ROLE OF ACIDS IN THE DEGRADATION OF ALKANOLAMINE DURING CO₂ AND H₂S REMOVAL PROCESS

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ABSTRACT

The formation of organic acid and inorganic acids in CO_2 and H_2S removal process are common phenomenon. Amines are basic in nature, which react easily with the acidic components to form heat stable salts and other degradation products. Heat stable salt and degradation products are problematic in the operation of CO_2, H_2S removal unit, as they reduce the solvent capacity to absorb CO_2 and H_2S, cause corrosion, foaming and solvent losses. This paper gives an insight on the degradation of amine solvent due to these acidic components and highlights the latest findings and research work carried out in this area of study.

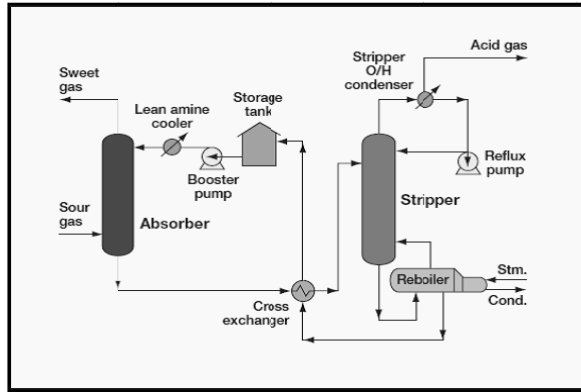*Keywords: acid; degradation; amine; alkanolamine; absorption; heat stable salt*

1. INTRODUCTION

Amines and alkanolamines are widely used in the natural gas refining for the sweetening of sour gas by absorbing the CO_2 and H_2S acidic gases. During the absorption process amine are highly degraded by this acidic oxide as a result amine loses its capacity to absorb these acidic gases. All acidic gases of natural gas composition play an important role to form amine to aldehyde and acids. Oxygen directly oxidized the amine and converted into carbonyl compounds like aldehyde or ketone or acid compound. Aldehydes react with water; in aqueous solution of formaldehyde is hydrated [1]. Aldehydes also react readily with primary amines. These reactions would not be significant with tertiary amines. In aqueous solution of monoethanolamine, formaldehyde will be present as an equilibrium mixture primarily in the form of imine with some hydrated aldehyde, carbinolamine, and aminal. Similar reactions can occur with other aldehydes such as hydroxyacetaldehyde. The imine formed from primary or secondary amines such as MEA may be subject to similar attack by radical oxidants. The presence of formaldehyde may also facilitate the oxidation of the amine molecule. Other less compounds easily hydrated to aldehydes, such as acetaldehyde and hydroxyacetaldehyde, react at room temperature with oxygen to produce the corresponding organic acid [2, 3]. The oxidation ususally takes place by a free radical chain mechanism. An initiator extracts a H from the α carbon to produce a free radical. The radical reacts with O₂ to produce a peroxyacid radical. The peroxyacid radical reacts with aldehyde to propagate the reaction with the production of the aldehyde

radical and a peroxyacid. So the prevention of amines loss is the major focus of interest for the chemical engineer. The prevention of amine losing by acid is the one of the condition for successful plant operation. This prevention of amine loss is also the key of economical benefit. Hence, to identify the alkanolamines degradations are important. Amine degradation compounds are quantified by chromatographic methods. Identification of degradation products is performed with several analytical methods like GC/MS, IC and HPLC etc. In some cases, synthesis of molecules is necessary to confirm structure of degradation products. The highest molecular weight compounds are identified with a high resolution mass spectrometry technique (FT-ICR/MS) with electrospray ionization (ESI). In some cases, NMR analyses are useful to determine compound structure. Formic, glycolic, acetic and oxalic acids, nitrite and nitrate are quantified by ion chromatography. The role of these acids and degradation path way was critically reviewed and a brief discussion was given by the following representation.

2. 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 sour gas sweetening plant was configured with absorber and regenerator. The temperature range is

40-60°C and 100-120°C at the absorber and the stripper respectively. Mainly amine solvents are used as absorbents for sweetening natural gas and for prolong use of this solvent that is transferred to the stripper by means of regenerating absorbed gases. Figure-1 represents a sweetening process of sour gas.

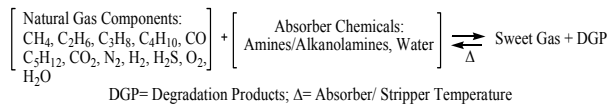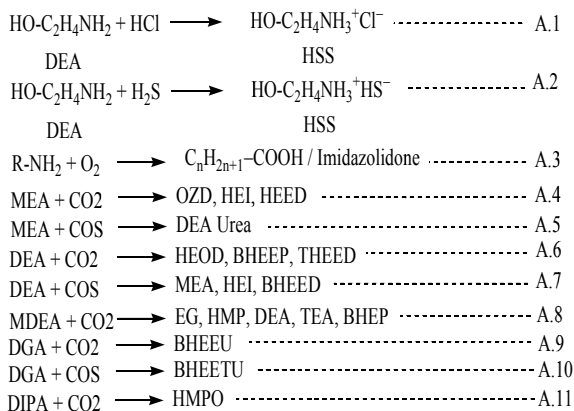Amines/Alkanolamines + Sour Gas → Swwet Gas

$$\left[\begin{array}{l}\text{Natural Gas Components:}\\ CH_4, C_2H_6, C_3H_8, C_4H_{10}, CO\\ C_5H_{12}, CO_2, N_2, H_2, H_2S, O_2,\\ H_2O\end{array}\right] + \left[\begin{array}{c}\text{Absorber Chemicals:}\\ \text{Amines/Alkanolamines, Water}\end{array}\right] \underset{\Delta}{\rightleftarrows} \text{Sweet Gas + DGP}$$

DGP= Degradation Products; Δ= Absorber/ Stripper Temperature

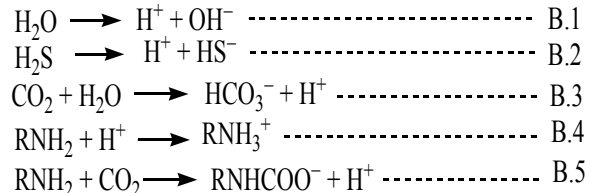**Figure. 1: Typical CO_2 absorption and desorption process [4]**

Sour gas components react with amine solvent during absorption-desorption cycles gradually at higher and lower temperature and some of these reactions (A.1 to A.11) are given in the following to show how DGP is formed [5].

$$HO\text{-}C_2H_4NH_2 + HCl \longrightarrow HO\text{-}C_2H_4NH_3^+Cl^- \quad \cdots\cdots\cdots \text{ A.1}$$
$$\text{DEA} \qquad\qquad\qquad\qquad \text{HSS}$$
$$HO\text{-}C_2H_4NH_2 + H_2S \longrightarrow HO\text{-}C_2H_4NH_3^+HS^- \quad \cdots\cdots\cdots \text{ A.2}$$
$$\text{DEA} \qquad\qquad\qquad\qquad \text{HSS}$$
$$R\text{-}NH_2 + O_2 \longrightarrow C_nH_{2n+1}\text{-}COOH / \text{Imidazolidone} \quad \cdots\cdots \text{ A.3}$$
$$MEA + CO2 \longrightarrow \text{OZD, HEI, HEED} \quad \cdots\cdots\cdots \text{ A.4}$$
$$MEA + COS \longrightarrow \text{DEA Urea} \quad \cdots\cdots\cdots \text{ A.5}$$
$$DEA + CO2 \longrightarrow \text{HEOD, BHEEP, THEED} \quad \cdots\cdots \text{ A.6}$$
$$DEA + COS \longrightarrow \text{MEA, HEI, BHEED} \quad \cdots\cdots \text{ A.7}$$
$$MDEA + CO2 \longrightarrow \text{EG, HMP, DEA, TEA, BHEP} \quad \cdots\cdots \text{ A.8}$$
$$DGA + CO2 \longrightarrow \text{BHEEU} \quad \cdots\cdots\cdots\cdots \text{ A.9}$$
$$DGA + COS \longrightarrow \text{BHEETU} \quad \cdots\cdots\cdots\cdots \text{A.10}$$
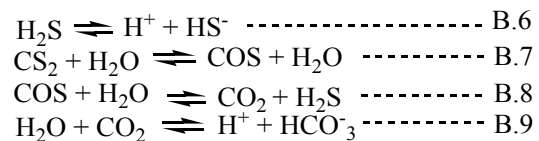$$DIPA + CO2 \longrightarrow \text{HMPO} \quad \cdots\cdots\cdots\cdots \text{A.11}$$

3. BASIC DEGRADATION CHEMISTRY

Degradation products are contaminants in solution that are derived from the breakdown of the base amine molecule and often caused reversibly and irreversibly to form totally different chemical species. Examples of

degradation products are ethylenediamine derivatives (THEED) [6], which can form when CO_2, COS or O_2 are in an amine system. The basic chemistry of degradation of alkanolamine is explained in the open literature [7] and these are given below. 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.

$$H_2O \longrightarrow H^+ + OH^- \quad \cdots\cdots\cdots\cdots \text{ B.1}$$
$$H_2S \longrightarrow H^+ + HS^- \quad \cdots\cdots\cdots\cdots \text{ B.2}$$
$$CO_2 + H_2O \longrightarrow HCO_3^- + H^+ \quad \cdots\cdots\cdots \text{ B.3}$$
$$RNH_2 + H^+ \longrightarrow RNH_3^+ \quad \cdots\cdots\cdots \text{ B.4}$$
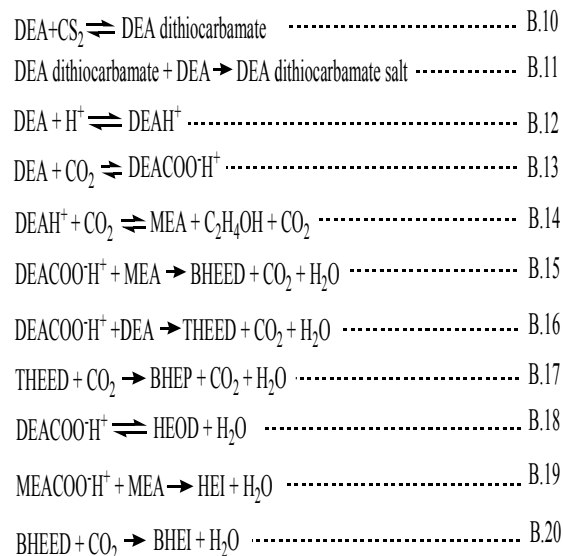$$RNH_2 + CO_2 \longrightarrow RNHCOO^- + H^+ \quad \cdots\cdots \text{ B.5}$$

The same reaction is also explained in the literature [8-10] for DEA degradation. These reactions are as follows. Hydrogen sulfide emitted hydrogen ion (Eq. B.6) in water and carbon dioxide as well as carbonyl sulfide and produces COS and H_2S respectively (Eq. B.7). This reaction causes additional reactions with DEA molecule.

$$H_2S \rightleftharpoons H^+ + HS^- \quad \cdots\cdots\cdots \text{ B.6}$$
$$CS_2 + H_2O \rightleftharpoons COS + H_2O \quad \cdots\cdots \text{ B.7}$$
$$COS + H_2O \rightleftharpoons CO_2 + H_2S \quad \cdots\cdots \text{ B.8}$$
$$H_2O + CO_2 \rightleftharpoons H^+ + HCO_3^- \quad \cdots\cdots \text{ B.9}$$

DEA molecule directly reacts with CS_2 and successively produces DEA thiocarbamate salt (Eq. B.10 & B.11). On the other hand it produces carbamate with CO_2 (Eq. B.13). DEA carbamate reacts with MEA and DEA and forms BHEED and THEED respectively. These two DGP further form 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 because the author assume that it has better absorption capacity. It is also assume that any amine system where higher molecular weight compound break down into lower molecular mass amine like MDEA or DEA to MEA that process will rich at the high absorption rate. Alkanolamines are oxidized and form aldehyde or ketone then formed acid. This acid finally forms HSAS. So to protect the formation of HSAS the intermediate reaction should be controlled at first. 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 over view of the reaction pathways of DEA are

mentioned below.

$$DEA + CS_2 \rightleftharpoons DEA \text{ dithiocarbamate} \quad \text{----------} \quad B.10$$

$$DEA \text{ dithiocarbamate} + DEA \rightarrow DEA \text{ dithiocarbamate salt} \quad \text{----------} \quad B.11$$

$$DEA + H^+ \rightleftharpoons DEAH^+ \quad \text{----------} \quad B.12$$

$$DEA + CO_2 \rightleftharpoons DEACOO^-H^+ \quad \text{----------} \quad B.13$$

$$DEAH^+ + CO_2 \rightleftharpoons MEA + C_2H_4OH + CO_2 \quad \text{----------} \quad B.14$$

$$DEACOO^-H^+ + MEA \rightarrow BHEED + CO_2 + H_2O \quad \text{----------} \quad B.15$$

$$DEACOO^-H^+ + DEA \rightarrow THEED + CO_2 + H_2O \quad \text{----------} \quad B.16$$

$$THEED + CO_2 \rightarrow BHEP + CO_2 + H_2O \quad \text{----------} \quad B.17$$

$$DEACOO^-H^+ \rightleftharpoons HEOD + H_2O \quad \text{----------} \quad B.18$$

$$MEACOO^-H^+ + MEA \rightarrow HEI + H_2O \quad \text{----------} \quad B.19$$

$$BHEED + CO_2 \rightarrow BHEI + H_2O \quad \text{----------} \quad B.20$$

4. ACID FORMATION REACTION IN AMINE SYSTEM

The reaction in this scheme was proposed to account for the presence of all the anions observed in this study. This acid formation mechanism could be applied to any alkanolamine. Also, it was noted that although the acid form of acetic, formic, glycolic, glyoxalic, and oxalic acids are shown in the following reaction, each of these anions are almost completely ionized to the amine heat stable salt in basic solutions. The literature [11] cited a oxidation reaction of MEA which are as follows.
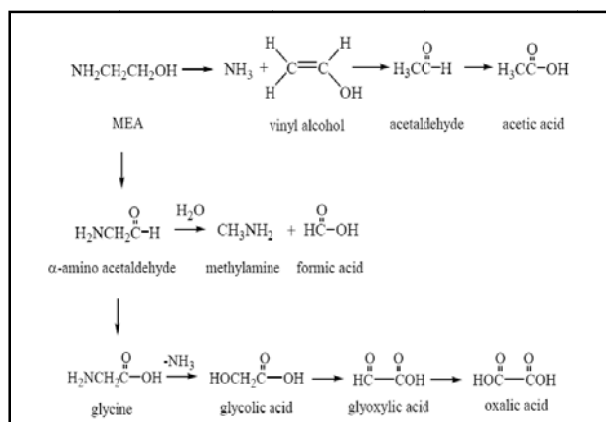
5. TYPICAL HSS IN AMINE SYSTEM

Heat stable salt (HSS) formation is another form of active amine loss. The amine and an acid form a salt that cannot be regenerated in the stripper [12, 13]. Strong acid anions such as formate, acetate, thiosulfate, thiocyanate, and chloride can tie up an amine molecule

to form a salt that is not capable of being regenerated by the addition of heat and are thus referred to as Heat Stable Salts. Not only do they tie up the amine and thereby reduce the acid gas carrying capacity, but they are also considered corrosive. However, there is still a considerable amount of confusion in the industry over the term "Heat Stable Salt". Some properties of common HSS is mentioned in Table -01 below.

Table-01: Common HSS in amine system [14]

Name of Ions	Chemical Formula	Origin of HSS anions	Limit ppm
Nitrate	NO_3	Inorganic	-
Nitrite	NO_2	Inorganic	-
Formate	CHO_2	Organic	500
Oxalate	C_2O_4	Organic	250
Acetate	$C_2H_2O_2$	Organic	1000
Sulfate	SO_4	Inorganic	500
Sulfite	SO_3	Inorganic	500
Phosphate	PO_4	Inorganic	-
Thiosulfate	S_2O_3	Inorganic	10,000
Thiocyanate	CNS	Inorganic	10,000
Glycolate	$C_2H_3O_3$	Organic	500
Malonate	$C_3H_3O_3$	Organic	500
Succinate	$C_4H_5O_4$	Organic	1000
Chloride	Cl	Inorganic	500

6. SPECIFIC DEGRADATION PRODUCTS BY ACID

While Heat Stable Salts (HSS) are common to all amine solvents, degradation products are solvent-specific [6, 15-17]. A description of common degradation products found in various gas treating solvents follows.

Formamides

N-formyl amines (formamides) are degradation products generally found in gas treating solutions that are based on primary and secondary amines [18]. Under certain conditions all primary and secondary amines react with the formic acid in solution (via dehydration) to form n-formyl amines. The data from process solutions containing formate as a HSS anion show that the following equilibrium relationship exists in the solution between the formate HSS and the n-formyl MEA (MEA-F) [19].

Formic Acid + MEA ⇔ MEA-F + Water

Since the above equation represents equilibrium, it is also possible to hydrolyze MEA-F back into MEA and

formic acid. The heat and water present in the stripper of the amine unit will generate a new equilibrium if removing one of the above components disturbs the balance of the equation.

HEED

HEED is a degradation product of MEA from reactions with CO_2. There is a wealth of literature on the reaction mechanisms and the corrosive nature of HEED [20]. While much of the literature has focused on MEA in CO_2 service only, HEED has been found in many combined systems treating H_2S and CO_2.

HEEU

HEEU is a degradation product of MEA that is not that well known since most of the literature has focused on degradation in CO_2 service. HEEU is formed via the same reaction pathway as HEED when COS is present in the gas [21].

Polymers

We generally find polymers when HEED, is present in MEA systems treating H_2S and CO_2. These polymers are formed from the reaction of HEED with MEA molecules to make longer chained ethylenediamines [22]. We also find polymers when THEED is present in DEA systems treating H2S and CO_2 [22].

BHEEU

BHEEU is an inert degradation product of DGA which formed in the presence of COS and CO_2 [21]. .Formation of BHEEU can be reversed by thermal reclaiming.

Morpholine

This is an inert degradation product of DGA that, while rare, can occur when the solution is subjected to high temperatures.

THEED

THEED is a well-known degradation product of DEA from reactions with CO_2. There is a wealth of literature on the reaction mechanisms and the corrosive nature of THEED [20, 21]. While much of the literature has focused on DEA in CO_2 service only, THEED has been found in combined systems treating H_2S and CO_2.

Bis-HEP

Bis-hydroxyethyl piperazine (Bis-HEP) is a well-known degradation product of DEA from reactions with CO_2. There is a wealth of literature on the reaction mechanisms of bis-HEP [20, 21]. While much of the literature has focused on DEA in CO_2 service only, bis-HEP has been found in combined systems treating H_2S and CO_2.

MEA

In the presence of certain chemical compounds (oxygen) or intermediates, it is possible to degrade or break down the DEA molecule to simpler amines. Monoethanolamine (MEA) is one of the simpler amines that may be formed from DEA degradation. It is important to monitor the level of MEA in the circulating DEA system due to Amine Stress Corrosion Cracking (ASSC) concerns associated with MEA. MEA will also generally further degrade in the system.

Bicine

Bis-(hydroxyethyl) glycine (Bicine) is a degradation product formed in the presence of DEA and unstable chemical intermediates, and is considered corrosive [23, 24].

DIPA-OX

Hydroxypropylmethyloxazolidone (HPMO or DIPA-OX) is a well-known degradation product of DIPA from reactions with CO_2. There is a wealth of literature on the reaction mechanism of DIPA-OX [20, 21, 25]. The literature also states that DIPA-OX is the endpoint of DIPA degradation in CO_2 service (due to steric hindrance), so polymers of DIPA are not supposed to be formed like they are with MEA and DEA.

MDEA Fragments

MDEA in Tail Gas Treating units (TGTU), Acid Gas Enrichment units (AGE), and in some main amine systems should be monitored for MDEA fragments. These include MMEA, DEA, Bicine and C^{2+} HSS anions [26]. It is also important to note that as ethanolamines (from MDEA degradation) accumulate in the solvent, they will generally undergo further degradation to compounds listed in the above sections. The presence of these primary and secondary amines may affect the gas treating selectivity of the amine solution.

Dimers

The literature states that steric hindrance prevents further degradation of DIPA-OX to diamines ("dimers"). However, we generally do find dimers in Sulfinol-D systems treating H_2S and CO_2. These "dimers" are similar to the diamines found in MEA and DEA systems, and are likely formed via the same pathway.

TIPA

TIPA may be found in systems treating H_2S and CO_2 utilizing Sulfinol-D, when evidence of oxygen degradation is present. Literature shows that when amines degrade they generally form simpler amines, but sometimes these simpler amines react with the base amine molecule (or others) to form a more complex amine [27].

7. COMMON DEGRADATION PRODUCTS AND EFFECT

All alkanolamine degradation products are not same in behavior, some of these are acidic and some of these are alkaline based. Depending on the nature of the degradation products these are classified as follows.

7.1 Acidic degradation product

Acidic degradation products are highly corrosive for plant unit, thus metallic unit of the gas sweetening plant is highly interactive by this product. So the acidic degradation products are very harmful among all degradation products. Heat stable salts are the common degradation products of amine stripping system and these are potentially corrosive. All of these amines degraded and formed carboxylic acids. These acids are capable of causing further chemical reaction with miscellaneous degradation products. By this reaction the concentration of contaminants increases continuously during absorption-desorption cycles and finally shows operational problems.

7.2 Basic degradation product

The alkaline degradation products are less corrosive than acidic or some of these are noncorrosive but both still have a bad impact on plant operation or even the neutral DGP has the same effect too. It increases the viscosity and as a result it highly inhibits the solution flow rate. This lower flow rate should affect the efficiency of the plant [28]. To accelerate the plant lower flow rate to satisfactory flow rate, high energy consumption is required. For this reason no degradation products are expected.

7.3 Ionic degradation product

The degradation product which contains charge at the chain end and it may be positive or negative these are defined as ionic degradation products. The literature is citied its effect on the plant performance [8, 29, 30]. Ionic degradation products are more porn to affect the plant performance because it is easily react with the components and form miscellaneous reaction products.

7.4 Polymeric degradation product

Many articles reflect a lot of information on polymeric degradation products but there is no specific polymer formation degradation reaction [31-33]. Polymeric degradation products identified by GC-MS detection may be neutral or living. Living polymer means it contains a functional group at the chain ends of the molecule which are capable of causing further chemical reaction with acidic oxide or any reactive unit. The literature cited very inadequate information regarding the polymerization reaction mechanism though it has a satisfactory detection report. Wide ranges of research on polymerization reaction are suggested to recover this literature gap. Literature [7] focused that THEED, Bicine, HSS, HE-Sarcocine, HEED, HEOD, BHEED and THEED are corrosive compounds [31, 34]. Actually these are corrosive because all of these are acidic or basic or contain a living functional group or oxazolidone ring at the chain end or in its structure.
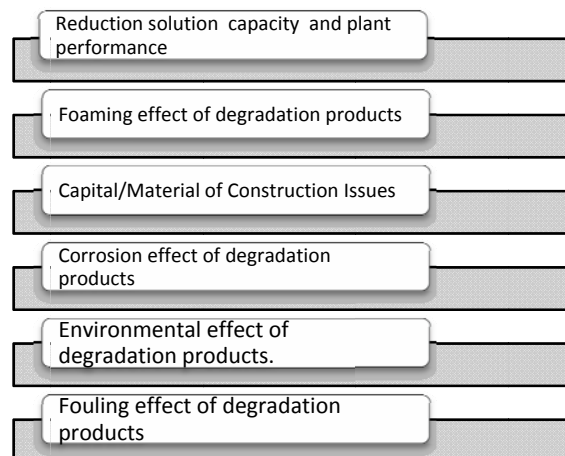
7.5 Neutral Degradation product

Neutral degradation products having no active functional group are very harmful for fouling effect. These degradation products are inactive and just move towards the entire solution direction. It also makes the solution more viscous. Neutral degradation products having no movement so there is a great probability to adhering with plant pipelines, as a result that place easily corrode or destroy. Carl and Haws studied the effect of neutral degradation products [35]

7.6 Volatile degradation product

Volatile degradation products are highly harmful to the environment. Generally these gases cause green house effect, world climate change and so on. The effects of the amine were well conducted in the literature [36] last year.

7.7 Common effect of DGP

The foaming behavior of degradation products was conducted by Thitakamol and Veawab [30, 37]. Corrosion behavior of degradation products were conducted by Dawodu and Meisen [31] and also conducted by the researchers [34, 36]. The recent article [34] pointed out several problems which occurred due to irreversible degradation reaction and mentioned below.

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

8. CONCLUSION

During the sour gas sweetening process a lot of solvent are losses by amine degradation. The

degradation products arises various difficulties and as a result the remediation of this problem has become a major focus of interest for the last few decades. HSAS neutralization techniques (vacuum distillation, electrodialysis, ion exchanges) are still being developed to improve plant efficiencies and reduce operation problems.

The literature mostly cited the heat stable salt and its minimization. HSAS are basically the reaction products of acid and amine. Amine is the main solvent; on the other hand an acid is the by product, if we control the acid formation in amine system then automatically reduces the HSAS formation. Acids can also be converted to acid amides by adding some additives. Because amides contain $CONH_2$ functional group this is capable to capture more acid gases. So we need further research on it to recover the research gap. The author suggested the acid remediation by converting into amides compound. Author also would like to put emphasis for the minimization of the acidic content inside the solution. The above mentioned contents of this review paper highlighted very important and recent information regarding alkanolamines degradation by acid. Knowledge of the reaction mechanism aids the development of procedures to minimize degradation or purify partially degraded solutions. Therefore, the overall representation would help to understand the role of both inorganic and organic acid on amine degradation.

ACKNOWLEDGEMENT

ABBREVIATIONS

NG	Natural gas
DIPA	Di-isopropanolamine
DEA	Diethanolamine
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
DGP	Degradation product
DGA	Diglycolamine
HSS	Heat stable salts
HSAS	Heat stable amine salts
AMP	Aminomethyl propanol
HEP	Hydroxyethyl piperazine
BHEED	*N,N*-Bis(hydroxyethyl) - ethylnediamine
BHEP	*N,N*-Bis(hydroxyethyl)-piperazine
HEOD	Hydroxyethyl-oxazolidone
THEED	*N,N,N*-Tris(hydroxyethyl)- ethylenediamine
BHEI	*N,N* Bis (hydroxyethyl)- imidazolidone
BHEEU	*N,N*-Bis(hydroxyethoxy-ethyl)urea
NMR	Nuclear magnetic resonance
GC-MS	Gas chromatography mass spectrometer
HPLC	High performance liquid chromatography
IC	Ion chromatography
FTIR	Fourier transforms infrared resonance spectrometer
HPLC-RID	High performance liquid chromatography-refractive index detector

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