the world (Prasad and Dhanya, 2011). Use of coal as a huge source of energy has become important because of its availability and low cost. According to intergovernmental panel on climate change (IPCC) report, a great number of coal-fired power plants operated in Canada and elsewhere in the world is coal-fired. The combustion of coal has been considered as a large production source of CO_2.

In the world, 30–40 % of total CO_2 emissions come from coal-fired power plants (Huang et al., 2010). A composition of flue gases in existing coal-fired power plants generally consists of considerable amount of N_2, 7-15 % CO_2, 2-12 % O_2 and small amount of NO_x, SO_2 and SO_3. As shown in Table 2.1, it is a typical flue gas composition after SO_2 scrubbing for coal-fired power plants (Chakma et al., 1995).

Table 2.1 Typical composition of flue gases after SO_2scrubbing (Chakma et al., 1995)

Composition in Coal-Fired	Mole %
CO_2	7-15
O_2	2-12
N_2	65-75
H_2O	5-15
SO_2	2-400 ppm
SO_3	1-10 ppm
NO_x	1-400 ppm
Particulates	0.1 - 0.5 ~rains/SCF

To reduce CO_2 emission in the flue gas of the coal fired power plant going into the atmosphere, one can integrate technology CO_2 capture to the coal-fired power plants as a schematic shown in Figure 2.1.
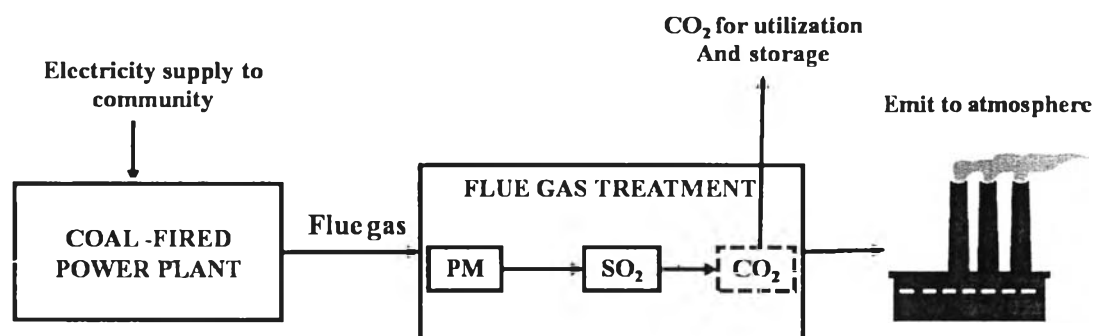
Figure 2.1 Schematic diagram of the integration of a CO_2 capture unit to a coal-fired power plant (Thitakamol *et al.*, 2007).

2.1 CO_2 Capture

A novel technology that could eliminate all CO_2 emissions is CO_2 capture and storage process (CCS). Lackner *et al.* (2010) summarized a basic of CCS consisting of three stages a) CO_2 separation (from combustion exhaust), b) CO_2 transportation (usually via pipeline), and c) CO_2 storage (such as urea production, underground storage, food and beverage industry, enhanced oil recovery, dry ice production, etc.). Spigarelli and Kawatra (2013) estimated the CO_2 capture cost of 70–90 % of the total operating costs of a CCS system. CO_2 capture technologies can be classified into pre-combustion, post-combustion and oxy-fuel combustion (Wang *et al.*, 2011). Each technology has its own advantages and disadvantages and is at different stages of development.

Pre-combustion capture is CO_2 capture process before fossil fuel combustion which it is integrated to gasification combined cycle (IGCC) power plants. In the first step of gasification, it produces "synthesis gases" and creates a high pressure converting to CO_2/H_2 gas stream which CO_2 is separated out and H_2 can be used for source energy (Thambimuthu *et al.*, 2010). The advantage of IGCC

power plant is the highest energy efficiency, and the penalties introduced by CO_2 capture are the lowest as well. However, it is very difficult to retrofit IGCC technology to existing facilities and it is costly (Strube and Manfrida, 2011). At the current state of development, pre-combustion technology should only be applied if a new IGCC facility is being constructed (Spigarelli and Kawatra, 2013).

Oxy-combustion capture is CO_2 captured after fossil fuel combustion in an O_2 rich atmosphere, which suppressed the formation of NO_x after fossil fuel combusted and create CO_2/H_2O gas stream. CO_2 can easily be separated by cooling the flue gas stream to condense out the H_2O (Spigarelli and Kawatra, 2013). The main advantage of oxy-combustion is high purities of the CO_2 stream which can be reached, so that it is suitable for EOR (Coninck *et al.*, 2009). However, equipment needed to obtain the large volume of O_2 is costly to operate and retrofitting to existing facilities is difficult (Strube and Manfrida, 2011).

Post-combustion capture is CO_2 captured after fossil fuel combustion. Spigarelli and Kawatra (2013) found that this technology possess the greatest potential for near term implementation at fossil fuel power plants because they can be retrofitted to existing facilities with the least difficulty. In current chemical absorption with amines, it is the most mature technology for post-combustion.
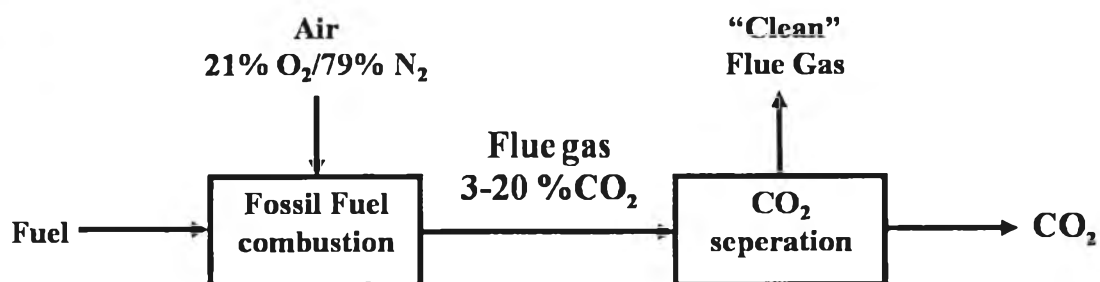

Figure 2.2 Simplified post-combustion capture block diagram (Spigarelli and Kawatra, 2013).

CO$_2$ instead of being discharged directly to the atmosphere, flue gases stream is passed through equipment which removes most of the CO$_2$ and the remaining flue gases are discharged to the atmosphere shown in Figure 2.2 (Spigarelli and Kawatra, 2013).

Technologies of CO$_2$ capture for post-combustion are current employed technologies including physical and chemical solvents, particularly monoethanolamine (MEA), adsorption onto solids, various types of membranes, and cryogenic separation.

The choice of suitable technology depends on the characteristics of the flue gases, which depend mainly on the power plant technology. The most commonly used post-combustion CO$_2$ capture is chemical absorption using alkanolamines solution techniques for low-pressure flue gas streams from coal-fired plant as substantiated by Bhown and Freeman (2011). Figure 2.3 shows distribution type of technology post-combustion CO$_2$ capture.
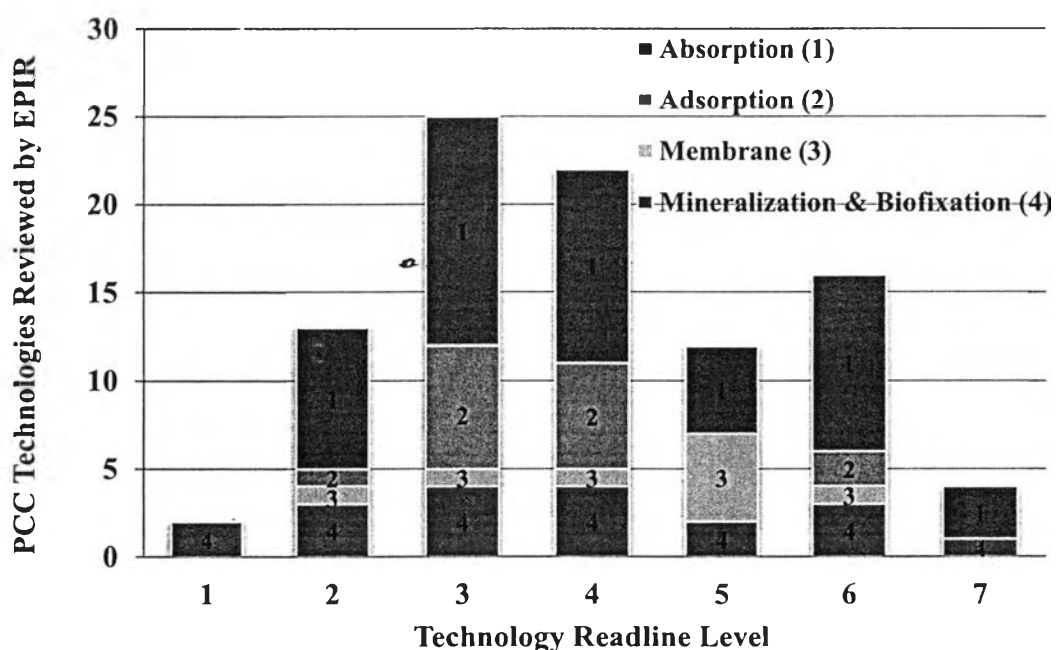
Figure 2.3 Distribution of post-combustion CO$_2$ capture technology types by TRL ranking (Bhown and Freeman, 2011).

2.1.1 Absorption

Absorption technologies are the most common CO_2 capture process currently used with post-combustion flue gases. It can be chemical and physical absorption.
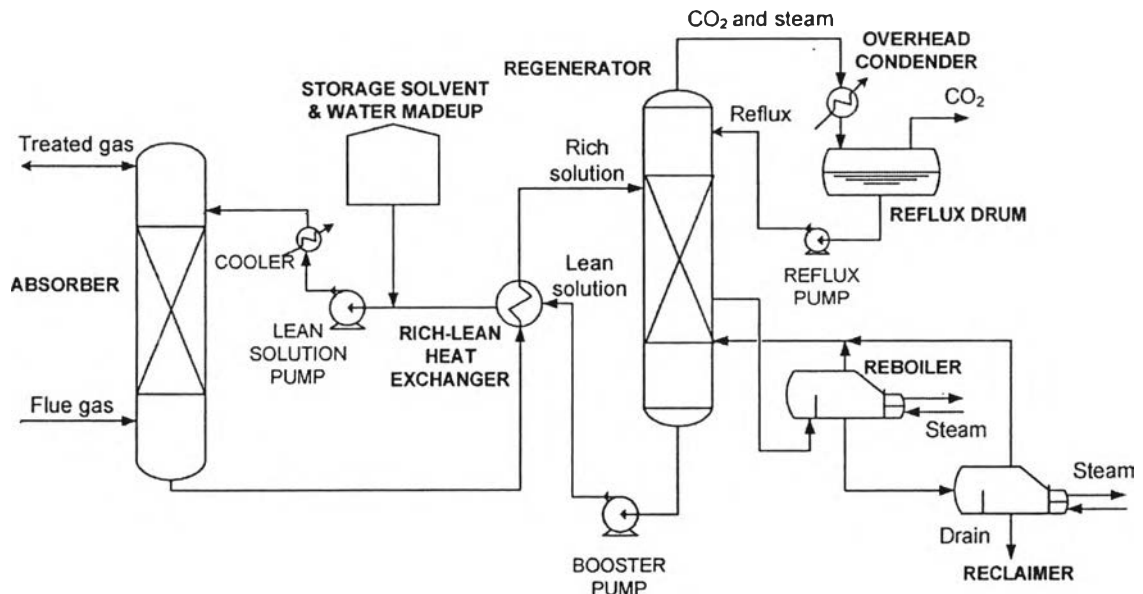
Figure 2.4 Schematic diagram of the typical absorption-based CO_2 capture unit (Thitakamol *et al.,* 2007).

Absorption is technology for capturing CO_2 from post-combustion flue gases of containing low partial pressures of CO_2 (3–20 %). In Figure 2.4 flue gas component comes into contact with the chemical solvent and CO_2 is absorbed from the gas phase into the liquid phase by chemical or physical absorption reaction to form a weakly bonded intermediate compound at condition low temperature and high pressure in an absorber. Then sweet gas or lean CO_2 in flue gas exits at the top of the absorber. In part of absorbent when absorbed CO_2 from flue gas, it changed from lean solution to rich solution or high concentration of CO_2. The rich solution was sent to the regenerator for recovering the lean solution by adding an application of heat production and hot stream from the reboiler. In the regeneration step, the rich solution is being heated, the pressure is decreased, and CO_2 is released at top of

stripper. The lean solution or low concentration of CO_2 as refer to the "rich solvent" was sent to bottom of regenerator and pass through heat exchanger for cooling before being sent back to the absorber to complete CO_2 capture cycle. The rich solution is repeatedly cycled and exposed to heat at the reclaimer, so it can be degraded.

Physical absorption differs from chemical absorption which the physical absorption requires high partial pressure of CO_2, so the physical absorption is a function of the solubility of CO_2 in the solvent without reacting between CO_2 and physical solvent. Factors which need to be considered when choosing a solvent are the solubility and reactive properties of the flue gases component in the solvent (Wang et al., 2011).

Currently commercial available technologies are chemical absorption. Several chemical absorption processes are different in the solvent used to capture CO_2. The four major processes are 1) amine absorption, 2) aqua ammonia absorption, 3) dual-alkali absorption, and 4) sodium carbonate (Na_2CO_3) slurry absorption. Amine absorption is commonly used to capture CO_2 in coal-fired power plant (Spigarelli and Kawatra, 2013).

2.2 Amine Absorbent

Conventional alkanolamines are classified as primary, secondary and tertiary alkanolamines depending on the number of substituting groups replacing hydrogen atoms of ammonia (NH_3). Some of the alkanolamines most commonly used in CO_2 capture are monoethanolamine (MEA), methyldiethanolamine (MDEA), 2-amino-2-methylpropanol (AMP), diglycolamine (DGA), diethanolamine (DEA) and di-isopropanolamine (DIPA) (Rochelle, 2009). Table 2.2 shows the examples of commonly commercial alkanolamines.

Table 2.2 Comparison the CO_2 absorption, vapor pressure, overall cost and corrosivity of MEA with commercial available amines (DEA, MDEA) (Rao and Rubin, 2002)

Amines	MEA (Primary Amine) $HOCH_2CH_2NH_2$	DEA (Secondary Amine) $HN(CH_2CH_2OH)_2$	MDEA (Tertiary Amine) $CH_3N(CH_2CH_2OH)_2$
CO_2 Absorption	High	Moderate	High
Vapor Pressure	High	Low	Low
Corrosivity	High	High	Low
Cost	Low	Low	High

In Table 2.2, there are several advantages of MEA, such as high CO_2 absorption and high vapor pressure (Rao and Rubin, 2002). Moreover it has high solubility in water, low viscosity, high kinetics at low CO_2 partial pressure and it is cheap. Although the MEA is commercially used in natural gas treatment, MEA requires a large amount of high energy for regeneration, high corrosivity and is degraded in the presence of O_2. These problems have been addressed through the use of alkanolamine which chemically react with the CO_2 during capture.

2.2.1 Monoethanolamine (MEA)

An aqueous MEA solution, important absorbent in the CO_2 removal process, has many advantages, such as high reactivity, low solvent cost, and high absorption capacity on a mass basis, reasonable thermal stability and relatively high biodegrade ability. Sometimes it can be improved by using an activator and mixing with other amines. MEA is a primary amine, the lightest molecule compared to the other amines, and high pH, which makes MEA high efficient to capture an acid gas. MEA chemically absorbs CO_2 with exothermic reaction. However, MEA degradation leads to irreversible side reactions mainly with CO_2 and O_2, and also with NO_x and SO_x which creates different problems in the process, such as solvent loss, formation of volatile compounds potentially dangerous for environment, foaming, fouling and especially corrosion (Islam *et al.*, 2010).

2.3 Amine Degradation

Compositions of flue gases from coal-fired power plant consist of CO_2, NO_x, O_2, SO_2 and SO_3. These impurities are removed by aqueous solutions of alkanolamines but plant and laboratory reports indicate that for a long period use, alkanolamines may be transformed into unwanted products which are not easily recovered. This phenomenon commonly referred to as "amine degradation" (Islam *et al.*, 2010).

It is important to understand degradation conditions that are varied within the gas treating plant. Bedell (2009) substantiated that different mechanisms may be involved in different parts of the plant, such as the highest O_2 concentration and the lowest temperature will occur in the absorber while the lowest O_2 concentration and highest temperature will occur in the reclaimer. The amine degradation can produce several negative effects on the operation of a CO_2 capture process as follows:

- Operating cost
  - The replacement cost of MEA system to be about 4 % of the total cost of CO_2 capture.
  - Viscosity increases with increase of MEA degradation and induces the costs associated with solvent pumping to increase.
- Performance
  - Increase of viscosity increases mass transfer limitations.
  - Formation of acidic degradation products will form heat stable salts which will reduce the solution's capacity for CO_2; thus, requires technologies to regenerate heat stable salts.
- Capital/material of construction issues
  - Acidic degradation products (HSS) are more corrosive; therefore, it requires materials resisting to corrosion which is more expensive for construction.

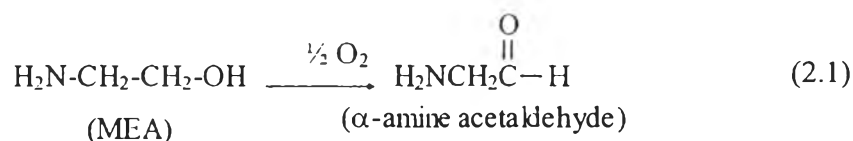Amine degradation can be systematized into two main reaction types

1) Amine oxidative degradation through

- Autoxidation pathways

- Oxidation in the presence of metal ions

2) Thermal degradation including reactions in the presence of CO_2.
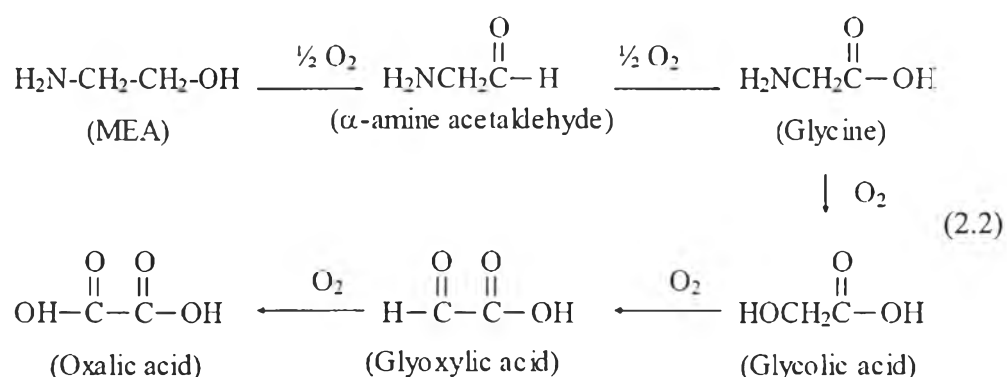
2.3.1 Oxidative Degradation

Oxidative degradation of alkanolamine solution is caused by the presence of O_2 or metal in the flue gases. Excess O_2 will enter in the absorber and this is where the most likely place "oxidative degradation" occurs. The oxidative degradation occurred by presence of dissolved O_2 into the liquid holdup at the bottom of absorber and is also catalyzed by metal ions. The degradation products will be oxidized into fragments of alkanolamine, such as ammonia, organic acids and oxidants. Major product of MEA oxidative degradation product is α-amine acetaldehyde as shown in Equation 2.1 (Supap *et al.*, 2011).

$$H_2N\text{-}CH_2\text{-}CH_2\text{-}OH \xrightarrow{\frac{1}{2} O_2} H_2NCH_2\overset{\overset{\displaystyle O}{\displaystyle \|}}{C}\text{-}H \qquad (2.1)$$

$$\text{(MEA)} \qquad \text{(α-amine acetaldehyde)}$$

Bedell (2009) proposed autoxidation of organic molecules without any specific catalyst. Autoxidation is a free radical chain reaction with O_2 to form the peroxide radical which leads to the production of imine (NH_2^+) and hydrogen peroxide (H_2O_2).

Rochelle and Chi (2001) proposed oxidative degradation with metal ions which resulted in much faster reactions. Bedell (2009) and Fredriksen and Jens (2013) explained mechanism of MEA degradation where the electron and hydrogen abstractions were proposed as pathways towards the degradation of MEA, however there are still gaps in the knowledge that require to be elucidated. Bedell (2009) substantiated that Fe, Cu, Cr, Ni and V ions were found to catalyze these paths.

One of the first oxidative fragmentation pathways of alkanolamine degradation using MEA was proposed by Jefferson Chemical (Hofmeyer *et al.,* 1965). The pathway reaction of MEA with initial O_2 is produce α- amine acetaldehyde intermediate as shown in Equation 2.2. α-Amineacetaldehyde was oxidized to glycine, glycolic acid, eventually to oxalic acid. Supap *et al.* (2011) commented that this mechanism was useful only proposed oxalic acid as a final product.

$$
\begin{array}{ccccc}
& & & \overset{\displaystyle O}{\underset{\displaystyle \|}{}} & & & \overset{\displaystyle O}{\underset{\displaystyle \|}{}} \\
H_2N\text{-}CH_2\text{-}CH_2\text{-}OH & \xrightarrow{\ \frac{1}{2}O_2\ } & H_2NCH_2C\text{—}H & \xrightarrow{\ \frac{1}{2}O_2\ } & H_2NCH_2C\text{—}OH \\
(MEA) & & (\alpha\text{-amine acetaldehyde}) & & (Glycine)
\end{array}
$$

$\Big\downarrow O_2$

$$(2.2)$$

$$
\begin{array}{ccccc}
\overset{\displaystyle O}{\underset{\displaystyle \|}{}}\ \overset{\displaystyle O}{\underset{\displaystyle \|}{}} & & \overset{\displaystyle O}{\underset{\displaystyle \|}{}}\ \overset{\displaystyle O}{\underset{\displaystyle \|}{}} & & \overset{\displaystyle O}{\underset{\displaystyle \|}{}} \\
OH\text{—}C\text{—}C\text{—}OH & \xleftarrow{\ O_2\ } & H\text{—}C\text{—}C\text{—}OH & \xleftarrow{\ O_2\ } & HOCH_2C\text{—}OH \\
(Oxalic\ acid) & & (Glyoxylic\ acid) & & (Glycolic\ acid)
\end{array}
$$

Several years later, Rochelle and Chi (2001); Bedell and Lepaumier *et al.* (2009) proposed the formation routes for formations of formic and acetic acids by adding pathways into the previous mechanism as shown in Equation 2.2. Acetic acid was thought to form by decomposition of MEA giving NH_3 and vinyl alcohol and then react to give acetaldehyde which finally converts to acetic acid. Formic acid was generated from fragmentation of α-amino acetaldehyde intermediate proposed from the previous mechanism. The modified mechanism by Supap *et al.* (2011) is shown in Equation 2.3.

$$H_2NCH_2CH_2OH \longrightarrow NH_3 + \underset{H}{\overset{H}{\underset{\diagdown}{}}}C{=}C\underset{OH}{\overset{H}{\diagup}} \longrightarrow CH_3\overset{O}{\overset{\|}{C}}{-}H \longrightarrow CH_3\overset{O}{\overset{\|}{C}}{-}OH$$

$$\text{(MEA)} \qquad\qquad\qquad \text{(Vinyl alcohol)} \qquad \text{(Acetaldehyde)} \qquad \text{(Acetic acid)}$$

$$H_2NCH_2\overset{O}{\overset{\|}{C}}{-}H \xrightarrow{H_2O} CH_3NH_2 + H{-}\overset{O}{\overset{\|}{C}}{-}OH \qquad\qquad (2.3)$$

$$\text{(α-Amino acetaldehyde)} \qquad \text{(Methylamine)} \quad \text{(Formic acid)}$$

$$H_2NCH_2\overset{O}{\overset{\|}{C}}{-}OH \longrightarrow HOCH_2\overset{O}{\overset{\|}{C}}{-}OH \longrightarrow H{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}OH \longrightarrow OH{-}\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}{-}OH$$

$$\text{(Glycine)} \qquad\quad \text{(Glycolic acid)} \qquad \text{(Glyoxylic acid)} \qquad \text{(Oxalic acid)}$$
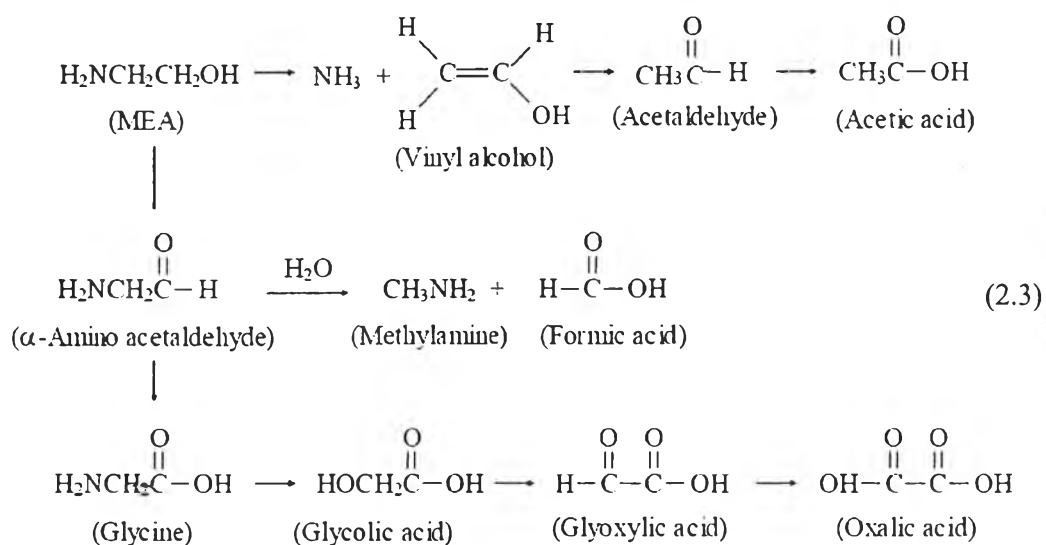
Voice and Rochelle (2013) studied the effects of metal ion catalysts (iron, manganese, and copper) on oxidative degradation of MEA in CO_2 capture and found that the oxidation rate increased by up to a factor of ten. The activation energy of the oxidation rate was 68–70 kJ/mol. Addition of 2 % CO_2 to the gas oxidation increased by a factor of five. The oxidation rate was found to be approximately first order in oxygen partial pressure. Addition of 50 ppm NO_2 or SO_2 to the reactor gas had a minimal effect on the degradation rate. The mass balance was closed within 5 % at high gas flow and within 20 % at low gas flow. Two-thirds of the degraded MEA in both systems was converted to NH_3. The final conclusion was that the dissolved metals and temperature are the most important factors to consider in oxidation of MEA.

Supap *et al.* (2011) studied MEA and major acidic degradation products, often detected in CO_2 capture process to understand the mechanistic roles of these acids in the oxidation process. These acids which are formic acid, acetic acid, glycolic acid and oxalic acid form major heat stable salts (HSSs) with MEA. The reaction of MEA and acetic acid was similar to MEA-formic acid which occurred immediately after the formation of acid and they occur in two forms, acetate of MEA and N-(2-hydroxyethyl)acetamide (HEA), in equilibrium as shown in Equation 2.4 (Supap *et al.*, 2011).

$$(2.4)$$
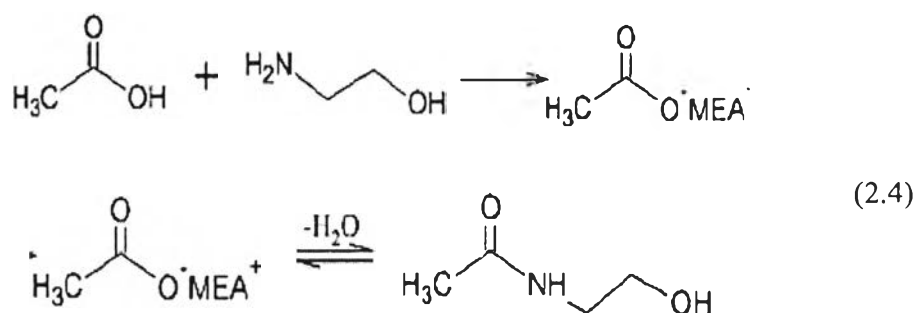
Another reaction was succinic acid and MEA forming a stable N-(2-hydroxyethyl)-succinimide through an intermediate of N-(2-hydroxyethyl)-succinamide as shown in Equation 2.5 (Supap *et al.*, 2011).


$$(2.5)$$
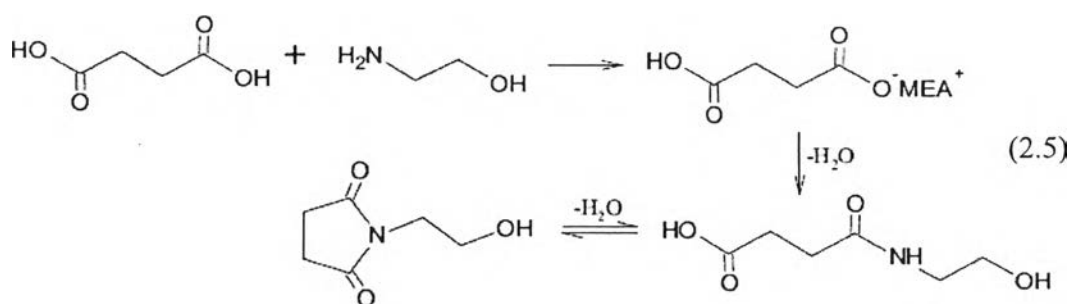
2.3.2 Thermal Degradation

Thermal degradation of alkanolamine solution in CO_2 captures process occurs at high temperature (>100 °C) and high partial pressure (20 MPa) of CO_2 in the absorber. High temperature will break chemical bonds and increases action rate of alkanolamine solution leading to successive thermal degradation productions, which also cause loss of alkanolamine solution in CO_2 captures process. Most of thermal degradation productions will be found in the bottom of reclaimer (Gouedard *et al.*, 2012). MEA, common alkanolamine for CO_2 capture is subjective to oxidative degradation. Davis (2009); Eide-Haugmo *et al.* (2011) studied the MEA loss due to thermal degradation at maximum temperature of 120 °C or temperatures below 200 °C. Zoannou *et al.* (2013) stated that carbamate was the MEA major thermal degradation products and can be formed to other degradation products by side reaction.

In the absorber, MEA reaction with CO_2 to form MEA carbamate which it is major thermal degradation product as shown in Equation 2.6 (Polderman *et al.*, 1955).

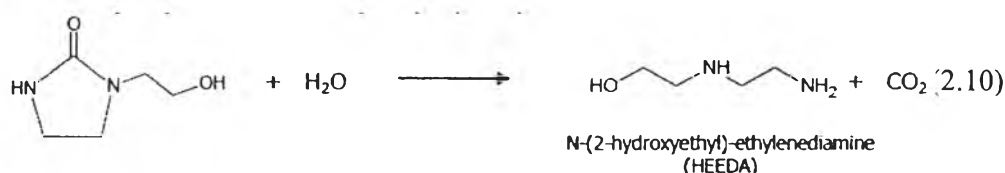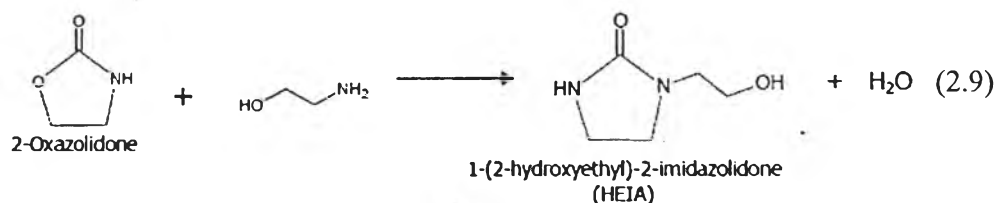$$\text{MEA} + CO_2 \rightleftharpoons \text{MEA Carbamate} \qquad (2.6)$$
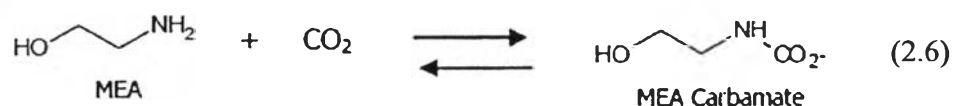
This process is normally reversed in the stripper, but it was proposed that this carbamate could go through a condensation reaction to form 2-oxazolidone as shown in Equation 2.7 (Polderman *et al.*, 1955).

$$\text{MEA Carbamate} \rightleftharpoons \text{2-Oxazolidone} + H_2O \qquad (2.7)$$
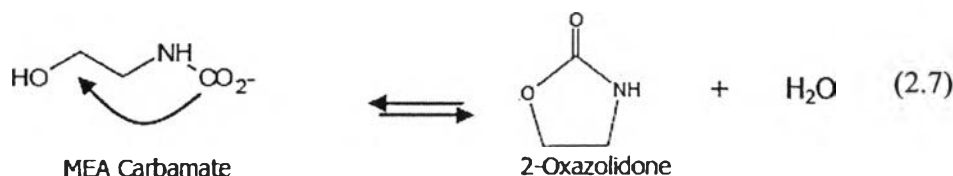
Yazvikova *et al.* (1975) found that MEA-carbamate can also react with another MEA and irreversibly dehydrolyze to form N,N'-di(2-hydroxyethyl)-urea as shown in Equation 2.8 (Polderman *et al.*, 1955).

$$\text{MEA Carbamate} + \text{MEA} \rightarrow \text{N,N'-di(2-hydroxyethyl)urea} + H_2O \qquad (2.8)$$
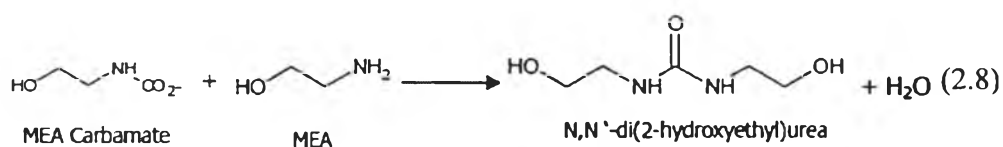
The former product of 2-oxazolidone can then react with MEA to form 1-(2-hydroxyethyl)-2-imidazolidone or HEIA shown in Equation 2.9 (Polderman *et al.*, 1955), and HEIA can then be hydrolyzed to form N-(2-hydroxy ethyl)-ethylenediamine referred as HEEDA as shown in Equation 2.10 (Polderman *et al.*, 1955).

$$\text{2-Oxazolidone} \quad + \quad \text{(HO—CH}_2\text{CH}_2\text{—NH}_2) \quad \longrightarrow \quad \text{1-(2-hydroxyethyl)-2-imidazolidone (HEIA)} \quad + \quad H_2O \quad (2.9)$$

$$\text{HEIA} \quad + \quad H_2O \quad \longrightarrow \quad \text{N-(2-hydroxyethyl)-ethylenediamine (HEEDA)} \quad + \quad CO_2 \quad (2.10)$$
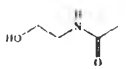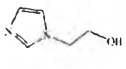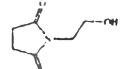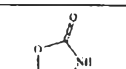
These four species (2-oxazolidone, N,N'-di(2-hydroxyethyl)-urea, HEIA and HEEDA) plus further polymerization products are the major products of thermal degradation which are difficult to regenerate under normal stripper conditions. The rate of formation of thermal degradation products is a function of temperature (faster kinetics), CO_2 loading (more carbamate present), and MEA concentration. Davis and Rochelle (2009) summarized HEIA, HEEDA and MEA makeup, the major total MEA loss. HEIA is the most stable and degradation product in highly degraded compound. Part of HEEDA make costs for regeneration in the stripper low at temperatures below 110 °C, but can become significant if the pressure in the stripper is increased.

Gillis *et al.* (1963) studied corrosion of MEA combination test. The combination of MEA main produced degradation products are cyclic urea of HEIA and diamine of HEEDA. The result showed that the diamine of HEEDA is significantly increasing passing through in liquid phase of corrosive test. In a separate corrosion test, HEEDA was a large factor in the corrosion of carbon steel equipment in an amine treating unit which one test showed over 300 times more iron in a solution of HEEDA and MEA compared to a comparable MEA solution.

The MEA degradation products are common found in the regeneration process shown in Table 2.3. Supap *et al.* (2006) identified and compared MEA degradation products in two systems, it is MEA with O_2 and MEA with O_2 and CO_2, and analyzed degradation products by GC-MS, HPLC-RID, and CE-DAD techniques. For GC-MS, it used an HP-35MS column for analysis of the degradation products and HP-Innowax column for analysis MEA. For HPLC-RID, it used a Nucleosil column with phosphate buffer for analysis of MEA and degradation products And for CE-DAD, it used phosphate and borate for electrolytes for analysis degradation products. The results received by these techniques are shown in Table 2.4.

Table 2.3 Major MEA degradation products (Gouedard *et al.*, 2012)

Chemical Structure	Name (Abbreviation)	Mw (g/mol)	References
	N-(2-hydroxyethyl)acetamide (HEA) or (N-acetylethanolamine)	103	Lepaumier *et al.* (2009a); Strazisar *et al.* (2009b)
	N-(2-hydroxethyl)imidazole (HEI)	112	Lepaumier *et al.* (2009a); Sexton and Rochelle (2011)
	N-(2-hydroxyethyl)-succinimide	143	Lepaumier *et al.* (2009b); Rooney *et al.* (1998b); Supap *et al.* (2011)
	2-oxazolidone (OZD)	87	Lepaumier *et al.* (2009a); Strazisar *et al.* (2003)

Table 2.4 Summary of degradation products suggested by the GC-MS technique and previously reported in literature (Supap *et al.,* 2006)

Degradation Products		Standard Verification	Reference
Compound	% Confidence		
Products Labeled in this work			
1-Methylazetidine	58		
D,L-homoserine lactone	86		
Imidazole	80	X	
N-(2-hydroxyethy) acetamide	83	X	Hofmeyer *et al.* (1965); Strazisar *et al.* (2003).
N-methyl formamide	40		Hofmeyer *et al.* (1965).
1,3-Dioxane	46		
2-Ethyl-1-imidazole	25		
5-Hydrazinocarbonyl-1-imidazole	53		
Uracil	35		
N-(2-hydroxyethyl)succinimide	72		Strazisar *et al.* (2003).
1-Amino-4-methylpiperazine	64		
2-Pyrolidinone	38		
1-Methyl-4-imidazole-5-carboxylic acid	50		

Table 2.4 Summary of degradation products suggested by the GC-MS technique and previously reported in literature (Supap *et al.,* 2006) (cont.)

Degradation Products		Standard Verification	Reference
Compound	% Confidence		
N-methylene ethanamine	25		
5-Aminovaleric acid	59		
D,L-aspartic acid	72		
2-[(2-Aminoethyl)amino] ethanol	92		
Ethylamine	43		
4,5-Dimethyloxazole	64		
18-Crown-6	47	X	
Ethylurea	38		
N-glycylglycine	59		
Dimethylhydrazone-2-propanone	72		
Additional Products Found in This Work			
Ammonia	30		Hofmeyer *et al.* (1965); Chi *et al.* (2002); Rooney *et al.* (1998).
Formic acid	86	X	Blanc *et al.* (1982); Rooney *et al.* (1998).

Table 2.4 Summary of degradation products suggested by the GC-MS technique and previously reported in literature (Supap *et al.*, 2006) (cont.)

Degradation Products		Standard	Reference
Compound	% Confidence	Verification	
Acetic acid	80	X	Blanc *et al.* (1982); Rooney *et al.* (1998).
Pyrimidine	86	X	
Acetamide	70	X	
2-Methylaminoethanol	75	X	Bello *et al.* (2005).
Acetaldehyde	65		Rooney *et al.* (1998).
Ethanol	80		
Oxalic acid			Hofmeyer *et al.* (1965); Rooney *et al.* (1998).
Glycolic acid			Hofmeyer *et al.* (1965); Rooney *et al.* (1998).
Bicine			Howard *et al.* (2001).

GC-MS is the most sensitive for analysis which it can detect greatest product. Confirmation of the results could be accomplished through the use of a combination of GC-MS, HPLC-RID, and CE-DAD. The GC-MS technique analyzed the degradation products using three different GC columns having widely different polarities. HP-35MS column of intermediate-polarity was the best performed for analysis the degradation products from the MEA with O_2 and MEA with O_2 and CO_2 degradation systems. HP-Innowax column of high-polarity was the best performed for analysis of MEA and HP-5MS column of non-polarity was unsuitable for all. A HPLC-RID technique using cation-exchanger was the best performed for contemporary analysis degradation product and MEA in this single column in a single run. CE-DAD using an electrolyte was unsuitable for analysis high concentration of MEA.

2.4 Methods for Removal of Amine Degradation Products

2.4.1 Electrodialysis

Electro-dialysis (ED) was first developed in the 1950s as a technology for desalting water. The technique involves the selective removal of charged species by flowing the contaminated ethanolamine solution between a stack of alternating positively and negatively charged ion exchange membranes. However, fouling of membrane and overall economics are concerned and become disadvantage in the separation of the degradation products (Dumée *et al.*, 2012).

2.4.2 Distillation

Distillation has an economic advantage when operating with very high concentrations of MEA degradation. In addition, there are low quantities of waste generated and it consumes low water and chemical. The distillation works better with the amines with low boiling points. The major disadvantage of distillation is the energy consumption needed to vaporize and distill over the amine solution. Distillation has poor economics for maintaining low concentrations of MEA degradation, because such a large volume of solvent must be distilled to remove a small amount of MEA degradation. MEA degradation can be separated as the bottom

residue in a reclaimer. Large energy input is needed to achieve this process (Dumée *et al.*, 2012).

2.4.3 Ion Exchange Resins (IEX)

Ion exchange resins are commonly used to remove ionic contaminants from the MEA degradation, such as the organic anions formed through oxidation or the sulfates and nitrates formed by reaction with acid gases. However, they are not able to remove uncharged contaminants such as those produced from thermal degradation. In addition, an operational cost is relatively high. Also, several researches have reported the belief that it will not work effectively for amine reclaimation or thermal degradation and become a major disadvantage of this technique (Dumée *et al.*, 2012).

2.5 Liquid-Liquid Extraction

Liquid-liquid extraction (LLE) is a process of transferring a solute from one liquid phase to another immiscible or partially miscible liquid in contact with the first. The two phases are chemically quite different, which leads to a separation of the components according to their distribution or partition between the two phases. Normally one phase is aqueous solution and the other phase is an organic solvent. This is different from distillation, in which the liquid is partially vaporized to create another (vapor) phase, but the two phases are similar chemically.

Differential extraction becomes more effective if the process is repeated a number of times using a small volume of the organic solvent each time, than by using the whole solvent in one lot, i.e. multiple extraction is more efficient than single extraction.

Basically, the MEA degradation products are various acid anions, such as formate, acetate, glycolate and oxalate. The carboxylic acids are acidic because of the hydrogen in the -COOH group which increases the acidity of the solution. Therefore, the alkaline solution (base ions) is selected for extraction of acid from the MEA degradation solution by acid-base reaction (Wasewar *et al.*, 2011)

This technology is a complex separation process. An additional component has to be introduced as extractant, which makes other subsequent separation steps necessary. A solvent extraction is often an organic liquid that can extract solute containing in an aqueous solution based on its solubility in a diluent and its selectivity of solute. Good diluents must possess a higher solubility of solute than the mixture, where the solute is originally 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 selection of the extractant is important for a reactive extraction process. The two most important characteristics are a high capacity and selectivity for the product compared with water. These two requirements are represented by the distribution coefficient and separation factor. The complexation between the extractant and the solute should also be strong enough to overcome the low activity of the solute in the aqueous phase, yet not so strong as to render regeneration difficult or impossible (Hong *et al.* 2001).

Yang *et al.* (1991) researched the extraction of carboxylic acids by using Alamine 336 (tertiary amine) and Aliquat 336 (a quaternary ammonium chloride) as extractants. The result showed that Aliquat 336 could extract both undissociated and dissociated acids under both acidic and basic conditions. However, extractant regeneration by striping may be difficult for Aliquat 336. For extraction with high concentration of Aliquat 336 with dilutent, it formed emulsion between aqueous phases and organic phase. Therefore, low efficiency of extraction due to low transfer between extractant and solute. They also reported that general diluent for Aliquat 336 was 2-octanol as had no apparent effects on extraction performance. The viscosity of Aliquat 336 in any diluent was extremely lower than that of pure Aliquat 336. Therefore, no emulsion formed between aqueous phase and organic phase when diluent was used, and transfer between two phases increased.

Bora and Dutta (1998) researched the extraction of 7-amino cephalosporanic acid (7-ACA). They used secondary amine (di-*n*-octylamine, Amberlite LA-1, and Amberlite LA-2), tertiary amine (tri-*n*-octylamine) and quaternary amine (Aliquat336) as extractants with butyl acetate as a solvent. In case of extraction with secondary and tertiary amines, the extraction efficiency of 7-ACA

decreased with the increase of pH. However, the extraction with Aliquat 336 provided extraction efficiency higher than those of secondary and tertiary amines in the above pH ranges. The success of this method depends upon the difference in solubility of a compound in various solvents. For a given compound, a solubility difference between solvents is quantified as the "reactive extraction".

2.5.1 Reactive Extraction

Reactive extraction is a separation process using the reactions between extractants and the substances extracted. In organic phase, the extractant reacts with substances in the aqueous phase. The reaction complexes formed are then solubilized in the organic phase. Extractants, such as aliphatic amine are mainly used in the solvent extraction of carboxylic acids. (Hong *et al.* 2001).

Organic solvents used for extraction was accounted for by three major phenomena 1) conventional oxygen-bearing and hydrocarbon extractant, 2) phosphorus-bonded oxygen-bearing extractant, and 3) high molecular weight aliphatic amines. Solvent extraction with conventional solvents such as alcohols, ketones, ethers, and aliphatic hydrocarbons is not efficient when applied to dilute, carboxylic acid solutions because of low aqueous phase solute in organic phase as refer to low distribution coefficients. However, carboxylic acid extractions with organophosphates, such as aliphatic amine have high distribution coefficients. And high aliphatic amine interactions with the acid allow formation of acid-amine complexes and thus provide high distribution coefficients.

In liquid–liquid extraction, a quantity of organic compound measured by distribution in between aqueous and organic phases is referring "the distribution or partition coefficient" as refer to K_D which is a ratio of the solubility of solute dissolved in organic phase to the solubility of substances dissolved in aqueous phase. The constant K_D, is essentially the ratio of the concentrations of the solute in the two different solvents, once the system reaches equilibrium. At equilibrium, the molecule of substances will distribute in the solvent. Inorganic and water soluble substances will stay in the aqueous phase and more organic molecules will remain in the organic phase.

There are many factors influent on the extraction concentrations of the acid and the extractant, and the type of extractant or diluent used. Since the extraction equilibrium is dependent on the concentration of undissociated acid in the aqueous phase, pH is also an important variable. The following reactions occur in the reactive extraction of carboxylic acids with aliphatic amine extractants (Yang *et al.*, 1991).

Ionization of the Carboxylic Acids in an Aqueous Solution

Carboxylic acids are weak acids. The general formula of a carboxylic acid is R-COOH with -COOH referring to the carboxyl group. When a carboxyl group is deprotonated (H^+), its conjugate base forms a carboxylate anion (R-COO⁻) as shown in Equation 2.11.

$$HA \leftrightarrow H^+ + A^-\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ (2.11)$$

The concentrations of hydrogen ion (H^+) or pH effected to dissociated acids (A⁻) and undissociated acids (HA) are the acid dissociation constant (K_a) which can be expressed as shown in Equation 2.12.

$$K_a = \frac{[H^+_{aq}]\cdot[A^-_{aq}]}{[HA_{aq}]}\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ (2.12)$$

Partition of the undissociated molecular acid between the two phases, aqueous (aq) and organic (org) at low pH values or high H^+ concentrations, the acid presence in the aqueous phase is mainly in the undissociated form, and the distribution coefficient is equal to Equations 2.13 and 2.14.

$$HA_{aq} \leftrightarrow HA_{org}\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ (2.13)$$

$$P = \frac{[HA]_{org}}{[HA]_{aq}} = K_1\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ (2.14)$$

Dimerization of the Dicarboxylic in the Aqueous Phase

Dicarboxylic acids are strong acids. The molecular formulas of dicarboxylic acids are HOOC-R-COOH. Dissociating of the second carboxyl group occurs less readily than the first. This effect arises because more energy is required to deprotonate anions than neutral molecules. Where H_2A is undissociate dicarboxylic acid, the second proton dissociated is defined as shown in Equations 2.15 and 2.16.

$$H_2A \leftrightarrow H^+ + HA \tag{2.15}$$

$$HA \leftrightarrow H^+ + A^- \tag{2.16}$$

Therefore, the dicarboxylic acid dissociation constant included K_{a1} and K_{a2} which are defined as shown in Equations 2.17 and 2.18.

$$K_{a1} = \frac{[H^+_{aq}] \cdot [HA^-_{aq}]}{[H_2A_{aq}]} \tag{2.17}$$

$$K_{a2} = \frac{[H^+_{aq}] \cdot [A^-_{aq}]}{[HA_{aq}]} \tag{2.18}$$

Partition of the undissociated molecular dicarboxylic acid between the two phases, aqueous (aq) and organic (org) at high pH values, is that the acid presence in the aqueous phase is mainly in the undissociated form, and the distribution coefficient is equal to Equations 2.19 and 2.20.

$$2HA_{org} \leftrightarrow HA_{2,org} \tag{2.19}$$

$$D = \frac{[HA]_{2,org}}{[HA]^2_{org}} = K_2 \tag{2.20}$$

In theoretical concept of carboxylic recovery with quaternary amine extraction, the molecule acid which is extracted by the extractant is bigger than the part of the extracted anions (carboxylate). Therefore, the concentration of

undissociated acid (HA) is a function of the acid can be extracted by amine extarctant at equilibrium system.

The overall of acid such as, undissociated and dissociated acids, are extracted from aqueous to organic phase at equilibrium that called "Distribution ratio", is defined as the ratio of the total concentrations of that carboxylic acid in the two phases. The overall distribution coefficient can be written as shown in Equation 2.21.

$$K_D = \frac{[TA]_{org\,total}}{[TA]_{aq\,total}} = \frac{[HA]_{org} + 2HA_{2,org}}{[HA]_{aq} + [A^-_{aq}]} = \frac{K_1 + K_2 \cdot K_a / [H^+]}{1 + K_a / [H^+]} \qquad (2.21)$$

Where $[TA]_{org\,total}$ and $[TA]_{aq\,total}$ are the total concentrations of the acid in the organic and aqueous phases, respectively.

The degree of extraction (E %) of carboxylic acid is expressed as shown in Equation 2.22.

$$E\% = K_D \times \frac{100}{(1 + K_D)} \qquad (2.22)$$

The mechanism of the reactive extraction is interaction between carboxylic acid (HA) and quaternary ammonium chloride, $(R4N^+Cl^-)$ which can be explained using the mass action law. Basically, interactions with acid-base extraction occur in the intermediate at equilibrium situation that there are some molecule acids connecting with molecule base of quaternary amine.

The extraction of acid with an amine solvent occurs by H-bonding or ion pair formation, which takes place only with the undissociated part of the acid. The portion of dissociated acid is generally negligible in the aqueous phase. The interfacial reaction between acid molecules and molecule of quaternary amine is given by Equation 2.23,

$$HA_{aq} + (R_4N^+Cl^-)_{org} \leftrightarrow (HA{:}R_4N^+Cl^-)_{org} \qquad (2.23)$$

The complexation consisted of more than one acid per amine, which was a common behavior for monocarboxylic acids. The ratio of complex formation was depended on the diluents. Diluents provide the solution of the extractants and also general and specific solvation to the acid-extractant complexes formed. Solvation of the whole extractant-acid complex is based on dipole-dipole interaction and was found to play an important role in the neutralization reaction between acid and extractant, which is promoted by increasing the polarity of the diluent (Waseware *et al.*, 2011).

In the equilibrium, the molecules of extractant are computed by applying law of mass action that is the ratio between concentrations of extractant molecules and the concentration of carboxylic acids species, according to the general equation of interaction between 2 phases. Therefore, extraction the undissociated molecules of acid by amine interaction is equilibrium complexation equal to Equation 2.24.

$$K_E = \frac{(HA:R_4N^+Cl^-)_{org}}{HA_{aq}(R_4N^+Cl^-)_{org}} \tag{2.24}$$

2.6 Literature Review

Gouedard *et al.* (2012) summarized alkanalamine degradation products. In case of MEA, ammonia,N-(2-hydroxyethyl)-piperazin-3-one (HEPO) and N-(2-hydroxyethyl)-2-(2-hydroxyethylamino)-acetamide (HEHEAA) are the main identified degradation products in pilot plants. Among lab studies, the most cited degradation products are ammonia, carboxylic acids, N-(2-hydroxyethyl)-formamide (HEF), N-(2-hydroxyethyl)-acetamide (HEA) and N-(2-hydroxyethyl)-imidazole (HEI) for oxidative degradation, and oxazolidin-2-one (OZD), N-(2-hydroxyethyl)-ethylenediamine (HEEDA) and N-(2-hydroxyethyl)-imidazolidin-2-one (HEIA) for thermal degradation.

Yang *et al.* (1991) studied extractions of carboxylic acids by tertiary and quaternary amines under various equilibrium pHs ranging from 2.0 to 8.5. Alamine 336 and Aliquat 336 used in this research, the result showed that Aliquat336 could

extract both undissociated and dissociated acids and can be used under both acidic and basic conditions. However, extractant regeneration by striping may be difficult for Aliquat 336. For extraction with concentration greater 25 % of Aliquat 336 in diluent, an emulsion phase was also observed at the interface between the aqueous and organic phases when the equilibrium pH of the aqueous phase was lower than 3.0. The formation of emulsion not only affects the equilibrium, but also causes difficulty in separating the two phases. They also reported that the use of 2-octanol as a diluent had no effects on extraction efficiency for Aliquat 336. Nevertheless, the use of a diluent with Aliquat 336 can improve the physical properties of the extractant, which Aliquat 336 in any diluent was decreased viscosity. Also, the surface tension that arises at the interface of the two phases was decreased when a diluent was used, which allows the two phases to separate faster.

Kyuchoukov *et al.* (2001) studied the extraction of lactic acid by mixed extractant consist of tri-n-octylamine and Aliquat 336 in decanol, which result shown that more efficient in the extraction of lactic acid. After extraction, the aqueous phase had a higher pH value in comparison with that of the initial solution.

Akkarachalanont *et al.* (2012) studied the process for regenerating amine-based solvents from impurities, degradation products and HSSs in CO_2 capture process. Liquid-liquid extraction is a process for regenerating the lean amine solvent, using extractant and diluent. Example of reaction composition consist of extractant (Aliquit 336) and diluent (1-octylamine) for the extraction of HSSs and HSSs in MEA solution, the extract ability of HSSs in the aqueous phase without MEA was better than that with the MEA solution. The mixed extractant could reduce added chloride⁻ better than the 2-step extarction technique and the use of extractant alone. And presence of CO_2 into the MEA solution reduced the extraction efficiency.

Suppaibulsuk *et al.* (2013) studied the effect of different extraction diluents (1-octanol, 2-ethyl-hexanol, 1-heptanol, 1-hexanol and 1-pentanol) to extract HSS, i.e. acetate, formate, glycolate, and oxalate from aqueous monoethanolamine (MEA) solution. The diluent are selected based on their solvation power, which helps transfer of HSS from the aqueous amine to organic diluent. The result of this work prefers the 2-ethyl-hexanol for the optimized diluents.

Teptakob *et al.* (2014) studied the extraction equilibrium of heat stable salt in MEA absorption solution in CO_2 capture. The efficient extraction of HSSs from the lean MEA solvent can increase but in the presence of CO_2 and MEA absorption efficiency of extraction decrease. In addition different temperature can be different result, increase temperature will increase efficiency of extraction.

From the literature review, the neutral MEA degradation products accumulations in the amine solution present many problems that needed to be taken care of. These products have no ability to absorb CO_2 and must be removed from the MEA solvent because they reduce the efficiency of the absorption process. A commercial removal process of MEA degradation products is based on distillation, which consumes a large quantity of energy, thus economically unattractive. A liquid-liquid extraction technique shows a potential in replacing the conventional distillation as it can be achieved at atmospheric and lower temperature conditions (e.g. 1 atm and 25-60 °C). Also, the technique can be possibly applied to separate the neutral MEA degradation products in amine used for CO_2 capture due to its successful use in other applications as shown in Table 2.5.

Therefore, the objective of this research is to use the liquid-liquid-extraction to separate neutral MEA degradation products such as imidazole, N-acethylethanolamine, 2-oxazolidone and N-(2-hydroxyethyl)-succinimide) from the MEA absorption solution. The selection of Aliquat336 as the extractant in 2-ethyl-1-hexanol diluent in this research was based on the studies of Yang *et al.* (1991); Akkarachalanont *et al.* (2012); Suppaibulsuk *et al.* (2013) Effects of temperature and CO_2 loading were also investigated.

Table 2.5 Summary of literature review

Extractants	Diluents	Detected Components	References
• Alamine 336 Aliquat 336 (Cl⁻) Ammonium chloride	kerosene 2-octanol	Carboxylic acid	Yang *et al.*, 1991
Mixed extractants: TOA and Aliquat 336 (Cl⁻)	decanol	Lactic acid	Kyuchoukov *et al.*, 2001
Aliquat 336 (Cl⁻) Aliquat 336 (OH⁻)	1-octylamine	HHSs	Akkarachalanont *et al.*, 2012
	1-octanol 2-ethyl-hexanol 1-heptanol 1-hexanol 1-pentanol	HHSs	Suppaibulsuk *et al.*, 2013
Aliquat 336 (OH⁻)	2-ethyl-1-hexanol	HHSs	Teptakob *et al.* (2014)