Review

Degradation studies of amines and alkanolamines during sour gas treatment process

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Aqueous solutions of alkanolamines are widely used for the removal of acidic gases such as H_2S, CO_2, COS and CS_2 in the sour gas treatment process. In spite of the resistance of alkanolamines to chemical breakdown, plant and laboratory reports indicate that, on prolonged use, alkanolamines may be transformed into undesirable products from which the amines are not easily recovered. This phenomenon, commonly referred to as 'amine degradation', not only leads to amine losses, but may also contribute to operational problems such as foaming, corrosion, high solution viscosity and fouling as a result of decreasing the plant life. Amine based gas purification plants having absorption and stripping system, solvents are degraded at these two units mainly by oxidative degradation at absorber condition and thermal degradation at stripper condition. Identification of amine degradation routes, remediation of degradation, types of degradation products and studies on degradation reaction mechanism becomes essential for successful plant operation. Gas chromatography-mass spectrometry (GC-MS), ion chromatograph (IC), high performance liquid chromatography (HPLC), nuclear magnetic resonance spectroscopy (NMR) and Fourier transform infrared absorption spectrometry (FT-IR) are extensively used to identify the various degradation products. A comprehensive review of the latest research activities on alkanolamines degradation, best method for identification, various properties of degradation products and their classification is presented in this paper. This study would help to develop better understanding of amine degradation.

Key words: Degradation, alkanolamines, absorption, stripping, sour gas.

INTRODUCTION

Natural and refinery gases typically contain acid gases in concentrations ranging from a few parts per million to tens of volume percent. The major acid gases are hydrogen sulfide (H_2S) and carbon dioxide (CO_2).

The toxicity of H_2S, and the lack of heating value of CO_2, NG or LPG must be purified prior to liquification and use, because of the corrosivity of acidic gases in the presence of water. Amines and alkanolamines are widely used in natural gas refining for the sweetening of sour gas by removing CO_2 and H_2S. In the amine based purification plant alkanolamines of primary significance include monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), di-2-propanolamine (DIPA) and diglycolamine (DGA). For the

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last two decades the sterically hindered amine such as AMP (2-amino-2-methyl-1-propanol) has been suggested as an attractive solvent for the removal of acid gases. The advantages of AMP include high equilibrium loading capacity (Davis and Gary Rochelle, 2009). Aqueous MDEA solution is used as a solvent for selectively absorbing H_2S (Lepaumiera et al., 2009; Blauwhoff et al., 1984; Closmann, 2009; Klare et al., 2000; Shahi et al., 1994; Lepaumier et al., 2009a; Saleem and Essa, 2010). However, in removing acid gases with alkanolamines and regenerating them, undesirable compounds are likely to be produced by the irreversible transformation of alkanolamines, which is called degradation.

Degradation causes a loss of alkanolamine, and it may also contribute to operational problems such as foaming, corrosion and fouling. While some loss is expected in all operations, extreme losses can negatively impact economics of operating any amine unit. Degraded DEA solutions usually contain hydroxyethyl oxazolidone (HEOD) bis (hydroxyethy) piperazine (BHEP) and tris-(hydroxyethyl) ethtlendiamine (THEED), together with low concentrations of various higher boiling compounds (Dawodu and Meisen, 1996, 1993; Shahi et al., 1994; Choy and Meisen, 1980; Dawodu and Meisen, 1991; Dawodu and Axel Meisen, 1994). The degraded solution of MDEA or MDEA/PZ contains EG, DEA, TEA, DMAE, HMP, BHEP, MP and DMP (Lepaumier et al., 2009a; Lepaumier et al., 2009c, b; Oh et al., 2003; Amiri et al., 2007; Carlson et al., 2001; Haws and Jenkins, 2000). Literature cited sufficient information on MEA degradation products including volatile and solid substances. It contains more than 15 different degradation products identified by many researchers (Strazisar et al., 2003; Supap et al., 2006; Lepaumier et al., 2009c, b; Sexton and Rochelle, 2009; Davis, 2009; Sexton and Rochelle, 2010; Strazisar et al., 2010; Haws, 2010). Haws (2010) noted that the degraded solution of DGA contains BHEEU and BHEETU, DIPA contains HMPO. In addition to these impurities, resulting from acid gas induced amine degradation, industrial amine solutions frequently contain other contaminants such as suspended solids, dissolved hydrocarbons, sodium and chloride ions, iron sulfide, foam suppressants, corrosion inhibitors and heat stable salts. The accumulation of contaminants in amine solutions creates major operational problems including degradation (Lepaumier et al., 2009a), foaming (Thitakamol et al., 2009; Pauley and Reza Hashemi, 1998; Amiri et al., 2007), fouling (Axel Meisen and Abdi, 2010), corrosion (Dawodu and Meisen, 1996), a reduction in active amine content also causes an increase in solution viscosity. The chemical and physical nature of the contaminants makes the development of purification schemes inherently difficult. In this regards, an overview of the degradation process of amines solvents, degradatio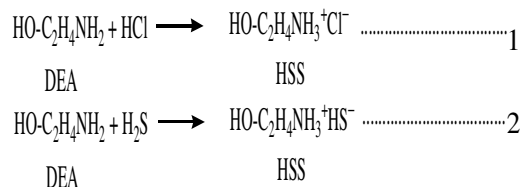n reaction mechanism, impact of degradation products and methodology of DGP identification is very important for a better understanding of amine and alkanolamine based absorption and stripping systems.

The main objectives of this review work are to represent the basic degradation study of MEA, DEA, MDEA and PZ with possible degradation pathways. Additionally this work also explains the major cause and effect of degradation products.

AMINE BASED ABSORPTION AND STRIPPING SYSTEM

For over seventy years, the alkanolamine process has been considered the best approach in removing H_2S and CO_2 for the purpose of purification and separation. It is based on the reaction between weak acid (H_2S and/or CO_2) and weak base (alkanolamines) to give a water soluble amine acid gas salt. An amine based natural gas sweetening plant was configured with absorber and regenerator. The temperature range is 40 to 60°C and 100 to 120°C at the absorber and the stripper, respectively. The sweet gas obtained from the absorber alternatively exhausts sour gas components at the stripper. Figure 1 represents a sweetening process of sour gas.

Mainly, amine solvents are used as absorbents in the absorber for sweetening natural gas and for prolong use of this solvent that is transferred to the stripper by means of regenerating absorbed gases. Absorption and desorption are the common process in these two units occurring continuously during the circulation of amine solvent. Natural gas containing several acidic oxides is very harmful for environment and plant operation and for this reason, these are removed prior to use. Sour gases react with amine solvent during absorption-desorption cycles gradually at higher and lower temperature and some of these reactions are given on how the DGP is formed as follows (Haws, 2010):

$$HO\text{-}C_2H_4NH_2 + HCl \longrightarrow HO\text{-}C_2H_4NH_3^+Cl^- \quad \text{.....................................} 1$$
$$\text{DEA} \qquad\qquad\qquad\qquad \text{HSS}$$

$$HO\text{-}C_2H_4NH_2 + H_2S \longrightarrow HO\text{-}C_2H_4NH_3^+HS^- \quad \text{.................................} 2$$
$$\text{DEA} \qquad\qquad\qquad\qquad \text{HSS}$$

The degradation reactions 3 to 11 showed formation of various degradation products of most common industrially used alkanolamine with acid gas components. The degradation reaction 7 also showed that DEA degraded into MEA and on the other hand MDEA was degraded to EG, DEA and TEA (reaction 8). Low molecular weight
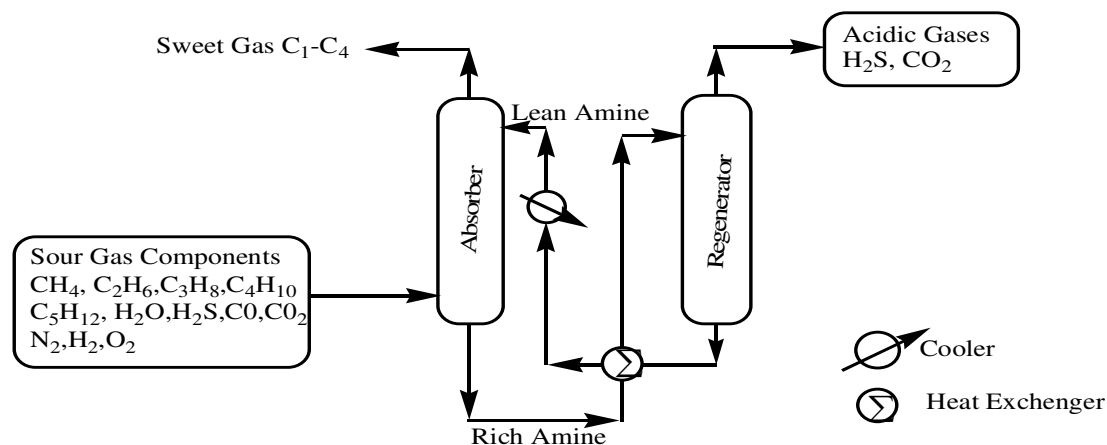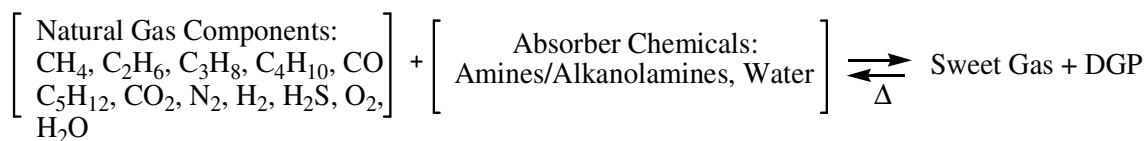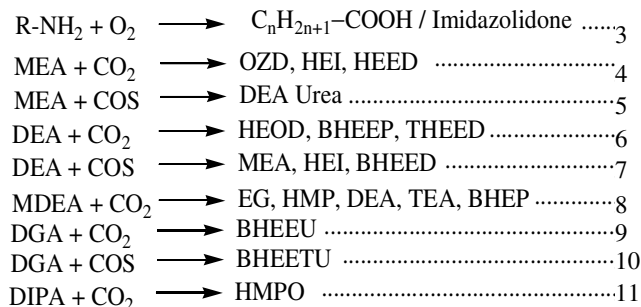
Figure 1. Sour gas sweetening process.

amine MEA is not degraded into amine but it directly forms DGP like OZD, HEI and HEED (Reaction 4). So, the higher molecular weight amines are degraded into low molecular weight amines but low molecular weight amines are not. This phenomenon of producing amines most probably accelerates the absorption process. For this reason, recently, many researchers (Lepaumier et al., 2009c, b) recommended higher molar mass amines like MDEA, DIPA and AMP in sour gas sweetening process for its high resistance to degradation and good absorption capacity.

$$R\text{-}NH_2 + O_2 \longrightarrow C_nH_{2n+1}\text{-}COOH \,/\, \text{Imidazolidone} \dots\dots 3$$
$$MEA + CO_2 \longrightarrow OZD, HEI, HEED \dots\dots\dots\dots\dots 4$$
$$MEA + COS \longrightarrow DEA \text{ Urea} \dots\dots\dots\dots\dots 5$$
$$DEA + CO_2 \longrightarrow HEOD, BHEEP, THEED \dots\dots 6$$
$$DEA + COS \longrightarrow MEA, HEI, BHEED \dots\dots\dots 7$$
$$MDEA + CO_2 \longrightarrow EG, HMP, DEA, TEA, BHEP \dots 8$$
$$DGA + CO_2 \longrightarrow BHEEU \dots\dots\dots\dots\dots 9$$
$$DGA + COS \longrightarrow BHEETU \dots\dots\dots\dots 10$$
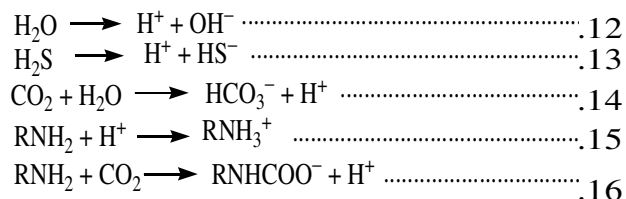$$DIPA + CO_2 \longrightarrow HMPO \dots\dots\dots\dots\dots 11$$

This absorption reactions cause a lot of solvent degradation with various difficulties and as a result, the remediation of this problem has become a major focus of interest for the last few decades. Large numbers of

articles have been published in the field of degradation in the last three decades. The prevention of amine loss, amine degradation is one of the conditions for successful plant operation and also the key to economic benefits. Hence, it is very important to identify the route of amine degradation.

CHEMISTRY OF AMINE DEGRADATION

The basic chemistry of degradation of alkanolamine is explained in the open literature (Wenten, 2010) and these are given as follows. In the following chemical reaction, it is clear that amines occur due to the protonation and carbamate formation reaction brought about by the hydrolysis of water and acids.

$$H_2O \longrightarrow H^+ + OH^- \dots\dots\dots\dots\dots 12$$
$$H_2S \longrightarrow H^+ + HS^- \dots\dots\dots\dots\dots 13$$
$$CO_2 + H_2O \longrightarrow HCO_3^- + H^+ \dots\dots\dots\dots 14$$
$$RNH_2 + H^+ \longrightarrow RNH_3^+ \dots\dots\dots\dots\dots 15$$
$$RNH_2 + CO_2 \longrightarrow RNHCOO^- + H^+ \dots\dots\dots\dots 16$$

The same reaction is also explained in the literature (Dawodu and Meisen, 1996; Choy and Meisen, 1980; Dawodu and Meisen, 1994) for DEA degradation.
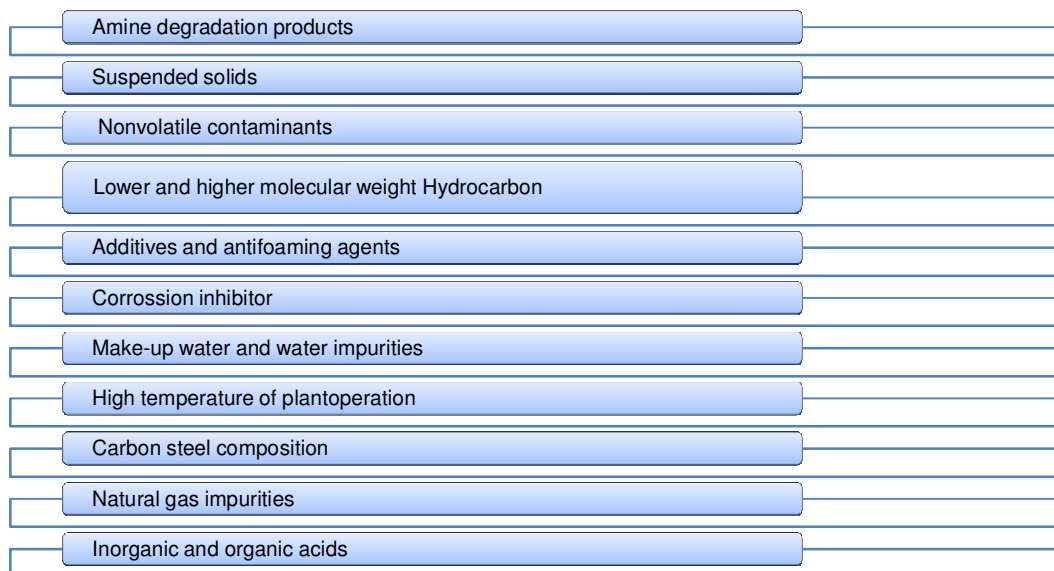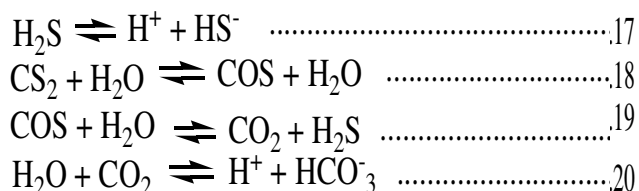
Figure 2. Causes of amine degradation.

Hydrogen sulfide emitted hydrogen ion (Reaction 17) in water and carbon dioxide as well as carbonyl sulfide and produces COS and H_2S, respectively (Reaction 18). This reaction causes additional reactions with DEA molecule.

These reactions are as follows:

$$H_2S \rightleftharpoons H^+ + HS^- \quad\dots\dots\dots\dots\dots\dots 17$$

$$CS_2 + H_2O \rightleftharpoons COS + H_2O \quad\dots\dots\dots\dots\dots 18$$

$$COS + H_2O \rightleftharpoons CO_2 + H_2S \quad\dots\dots\dots\dots\dots 19$$

$$H_2O + CO_2 \rightleftharpoons H^+ + HCO_3^- \quad\dots\dots\dots\dots\dots 20$$

DEA molecule directly reacts with CS_2 and successively produces DEA thiocarbamate salt (Reactions 21 and 22). On the other hand, it produces carbamate with CO_2 (Reaction 23). DEA carbamate reacts with MEA and DEA and forms BHEED and THEED, respectively. These two DGP further forms BHEI and BHEP with CO_2, respectively. HEOD is one of the familiar DGP of DEA and this is also from DEA carbamate. Protonated DEA molecule reacts with CO_2 and converts into MEA, ethanol and water. The formation of MEA is better for DEA system. However, there is insufficient information in this connection in the open literature. Ethanol can easily degrade to aldehyde and then an acid. This acid forms various acetate and ester compounds in amine system. An overview of the reaction pathways of DEA are mentioned as follows:

$$DEA + CS_2 \rightleftharpoons DEA\ dithiocarbamate \quad\dots\dots\dots\dots 21$$

$$DEA\ dithiocarbamate + DEA \rightarrow DEA\ dithiocarbamate\ salt \quad\dots\dots 22$$

$$DEA + H^+ \rightleftharpoons DEAH^+ \quad\dots\dots\dots\dots\dots 23$$

$$DEA + CO_2 \rightleftharpoons DEACOO^-H^+ \quad\dots\dots\dots 24$$

$$DEAH^+ + CO_2 \rightleftharpoons MEA + C_2H_4OH + CO_2 \quad\dots\dots 25$$

$$DEACOO^-H^+ + MEA \rightarrow BHEED + CO_2 + H_2O \quad\dots\dots 26$$

$$DEACOO^-H^+ + DEA \rightarrow THEED + CO_2 + H_2O \quad\dots\dots 27$$

$$THEED + CO_2 \rightarrow BHEP + CO_2 + H_2O \quad\dots\dots 28$$

$$DEACOO^-H^+ \rightleftharpoons HEOD + H_2O \quad\dots\dots 29$$

$$MEACOO^-H^+ + MEA \rightarrow HEI + H_2O \quad\dots\dots 30$$

$$BHEED + CO_2 \rightarrow BHEI + H_2O \quad\dots\dots 31$$

CAUSES OF AMINE DEGRADATION

Amines and alkanolamines can be degraded in many ways. During the absorption process, amines and alkanolamine are used for removing acidic oxide for as example CO, CS_2, CO_2, COS and H_2S. Water is the most widely used solvent for making amine solution, as this water is one of the causes of amine degradation. Based on the existing studies, the causes of amine degradation are shown in Figure 2. This extracted information would help to develop our research knowledge.

EFFECT OF DEGRADATION PRODUCTS

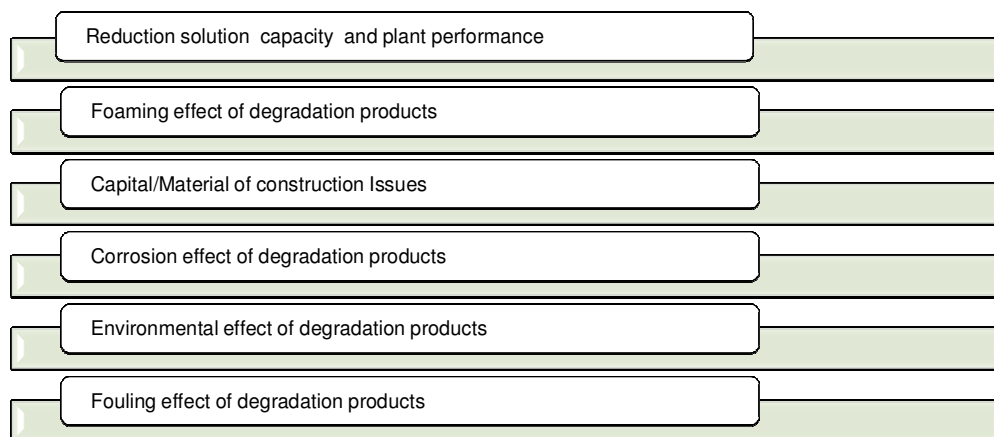Degradation is the undesirable phenomenon in the

Reduction solution capacity and plant performance

Foaming effect of degradation products

Capital/Material of construction Issues

Corrosion effect of degradation products

Environmental effect of degradation products

Fouling effect of degradation products
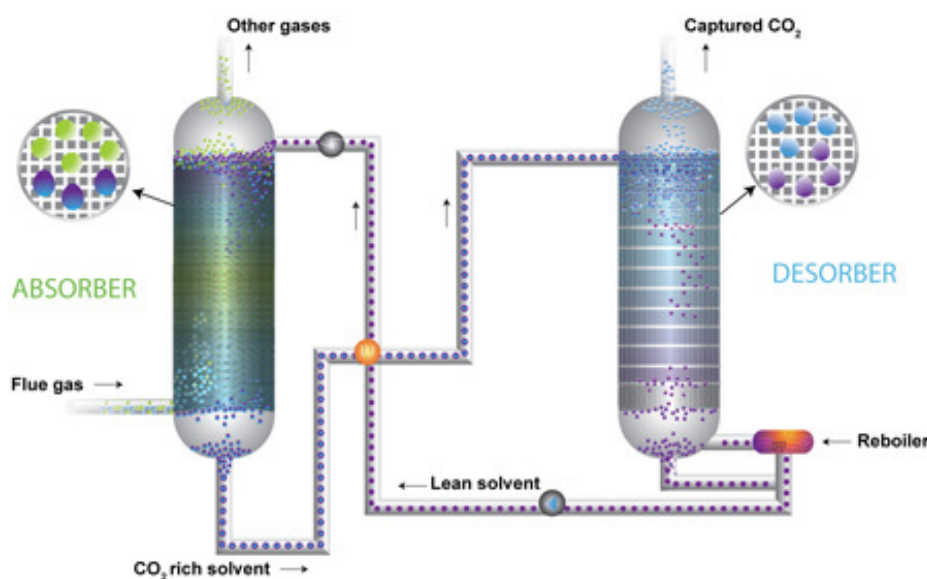
Figure 3. Problems irreversible degradation reaction.

Figure 4. Foam formations in the interior of the stripper by degradation products (CRC, 2010).

replacement of acidic oxides absorption. It is considered that degradation products are major problems during the plant operation (Figure 3). The foaming behavior of degradation products was conducted (Thitakamol et al., 2009; Thitakamol and Veawab, 2008; Goff and Rochelle, 2006). Corrosion behavior of degradation products were conducted by Dawodu and Meisen (1996) and also conducted by the following researchers (Franco et al., 2009; Bedella, 2009; Eide-Haugmo et al., 2009). The recent paper (Bedella, 2009) pointed out several problems which occurred due to irreversible degradation reaction.

Most of the degradation products and corrosion inhibitors in aqueous MEA solutions enhance foaminess coefficient. At the same time, the physical properties, namely surface tension, density and viscosity of solution, play a significant role in foaming tendency through foam formation and foam stability. Among physical properties, the foam height is the most sensitive to liquid viscosity followed by liquid density and surface tension, but not sensitive to gas density. A typical view of the foam formation is shown in the Figures 4 and 5.

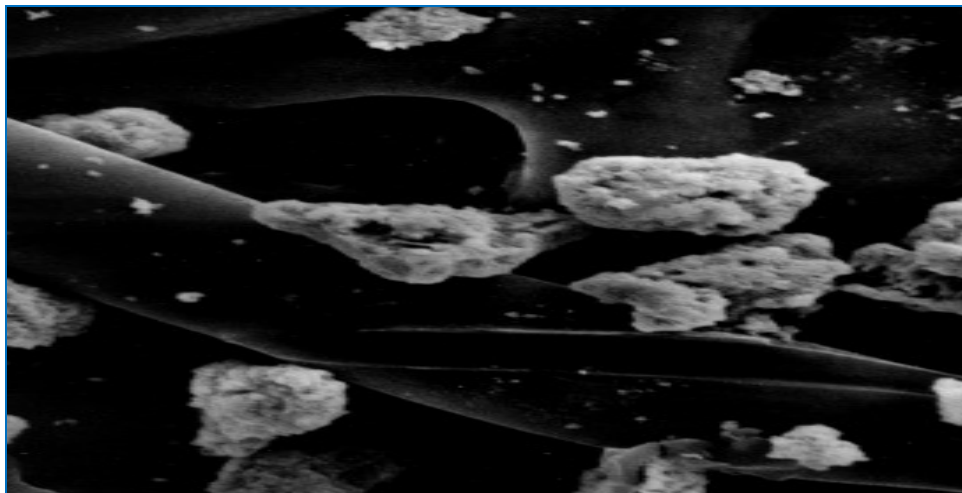Depending on the type of impurities, two major problems may arise, that is:

Figure 5. Foam formations by degradation products (Pauley and Reza Hashemi, 1998).

Figure 6. Crevice corrosion in the junction of pipelines (CTL, 2010).

1. The replacement cost of amine for an MEA system was shown by Saxena to be about 4% of the total cost of CO_2 sequestration. It should also be realized that solvents which are more expensive than MEA may have lower degradation rates or may reduce other cost factors such as energy or capital.

2. Increased viscosity caused by degradation could increase the costs associated with solvent pumping. On the other hand, acidic degradation products may be more corrosive and some diamines produced may act as chelants to remove protective films from metal surfaces. Such corrosivity, could necessitate more expensive construction materials. In the amine based NG gas purification industry, many operational problems occurred

including economical and environmental impact during this process. Acidic degradation products may also occur in this industry and as a result may also corrode pipelines. A typical view of crevice and pitting corrosion in industry is shown in Figures 6 and 7.

All amines and alkanolamines, and also their degradation products are not environmentally friendly. Eide-Haugmo conducted researches on the biodegradability and environmental effect of more than forty amines including alkanolammines like MEA, DEA, MDEA, AMP, etc., (Eide-Haugmo et al., 2009). Effect of degradation products on membrane gas absorption process conducted by Franco, noted that the presence of oxalic acid reduced the mass transfer rate of CO_2 in MEA
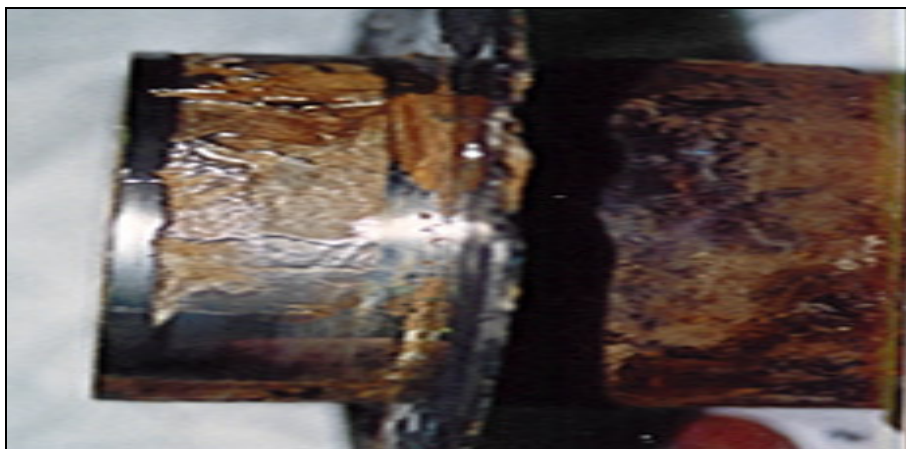
Figure 7. Pitting corrosion occuring at the end of the pipe junction (Internet, 2010b).

Figure 8. Fouling effect in the pipe line of gas sweetening plant (ARIANA, 2010; Internet, 2010a, 2009).

and most significantly followed by formic acid as well as acetic acid (Franco et al., 2009). Amine based purification plant emitted a lot of toxic volatile products which are very harmful for living organisms. Hence, considering all sides we should think about the environmental effect of degradation products and also further research in this area. Most of the articles highlighted the greenhouse effect of sour gases but not on all volatile degradation products. Formation of solid products and solid heat stable salts may create fouling deposits in piping, heat exchangers and reboilers (Figure 8). As a result, pressure drops will rise and the heat-transfer coefficient will fall, leading to increased overall energy costs for the plants. Cleaning of piping, heat exchangers and other infected areas are also expensive. It is therefore advisable to provide effective filtration to remove any solids

that may be present.

AN OVERVIEW OF THE DEGRADATION OF ALKANOLAMINES

Amine based absorption and stripping system with aqueous amine solution offers a competitive approach for capturing CO_2 from raw natural gas and coal-fired power plant flue gas. Carbon dioxide removal from flue gas is important to reduce greenhouse effect. CO_2 absorption with reversible chemical reaction using aqueous alkanolamines solution is currently the most appropriate method for low pressure CO_2 sources. In the last decades, alkanolamines have acquired a well established position in gas-treating for the removal of the acidic
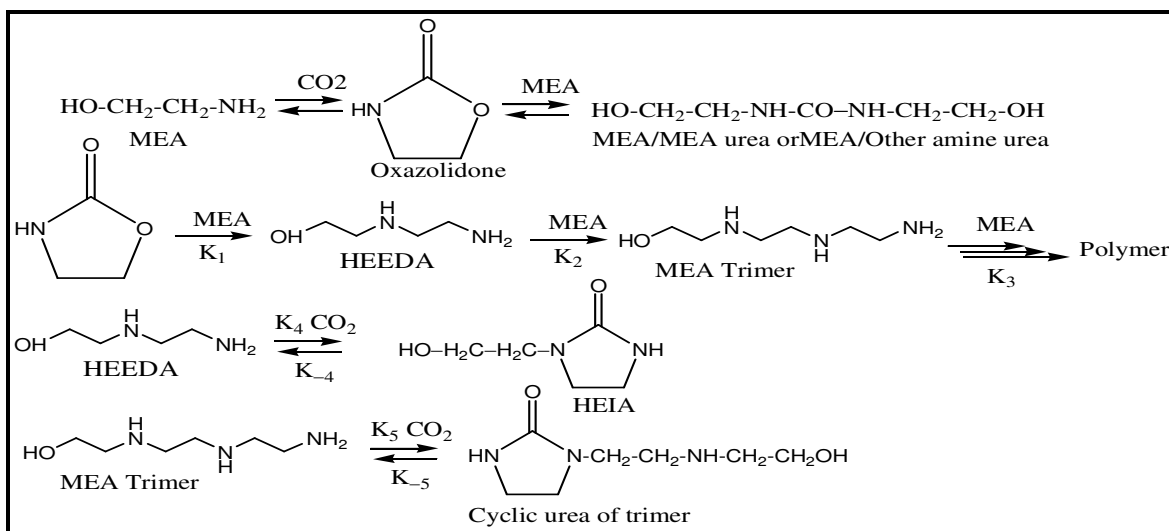
Figure 9. CO₂ induced degradation of MEA.

components H₂S and CO₂. Industrially, important alkanolamines are MEA, DEA, DIPA and MDEA. Among all known solvents, MEA is the benchmark molecule because of its properties towards CO_2 capture (low price, high water solubility, high absorption capacity and fast kinetic). However, a major problem associated with chemical absorption using alkanolamines is degradation through irreversible side reactions with CO_2, H_2S and O_2 which leads to numerous problems with the process: solvent loss, foaming, fouling, increased viscosity and corrosion. So, the degradation studies of alkanolamines are becoming very important for successful plant operation.

Degradation study of MEA and MEA blends

Amine based absorption and stripping system with aqueous amine solution offers a competitive approach for capturing CO_2 from raw natural gas and coal-fired power plant flue gas. Among these amine solutions, MEA is considered the base line solvent for this application (Hilliard 2008; Aron and Tsouris, 2005). For this consideration, aqueous monoethanolamine (MEA) is used extensively to remove CO_2 from flue gas.

Degradation route of MEA

In power plant flue gas stream, that contains 5 to 10% O_2, 10% CO_2; three types of degradation can occur. MEA degrades in the presence of O_2 and CO_2, resulting in extensive amine loss and equipment corrosion as well as

generating environmental impacts. This reaction produces high molecular weight degradation products and is expected to occur at the higher temperature region of the stripper. This reaction mechanism is different from Lepaumiers et al. (2009a, b, c) studies; there is a difference in their results with reference to polymeric and oligomer degradation product. Oligomer is formed from O_2/CO_2 induced degradation of MEA which was shown (Lepaumier et al., 2009a, b, c). On the other hand, Closmann (2009) talked about the formation of polymeric products. From this point, it has created divergent views on the formation of either polymer or oligomer. The degradation pathways of MEA are explained in the literature (Strazisar et al., 2003; Goff and Rochelle, 2004; Lepaumier et al., 2009a; Lepaumier et al., 2009c, b; Abdi, 1997; Lawal et al., 2005a; Strazisar et al., 2010) for protonation, polymerization and isomerization reaction and miscellaneous route regarding reactions. The CO_2 induced degradation of MEA is shown in Figure 9.

Effectively to prevent MEA degradation, a degradation prevention strategy needs to be formulated, and this requires knowledge of the degradation products, stoichiometry, mechanism and kinetics of the degradation process as a function of the various operating variables (Bello and Idem, 2006).

Degradation products of MEA

MEA is a very reactive solvent for gas absorption process; as a result, it shows high reaction rate with any components and form much DGP. The major problem is that the regeneration energy of MEA degradation products

Table 1. Degradation products of MEA induced by CO_2 (Strazisar et al., 2003).

No.	Name	Formula
1	N-formylethanolamine	$(C_3H_7NO_2)$
2	N-acetylethanolamine	$(C_4H_9NO_2)$
3	2-oxazolidone	$(C_3H_5NO_2)$
4	N-(hydroxyethyl)-succinimide	$(C_6H_9NO_3)$
5	N-(2-hydroxyethyl)-lanthamide	$(C_5H_{11}NO_3)$
6	1-hydroxyethyl-3-homopiperazine	$(C_7H_{14}N_2O_2)$
7	1-(2-hydroxyethyl)-2-imidazolidinone	$(C_5H_{10}N_2O_2)$
8	1-hydroxyethyl-2-piperazinone	$(C_6H_{12}N_2O_2)$
9	4-hydroxyethyl-2-piperizinone	$(C_6H_{12}N_2O_2)$
10	3-hydroxyethylamino-N-hydroxy-ethylpropanamide	$(C_7H_{16}N_2O_3)$
11	2-hydroxyethylamino-N-hydroxyethylacetamide	$(C_6H_{14}N_2O_3)$
12	Ammonia	(NH_3)
13	Acetic acid	$(C_2H_4O_2)$
14	Propionic acid	$(C_3H_6O_2)$
15	n-butyric acid	$(C_4H_8O_2)$
16	Monoethanolamine	(C_2H_7NO)
17	2,6-dimethyl-4-pyridinamine	$(C_7H_{10}N_2)$
18	2-imidazolecarboxaldehyde	$(C_4H_4N_2O)$
19	1-methyl-2-imidazolecarboxaldehyde	$(C_5H_6N_2O)$

Table 2. Degradation products of MEA induced by CO_2 and O_2 (Supap et al., 2006).

Major DGP of MEA induced by CO_2 and O_2

1-methylazetidine; D,L-homoserine lactone; Imidazole; N-(2 hydroxyethyl) -acetamide; N-methyl formamide; 1,3-dioxane; 2-ethyl-1H-imidazole; 5-hydrazinocarbonyl-1H-imidazole; Uracil; N-(2hydroxyethyl)succinimide; 1-amino-4 methyl piperazine; 2-pyrolidinone; 1-methyl-4-imidazole-5-carboxylic acid; N-methylene ethanamine; 5-aminovaleric acid; D,L-aspartic acid; 2-[(2-aminoethyl)amino] ethanol; ethylamine; 4,5dimethyloxazole; 18-crown-6; ethylurea; N-glycylglycine dimethylhydrazone-2-propanone; 1-(2-hydroxyethyl)-2-imidazolidinone

Additional DGP of MEA induced by CO_2 and O_2

Ammonia; formic acid; acetic acid; pyrimidine; acetamide; 2-methylaminoethanol; acetaldehyde; ethanol.

Other Products of MEA induced by CO_2 and O_2

Oxalic acid; glycolic acid; bicine

is high. The miscellaneous degradation products and their chemical formula are given in Tables 1 and 2.

Degradation of DEA and its blends

Diethanolamine (DEA) is an important alkanolamine successfully used within the 25 to 35 wt% range in natural gas sweetening plant for sour gas absorption. Degradation study of DEA with CO_2 to form various byproducts has been demonstrated as early as 1956.

There is a lot of information of DEA and its blends which are also reported in the literature (Lepaumier et al., 2009a; Blauwhoff et al., 1984; Klare et al., 2000; Dawodu and Meisen, 1996; Shahi et al., 1994; Choy and Meisen, 1980; Dawodu and Meisen, 1991, 1992; Kennard and Axel Meisen, 1983; Lepaumier et al., 2009c, b). DEA/MDEA and DEA/AMP also have an experience of sour gas absorption. The first blends MDEA/DEA have been used successfully in a wide variety of natural gas sweetening applications for 20 years. Poldermann and Steele (1956) discovered the following reaction mechanism
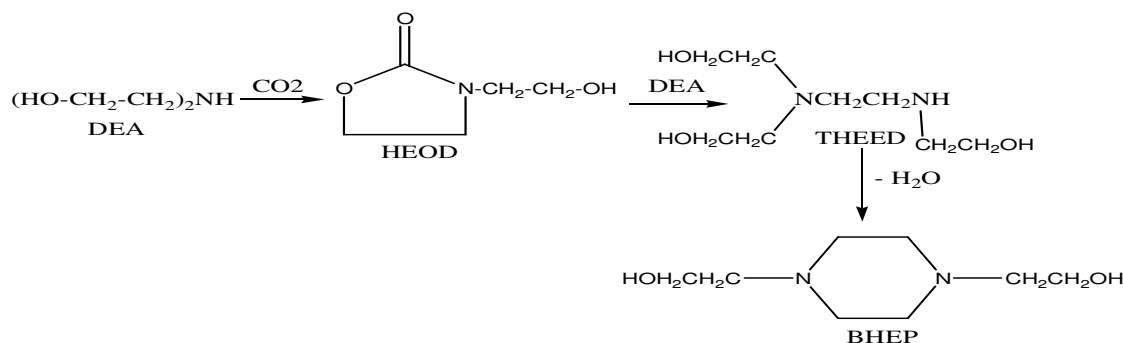
Figure 10. Reaction responsible for the degradation of DEA by CO_2.

during DEA/CO_2 degradation (Dupart et al., 1999).

Degradation reaction of DEA and DEA blend

A model was developed by Kennard (1983) to explain the formation of the main degradation products. The following reaction shows the major reactions which are believed to be responsible for the degradation of DEA by CO_2 (Figure 10). Certain reaction steps cannot be fully confirmed since they are based on the existence of DEA carbamate. Unfortunately, it was impossible to isolate and identify the carbamate, and certain aspects of the reaction mechanism therefore they remain conjectural. In general, the DEA degrades via three routes: the fast "molecular route", the slower "ionic route" and the very slow "thermal route". The molecular route involves CO_2 reacting directly with DEA to produce the carbamate, whereas the ionic route produces the carbamate from the amine salt R_2NH^{2+}- HCO_3^-. The carbamate then degrades slowly to produce THEED, which in turn loses water to form BHEP. HEOD is a side product, produced by internal dehydration of the carbamate and it is believed that the formation of HEOD does not contribute to the overall degradation of DEA. CO_2 appears to catalyze the degradation of DEA to THEED and of THEED to BHEP via the formation of carbamate complexes (Dupart et al., 1999).

Degradation products of DEA and DEA blend

Since DEA is a secondary alkanolamine, it has a reduced affinity to reaction with H_2S and CO_2. There are many degradation products which are formed and induced by several gases which are mentioned in Table 3. The degradation products of DEA are relatively low corrosive than those of MEA. Exposure to oxygen forms corrosive acids and on the other hand, COS and CS_2 induced

degradation of DEA produced relatively low corrosive products than O_2. DEA is not reclaimable under regenerator conditions (Meisen and Abdi, 2010); it decomposes below its boiling point at atmospheric pressure. Vacuum reclaimers, however, have been successfully used to reclaim DEA solutions (Meisen, 1996).
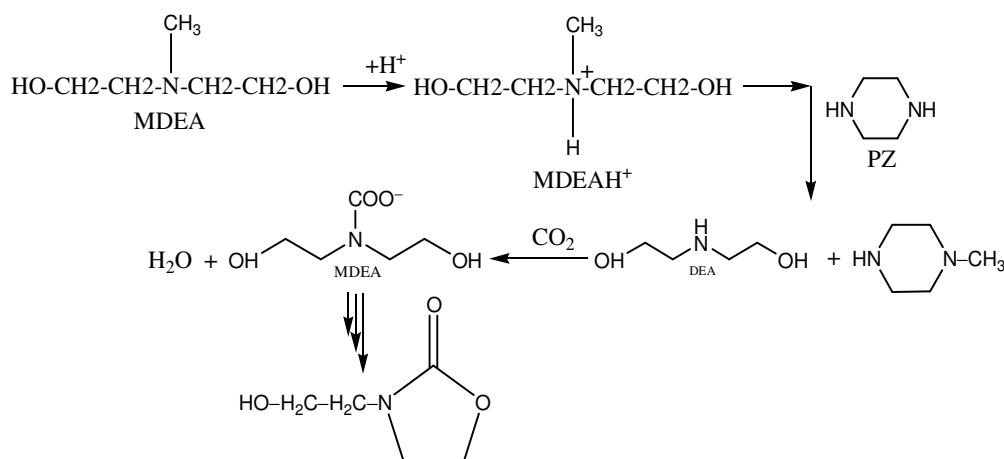
Degradation of MDEA and its blends

Among the all alkanolamines, MDEA as an absorption solvent of acid gases is widely used today because it possesses the characteristics such as higher H_2S selectivity, bigger absorption capacity, lower regeneration energy, smaller hot-degradation and low corrosion (Weiland et al., 2003). Many articles (Closmann et al., 2009; Klare et al., 2000; Shahi et al., 1994; Lepaumier et al., 2009c; Lawal et al., 2005b) were reported on the MDEA degradation induced by CO_2/O_2, CO_2/H_2S and CO_2, respectively. MDEA is a tertiary amine and commonly used in the 20 to 50 wt% range.

Degradation reaction of MDEA and MDEA blend

MDEA does not have a hydrogen atom attached to the nitrogen and cannot react directly with CO_2 to form carbamate. The CO_2 reaction can only occur after the CO_2 dissolves in water to form a bicarbonate radical, which then undergoes an acid-base reaction with the amine. At least six mechanisms for the CO_2-MDEA reaction have been proposed (Cornelissen, 1982; Barth et al., 1981; Danckwerts, 1979). MDEA can, however, react with H_2S by the same proton transfer mechanism of primary and secondary amines (Jou et al., 1982). There is a one CO_2 induced degradation of PZ and MDEA explained by Closmann (2009) and are presented reaction mechanism as shown in Figure 11.

Table 3. Degradation products of DEA induced by CS_2 (Dawodu and Meisen, 1996).

Symbol	Name	Formula
MEA	Monoethanolamine	C_2H_7NO
AMP	Aminomethyl propanol	$C_4H_{11}NO$
DGA	Diglycolamine	$C_4H_{11}NO_2$
HEP	Hydroxyethyl piperazine	$C_6H_{14}N_2O$
BHEED	N,N'-Bis(hydroxyethyl)-ethylenediamine	$C_6H_{16}N_2O_2$
DIPA	Di isopropanolamine	$C_6H_{15}NO_2$
DEA	Diethanolamine	$C_4H_{11}NO_2$
BHEP	N,N'-Bis(hydroxyethyl)-piperazine	$C_8H_{18}N_2O_2$
BHEED	N,N-Bis(hydroxyethyl)-ethylenediamine	$C_6H_{16}N_2O_2$
HEOD	Hydroxyethyl-oxazolidone	$C_5H_9NO_3$
HEI	Hydroxyethyl-imidazolidone	$C_6H_{11}NO_2$
THEED	N,N,N'-Tris(hydroxyethyl)-ethylenediamine	$C_8H_{20}N_2O_3$
BHEI	N,N'-Bis(hydroxyethyl)-imidazolidone	$C_7H_{14}N_2O_3$
DEAC	Diethanolamine carbamat	$C_5H_{12}NO_4$
MEAC	Monoethanolamine carbamat	$C_3H_8NO_3$
DEADTC	Diethanolamine dithiocarbamate	$C_5H_{11}NS_2$
DEADTCS	Diethanolamine dithiocarbamate salt	$C_9H_{22}N_2O_4S_2$
AEEA	Aminoethylethanolamine	$C_4H_{12}N_2O$

Figure 11. CO_2 induced degradation of PZ and MDEA.
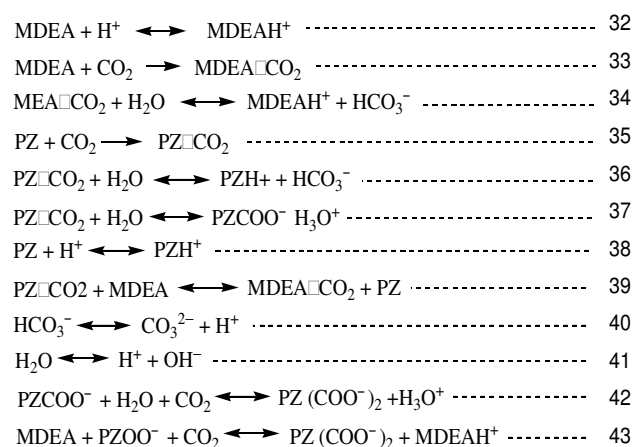
Degradation products of MDEA and MDEA blend

While MDEA was initially thought of as non degradable, recently it has been shown in many articles that it will often degrade in TGTU services, and efforts are being reflected on improved reclaiming options for solvent quality control. MDEA molecule degraded into HSS, DEA, MMEA and bicine. Bis-(hydroxyethyl) glycine (Bicine) is a degradation product formed in the presence of DEA and unstable chemical intermediates. It is considered as a corrosive DGP and may be removed by vacuum distillation. It has been shown that ion exchange is not very effective in removing this compound since it is either dipolar or a zwitterions (essentially meaning it may behave as an anion or a cation depending on the pH of the solution). Monomethylethanolamine (MMEA) is one of the simpler amines that may be formed from MDEA degradation, since MMEA is a secondary amine; it will react directly with CO_2 and will begin to affect the performance of the MDEA solvent. Diethanolamine (DEA) is also one of the simpler secondary amines that may be formed from MDEA. Since DEA is a secondary amine, it

will react directly with CO_2 and will begin to affect the performance of the MDEA solvent.

Degradation of miscellaneous amines

In the revolution of engineering science, piperazine (PZ) has become the most familiar chemical in purification and in the separation process. Hence, aqueous PZ has been investigated as a novel amine solvent for carbon dioxide absorption (Freeman et al., 2010). PZ is a cyclic aliphatic diamine containing two substituted hydrogen atoms in its molecular structure specifically in the first and fourth positions. This H-atom is capable of reacting with other components and as a result is degraded by contaminants. The absorption reaction of MDEA/PZ is explained by Lensen (2004) which is given as follows:

$$MDEA + H^+ \longleftrightarrow MDEAH^+ \quad \text{-----------------------------} \quad 32$$

$$MDEA + CO_2 \longrightarrow MDEA\Box CO_2 \quad \text{-----------------------------} \quad 33$$

$$MEA\Box CO_2 + H_2O \longleftrightarrow MDEAH^+ + HCO_3^- \quad \text{------------------} \quad 34$$

$$PZ + CO_2 \longrightarrow PZ\Box CO_2 \quad \text{-------------------------------------} \quad 35$$

$$PZ\Box CO_2 + H_2O \longleftrightarrow PZH+ + HCO_3^- \quad \text{------------------------} \quad 36$$

$$PZ\Box CO_2 + H_2O \longleftrightarrow PZCOO^- \ H_3O^+ \quad \text{-------------------------} \quad 37$$

$$PZ + H^+ \longleftrightarrow PZH^+ \quad \text{-------------------------------------} \quad 38$$

$$PZ\Box CO2 + MDEA \longleftrightarrow MDEA\Box CO_2 + PZ \quad \text{------------------} \quad 39$$

$$HCO_3^- \longleftrightarrow CO_3^{2-} + H^+ \quad \text{-------------------------------------} \quad 40$$

$$H_2O \longleftrightarrow H^+ + OH^- \quad \text{-------------------------------------} \quad 41$$

$$PZCOO^- + H_2O + CO_2 \longleftrightarrow PZ\,(COO^-)_2 + H_3O^+ \quad \text{--------------} \quad 42$$

$$MDEA + PZOO^- + CO_2 \longleftrightarrow PZ\,(COO^-)_2 + MDEAH^+ \quad \text{---------} \quad 43$$

SOLVENT BLENDS

Since the mid-1980's, in order to further improve absorption performance of MDEA solvent, blended alkanolamine solvents have been developed by adding another alkanolamine into MDEA. These blended solvents include MDEA-MEA, MDEA-DEA, MDEA-DIPA, MDEA-DGA and MDEA-AMP (Pacheco et al., 2000; Mandal et al., 2001; Xia et al., 2003; Rinker, 1997). The blended solvents have the compatibility of advantages of single solvent in blended solvents (Aroonwilas and Veawab, 2004). Example, a blended solvent, which consists of a mixture of primary or secondary amine with MDEA, combines the higher CO_2 reaction rates of the primary or secondary amine with the higher CO_2 loading capacity of the MDEA. Thus, the blended solvent providing both higher CO_2 reaction rate and higher CO_2 equilibrium capacity may result in substantial lower solvent circulation rates compared to a single solvent. So the development of a new solvent for maximum CO_2

absorption can be considered as a great invention of sour gas sweetening process. A large amount of experimental work (Dawodu and Meisen, 1996; Dawodu and Meisen, 1994; Lawal and Idem, 2006; Davis, 2009; Sexton and Rochelle, 2010; Lawal et al., 2005a; Oh et al., 2003) has been done over the past few years to characterize new solvents with respect to different properties such as solubility, absorption, capacity, amine volatility, etc. Amines and alkanolamines are among several solvents that have been investigated and current research is focused on designing a chemically stable, less corrosive solvent with fast reaction rates and low heats of absorption to minimize energy requirements for the regeneration of the solvent. Recently, most of the scientists have shown an increased interest in the use of mixed amine solvents in gas - treating processes. Blends comprising of primary, secondary, or tertiary amines have been suggested for the industrial gas sweetening processes (Abdi et al., 2005). Some new amine blends (TBEE, APM, DIPATBG and TBE) have been focused upon as having no sufficient reports. Hence we should continue to get information on it about degradation, modeling, design, absorption, adsorption, kinetics, mechanism and various comparative sweetening capa-cities. It was also mentioned that there are no aromatic amines or unsaturated aliphatic or aromatic amines in open literature for degradation study including CO_2 capture technology. These amines have better absorption capacity with better resistance to degradation.

CONCLUSION

Amine degradation is an ongoing research area till date, as there are many unknown areas to be discovered. Recovery techniques are still being developed to improve recovery efficiencies, reduce environmental impacts and operating problems of the reclaiming units. The aforementioned contents of this review paper highlighted very important and recent information regarding alkanolamines degradation, degradation path ways, degradation products and effect of degradation.

RECOMMENDATION

The author would like to recommend working with three component amine (aliphatic and aromatic) blends for decreasing degradation, amine losses, corrosion and miscellaneous side reaction. Many researches and experiments were conducted on degradation but there is no paper on heterocyclic aliphatic and heterocyclic aromatic amines. The author also predicted that this amine also has the best thermal stability and resistance to degradation properties. Therefore, we have to take this

information into consideration and implement accordingly. PZ has become an ideal solvent because, it has two amine functional groups in its structure. So, the author recommends working with higher molecular weight polyamine (cyclic and straight) compounds.

ACKNOWLEDGEMENTS

Abbreviations: DGP, Degradation products; **HSS,** heat stable salts; **EG,** ethylene glycol; **TEA,** triethanolamine; **PZ,** piperazine; **MEA,** monoethanolamine; **THEED,** triethylenediamine; **HEI/HEIA,** hydroxyethylimidazolidone or 1-(2-Hydroxyethyl)-2-imidazolidinone; **MEA,** monoethanolamine; **AMP,** aminomethyl propanol; **DGA,** diglycolamine; **HEP,** hydroxyethyl piperazine; **BHEED,** N,N-Bis(hydroxyethyl) ethylnediamine; **DIPA,** di-isopropanolamine; **DEA,** diethanolamine; **BHEP,** N,N-Bis(hydroxyethyl)-piperazine; **HEOD,** hydroxyethyl-oxazolidone; **HEI,** hydroxyethyl-imidazolidone; **THEED,** N,N,N-Tris(hydroxyethyl) ethylenediamine; **BHEI,** N,N-Bis(hydroxyethyl) imidazolidone; **DEAC,** diethanolamine carbamate; **MEAC,** monoethanolamine carbamate; **DEADTCS,** diethanolamine dithiocarbamate; **AEEA,** aminoethylethanolamine; **DEA,** diethanolamine; **MDEA,** methyldiethanolamine; **NG,** natural gas; **HEEDA,** hydroxyethyletylenediamine; **LPG,** liquefied petroleum gas; DGA, diglycolamine; **BHEEU,** N,N-Bis(hydroxyethoxy-ethyl)urea; **BHEETU,** N,N-Bis(hydroxyethoxy-ethyl)thiourea; **HPMO,** hydroxypropylmethyl-oxazolidone; **TMPDA,** N,N,N′,N′-Tetramethylpropylene diamino; **TMBDA,** N,N,N′,N′-Tetramethylbutylene diamino; **PMDETA,** N,N,N′,N′,N″-Pentamethyl diethylene triamine; **PMDPTA,** N,N,N′,N′,N″ -Pentamethyl dipropylenetriamine; **TMEDA,** N,N,N′,N′-Petramethyl ethylenediamine; **NMR,** nuclear magnetic resonance; **GC-MS,** gas chromatography mass spectrometer; **GC,** gas chromatography; **HPLC,** high performance liquid chromatography; I**C,** ion chromatography; **FTIR,** Fourier transform infrared spectrometer; **HPLC-RID,** high performance liquid chromatography-refractive index detector; **CE-DAD,** capillary electrophoresis-Diode array detect.

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