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Development of A Novel Reclaiming Process for Degraded Solvents and Glycols from Industrial Gas Processing and Purification

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Development of A Novel Reclaiming Process for Degraded Solvents and Glycols from Industrial
Gas Processing and Purification

by

Huitian Ju

A THESIS

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Abstract

Densities, viscosities, refractive indices and electrical conductivities of both artificial degraded and industrial degraded MEA solutions were measured at standard temperature of 298.15 K or 293.15 K. These measurement data are not currently available for the degraded MEA solutions and the reported values are particularly important for monitoring solvent quality and plant performance.

A new reclaiming process was developed to continuously separate degradation products and other types of impurities from the solvent. The detailed analysis of the feed stream, the recovered product stream, and the waste stream showed that this novel reclamation technology is capable of removing most of undesirable impurities and restoring the solvent to its original purity at a high recovery rate. The data would be useful for scaling-up and designing the commercial reclaimers, which can meet the solvents' cleanup targets at low expenditures, low energy consumption, and minimum waste for disposal.

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Credit also goes to Dr. Ahmed Aboudheir, Dr. Walid ElMoudir and Pawan Kundra from HTC Pureenergy Inc., who are more knowledgeable and skilled in the reclamation setup than I could ever dream of being. Without their help and insight, I would have spent way more time trying to set up my equipment.

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Last but not least, I need to thank all my friends who have been very supportive and helpful during my difficult time. Their companionship made my time in Calgary very unforgettable.

Dedication

This thesis is dedicated to my beloved parents for their unconditional love and support of all time.

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List of Symbols, Abbreviations and Nomenclature

Symbol	Definition
A_0	Fitting parameter in Equation (3.4)
A_1	Fitting parameter in Equation (3.4)
A_2	Fitting parameter in Equation (3.4)
A_3	Fitting parameter in Equation (3.4)
k	Electrical conductivity [$\text{mS}\cdot\text{cm}^{-1}$]
M_A	Mass of species A [g]
M'_{DP}	Mass of other degradation products which are not heat stable salts (HSSs)
MW_A	Molecular weight of species A
n_A	Amount of species A [mole]
n_D	Refractive index
P	Pressure [Pa]
T	Temperature [k]
w_{amine}	Amine mass fraction
w_{DP}	Total degradation products mass fraction
w'_{amine}	Solvent concentration (mass fraction)
w'_{HSS}	Heat stable salts (HSSs) content (mass fraction)
w'_{Water}	Water content (mass fraction)

Greek Symbols	Definition
α	CO ₂ loading
ρ	Density [kg·m ⁻³]
η	Viscosity [mPa·s]

Abbreviation	Definition
AAD	Average absolute percentage deviation
AEHEIA	N-(2-aminoethyl)-N'-(2-hydroxyethyl)-imidazolidinone
Al	Aluminum
ASTM	American Society for Testing and Materials
B	Boron
BHEI	1,3-bis(2-hydroxyethylamino)-1H-imidazol-3-ium
BHEOX	N,N'-bis(2-hydroxyethyl)-oxalamide
Bis-HEP	Bis-hydroxyethylpiperzine
Ca	Calcium
CFCs	Chlorofluorocarbons
CH ₄	Methane
CO ₂	Carbon dioxide
DEA	Diethanolamine
DEG	Diethylene glycol
DHU	N-N-di(hydroxyethyl)-urea
DP	Degradation products
EG	Ethylene glycol
Fe	Iron
GC-MS	Gas Chromatography - Mass Spectrometry

GHG	Greenhouse gas
HCl	Hydrochloric acid
HDPE	High-density polyethylene
He	Helium gas
HEA	N-(2-hydroxyethyl)-acetamide
HEED	Hydroxyethylethylenediamine
HEEDA	N-(2-hydroxyethyl)-ethylenediamine
HEEU	Hydroxyethylethylenediamine Urea
HEF	N-(2-hydroxyethyl)-formamide
HEGly	N-(2-hydroxyethyl)-glycine
HEHEAA	N-(2-hydroxyethyl)-2-(2-hydroxyethylamino)-acetamide
HEI	N-(2-hydroxyethyl)-imidazole
HEIA	N-(2-hydroxyethyl)-imidazolidinone
HEO	2-(2-hydroxyethylamino)-2-oxoacetic acid
HEPO	4-(2-hydroxyethyl)-piperazin-2-one
HES	N-(2-hydroxyethyl)-succinimide
HFCs	Hydro fluorocarbons
HHEA	2-hydroxy-N-(2-hydroxyethyl)-acetamide
HSSs	Heat stable salts
IC	Ionic chromatography
ICP	Inductively Coupled Plasma
K	Potassium
KOH	Potassium hydroxide
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
MEG	Monoethylene glycol
Mg	Magnesium

MMEA	N-Methyl monoethanolamine
Mo	Molybdenum
Na	Sodium
NaOH	Sodium hydroxide
N ₂ O	Nitrous oxide
OPEC	Organization of the Petroleum Exporting Countries
OZD	2-oxazolidinone
Pb	Lead
PFA	Polyfluoroalkoxy
PFCs	Perfluorocarbons
PG	Propylene glycol
SF ₆	Sulphur hexafluoride
Si	Silicon
TEA	Triethanolamine
TEG	Triethylene glycol
THEED	Tris- Hydroxyethylethylenediamine
Zn	Zinc

Chapter 1: Introduction

1.1 Greenhouse Gas Effect and Carbon Dioxide Contribution

Greenhouse gas (GHG) can absorb and emit radiation within the thermal infrared range in the atmosphere. According to Rao and Riahi (2006), the primary GHGs are carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O), hydro fluorocarbons (HFCs), perfluorocarbons (PFCs), chlorofluorocarbons (CFCs) and sulphur hexafluoride (SF₆). The contribution of each GHG to the overall greenhouse gas effect depends on its emission volume and individual greenhouse potential. CO₂ has been considered as one of the most influential greenhouse gases due to its second largest emission volume, following water vapor (Songolzadeh et al., 2014). Predicted by International Panel on Climate Change (IPCC), the atmosphere may contain up to 570 ppmv CO₂ by the year of 2100, as a result of which the mean global temperature will increase by round 1.9 K (Stewart and Hessami, 2005).

Fossil fuel combustion is the main contributor of CO₂ emission to the atmosphere (Quadrelli and Peterson, 2007). Reported by the Organization of the Petroleum Exporting Countries (OPEC, 2010), there would be an increasing demand for energy in the world. Fossil fuels contribute to more than 85 percent of the world energy demand (Yang et al., 2008). As a result, increasing amount of CO₂ will be produced.

1.2 CO₂ Removal Methods

To reduce carbon dioxide emission, various CO₂ removal methods have been under intensive research and development, such as absorption, adsorption, membrane-based separation and cryogenics.

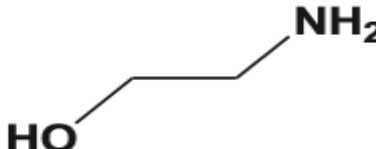
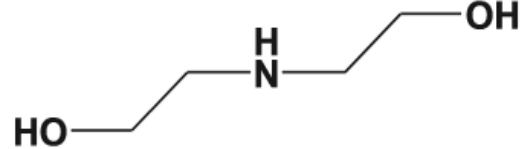
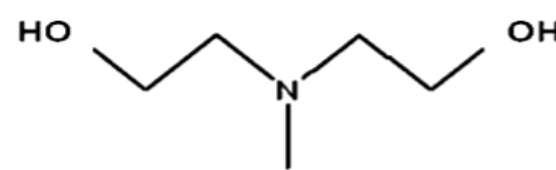
1.2.1 Absorption

Absorption technology uses liquid absorbents to physically and/or chemically absorb the CO₂ gas (Ren et al., 2010). When it is physical absorption, the mass transfer takes place at the interface between the absorbent and CO₂, at a rate depending on the solubility of CO₂ into the absorbent, the working pressure and temperature (Babamohammadi et al., 2014). In a typical physical absorption-desorption process, CO₂ is absorbed under high temperature and low pressure and

desorbed under higher temperature and lower pressure (Rosli et al., 2017). There are several currently existing commercial processes which employ physical absorption, including Selexol, Rectisol, Purisol and Fluor process (Yu et al., 2012). On the other hand, when chemical absorption takes place, chemical reaction happens between the absorbed CO₂ gas and the absorbent. Sometimes, the chemical absorption combines with the physical absorption.

The chemical absorption based on alkanolamine solutions is the most widely developed and ready to use technology. In industry of natural gas, monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA) have been widely employed to capture CO₂ for more than 60 years. The formulae of these three alkanolamines are shown in Table 1.1.

Table 1.1 Formulae of Alkanolamines Commonly Used for CO₂ Capture

Alkanolamine	Formulae
MEA	
DEA	
MDEA	

Alkanolamine solutions can be categorized into three classes depending on how many hydrogen atoms in ammonia are replaced by alkyl groups. Primary alkanolamine arises when only one hydrogen atom is replaced, such as MEA. Secondary alkanolamine such as DEA, has two

hydrogen atoms replaced by alkyl substituents. In tertiary alkanolamine, all three hydrogen atoms are replaced by organic substituents. MDEA is one example.

Chemical absorption using alkanolamine solutions involves the reaction between CO₂ and alkanolamine solvent to form weakly bonded intermediate compounds. The intermediate compounds can be broken down with high temperature and thus release the solvent back (Dumee et al., 2012). The reactions between the alkanolamine solvents (primary, secondary and tertiary) and CO₂ are shown in Table 1.2, according to Awais (2013), Sutar et al. (2012), ElMoudir et al. (2012) and Kierzkowska-Pawlak (2010).

Table 1.2 Reactions between Alkanolamine Solvents and CO₂ Gas

Type of alkanolamine	Reaction
Primary	$2\text{RNH}_2 + \text{CO}_2 \leftrightarrow \text{RNH}_3^+ + \text{RNHCOO}^-$
Secondary	$2\text{R}_2\text{NH} + \text{CO}_2 \leftrightarrow \text{R}_2\text{NH}_2^+ + \text{R}_2\text{NCOO}^-$
Tertiary	$\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3$
	$\text{H}_2\text{CO}_3 + \text{R}_3\text{N} \leftrightarrow \text{R}_3\text{NH}^+ + \text{HCO}_3^-$

1.2.2 Adsorption

Adsorption is a physical and/or chemical process. The adsorption process completes when CO₂ leaves the gas phase and attaches itself to a solid phase. In industry, the total process involves two steps. Firstly, CO₂ is selectively removed from a gas stream by the adsorbent, such as activated carbon, zeolites, alumina or metallic oxides. Then either by reducing pressure or by increasing temperature, the used adsorbent can be regenerated to maintain its high adsorption capability (Yu et al., 2012).

However, adsorption is not suitable for the acid gas removal within a large-scale power plant. Besides, most available adsorbents have low selectivity of CO₂ gas, as a result of which the gas phase must have high CO₂ concentration in order to achieve an efficient gas treatment.

1.2.3 Membrane-based Separation

Membrane-based separation is a relatively new technology. The permeation rates of different constituent species in the gas mixture are diversified. As a result, membranes can act as semi-permeable barriers to selectively remove the target gas of CO₂ from the flue gas stream (Koros and Fleming, 1993; Pfaff and Kather, 2009). There are various types of membrane materials, such as polymeric, inorganic and zeolite.

For membrane-based separation, no regeneration energy is required, and no waste streams are produced. However, the selectivity of this technology is relatively low. What's more, membranes can be easily plugged with impurities in the gas stream.

1.2.4 Cryogenics

Cryogenics is a physical process. By fractional condensation and distillation at low temperature, CO₂ can be liquefied and removed from the gas stream, according to Collaudin and Rando (2000). The captured CO₂ gas comes in the liquid phase, which is better to be transported or injected in the oil reservoir. With the capital expense of refrigeration taken into consideration, cryogenics is suitable to be applied into CO₂ removal when the CO₂ concentration is high in the gas mixture.

1.3 Post-combustion CO₂ Capture Process

In fact, the chemical absorption is the only technology which has gone into the industrial scale since the end of 1970s (Strazisar et al., 2003; Duke et al., 2009). For instance, Aboudheir and ElMoudir (2013), and ElMoudir et al. (2014) reported data and information on two operating plants utilizing the chemical absorption technology based on monoethanolamine solvent to remove CO₂ from flue gas. A typical process flow diagram for post-combustion CO₂ capture from flue gas stream by chemical absorption based on alkanolamine solvents is shown in Figure 1.1.

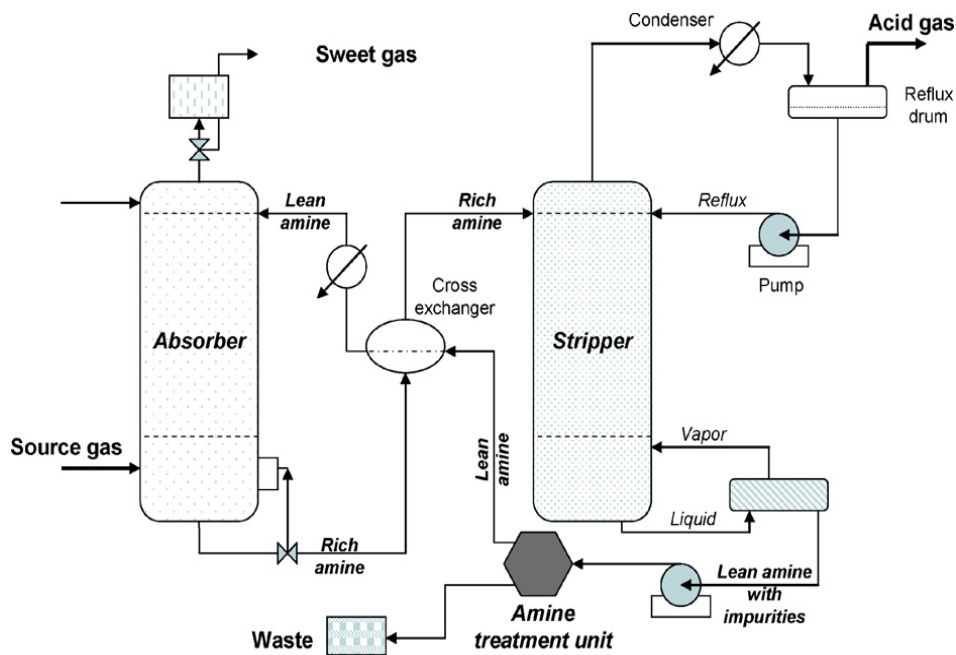
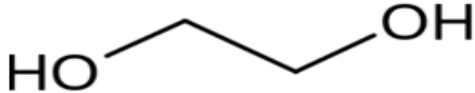
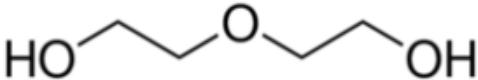
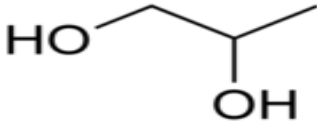
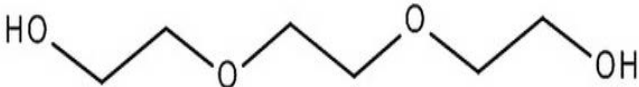


Figure 1.1 Process flow diagram for post-combustion CO₂ capture from flue gas stream by chemical absorption (Dumee et al., 2012)

As can be seen from Figure 1.1, the whole process involves two major steps: absorption and stripping. At first, in a packed or tray column named absorber, the cooled flue gas rich of CO₂ coming from the bottom of the absorber is counter-currently brought into contact with the lean amine solvent (containing small amount of CO₂). After that, alkanolamine solvent is loaded with a large amount of CO₂, as a result of which it becomes CO₂-rich alkanolamine solvent. The treated flue gas which reaches the requirement, will be vented to the atmosphere. Before going to the stripper, the rich solvent exchanges heat with regenerated hot lean amine in a cross-heat exchanger. The heated rich solvent is then sent to another column named stripper which thermally regenerates the alkanolamine solvent by removing the CO₂ gas from the solvent. In the stripper, heat is provided by the stripping steam generated inside a reboiler, and the steam breaks the weak chemical bond between amine and CO₂. The alkanolamine solvent coming down from the stripper, which becomes lean amine solvent due to low CO₂ content after stripping, is regenerated and ready for another absorbing-desorbing cycle. The gas which mainly contains CO₂ and water is released from the top of the stripper and condensed in the overhead condenser to maintain the water balance. Then the pure CO₂ gas is compressed and sent for subsequent transportation and storage.

However, the CO₂ gas flowing to the CO₂ compression unit usually presents a moderate level of moisture, which requires dehydration treatment before going to the export pipeline, in order to prevent potential hydrate formation, two-phase flow and corrosion in the export line. Glycols are also used as antifreeze. Glycols such as monoethylene glycol (MEG), diethylene glycol (DEG), propylene glycol (PG) and triethylene glycol (TEG) are the most widely used. Table 1.3 displays the formulae of these four glycols.

Table 1.3 Formulae of Glycols Widely Used

Type of Glycol	Formulae
MEG	
DEG	
PG	
TEG	

1.4 Degradation of Alkanolamine and Glycol Solvents

1.4.1 Degradation of Alkanolamine Solvents

Alkanolamine solvents, whether they are single, mixed or formulated, are subjected to degradation within the gas purification processes. Exposed to impurities in the flue gas stream such as O₂, NO_x (NO and NO₂) and SO_x (SO₂ and SO₃) in the absorber and high temperature in the reboiler,

alkanolamine solvents can experience chemical and thermal degradation according to Strazisar et al. (2003), ElMoudir et al. (2012) and ElMoudir et al. (2014). After several absorbing-desorbing cycles, the alkanolamine solvents can be loaded with different types of impurities and degradation products.

The major kinds of degradation products which draw wide attention are heat stable salts (HSSs) due to their great impact on the plant equipment and operation. They are formed mainly from the formation of ionic degradation products of organic acids such as acetic and formic acids due to the solvent degradation reactions with O₂ and other impurities (Blanc et al., 1981; Bacon, 1987; Strazisar et al., 2003). Once these organic acids formed, they react immediately with the alkanolamine solvent to form complex salts called heat stable salts (formate or acetate with amine solvent). These salts cannot be thermally broken down and thus fail to release the solvent back, directly leading to the reduced solvent absorption capacity. Other potential degradation products include diamines, urea, imidazolidone and amides.

1.4.2 Degradation of Glycols

Glycols are susceptible to thermo-oxidative degradation reactions which will produce organic acids. Although there is little information about the composition of acidic degradation products, the potential thermo-oxidative degradation products of ethylene glycol (EG) and propylene glycol (PG) include glycolic acid, formic acid, carbonic acid, oxalic acid and acetic acid (Brown et al., 1987).

1.5 Operational Problems Raised by Accumulation of Degradation Products

The accumulation of degradation products can give rise to great operational problems in the whole CO₂ capture process. The potential operating problems and failures are summarized and listed below.

1. Reduced solvent capacity due to the solvent loss and the formation of degradation products (Cummings and Mecum, 2000).
2. Change of the solvent characteristics and performance caused by change of solvent properties, such as density and viscosity.

3. Foaming and increased foaming tendency in the absorber and stripper (Ballard, 1966; Cummings, Smith and Nelsen, 2007; Harston and Ropital, 2007).
4. Corrosivity and increased corrosivity tendency due to the accumulation of corrosive species such as heat stable salts (Ballard, 1966; Cummings and Mecum, 2000; Cummings, Street and Lawson, 2003).
5. Fouling in the heat exchangers and column internals due to corrosion and the accumulation of degradation products (Kohl and Nielsen, 1997).
6. Increased frequency of the replacement of mechanicals and the activated carbon filters due to the accumulation of degradation products and heat stable salts, leading to the increase in the operating and maintenance costs (Kohl and Nielsen, 1997).

1.6 Reclamation Methods

To maintain smooth operations in the plant, degradation products must be removed from the system. Major reclamation technologies include ion exchange, electrodialysis and thermal reclamation. Detailed explanation will be presented in Chapter 2.4.

Ion exchange and electrodialysis are capable of removing only ionized degradation products like heat stable salts. They fail to remove nonionic degradation products, as a result of which some operational problems still exist (ElMoudir et al., 2012).

Thermal reclamation can remove both ionic and nonionic degradation products. Therefore, it is the only feasible option for solvent reclamation. However, compared with the first two reclamation technologies, thermal reclamation consumes more time and energy. What's more, to meet the specific requirement, steam would recycle in the plant by distillation effect, but this can cause an interruption in the water balance (ElMoudir, 2012). Besides, in order to reduce the capital and operational expenditures, the existing thermal reclaiming technology needs further improvements in increasing the solvent recovery rate, reducing the solvent loss and utility consumptions, eliminating the contaminants from the recovered solvent, and extending the operating lifespan.

1.7 Objectives

This thesis has two research goals. Firstly, have a better understanding of the impact of solvent concentration, degradation products content and CO₂ loading on the physical properties of MEA solvents. Besides, develop a new reclaiming process for degraded alkanolamine and glycol solvents. To achieve these goals, the research work demonstrated in this thesis was conducted in accordance with the following specific objectives:

- Measure densities, viscosities, refractive indices and electrical conductivities of both artificial degraded and industrial degraded monoethanolamine (MEA) solutions at standard temperature of 298.15 K or 293.15 K to understand the impact of solvent concentration, degradation products content and CO₂ loading on the physical properties of MEA solvent
- Design and develop a continuously operating reclaiming setup for the reclamation of the degraded alkanolamine and glycol solvents from industrial gas processing and purification process
- Reclaim the degraded solvents of monoethanolamine (MEA) and monoethylene glycol (MEG) from the working plant in Canada to see the reclamation efficiency of the newly developed reclaimer

1.8 Thesis Organization

This thesis is composed of five chapters.

In Chapter 1, an overall scenario of the global carbon dioxide emission and various kinds of CO₂ capture technologies are reviewed. The knowledge of post-combustion CO₂ capture using alkanolamine solvents as absorbents and glycols for dehydration is introduced. The operational problems raised by the accumulation of degradation products during the process of CO₂ capture are put forward. The pros and cons of three most frequently used reclamation technologies are also displayed. Based on all the discussions, the motivation for this study is delivered and the objectives are stated.

Chapter 2 presents the literature review of degradation of alkanolamine solvents and glycols. The kinds of degradation products that normally exist and the reasons why they would be generated

are discussed. It is also reviewed what operational problems could be raised by the accumulation of degradation products. The reason why thermal reclamation technology stands out among the most widely used reclamation methods (ion exchange, electro dialysis and thermal reclamation) and the problems of the currently existing thermal reclamation technology are explained as well.

Chapter 3 shows the physical properties (density, viscosity, refractive index and electrical conductivity) of degraded MEA solvents at standard temperature of 298.15 K or 293.15 K. Two kinds of degraded MEA solvents were employed in this work: artificial degraded and industrial degraded. Empirical correlations were developed to allow the degradation level roughly estimated with a simple property measurement without any complex chemical analysis or extra costs.

In Chapter 4, the novel thermal reclaimer is introduced. To demonstrate the efficiency of this reclaimer, degraded solvents of monoethanolamine (MEA) and monoethylene glycol (MEG) were reclaimed in this reclaimer. The detailed analysis of the feed stream, the recovered product stream, and the waste stream showed that this reclaimer was able to remove most of undesirable impurities from degraded alkanolamine or glycol solvent and restore the solvent to almost its original purity at a high recovery rate and minimum energy consumption.

The conclusions and suggestions are discussed in Chapter 5.

Chapter 2: Literature Review

2.1 Degradation of Alkanolamine Solvents

As illustrated in Chapter 1, alkanolamine solvents can experience two kinds of degradation: thermal degradation and chemical degradation. Chemical degradation falls into two categories: oxidative degradation and carbamate degradation.

2.1.1 Thermal Degradation

Thermal degradation occurs when the working temperature reaches the decomposition temperature of the solvent. However, for most of the alkanolamine and glycol solvents, their decomposition temperatures are usually lower than their boiling points, according to Dow (1962) and Maddox and Morgan (1998). Different kinds of solvents degrade at different temperatures. MEA was found to be most sensitive to high temperature. It would thermally degrade at approximately 420.15 K (Dow, 1962). Meisen and Kennard (1982) reported that the thermal decomposition temperature of DEA was higher than that of MEA, up to 477.15 K. It has been found that the thermal decomposition temperature was also related to the solvent concentration. Reported by Dow (1962), diluting solvent with water would increase the thermal decomposition temperature.

Thermal degradation can be eliminated by proper design of the reboiler and hot sections in the CO₂ capture plants. It has been reported that the major thermal degradation products are ammonia, cyclic compounds and polymers (Bacon, 1987).

2.1.2 Oxidative Degradation

Compared with thermal degradation, oxidative degradation is more complicated. Oxidative degradation takes place when the solvent is exposed to the flue gas impurities such as O₂, NO_x (NO and NO₂) and SO_x (SO₂ and SO₃) (Bacon, 1987; Kohl and Nielsen, 1997; Vevelstad, 2013). Hofmeyer et al. (1956) did the study on the reaction between MEA solvents and O₂ and found that the degradation products included formic acid, formamides, ammonia and high molecular weight polymers. Blanc et al. (1981) found that the HSSs formed in the DEA or MDEA system were acetic acid, formic acid, propionic acid and oxalic acid. Bacon (1987) gave the general equation about the reaction between the alkanolamine solvent and O₂, which is shown in Eq. (2.1).



Heat Stable Salts (HSSs)

The major kinds of degradation products which draw the widest attention are heat stable salts (HSSs) because of their great impact on the plant equipment and operation. Currently, there is still confusion over the definition of HSSs. However, the following definition of HSSs is widely accepted: strong acidic anions formed from the degradation of amine can react with amine solvents to form salts that cannot be regenerated by the high temperature in the stripper (Cummings and Smith, 2010). The reactions of HSSs formation for primary, secondary and tertiary alkanolamine solvents are explained in Table 2.1, according to ElMoudir et al. (2012).

Table 2.1 Reactions of HSSs Formation

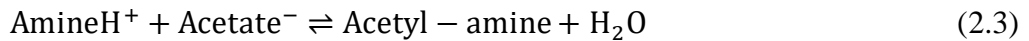
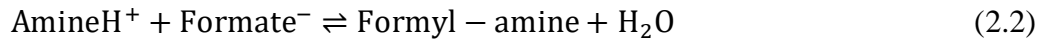
Type of alkanolamine	Reaction (formic acid as an example of the organic acid formed)
Primary	$\text{RNH}_2 + \text{HO}_2\text{CH} \rightarrow (\text{RNH}_3)^+ + (\text{O}_2\text{CH})^-$
Secondary	$\text{R}_2\text{NH} + \text{HO}_2\text{CH} \rightarrow (\text{R}_2\text{NH}_2)^+ + (\text{O}_2\text{CH})^-$
Tertiary	$\text{R}_3\text{N} + \text{HO}_2\text{CH} \rightarrow (\text{R}_3\text{NH})^+ + (\text{O}_2\text{CH})^-$

The cations of all these salts are the protonated amines. Hence these alkanolamine solvents bonded in the HSSs are not capable of capturing CO₂ gas any more. Commonly recognized HSSs include acetate, formate, sulfate, chloride, nitrate, glycolate and nitrite. The accumulation of HSSs in the solvents can result in reduced acid gas absorbing capacity. It can also contribute to corrosion, fouling, plugging and foam stabilization. According to Smith et al. (2009), the recommended level of HSSs for the most trouble-free operations would be 5000 ppm or less.

Other Degradation Products

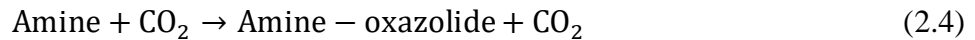
Other degradation products are usually inert molecules with amines being part of them. However, they can be polar or strong chelators of iron, which can cause the corrosion of the system. They can also lead to other problems like increased foaming and fouling.

In a primary or secondary amine system, amines form amides with carboxylic acids. The amides commonly found in the amine system are formamide and acetamide. The formation of these amides can be explained by the following two equations (Cummings and Mecum, 2000).



As can be seen from these two equations, the loss of 1 mol amine results from the formation of 1 mol amide. Temperature, residence time, pH and solvent concentration can affect the formation of amides.

Another kind of degradation product normally found in the primary or secondary amine system is oxazolidone. The formation of oxazolidone is depicted by Eq. (2.4) (Cummings et al., 2003). It can be seen from this equation that the formation of 1 mol oxazolidone can also contribute to the loss of 1 mol amine.



In the system of tertiary amine, amino acids can be formed. According to Cummings et al. (2003), bicine $\{(\text{HOCH}_2\text{CH}_2)_2\text{NCH}_2\text{CO}_2\text{H}\}$ was detected in the MDEA system. Hydroxyethylsarcosine $\{(\text{HOCH}_2\text{CH}_2)\text{N}(\text{CH}_3)(\text{CH}_2\text{CO}_2\text{H})\}$ has been found in the N-Methyl monoethanolamine (MMEA) system (Cummings et al., 2007). Because amino acids are able to hold iron in solution with the effect of H_2S , they can cause corrosion.

2.1.3 Carbamate Degradation

Although the main reaction between alkanolamine solvents and CO_2 gas is the formation of carbamate, which is regenerable under high temperature in the stripper, a small amount of CO_2 can also act as the reactant in the degradation reactions (Ballard, 1966).

For primary amines like MEA, the carbamate degradation products are imidazolidone, diamines and urea (Polderman et al., 1955). MDEA may not degrade under the influence of CO₂ (Kohl and Nielsen, 1997), but after it is protonated, it will still experience carbamate degradation (Critchfield and Rochelle, 1987). As a result, in the mixed solvent of MEA and MDEA, MDEA will be protonated by the protonated MEA, and finally degrade with small portion of CO₂ (Astarita, 1983).

2.1.4 Summary

According to published papers (Dumee et al., 2012; Nurrokhmah et al., 2013; Fytianos et al., 2016; Gouedard et al., 2012; Rey et al., 2013), a summary of the potential degradation products of MEA solvent is presented in Table 2.2.

Table 2.2 Potential Degradation Products of MEA Solvent

Name	Abbreviation	CAS
Formic acid/Formate		64-18-6
Acetic acid/Acetate		64-19-7
Glycolic acid/Glycolate		79-14-1
Oxalic acid/Oxalate		144-62-7
Bicine		150-25-4
Formamide		75-12-7
Acetamide		60-35-5
Formaldehyde		50-00-0
Acetaldehyde		75-07-0
Ammonia/Ammonium		7664-41-7
Sulfate		14808-79-8
Chloride		16887-00-6
Nitrite		14797-65-0
2-oxazolidinone	OZD	497-25-6
N-(2-hydroxyethyl)-ethylenediamine	HEEDA	111-41-1
N-(2-hydroxyethyl)-imidazolidinone	HEIA	3699-54-5

N-(2-aminoethyl)-N'-(2-hydroxyethyl)- imidazolidinone	AEHEIA	No CAS
N-(2-hydroxyethyl)-imidazole	HEI	1615-14-1
N-(2-hydroxyethyl)-formamide	HEF	693-06-1
N-(2-hydroxyethyl)-acetamide	HEA	142-26-7
2-hydroxy-N-(2-hydroxyethyl)-acetamide	HHEA	3586-25-2
N,N'-bis(2-hydroxyethyl)-oxalamide	BHEOX	1871-89-2
4-(2-hydroxyethyl)-piperazin-2-one	HEPO	23936-04-1
N-(2-hydroxyethyl)-glycine	HEGly	5835-28-9
N-(2-hydroxyethyl)-2-(2- hydroxyethylamino)-acetamide	HEHEAA	144236-39-5
1,3-bis(2-hydroxyethylamino)-1H-imidazol- 3-ium	BHEI	461044-72-4
Diethanolamine	DEA	111-42-2
2-(2-hydroxyethylamino)-2-oxoacetic acid	HEO	5270-73-5
N-(2-hydroxyethyl)-succinimide	HES	18190-44-8
N-N-di(hydroxyethyl)-urea	DHU	15438-70-7
Pyrimidine		289-95-2
2-methylaminoethanol		109-83-1
ethanol		64-17-5
Vinyl alcohol		557-75-5
Glycine		56-40-6
Hydroxy-acetaldehyde		141-46-8
Glyoxylic acid/Glyoxylate		298-12-4
Oxalamide		471-46-5
2-methyl-aminoethanol	MMEA	109-83-1
Oxiran		75-21-8

2.2 Degradation of Glycols

Currently, there is limited information about the degradation of glycols in the literature. Besides, the existing findings show different results. It was reported by Collins et al. (1964) that the thermal oxidative degradation products of MEG were expected to include glycolic, glyoxylic, oxalic and formic acids. However, in another study of theirs, only glycolic and formic acids were found and the major degradation products were formic acids. On the contrary, Diegle et al. (1980) reported that glycolic acid was the main acidic degradation product of MEG.

Even fewer findings about the degradation products of PG have been published. According to Sullivan (1980), the glycolic and formic acids would be expected as the degradation products of PG. However, there were no supporting experimental results. The potential thermo-oxidative degradation products of MEG and PG are listed in Table 2.3, according to Rossiter et al. (1983), Diegle et al. (1980) and Beavers et al. (1980).

Table 2.3 Potential Thermo-Oxidative Degradation Products of EG and PG

Potential degradation products of MEG	Potential degradation products of PG
Glycolic acid (HOCH_2COOH)	Lactic acid ($\text{CH}_3\text{CH}(\text{OH})\text{COOH}$)
Glyoxylic acid (HCOCOOH)	Pyruvic acid (CH_3COCOOH)
Formic acid (HCOOH)	Formic acid (HCOOH)
Carbonic acid (HOCOOH)	Carbonic acid (HOCOOH)
Oxalic acid (HOCCOOH)	Oxalic acid (HOCCOOH)
	Acetic acid (CH_3COOH)

2.3 Problems Raised by the Accumulation of Degradation Products

When new or reclaimed solvents are used, the quantity of degradation products must be very low. However, as degradation products accumulate, systems may show some operational problems like reduced solvent capacity, change of solvent properties, foaming, corrosivity, fouling and increased energy demand.

2.3.1 Reduced Solvent Capacity

When degradation takes place, 1 mol degradation products can be formed at the expense of at least 1 mol amine. As a result, the quantity of amine that is available to absorb CO₂ gas from the flue gas decreases. Consequently, this can always directly reduce the working efficiency of the CO₂ capture plant.

2.3.2 Change of the Solvent Properties

As the level of degradation products builds up, the physical and chemical properties of the solvent will change. Solvent physical properties like density and viscosity, are always the major parameters when it comes to the equipment design in the CO₂ capture plant. They are closely related to column diameter, velocity and pressure drop in the column (Stichlmair, 1989), mass transfer correlations and mass transfer area (Wang et al., 2005). When density and viscosity of alkanolamine solvent have been determined, the types of pipes, liquid pumps and heat transfer equipment are accordingly selected and/or designed (Jassim et al., 2007). Therefore, some operational problems may occur in pipes, pumps and heat transfer equipment as well as to the plant instruments when the values of density and viscosity change with the accumulation of degradation products.

2.3.3 Foaming

Foaming is usually the primary indicator of the contamination problems, as it can take place with small amounts of hydrocarbon, degradation products, solid particulates, or injected chemicals like antifoam (Singh et al., 2016). Foaming is a structure of expanded liquid surface area with gas (Cummings et al., 2003). The generation of surface area in the liquid needs energy to overcome the surface tension. Dissolved contaminants and degradation products can help lower the surface tension and thus increase the foaming tendency in the solvent system.

2.3.4 Corrosivity

According to Kittel et al. (2012), various parameters can influence the corrosivity of alkanolamine solvent, including temperature, CO₂ loading, solvent type, and the concentration of the degradation products and contaminants in the solvent. Temperature generally plays an extremely important role in corrosion phenomena. When the operating temperature increases by 10 to 20 K, the corrosion rate is normally doubled (Kittel and Gonzalez, 2014). Once the alkanolamine solutions are loaded with CO₂, they can lead to corrosion, which can be explained by Eq.s (2.5) and (2.6) (ElMoudir, 2012). Increasing the CO₂ loading increases the corrosivity of the solutions (DuPart et al., 1993a, 1993b)



When loaded with the same quantity of CO₂, primary amine is more corrosive than secondary and tertiary amines because it is more difficult to strip CO₂ from primary amine than from secondary and tertiary amines (Kittel et al., 2012). The effect of the degradation products, especially heat stable salts (HSSs) on corrosion, has been well documented through laboratory tests. When the accumulation of degradation products occurs, the system becomes more corrosive.

Kohl and Nielsen (1997) reported that the possible corrosive locations include the bottom of the absorber, rich/lean heat exchangers, stripper, reboiler and reclaimer.

2.3.5 Fouling

With excessive quantity of corrosion products, degradation products and contaminants, fouling can take place. Fouling can lead to poor liquid gas contact in the absorber and reduce the heat transfer performance of the reboiler and hot sections in the plants (Haws, 2001).

2.3.6 Increased Energy Demand

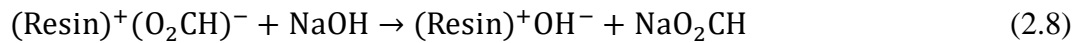
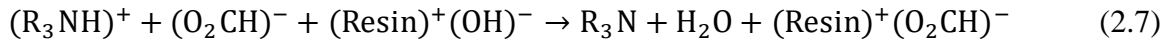
According to Hatcher et al. (2006), contaminated solvents will lead to increased energy consumption due to high false CO₂ loading, or the presence of degradation products that are stronger than amine loaded with CO₂. Besides, high circulation rate is implemented to maintain the same CO₂ removal efficiency when degradation products have accumulated in the solvents.

2.4 Reclamation Methods

2.4.1 Ion Exchange

Ion exchange technology commonly purifies liquids by removing dissolved ionic contaminants to the solid like strong base resin (Dumee et al., 2012). The removed ions are replaced with the equivalent amount of hydroxide ions from the resin (Shao et al., 2002; Jouravleva et al., 2000).

Ion exchange technology has been integrated to the treatment of the contaminated alkanolamine solutions. A typical example is AmiPur unit by M/S Eco-tec, Canada. When ion exchange technology is used to treat contaminated amine solvents from CO₂ capture application, solvents would firstly go through the resin which has been pretreated with a strong base like sodium hydroxide (NaOH). The hydroxide ions from the resin would exchange with anions from HSSs, returning the free amine and water to the amine system. After that, the HSSs anions are removed from the resin by regeneration with caustic, which produces biodegradable sodium salts, which are friendly to the waste water treatment system (Verma and Verma, 2009). These two steps are shown in the following two equations (ElMoudir et al., 2012; Wang et al., 2015).



The ion exchange technology is a good option for the amine solvents with low concentration of salts. It is capable of effectively removing ionized impurities and achieving high amine recovery (higher than 99%) (Cummings et al., 2007). Besides, it is less time and energy consuming. However, this technology cannot be regarded as an optimum choice for amine solvents from CO₂ capture. First of all, high level of CO₃²⁻ and HCO₂⁻ could be adsorbed in the resin, competing with HSS anions and leading to the reduced efficiency of this technology. Besides, in addition to ionized impurities, there are other degradation products which would have negative effect on the system. These degradation products are nonionic, which cannot be removed by ion exchange technology.

2.4.2 Electrodialysis

Electrodialysis is a separation process where an electrical potential difference is used as the driving force to facilitate the removal of ionic substances in the aqueous solution (Lim et al., 2014). A

stack of alternating cation-selective and anion-selective membranes between two electrodes contain electrically charged functional sites so that they are selective and allow the passage of either anions or cations, but not both. This removal method has been considered as an effective method for removal of HSSs from degraded alkanolamine solutions (Volkov et al., 2014). The first electro dialysis process, UCARSEP, was developed by Union Carbide (now owned by the Dow Chemical Company) for the purification of alkanolamine solvents used in natural gas processing (Lim et al, 2014; Parisi and Bosen, 2006).

There are four major factors that can dramatically affect the performance of electro dialysis: membrane type, surface area, type of the treated solvent, and applied current (ElMoudir et al., 2012). Although electro dialysis can achieve high removal efficiency of ionic degradation products like HSSs, it has some disadvantages. The contaminated solvents need to be filtered first before travelling to the electro dialysis unit to avoid the problem of plugging. Besides, this technology fails to remove nonionic degradation products which are also present in the solvent system. What's more, the water loss can occur due to osmosis, which can affect water balance in the system. Thus, electro dialysis cannot be considered as an optimum option to reclaim the degraded amine/glycol solvents.

2.4.3 Thermal Reclamation

Thermal reclamation uses heat energy to evaporate amine/glycol from the high-boiling degradation products to purify the amine/glycol solvent (Wang et al., 2014). Thermal reclamation can be conducted either on the stream withdrawn from the solution leaving the stripper (on-site) or off-site at the reclaiming plant. One example of on-site reclaimer is Delta Reclaimer, a patented reclaimer developed by HTC CO₂ Systems Corp., which can efficiently reclaim amine/glycol solvents (ElMoudir et al., 2014). Figure 2.1 shows Delta Reclaimer integrated in the CO₂ capture plant.

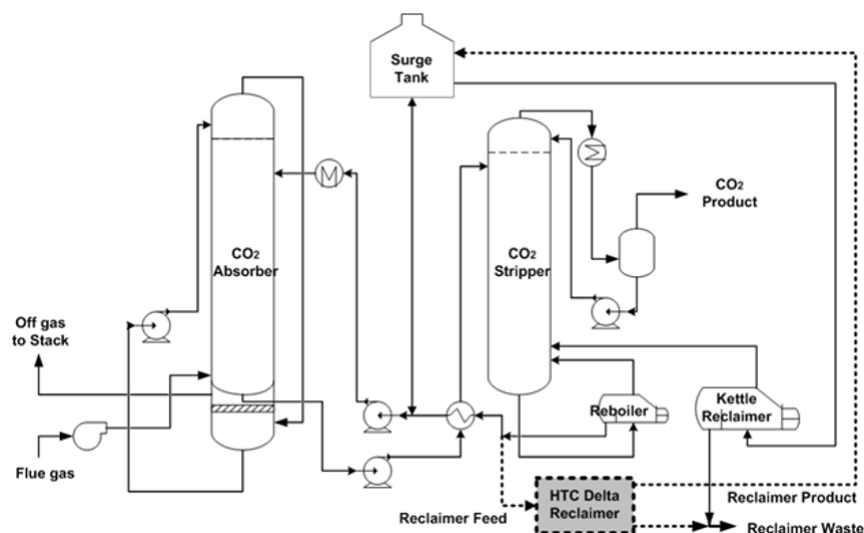


Figure 2.1 Delta reclaimer integrated in the CO₂ capture plant (ElMoudir et al., 2014)

Two important operating factors of thermal reclamation are temperature and pressure. The desired working temperature depends on the type of the solvent to be treated. Different types of amine/glycol solvents have different thermal stability; the working temperature should be carefully controlled, lower than the specific temperature which would lead to the thermal degradation of the treated solvent. The reclamation of MEA usually takes place under atmospheric pressure; however, for those solvents with high boiling points like DEA and MDEA, they are usually reclaimed under vacuum pressure.

Before going to the thermal reclaimer, the degraded amine would firstly be mixed with a strong base such as caustic soda to release amine trapped in HSSs (Blake and Rothert, 1962; Rooney, 1999). After the reclamation is done, the reclaimer needs to be drained and cleaned. The waste is considered toxic due to high levels of degradation products.

Compared with ion exchange and electrodialysis, thermal reclamation is more suitable for the reclamation of amine and glycol because it can remove both ionic and nonionic degradation products. Besides, it consumes less water and fewer chemicals. However, this technology still has some limitations. For those with low level of contamination, thermal reclamation needs higher capital expenditures. Besides, the solvent loss could be high in the hazardous waste.

2.4.4 Summary

A comparative summary of ion exchange, electro dialysis and thermal distillation is presented in Table 2.4.

Table 2.4 Comparison of Reclamation Methods

	Ion Exchange	Electrodialysis	Thermal Reclamation
Capability	Removal of ionic impurities	Removal of ionic impurities	Removal of both ionic and non-ionic impurities
Operational Principle	Ions exchanged with hydroxide ions from resin	Ions removed by electro dialysis	Vaporization of amine/glycol from degradation products
Advantages	Effective removal of ionic degradation products; High solvent recovery; Less time and energy consuming	High removal efficiency of ionic degradation products	Effective removal of non-ionic degradation products; Consumption of less water and fewer chemicals
Limitations	Failure to remove non-ionic degradation products	Pretreatment to avoid plugging; Failure to remove nonionic degradation products; Loss of water due to osmosis	Higher capital expenditures when contamination level is low; High solvent loss in the waste; Hazardous waste

Waste Products	Dilute aqueous stream containing removed ions	Aqueous brine containing removed ions	Aqueous stream containing salts, non-volatile organics and some solvent
Volume of Wastes	High to moderate	Moderate	Low
Amine Recovery	>99%	98%	85-95%

Chapter 3: Density, Viscosity, Refractive Index, and Electrical Conductivity of Degraded Monoethanolamine Solutions at Standard Temperatures

3.1 Introduction

In this chapter, the artificial degraded and industrial degraded MEA solvents were both analyzed to understand the impact of solvent mass fraction, degradation products content and CO₂ loading on the physical properties of MEA solvent at standard temperatures. For the physical properties of refractive index and electrical conductivity, the standard temperature is 293.15 K as they were normally measured under this temperature, which can be found in most open literature articles. On the other hand, density and viscosity were typically measured at the temperature of 298.15 K.

3.2 Experimental Section

3.2.1 Materials

Table 3.1 lists the information of the reagents employed in this work. Acetic acid and formic acid were used to create HSSs in the artificial degraded solvents. N-Acetyethanolamine, a type of amide, is one of the major degradation products of MEA solvent. The standard solutions of 0.5 mol·L⁻¹ hydrochloric acid (HCl) and 0.5 mol·L⁻¹ sodium hydroxide (NaOH) were used for volumetric titration. For water content determination, Hydranal-Composite 5 and Hydranal-Solver (Crude) Oil were used.

Table 3.1 Reagent Description Table

Chemical name	Source	Mole fraction/weight percent purity
Monoethanolamine (MEA)	Huntsman	> 99.5 % (weight percent)
carbon dioxide (CO ₂)	Praxair	99.99 % (mole fraction)
acetic acid	Sigma-Aldrich	> 99.7 % (weight percent)
formic acid	Fisher Scientific	> 98 % (weight percent)

N-Acetyethanolamine	Sigma-Aldrich	90 % (weight percent)
0.5 mol·L ⁻¹ hydrochloric acid (HCl)	BDH Chemicals	± 0.01
0.5 mol·L ⁻¹ sodium hydroxide (NaOH)	BDH Chemicals	± 0.01
Hydranal-Composite 5	Honeywell	< 70 % (weight percent)
Hydranal-Solver (Crude) Oil	Honeywell	< 60 % (weight percent)

3.2.2 Sample Preparation

The concentrated MEA solution was diluted to different required amine mass fraction ($M_{\text{Amine}}/(M_{\text{Amine}}+M_{\text{Water}})$), $w_{\text{amine}} = (0.20 \text{ to } 0.40)$, by using deionized distilled water (Supap et al., 2006). The maximum MEA mass fraction is limited to 0.40 as CO₂-loaded MEA solvent at higher mass fraction can have negative effect on CO₂ capture due to high viscosity and the increased potential of corrosion problems. The exact amine mass fraction of each diluted solution was determined by volumetric titration with standard solution of 0.5 mol·L⁻¹ HCl to the endpoint determined by both methyl orange indicator and pH meter.

The solutions with high CO₂ loading (> 0.5) were prepared by gently bubbling CO₂ gas stream in the solvent with required amine mass fraction. Solvents with different CO₂ loading were then prepared by diluting an aqueous amine solution of selected mass fraction and high CO₂ loading with a CO₂-unloaded amine solution with the same amine mass fraction to get the required CO₂ loading value ($n(\text{CO}_2)/n(\text{MEA})$), $\alpha = (0 \text{ to } 0.5)$. The exact CO₂ loading value of each solution was determined by the volumetric titration with standard solution of 0.5 mol·L⁻¹ NaOH to the endpoint determined by a pH meter.

By adding certain amount of formic acid, acetic acid and N-Acetyethanolamine in each solution, at equivalent percentage of 1/3 each to simulate the degradation products, the artificial degraded solvents were prepared. The range of the total degradation products mass fraction ($M_{\text{DP}}/(M_{\text{Amine}}+M_{\text{Water}}+M_{\text{DP}})$), $w_{\text{DP}} = (0 \text{ to } 0.02)$ was selected based on the maximum expected level of HSS contamination found in a typical CO₂ capture plant (ElMoudir et al., 2014).

3.2.3 Sample Analysis

For each industrial degraded MEA solvent, the solvent concentration (mass fraction) w'_{amine} , given as $(M_{\text{Amine}}/(M_{\text{Amine}}+M_{\text{Water}}+M_{\text{CO}_2}+M_{\text{DP}}))$ and CO_2 loading α were determined by volumetric titration with standard solution of $0.5 \text{ mol}\cdot\text{L}^{-1}$ HCl and $0.5 \text{ mol}\cdot\text{L}^{-1}$ NaOH to the endpoint determined by a pH meter. However, it needs to be noticed that this solvent concentration w'_{amine} is totally different from the amine mass fraction w_{amine} . After a full reflux distillation to strip all CO_2 in the sample, the same titration method of CO_2 loading was employed to determine the heat stable salts (HSSs) content (mass fraction) w'_{HSS} , $(M_{\text{HSS}}/(M_{\text{Amine}}+M_{\text{Water}}+M_{\text{CO}_2}+M_{\text{DP}}))$, in each industrial degraded MEA solvent. There were other kinds of degradation products except HSSs in each solvent that could not be determined by any titration method. The water content (mass fraction) w'_{Water} $(M_{\text{Water}}/(M_{\text{Amine}}+M_{\text{Water}}+M_{\text{CO}_2}+M_{\text{DP}}))$ of each sample was determined by a Karl Fischer titrator. The amine mass fraction w_{amine} and the total degradation products mass fraction w_{DP} mentioned above can be calculated by the following two equations, in which MW_{Amine} and MW_{CO_2} are the molecular weights of amine and CO_2 .

$$w_{\text{amine}} = \frac{w'_{\text{amine}}}{w'_{\text{amine}}+w'_{\text{Water}}} \quad (3.1)$$

$$w_{\text{DP}} = 1 - \frac{MW_{\text{amine}} \times (w'_{\text{Water}} + w'_{\text{amine}})}{MW_{\text{amine}} - MW_{\text{CO}_2} \times \alpha \times w'_{\text{amine}}} \quad (3.2)$$

3.2.4 Apparatus and Procedure

Density Measurements

Density measurements were conducted by using an Anton Paar density meter (DMA 4500) at temperature of 298.15 K. This density meter was calibrated with nitrogen and degassed water every time before the use of the machine. The specified repeatability of the density value and the integrated temperature measurement are $\pm 0.01 \text{ kg/m}^3$ and $\pm 0.01 \text{ K}$ respectively. The accuracy in the density measurement is estimated to be $\pm 0.05 \text{ kg/m}^3$. The density measurement for each solvent was made in triplicate and the average value was reported for further analysis.

Viscosity Measurements

Viscosities of artificial degraded and industrial degraded MEA solvents were measured with a rotational viscometer (model SMART, Fungilab S.A.). The instrument contains a measuring cell, which is connected with a thermostatic bath to allow the samples tested at standard temperature of 298.15 K. The rotational viscometer used a spring to measure the torque needed to rotate a spindle immersed in the cell, which contained the sample. The instrument converted the measured torque to viscosity and recorded it. The rotation speed of the spindle was adjusted to better measure the value of kinetic viscosity. The specified repeatability of the viscosity value is 0.2 % and the temperature precision is ± 0.1 K. All the measurements were made in triplicate and the average values were considered for further analysis.

Refractive Index Measurements

The refractive indices were measured with a digital refractometer (model PA230X, MISCO Refractometer) at the temperature of 293.15 K. This automatic digital refractometer had 2-point level I certified calibration and was in compliance with manufacturer's specifications to a stated uncertainty of ± 0.0001 refractive index. The refractive index measurements were made in triplicate and the average values were recorded.

Electrical Conductivity Measurements

Regarding the electrical conductivity, the measurements were conducted by the traceable expanded range conductivity meter (model 09-328, Fisher Scientific) at 293.15 K. The calibration was done using the traceable conductivity calibration standards. In the experimental procedure, about 5 mL of the solution and the electrode were sealed in a 10-mL glass tube placed in the bath. Its accuracy is ± 0.4 %. The measurements of electrical conductivity were made in triplicate and the average values were considered.

Water Content Measurements

The water content of each industrial degraded MEA solvent was determined by a Karl Fischer titrator (870 KF Titrino Plus, Metrohm). This titrator was calibrated with a standard solution of sodium tartrate. Hydranal-Composite 5 and Hydranal-Solver (Crude) Oil were respectively used as the titrating agent and media. It can reliably and precisely be used for volumetric water

determinations with water contents from a few ppm to 100 %. Each water content measurement was made in triplicate and the average value was considered.

3.3 Results and Discussion

3.3.1 Measurements of Pure Monoethanolamine and Pure Water

A comparison between experimental data of density, viscosity, refractive index, and electrical conductivity of pure components and data obtained by other researchers was performed and summarized in Table 3.2. A good agreement between the experimental data and those from literature is observed, which validates the experimental procedures and apparatus used in this work. However, electrical conductivity of pure MEA by other authors has not been found in the literature.

Table 3.2 Comparison between Measured and Literature Data of Density (ρ), Viscosity (η), Refractive Index (n_D), and Electrical Conductivity (k) for Pure Components at Standard Temperature $T = 298.15$ or 293.15 K ^a

Property/Unit	T/K	MEA		Water	
		exptl.	lit.	exptl.	lit.
$\rho/\text{kg}\cdot\text{m}^{-3}$	298.15	1012.0	1011.9 (Han et al., 2012)	997.0	997.0 (Maham et al., 1994)
			1012.3 (Amundsen et al., 2009)		997.0 (Pagé et al., 2013)
			1011.8 (Maham et al., 1994)		997.1 (González et al., 2007)
			1012.0 (Álvarez et al., 2010)		997.1 (García-Abuín et al., 2013)

			1012.1 (Li et al., 2013)		
$\eta/\text{mPa}\cdot\text{s}$	298.15	18.750	18.740 (García-Abuín et al., 2013)	0.890	0.891 (García-Abuín et al., 2013)
			18.980 (Mandal et al., 2003)		0.890 (González et al., 2007)
n_D	293.15	1.4560	1.4560 (Taib and Murugesan, 2011)	1.3330	1.3330 (Tseng and Thompson, 1964)
			1.4539 (Tariq et al., 2009)		
$k/\text{mS}\cdot\text{cm}^{-1}$	293.15	0.000	0.000 (Alam et al., 2011)		

^a Combined uncertainties u_c are $u_c(\rho) = 1 \text{ kg}\cdot\text{m}^{-3}$, $u_r(\eta) = 0.16$, $Uc(n_D) = 0.002$, and $Uc(k) = 0.01 \text{ mS}\cdot\text{cm}^{-1}$ (level of confidence = 0.95).

3.3.2 Measurements of Monoethanolamine and Water Mixtures

The densities, viscosities, refractive indices and electrical conductivities of MEA-water mixtures were measured at each standard temperature and reported in Table 3.3. The presented data of density, viscosity and refractive index were compared with those of the available literature at standard temperatures. A good agreement was found as illustrated in Figure 3.1-3.3.

Table 3.3 Density (ρ), Viscosity (η), Refractive Index (n_D) and Electrical Conductivity (k) Changing with the Amine Mass Fraction (w_{amine}) for the MEA + Water Binary Mixture, at Standard Temperature $T = 298.15$ or 293.15 K and Pressure $P = 0.1$ MPa ^a

w_{amine}	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\eta/\text{mPa}\cdot\text{s}$	n_D	$k/\text{mS}\cdot\text{cm}^{-1}$
	298.15 K		293.15 K	

0.00	997.0	0.89	1.3330	
0.20	1007.1	1.70	1.3587	1.020
0.30	1012.9	2.60	1.3720	0.720
0.40	1018.3	3.50	1.3854	0.461
0.50	1022.1	5.40	1.3975	0.290
0.60	1025.1	9.67	1.4126	0.111
0.70	1026.5	12.26	1.4230	0.089
0.80	1024.7	20.39	1.4368	0.034
0.90	1020.4	19.45	1.4444	0.032
1.00	1012.0	18.75	1.4560	0.031

^a Combined uncertainties u_c are $u_c(\rho) = 1 \text{ kg}\cdot\text{m}^{-3}$, $u_r(\eta) = 0.16$, $Uc(n_D) = 0.002$, and $Uc(k) = 0.01 \text{ mS}\cdot\text{cm}^{-1}$ (level of confidence = 0.95).

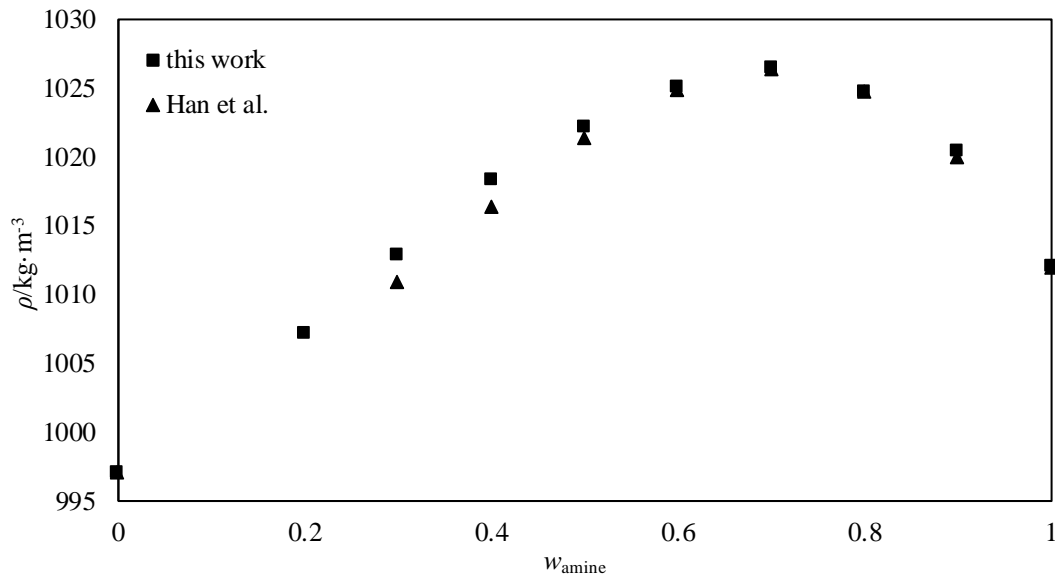


Figure 3.1 Comparison of measured density ρ data with published data for MEA + water system as a function of MEA mass fraction w_{amine} at 298.15 K.

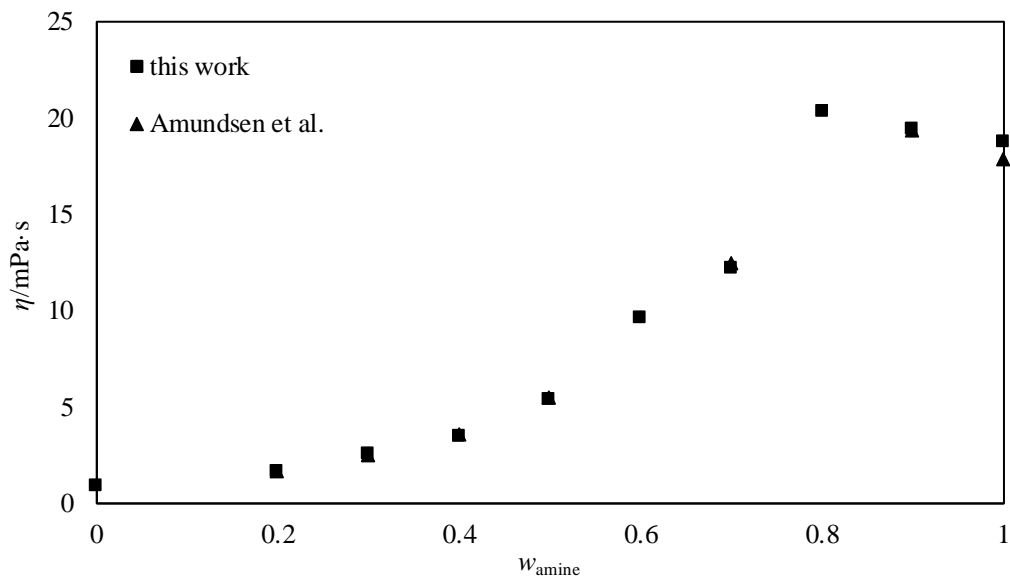


Figure 3.2 Comparison of measured viscosity η data with published data for MEA + water system as a function of MEA mass fraction w_{amine} at 298.15 K.

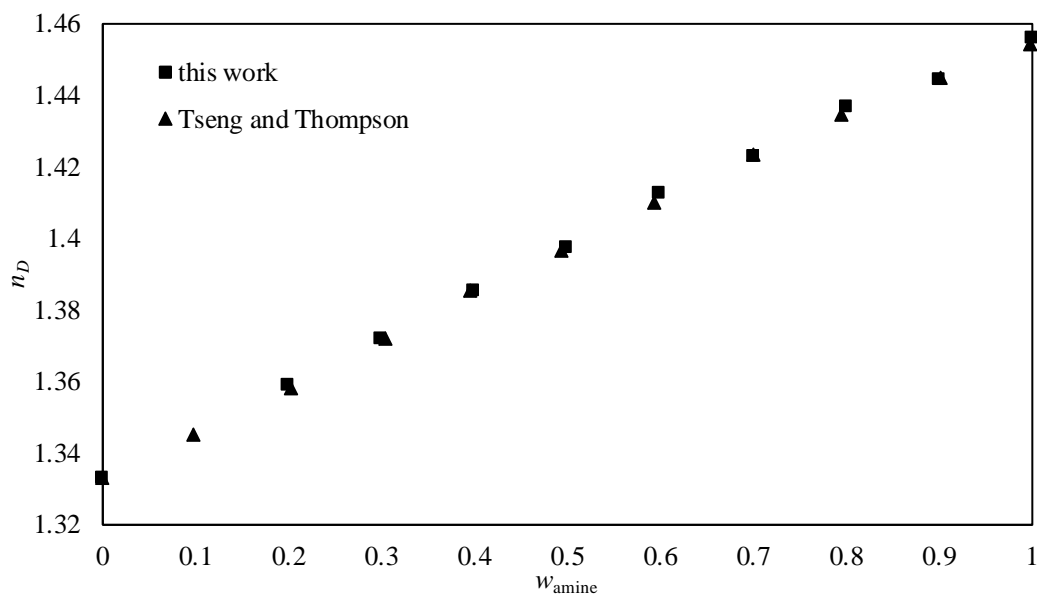


Figure 3.3 Comparison of measured refractive index n_D data with published data for MEA + water system as a function of MEA mass fraction w_{amine} at 293.15 K.

Unlike density, viscosity and refractive index, there are very few publications about electrical conductivity of MEA solutions. The electrical conductivity of MEA solutions with very low solvent concentration (lower than $0.5 \text{ mol}\cdot\text{L}^{-1}$) was reported (Han and Wee, 2014; Han and Wee, 2013). Figure 3.4 shows electrical conductivity increases slightly when solvent is diluted from very high concentration to a relatively low concentration. However, a huge increase can be witnessed when MEA mass fraction is much lower and a steep increase can be predicted when solvent reaches infinite dilution.

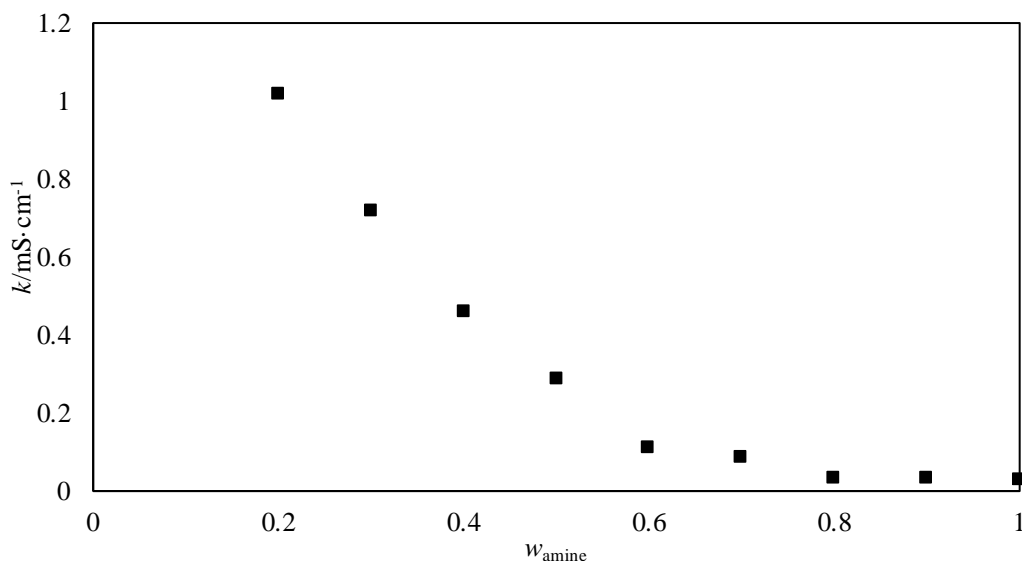
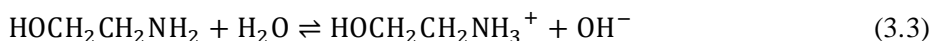


Figure 3.4 Measured electrical conductivity k data for MEA + water system as a function of MEA mass fraction w_{amine} at 293.15 K.

This phenomenon can be explained by the Debye-Huckel theory (Herbert, 1943). The dissociation constant of concentrated MEA at 298.15 K is 9.50. Hence, unlike strong bases, MEA is a weak base which can only have very small dissociation in the water solution, shown in Eq. (3.3). Adding water can contribute to a higher level of dissociation.



3.3.3 Measurements of Artificial and Industrial Degraded Monoethanolamine Solutions

The measurements of density, viscosity, refractive index and electrical conductivity of artificial degraded and industrial degraded MEA solutions under standard temperatures are given in Tables 3.4 and 3.5, respectively. For the artificial degraded MEA solutions, they have amine mass fraction (w_{amine}) from 0.2 to 0.4, CO₂ loading (α) from 0 to 0.5, and total degradation products content (w_{DP}) from 0 to 0.02.

Table 3.4 Density (ρ) and Viscosity (η) at 298.15 K, Refractive Index (n_D) and Electrical Conductivity (k) at 293.15 K, of Artificial Degraded MEA Solutions Changing with MEA Mass Fraction (w_{amine}), Total Degradation Products Mass Fraction (w_{DP}), and CO₂ Loading (α) at Pressure $P = 0.1$ MPa ^a

α	$\rho/$ kg·m ⁻³	$\eta/$ mPa·s	n_D	$k/$ mS·cm ⁻¹	$\rho/$ kg·m ⁻³	$\eta/$ mPa·s	n_D	$k/$ mS·cm ⁻¹	$\rho/$ kg·m ⁻³	$\eta/$ mPa·s	n_D	$k/$ mS·cm ⁻¹
	$w_{\text{DP}} = 0$ ($w_{\text{amine}} = 0.20$)				$w_{\text{DP}} = 0.01$ ($w_{\text{amine}} = 0.20$)				$w_{\text{DP}} = 0.02$ ($w_{\text{amine}} = 0.20$)			
0	1007.1	1.70	1.3587	1.02	1011.1	1.70	1.3604	5.72	1014.9	1.80	1.3616	9.85
0.15	1029.0	1.80	1.3642	11.90	1032.5	1.80	1.3657	15.82	1035.5	1.90	1.3669	19.44
0.25	1045.9	1.90	1.3676	18.04	1049.4	2.00	1.3691	21.59	1052.0	2.00	1.3701	24.59
0.35	1059.0	2.10	1.3709	23.54	1062.7	2.10	1.3725	26.77	1065.4	2.20	1.3736	29.92
0.50	1081.0	2.20	1.3752	30.80	1084.5	2.30	1.3764	33.30	1086.3	2.40	1.3775	35.90
	$w_{\text{DP}} = 0$ ($w_{\text{amine}} = 0.30$)				$w_{\text{DP}} = 0.01$ ($w_{\text{amine}} = 0.30$)				$w_{\text{DP}} = 0.02$ ($w_{\text{amine}} = 0.30$)			
0	1012.9	2.60	1.3720	0.72	1016.8	2.70	1.3738	3.69	1020.0	2.90	1.3751	7.31
0.15	1044.2	2.90	1.3809	11.75	1047.3	3.00	1.3822	15.68	1050.0	3.20	1.3836	17.29
0.25	1065.0	3.10	1.3863	17.71	1067.4	3.20	1.3873	21.72	1069.6	3.30	1.3882	22.34
0.35	1085.1	3.30	1.3913	21.93	1086.6	3.50	1.3923	26.35	1088.2	3.70	1.3933	27.76
0.50	1105.0	3.90	1.3978	27.40	1106.2	4.10	1.3987	32.30	1107.1	4.20	1.3996	33.30
	$w_{\text{DP}} = 0$ ($w_{\text{amine}} = 0.40$)				$w_{\text{DP}} = 0.01$ ($w_{\text{amine}} = 0.40$)				$w_{\text{DP}} = 0.02$ ($w_{\text{amine}} = 0.40$)			
0	1018.3	3.50	1.3854	0.46	1024.2	3.70	1.3865	2.92	1026.6	3.80	1.3878	5.31
0.15	1058.9	4.20	1.3960	11.71	1061.8	4.50	1.3971	13.27	1064.5	4.80	1.3980	14.84
0.25	1086.6	4.70	1.4029	16.80	1088.4	5.00	1.4039	17.75	1090.2	5.20	1.4046	19.04
0.35	1112.3	5.70	1.4101	20.24	1114.0	6.00	1.4110	21.07	1115.1	6.20	1.4118	23.71
0.50	1138.2	6.70	1.4180	23.33	1139.8	6.90	1.4188	23.76	1140.7	7.10	1.4197	27.79

^a Combined uncertainties u_c are $u_c(\rho) = 1$ kg·m⁻³, $u_r(\eta) = 0.16$, $Uc(n_D) = 0.002$, and $Uc(k) = 0.01$ mS·cm⁻¹ (level of confidence = 0.95).

Table 3.5 Density (ρ) and Viscosity (η) at 298.15 K, Refractive Index (n_D) and Electrical Conductivity (k) at 293.15 K, Solvent Concentration (w'_{amine}), HSSs Content (w'_{HSS}), Water Content (w'_{water}), CO₂ Loading (α), MEA Mass Fraction (w_{amine}), and Total Degradation Products Mass Fraction (w_{DP}) of Industrial Degraded MEA Solutions at Pressure $P = 0.1$ MPa ^a

w'_{amine}	w'_{HSS}	w'_{Water}	α	w_{amine}	w_{DP}	$\rho/\text{kg}\cdot\text{m}^{-3}$	$\eta/\text{mPa}\cdot\text{s}$	n_D	$k/\text{mS}\cdot\text{cm}^{-1}$
0.151	0.0038	0.786	0.517	0.161	0.0069	1062.6	2.00	1.3701	28.98
0.140	0.0048	0.849	0.063	0.142	0.0050	1016.3	0.30	1.3558	7.99
0.159	0.0047	0.807	0.239	0.165	0.0066	1037.9	1.10	1.3642	18.59
0.163	0.0029	0.807	0.214	0.168	0.0048	1033.4	1.10	1.3619	17.56
0.160	0.0050	0.807	0.244	0.165	0.0052	1037.9	1.20	1.3642	18.97
0.151	0.0042	0.776	0.597	0.163	0.0082	1082.9	2.30	1.3727	35.70
0.150	0.0053	0.794	0.452	0.159	0.0073	1057.1	1.80	1.3683	28.24
0.151	0.0047	0.769	0.676	0.164	0.0074	1083.1	2.50	1.3727	35.40
0.149	0.0037	0.820	0.239	0.154	0.0052	1032.4	1.00	1.3600	18.41
0.162	0.0049	0.804	0.248	0.168	0.0051	1039.7	1.20	1.3646	19.91
0.154	0.0028	0.820	0.193	0.158	0.0050	1030.3	1.00	1.3611	15.80
0.126	0.0043	0.808	0.680	0.135	0.0050	1080.8	2.10	1.3662	34.40
0.152	0.0049	0.769	0.675	0.165	0.0059	1083.0	2.50	1.3728	35.40
0.159	0.0051	0.806	0.245	0.165	0.0075	1038.0	1.20	1.3643	18.73
0.148	0.0052	0.772	0.692	0.161	0.0069	1083.1	2.50	1.3728	35.40
0.159	0.0051	0.805	0.245	0.165	0.0077	1039.8	1.20	1.3646	19.80

0.152	0.0041	0.817	0.235	0.157	0.0050	1032.3	1.00	1.3599	18.15
0.143	0.0046	0.842	0.073	0.145	0.0074	1016.1	0.40	1.3558	8.24
0.171	0.0038	0.801	0.193	0.176	0.0043	1033.3	1.20	1.3619	17.76

^a Combined uncertainties u_c are $u_c(\rho) = 1 \text{ kg}\cdot\text{m}^{-3}$, $u_r(\eta) = 0.16$, $Uc(n_D) = 0.002$, and $Uc(k) = 0.01 \text{ mS}\cdot\text{cm}^{-1}$ (level of confidence = 0.95).

Density, viscosity, refractive index and electrical conductivity of the artificial degraded MEA solutions with the same MEA mass fraction show an increase with increasing degradation products content or CO₂ loading. Both the increasing degradation products content and CO₂ loading can increase the molecular interactions, which can increase the density, viscosity, refractive index and electrical conductivity. In the case of viscosity, the increasing molecular weight of solutes is another contributor to the increased viscosity value. From Figures 3.5 to 3.12, linear increasing of density, viscosity, refractive index and electrical conductivity in artificial degraded solvents can be witnessed with increasing solvent mass fraction, degradation products content and CO₂ loading.

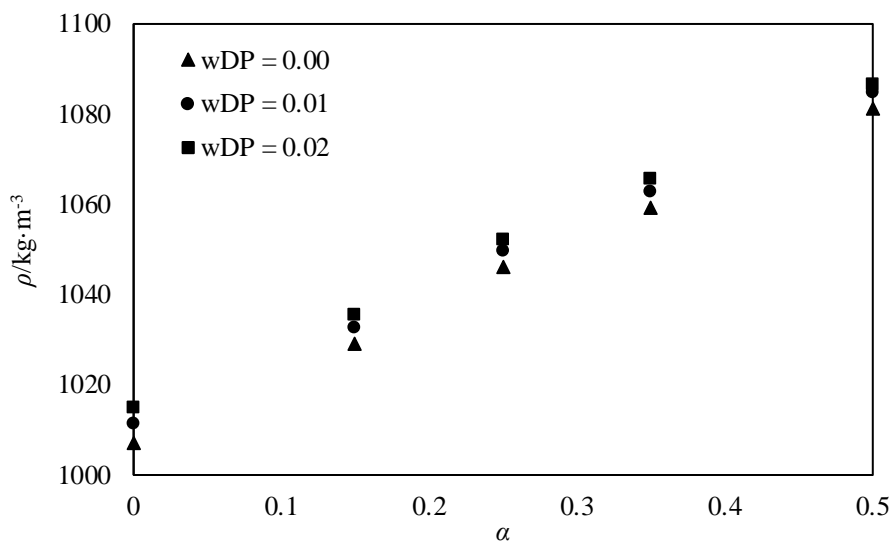


Figure 3.5 Measured density ρ of artificial degraded MEA solutions with mass fraction w_{amine} of 0.2 as a function of CO₂ loading α at 298.15 K.

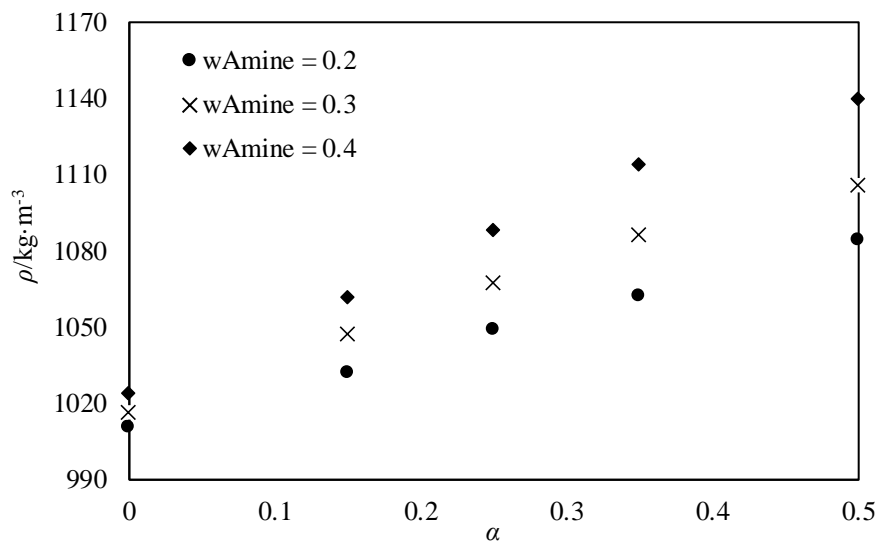


Figure 3.6 Measured density ρ of artificial degraded MEA solutions with degradation products content w_{DP} of 0.01 as a function of CO_2 loading α at 298.15 K.

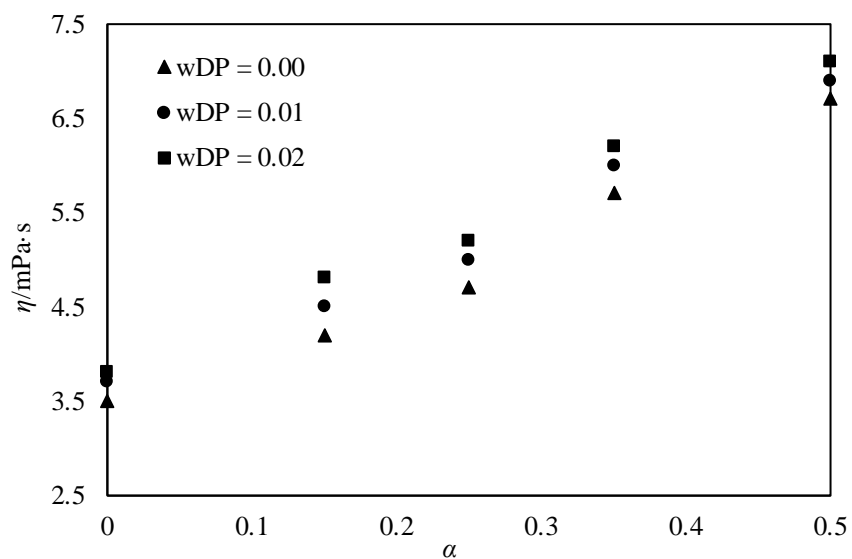


Figure 3.7 Measured viscosity η of artificial degraded MEA solutions with mass fraction w_{amine} of 0.4 as a function of CO_2 loading α at 298.15 K.

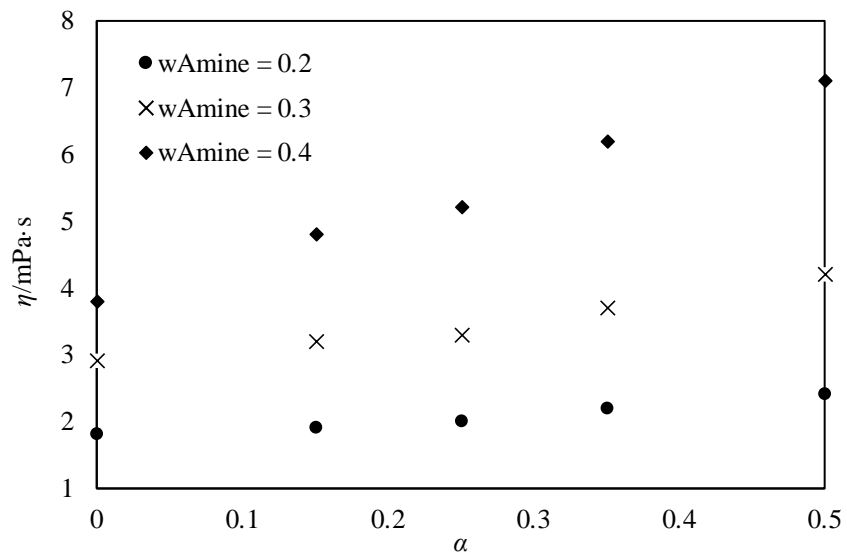


Figure 3.8 Measured viscosity η of artificial degraded MEA solutions with degradation products content w_{DP} of 0.02 as a function of CO₂ loading α at 298.15 K.

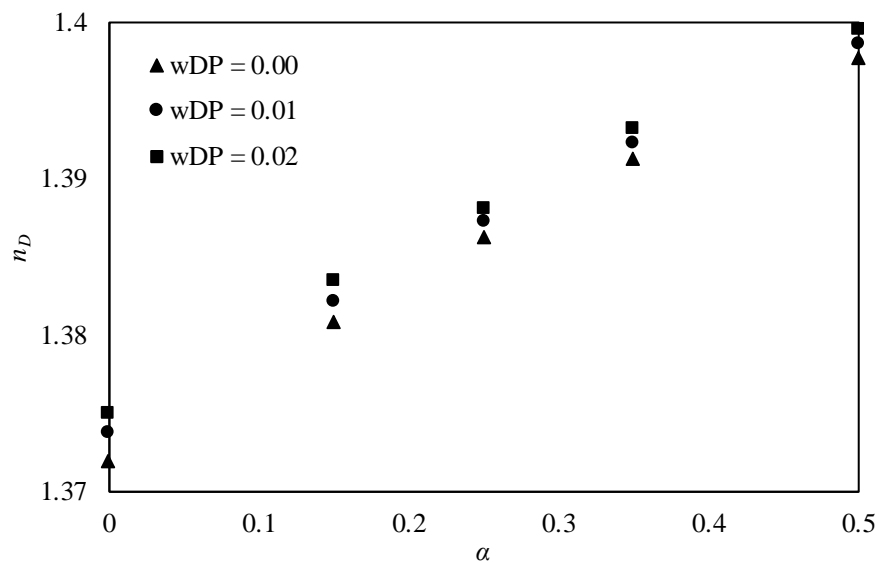


Figure 3.9 Measured refractive index n_D of artificial degraded MEA solutions with mass fraction w_{amine} of 0.3 as a function of CO₂ loading α at 293.15 K.

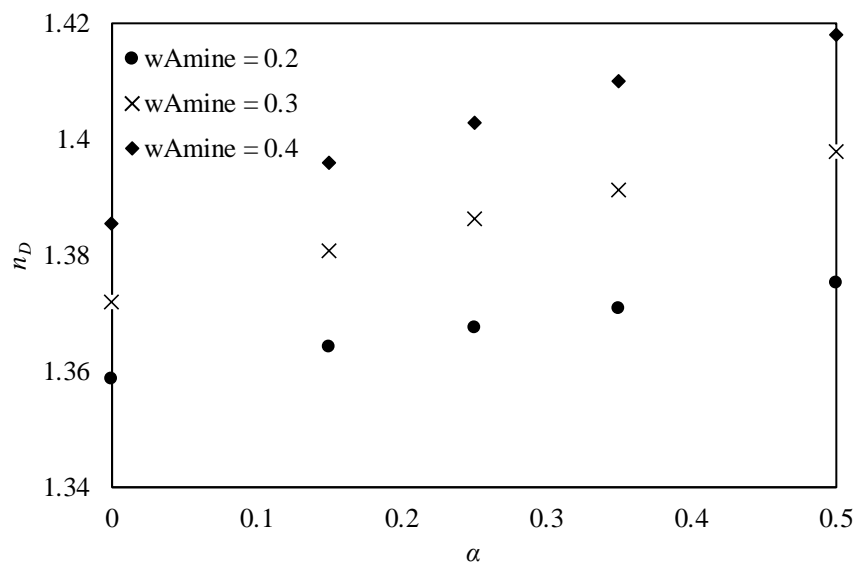


Figure 3.10 Measured refractive index n_D of artificial degraded MEA solutions with degradation products content w_{DP} of 0.00 as a function of CO_2 loading α at 293.15 K.

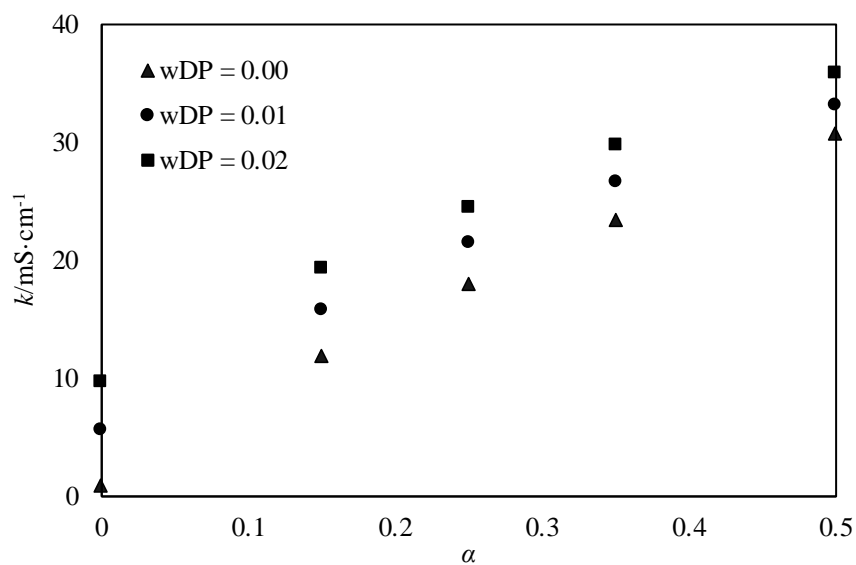


Figure 3.11 Measured electrical conductivity k of artificial degraded MEA solutions with mass fraction w_{amine} of 0.2 as a function of CO_2 loading α at 293.15 K.

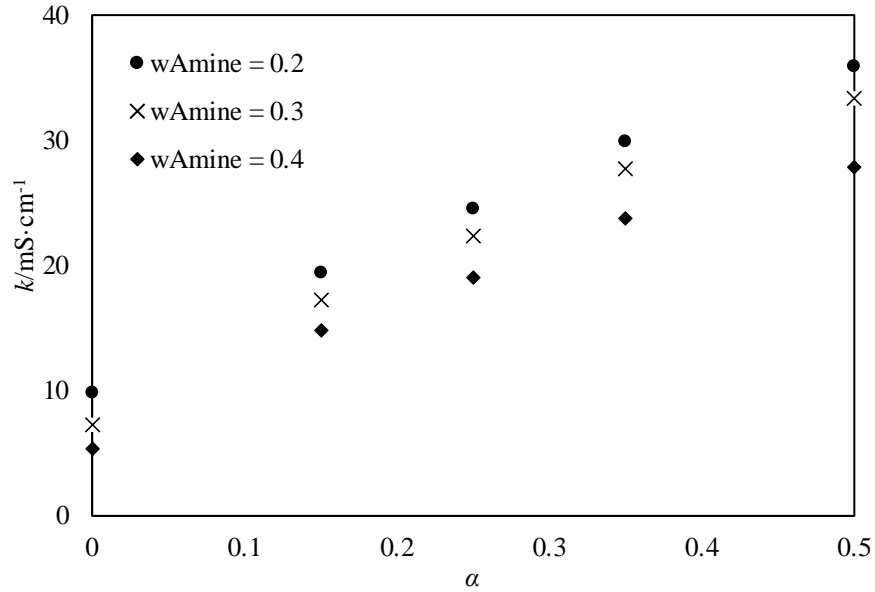


Figure 3.12 Measured electrical conductivity k of artificial degraded MEA solutions with degradation products content w_{DP} of 0.02 as a function of CO₂ loading α at 293.15 K.

Hence to roughly estimate the degradation level with a simple density, viscosity, refractive index or electrical conductivity measurement without any complex chemical analysis or extra costs, a linear polynomial of the following form was developed to correlate density, viscosity, refractive index or electrical conductivity with MEA mass fraction, degradation products content and CO₂ loading at standard temperature based on data of both artificial and industrial degraded solvents. For the mixtures of MEA and water, it can be observed that density, viscosity, refractive index and electrical conductivity do not change linearly with the solvent mass fraction for the whole solvent mass fraction range. However, from Figures 3.1 to 3.4, it can be seen that those four physical properties do change linearly with the solvent mass fraction when the value of the solvent mass fraction is within a narrow range of 0.2 to 0.4.

$$\text{Physical Property} = A_0 + A_1 w_{\text{amine}} + A_2 w_{\text{DP}} + A_3 \alpha \quad (3.4)$$

where A_0 , A_1 , A_2 and A_3 are the optimized coefficients estimated by the least-squares method and the values are listed in Table 3.6. The average absolute percentage deviation (AAD) was estimated according to the following equation

$$\text{AAD} = \frac{\sum_1^n \left| \frac{x_{\text{exp}} - x_{\text{calc}}}{x_{\text{exp}}} \right|}{n} \times 100 \% \quad (3.5)$$

Table 3.6 Fitting Parameters (A_0, A_1, A_2 and A_3) of Eq (3.4) and Average Absolute Percentage Deviations (AAD) for the Empirical Correlations of Density (ρ), Viscosity (η), Refractive Index (n_D) and Electrical Conductivity (k) for Artificial and Industrial Degraded MEA Solutions

properties	units	T/K	samples	A_0	A_1	A_2	A_3	AAD
ρ	kg·m ⁻³	298.15	artificial	959.955	187.767	258.667	188.272	0.526 %
			industrial	983.444	143.688	718.579	106.353	0.166 %
η	mPa·s	298.15	artificial	-2.323	16.033	14.667	3.464	11.149 %
			industrial	-1.891	13.727	10.095	3.078	1.872 %
n_D	-	293.15	artificial	1.321	0.174	0.114	0.0493	0.129 %
			industrial	1.323	0.186	0.713	0.0215	0.054 %
k	mS·cm ⁻¹	293.15	artificial	9.755	-22.067	270.133	51.095	28.575 %
			industrial	-9.984	110.699	89.966	41.155	4.104 %

It is found that for each physical property, AAD of industrial degraded MEA solutions is much lower than that of artificial degraded MEA solutions. It means the physical properties of density, viscosity, refractive index and electrical conductivity for industrial degraded MEA solutions fit better with the linear equations. One reason might be that compared with the artificial degraded MEA solutions, the industrial degraded MEA solutions have more narrow ranges of the solvent mass fraction and degradation products content. The fact that industrial degraded MEA solutions have more kinds of degradation products could be another reason.

Besides, when there is no MEA, degradation products or CO₂ in the solution, the solution becomes pure water. As a result, the value of each A_0 should be the value of each physical property for the pure water. However, it is not the case. The fact that the physical properties of pure water were not taken into consideration when the empirical correlations were developed could be one reason. In

other words, the developed empirical correlations cannot be used to estimate the physical properties of the pure water.

For density and viscosity, A_1 and A_3 of industrial degraded MEA solutions are smaller than those of artificial degraded MEA solutions. However, for density, A_2 of industrial degraded MEA solutions is larger than that of artificial degraded MEA solutions while for viscosity, A_2 of industrial degraded MEA solutions is smaller than that of artificial degraded MEA solutions. Thus, the density of the real degraded MEA solutions increase more dramatically with the increase of the degradation products content. The refractive index of the industrial degraded solutions also increases more dramatically with an increasing degradation products content, compared with the artificial degraded solutions. However, things are a little different when it comes to electrical conductivity. The electrical conductivity of artificial degraded MEA solutions decreases with the increase of the MEA mass fraction, which shows the same trend with the clean MEA solutions. On the contrary, the A_1 value of the industrial degraded MEA solutions is positive, which means that the electrical conductivity of industrial degraded MEA solutions increases when the MEA mass fraction increases. Besides, the electrical conductivity of the artificial degraded MEA solutions increases more dramatically with the increase of the degradation products.

Additional fourteen degraded MEA solvents from the working CO₂ capture plant in the USA were analyzed and the measured density data were used to determine the predictability of the two developed correlations. The result is presented in Figure 3.13.

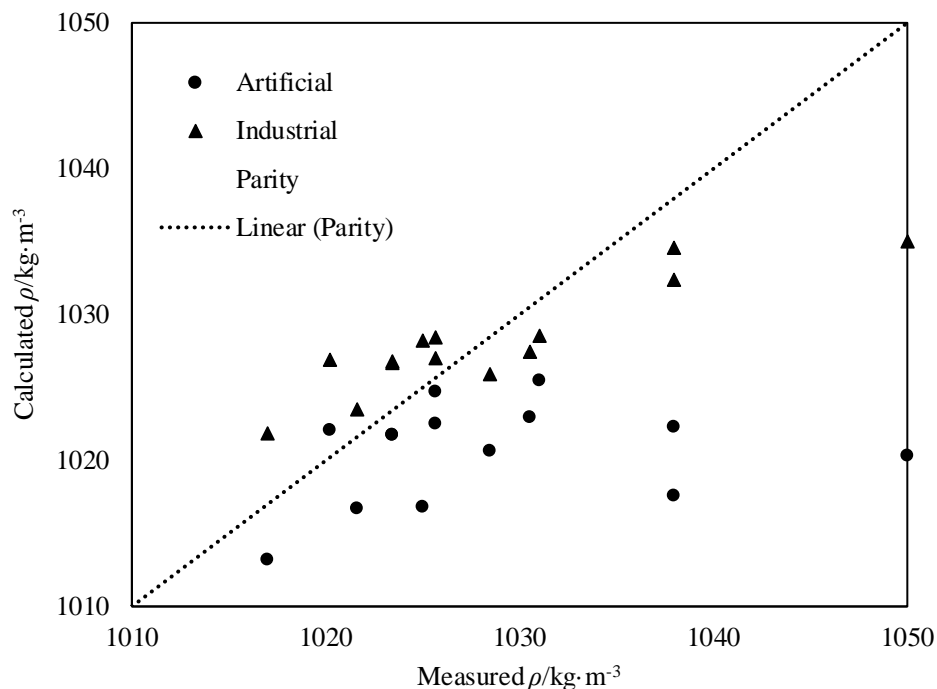


Figure 3.13 Parity chart compares the measured density ρ data for real degraded MEA solvents with the calculated densities from the equations developed from artificial degraded and industrial degraded solvents.

The average absolute percentage deviation is 0.778 % between the measured values and the calculated values from the equation developed from artificial degraded solvents. On the other hand, the average absolute percentage deviation is 0.412 % between the measured values and the calculated values from the equation developed from industrial degraded solvents. The empirical correlation of the industrial degraded MEA solvents is more reliable to estimate the density than that of the artificial degraded solvents. The fact that the MEA mass fraction, w_{amine} , and degradation products content, w_{DP} , of industrial degraded MEA solvents have a much narrower range results in a more accurate adjusted physical property equation.

3.4 Conclusions

Densities, viscosities, refractive indices and electrical conductivities of artificial degraded and industrial degraded MEA solutions were measured at standard temperature of 298.15 K or 293.15 K. This allows to quantify the impact of degradation products on the physical properties. The measured physical properties show a significant dependence on solvent mass fraction, degradation

products content and CO₂ loading. They change linearly with increasing solvent mass fraction, degradation products content and CO₂ loading. Empirical correlations were developed to allow the degradation level roughly estimated with a simple property measurement without any complex chemical analysis with extra costs.

Chapter 4: Reclamation of Degraded Alkanolamine and Glycol Solvents Used for CO₂ Capture Systems

4.1 Introduction

This chapter presents the novel thermal reclaimer. It is a simple vacuum setup which is able to remove most of undesirable impurities from degraded alkanolamine/glycol solvent and restore the solvent to its original purity at a high recovery rate and minimum energy consumption. To demonstrate the efficiency of this reclaimer, degraded solvents of monoethanolamine (MEA) and monoethylene glycol (MEG) obtained from the working plants were used as feeds of the reclaimer. The detailed analysis of the feed stream, the recovered product stream, and the waste stream were carried out and the result was presented and discussed in this work.

4.2 Process Description of the Reclaimer

The process flow diagram of the new reclaimer is shown in Figure 4.1 and Figure 4.2.

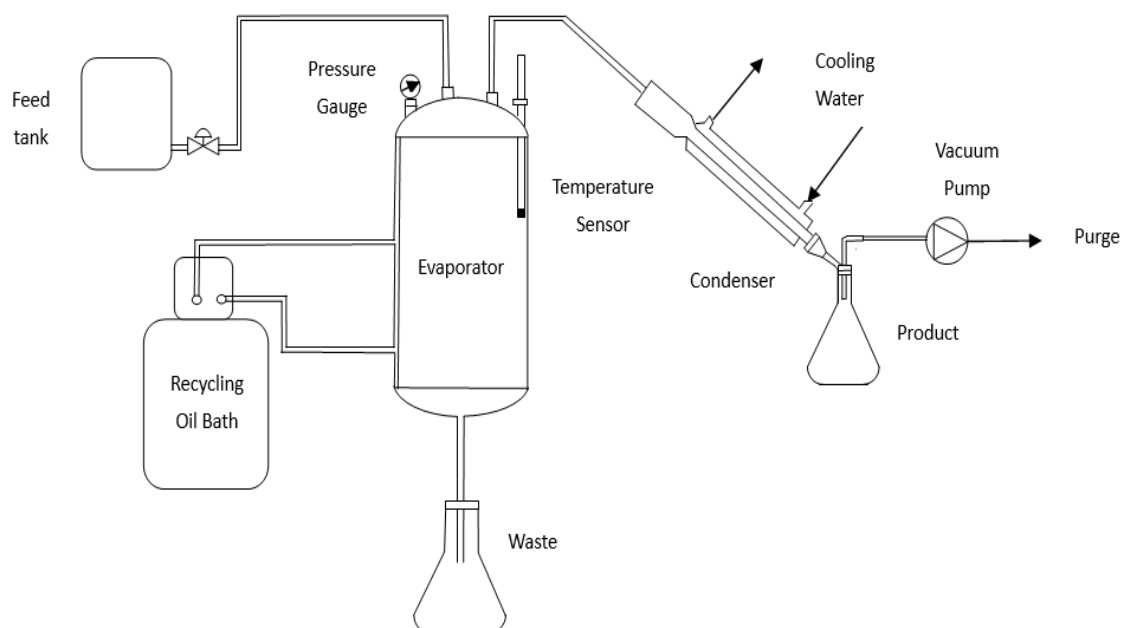


Figure 4.1 Process flow diagram of the new reclaiming unit



a) the vacuum pump, cooling system and feed tank b) principal part of reclaimer

Figure 4.2 General view of the reclaimer

This reclaimer consisted of a feed tank which stored the degraded feed of MEA or MEG. For degraded MEA solvent, it was mixed with chemical solution of 50% (mass weight) sodium hydroxide (NaOH) in advance to liberate amines from HSSs in the degraded solvent. The amount of NaOH added depended on the HSSs content of the degraded MEA solvent. The reclaimer also included an evaporator where thermal distillation took place. The heat energy was provided by the hot oil, which came from the recycling oil bath and then travelled in the jacket of the evaporator. Because degradation products and contaminants had higher boiling points, they would be left in the evaporator when the target solvent and water evaporated. The reclaimed product was condensed in the condenser unit and finally collected in the product flask. The setup also included a recycling cooling system which could efficiently condense all the vapor.

At the beginning of the reclamation process, the production rate was really high while the concentration of the solvent in the product was low. After a while, the production rate slowed down while the solvent concentration increased gradually. The system gradually reached steady

state when the production rate remained almost stable and the solvent concentration of the reclaimed product was almost equal to the feed concentration.

Most of the alkanolamine and glycol solvents cannot be reclaimed in the atmospheric pressure because their boiling points are higher than their degradation temperatures under the atmospheric pressure. A vacuum pump was thus used to main the vacuum pressure. When the waste became highly concentrated, it would be withdrawn from the bottom of the evaporator and get collected. During the steady state of the reclamation, feed was frequently added to the evaporator to make the liquid level inside the evaporator almost stable.

The main operating parameters of the test campaigns for degraded MEA and MEG solvents are summarized in Table 4.1.

Table 4.1 Operating Parameters of the Test Campaigns for Degraded MEA and MEG Solvents

Parameters	Unit	Value	
		MEA	MEG
Hot oil temperature	K	413.15	445.15
Operating pressure of reclaimer	KPa	38.00	20.00
Cooling water temperature	K	281.15	279.15

4.3 Analysis of the Solvent Samples

To validate the efficiency of the new reclaimer, 10 reclaimed products during the steady state were collected to be analyzed, along with one feed sample and two samples of the waste. The routine

analysis for both MEA and MEG samples included the physical and chemical property measurements. For MEA samples, MEA concentration, HSSs content and CO₂ loading were also routinely analyzed. The detailed information for analysis is given in Chapter 3.

4.3.1 Gas Chromatography – Mass Spectrometry (GC-MS) Technique

This technique has been developed to detect the degradation products of MEA solvents by Supap et al. (2006). The sample solution is injected into the GC inlet where it can be vaporized. The vaporized sample flows through the column with the carrier gas and its molecules are separated by virtue of their relative interaction with the coating of the column and the carrier gas. Different molecules elute from the column at different times. In MS, those molecules are captured, ionized and detected. More detailed description about this technique used in this work is summarized below.

The GC system (7980 A) combined with an inert Mass Selective Detector (5975) was obtained from Agilent Technologies. The Agilent J&W DB-WAX Ultra Inert Capillary GC Column, which worked well for more volatile and more polar components, was used in GC. It had the dimension of 0.25-mm diameter × 30-m length and could stand high temperature of up to 523.15 K. A 1- μ l sample was introduced to GC by an autoinjector. Before the injection of the sample, the sample was filtered by a membrane filter at first to avoid column fouling. Helium of ultra-high purity was used as the carrier gas in the column. After introducing the sample, start the GC-MS operating condition immediately.

The GC-MS operating condition was set up according to the paper of Supap et al. (2006). The initial temperature and the final temperature of the oven were set at 373.15 K and 513.15 K respectively. This final temperature was high enough to ensure complete elution while lower than the limiting temperature of the column to avoid any damage of the column. The ramp rate was set to be 7 K/min. The final temperature of 513.15 K was kept as long as 45 min so that all the degradation products could be completely eluted. The sample was injected using a split mode with a split ratio of 30:1 at the GC inlet temperature of 523.15 K. The temperature of GC-MS interface, MS quadrupole, and MS source was set at 523.15 K, 423.15 K and 503.15 K respectively. The gas saver mode was on.

4.3.2 Other Analysis

Other detailed analysis was conducted in Polaris Laboratories, which included total hardness, freezing point, visual test, specific conductance, boiling point, and total dissolved solids. For MAG samples, the solvent concentration of each sample was determined by ion chromatography (IC). For both MEA and MEG samples, it is very important to know the elemental concentrations of the corrosion metals of iron (Fe), aluminum (Al), lead (Pb) and zinc (Zn), the contaminants like calcium (Ca) and magnesium (Mg), the corrosion inhibitors of silicon (Si), phosphates (PO_4^{3-}), boron (B) and molybdenum (M), and the carrier salts of sodium (Na) and potassium (K) by using inductively coupled plasma (ICP). The contents of HSSs for MEA samples and the contents of organic degradation products for MEG samples are also of great importance, which was also determined by ion chromatography (IC).

4.4 Results and Discussion

4.4.1 Monoethylene Glycol (MEG)

The solvent color is a visual indicator of the solvent purity. Figure 4.3 shows the colors of the waste, the reclaimed product and the feed. The fresh MEG solvent, whether pure or dissolved in water, should be clear and colorless. From Figure 4.3, the reclaimed product is clear, which indicates the large removal of degradation products and impurities. Darker color of the sample usually indicates higher level of degradation. Because the waste has the highest solvent contamination, it is observed as opaque black.



Figure 4.3 General view of the waste (left), the reclaimed product (middle) and the feed (right)

The visual tests also show that there is no non-magnetic precipitation in the reclaimed solvents. However, minor flocculant and flake have been tested in the feed and the waste.

The element compositions of impurities in 10 reclaimed products, feed and two waste fluids are summarized and listed in Table 4.2. As can be seen from Table 4.2, the reclaimed products are found free of corrosion metals of Fe, Al, Pb and Zn, contaminants of Ca and Mg, corrosion inhibitors of B and Mo, and carrier salts of Na and K. Although corrosion inhibitors of Si and PO_4^{3-} still exist in the reclaimed products, their contents in the reclaimed products are very low, compared with those in the degraded feed.

Besides, the value of each element composition is quite stable in different reclaimed products, which proves that reclaimed solutions collected during the steady state are almost the same. The silicon contents of the reclaimed products range from 3 to 7 ppm and the phosphate contents are also within a narrow range of 6 to 15 ppm.

To better evaluate the performance of the reclaimer, Figure 4.4 is presented, in which the average values for product and waste are employed. From Figure 4.4, most element compositions are higher in the waste than in the feed. This phenomenon makes sense as those impurities could not be evaporated during the reclamation process and thus gradually got accumulated in the waste. However, the concentrations of Al and Ca are higher in the feed. It should be mentioned that the liquid inside the evaporator had two layers after an extended period of reclamation. The upper

layer was dark brown liquid while the layer in the bottom was a dense layer with black creamy color. When the waste was collected for the analysis, the upper layer was easier to travel and get collected as it had lower viscosity. These impurities of Al and Ca may get accumulated more easily in the lower layer and thus have lower concentration in the collected waste.

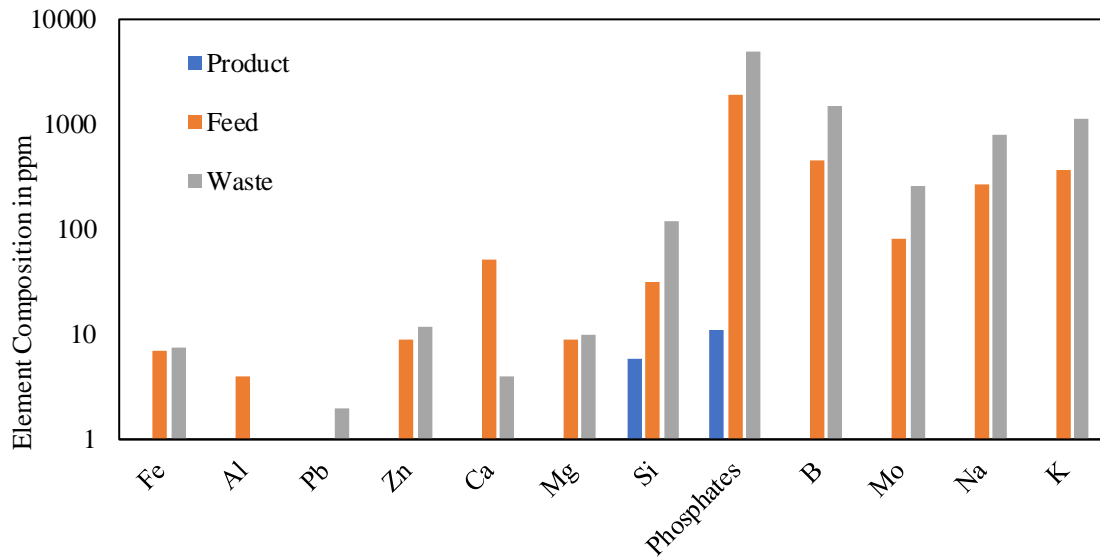


Figure 4.4 Change of element compositions found in the product, the feed and the waste

Table 4.2 Element Composition (ppm) of the Reclaimed Products, the Feed and the Wastes for MEG Solvents

Element (ppm)	Product #										Feed	Waste #	
	1	2	3	4	5	6	7	8	9	10		1	2
Fe	0	0	0	0	0	0	0	0	0	0	7	8	9
Al	0	0	0	0	0	0	0	0	0	0	4	0	0
Pb	0	0	0	0	0	0	0	0	0	0	1	2	2
Zn	0	0	0	0	0	0	0	0	0	0	9	12	12
Ca	0	0	0	0	0	0	0	0	0	0	51	1	7
Mg	0	0	0	0	0	0	0	0	0	0	9	10	10
Si	6	6	7	3	4	6	6	7	7	6	32	98	143
PO ₄ ³⁻	12	12	12	9	12	12	15	9	12	6	1907	4507	5301
B	0	0	0	0	0	0	0	0	0	0	457	1334	1616
Mo	0	0	0	0	0	0	0	0	0	0	80	231	283
Na	0	0	0	0	0	0	0	0	0	0	2690	7200	8760
K	0	0	0	0	0	0	0	0	0	0	3720	10230	12490

The result of property measurements for the reclaimed products, the feed and the wastes of MEG solvents is presented in Table 4.3. As can be seen from Table 4.3, the solvent concentration of each reclaimed product is equal or very close to the feed concentration, which proves the low solvent loss of this reclaimer.

The freezing point of the feed is slightly lower than that of the reclaimed product due to higher level of degradation products as degradation products, especially organic acids, can decrease the freezing point of the solvent. Hence, the relatively higher freezing point of the reclaimed product can confirm that some degradation products have been moved.

The specific conductance can also be used to demonstrate the product quality. The specific conductance values of the reclaimed products range from 66 to 127 μS while the specific conductance of the feed is much higher, 4550 μS . The decreased specific conductance of the reclaimed product is caused by the removal of degradation products like organic acids as they can conduct electricity.

Also seen from Table 4.3, the total hardness of the reclaimed product is 0 ppm, which confirms the complete removal of divalent cations of mainly calcium and magnesium. The physical properties of refractive index, density and viscosity are closely related to the degradation products content of the solvent. From Table 4.3, for the physical properties of refractive index and viscosity, there is not much difference between the reclaimed product and the degraded feed. Both refractive index and viscosity of the product are slightly lower than those of the feed. However, the density of the product is much lower than that of the feed due to the removal of the heavy degradation products and impurities. Because the degradation products content of the waste is much higher than that of the feed or the product, the refractive index, density, and viscosity of the waste are much larger than those of the feed or the product.

Table 4.3 Basic Testing Result of the Reclaimed Products, the Feed and the Wastes for MEG Solvents

Testing	Unit	Product #										Feed	Waste #		
		1	2	3	4	5	6	7	8	9	10		1	2	
Freezing point	K	235.37	235.37	237.04	235.37	237.04	235.37	235.37	235.37	235.37	235.37	235.37	232.59	250.93	250.93
Boil point	K	380.37	380.37	380.37	380.37	380.37	380.37	380.37	380.37	380.37	380.37	380.37	380.93	428.15	428.15
Solvent concentration	%	51	51	50	51	50	51	51	51	51	51	51	51	99	99
pH		9.0	8.8	8.9	9.4	9.2	8.9	9.0	8.8	8.8	8.9	8.4	8.4	9.9	10.2
Total hardness	ppm	0	0	0	0	0	0	0	0	0	0	159	2	21	
Specific conductance	μS	127	76	73	67	66	85	91	80	76	89	4550	1525	1650	
Refractive index		1.3849	1.3851	1.3848	1.3854	1.3846	1.3849	1.3855	1.3852	1.3850	1.3854	1.3868	1.4357	1.4379	
Density	kg/m ³	1066.2	1066.5	1065.9	1066.8	1065.8	1066.6	1066.9	1066.5	1066.6	1067.0	1075.9	1135.5	1141.3	
Viscosity	mPa·s	5.4	5.4	5.2	5.1	5.3	5.4	5.4	5.2	5.3	5.2	5.6	32.6	34.9	

The contents of organic degradation products for 10 reclaimed products, feed and two wastes are summarized and presented in Table 4.4. As can be seen from Table 4.4, the degradation product anions of glycolate and nitrite have been eliminated in all reclaimed products. The anion of acetate has been totally removed in most of the products. For all reclaimed products, the concentration of sulfate or chloride is almost the same, around 6 ppm. The concentration of the nitrate is also stable in each product, 13 ppm. However, the concentration of the formate is not stable in different products, ranging from 0 to 42 ppm.

To better evaluate the removal efficiency of the reclaimer for the individual degradation products, Figure 4.5 is presented, in which the average values for the product and the waste are employed. Although there are still anions of sulfate, chloride, nitrate, formate, and acetate in the reclaimed products, their contents in the products are much lower, compared with those in the feed, as can be seen in Figure 4.5.

For most of the ionic degradation products, their contents are much higher in the waste than in the feed. This phenomenon is most obvious for the anions of nitrate and glycolate, as their contents in the feed are lower than 1000 ppm while in the waste, their contents are around 3000 ppm. However, there are more degradation products of nitrite in the feed than in the waste. The possible reason can be that this kind of degradation product accumulate more easily in the lower layer of the liquid inside the evaporator while upper layer is more easily to be collected.

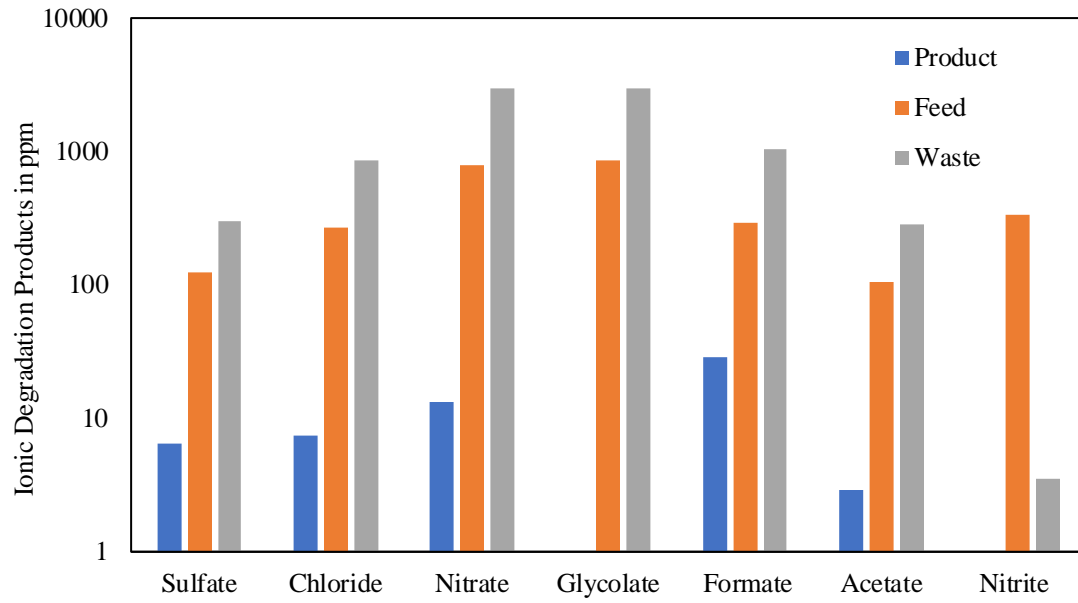


Figure 4.5 Change of contents of ionic degradation products in the product, the feed and the waste

Table 4.4 Degradation Products Contents of the Reclaimed Products, the Feed and the Wastes for MEG Solvents

Degradation products (ppm)	Product #										Feed	Waste #	
	1	2	3	4	5	6	7	8	9	10		1	2
Sulfate	7	6	6	6	6	6	7	7	6	7	123	308	292
Chloride	6	6	6	6	6	6	6	6	6	6	271	808	922
Nitrate	13	13	13	13	13	13	13	13	13	13	779	2839	3139
Glycolate	0	0	0	0	0	0	0	0	0	0	858	2683	3211
Formate	42	36	25	11	0	32	32	40	32	35	291	964	1121
Acetate	27	1	0	0	0	0	1	0	0	0	106	277	286
Nitrite	0	0	0	0	0	0	0	0	0	0	339	7	0

4.4.2 Monoethanolamine (MEA)

The colors of the waste, recovered product and the feed are shown in Figure 4.6. At first, it needs to be mentioned that the clean MEA solvent, whether pure or dissolved in deionized water, is pure and colorless. As can be seen from Figure 4.6, the reclaimed product is pure and colorless, which indicates the removal of degradation products and contaminants. The feed is in the color of clear fluorescent orange while the waste is opaque dark red. Darker color of the solvent normally results from higher level of degradation. Thus, higher level of degradation products in the waste can be assumed.

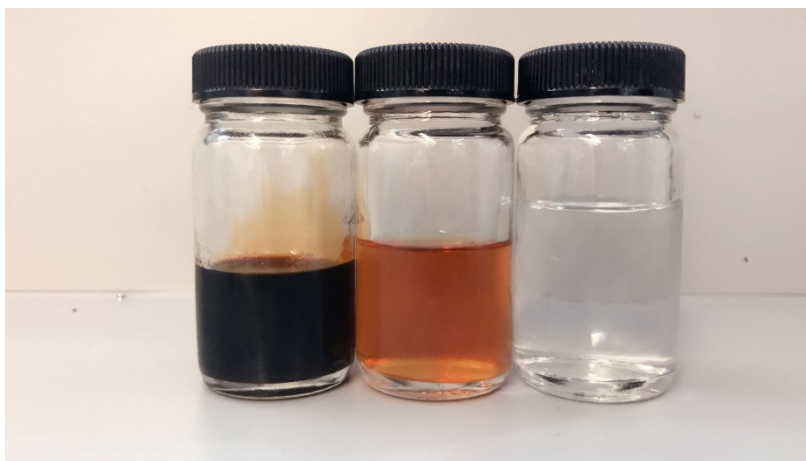


Figure 4.6 General view of the waste (left), the reclaimed product (right) and the feed (middle)

Besides, the feed also shows slight foaming tendency while the reclaimed products do not show foaming tendency at all. The foaming tendency of the degraded feed results from the high level of degradation products and contaminants. The fact that the reclaimed products do not foam is an indicator that the degradation level in the product is quite low.

The element compositions of 10 reclaimed products, feed and two waste fluids are summarized and listed in Table 4.5. As can be seen from Table 4.5, it only includes the element compositions of Fe, Ca, Si, PO_4^{3-} and Na as there are no other elements of Al, Pb, Zn, Mg, B, Mo and K in the degraded feed. Compared with the MEG feed, the MEA feed has lower level of these impurities.

In all reclaimed products, the impurity elements of Fe, Ca and PO_4^{3-} have been completely removed. The concentrations of Si are quite stable in the products, around 1ppm, slightly lower than that in the feed. The concentrations of Na in the products range between 0 to 3 ppm, almost half of Na concentration in the feed. The differences of the element compositions among the feed, product and the waste can be seen from Figure 4.7, in which the average values for product and waste are employed.

Because the impurities can get accumulated in the evaporator during the reclamation process, the concentrations of these elements in the wastes are much higher than those in the feed or reclaimed products. It also needs to be mentioned that the concentration of Na is very high in the wastes, much higher than that in the feed. The addition of 50% sodium hydroxide (NaOH) in advance to liberate amines from HSSs in the degraded feed can be one of the reasons.

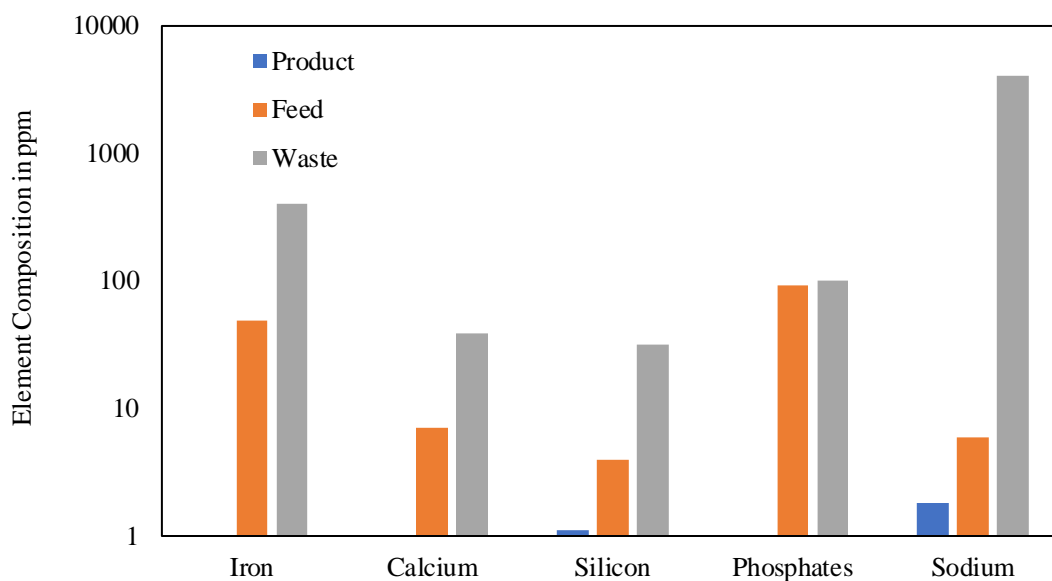


Figure 4.7 Change of element compositions found in the product, the feed and the waste

Table 4.5 Element Composition (ppm) of the Reclaimed Products, the Feed and the Wastes for MEA Solvents

Element (ppm)	Product #										Feed	Waste #	
	1	2	3	4	5	6	7	8	9	10		1	2
Fe	0	0	0	0	0	0	0	0	0	0	49	399	397
Ca	0	0	0	0	0	0	0	0	0	0	7	39	38
Si	1	1	1	1	1	1	3	1	1	0	4	34	30
PO ₄ ³⁻	0	0	0	0	0	0	0	0	0	0	92	93	96
Na	0	3	3	0	3	3	0	3	3	0	6	4133	4081

The properties of the reclaimed products, the feed and the wastes are presented in Table 4.6. As can be seen from Table 4.6, the freezing points of the reclaimed products are almost stable, ranging from 264.26 to 265.37 K, slightly higher than that of the degraded feed. The relatively lower freezing point of the feed results from higher level of degradation.

Due to the large removal of degradation products, especially organic acids, the pH values of the reclaimed products are higher than that of the feed. The total hardness of each reclaimed product is 0 ppm, which confirms the complete removal of divalent cations of mainly calcium and magnesium.

The physical properties of specific conductance, refractive index, density and viscosity are closely related to the degradation products content of the solvent. For 10 reclaimed products, the highest specific conductance value is 6540 μS . This value is much lower than the specific conductance of the feed, due to the removal of ionic degradation products, which can easily conduct electricity.

Normally, the larger value of density, viscosity or refractive index indicates higher level of degradation. From Table 4.6, the density, viscosity and refractive index of each reclaimed product are smaller than those of the feed. This result also proves the removal of degradation products.

Table 4.6 Properties of the Reclaimed Products, the Feed and the Wastes for MEA Solvents

Testing	Unit	Product #										Feed	Waste #	
		1	2	3	4	5	6	7	8	9	10		1	2
Freezing point	K	264.82	264.26	264.82	264.82	264.82	264.82	264.26	264.82	265.37	264.82	260.37	250.93	250.93
Boil point	K	374.82	374.82	374.82	374.82	374.82	374.82	374.82	374.82	374.82	374.82	375.37	428.15	428.15
pH		11.5	11.4	11.3	11.0	10.9	10.9	10.9	10.9	10.8	10.7	10.3	11.3	11.2
Total hardness	ppm	0	0	0	0	0	0	0	0	0	0	17	108	105
Specific conductance	μS	1329	1660	2010	4240	4780	4950	5220	5440	5450	6540	15480	596	851
Density	kg/m ³	1005.4	1009.7	1007.9	1006.0	1005.6	1005.4	1006.8	1005.6	1005.4	1005.6	1030.0	1174.3	1195.4
Refractive index		1.3522	1.3534	1.3530	1.3525	1.3524	1.3523	1.3529	1.3526	1.3522	1.3524	1.3622	1.4774	1.4743
Viscosity	mPa·s	4.2	4.5	3.7	3.8	3.9	3.7	4.2	4.2	3.9	4.1	5.3	440.1	444.5

The result of routine analysis of the solvent concentration, HSSs content and CO₂ loading is presented in Table 4.7. For the degraded feed, the solvent concentration is 15.270% (weight percent). The solvent concentrations of the products are within a narrow range of 14.942% to 16.071%, close to the solvent concentration of the feed. However, the solvent concentrations of the wastes are very high, around 78%, which means that when the system reaches steady state, the liquid within the evaporator is highly concentrated. This concentrated solvent cannot evaporate under the working temperature and pressure and thus works as a heat source, providing heat for the feed constantly entering into the evaporator.

The HSSs contents of the products are almost the same, around 0.061% (weight percent as MEA). This value is much lower than the HSSs content of the feed, which proves that this new reclaimer can efficiently remove most of the HSSs in the degraded MEA solvents.

As also can be seen from Table 4.7, the CO₂ loading of the degraded feed is 0.203 mol per mol MEA solvent. When it comes to the reclaimed products, the values of the CO₂ loading are very low, ranging from 0.004 to 0.048 mol per mol MEA solvent. This proves that after the reclamation process, the CO₂ capture capacity of the recovered MEA solutions can be restored.

Table 4.7 Routine Analysis Result of the Reclaimed Products, the Feed and the Wastes for MEA Solvents

Testing	Unit	Product #										Feed	Waste #	
		1	2	3	4	5	6	7	8	9	10		1	2
Solvent Concentration	wt%	15.330	16.071	15.625	14.978	15.043	15.046	15.086	14.942	15.006	15.003	15.270	78.158	78.429
HSSs content	wt% as solvent	0.000	0.060	0.050	0.061	0.061	0.061	0.061	0.061	0.061	0.061	0.500	-	-
CO ₂ loading	mol/mol solvent	0.004	0.004	0.005	0.020	0.036	0.027	0.031	0.034	0.032	0.048	0.203	-	-

Table 4.8 HSSs Contents of the Reclaimed Products, the Feed and the Wastes for MEA Solvents

Degradation products (ppm)	Product #										Feed	Waste #	
	1	2	3	4	5	6	7	8	9	10		1	2
Sulfate	5	4	3	14	5	5	11	4	4	18	40	30	43
Chloride	6	6	6	0	6	6	6	6	6	6	9	52	50
Nitrate	0	13	13	13	13	13	13	13	13	0	54	426	418
Glycolate	0	136	135	194	210	205	230	242	207	233	325	163	158
Formate	0	3	2	5	17	7	6	11	16	8	580	687	674
Acetate	0	16	14	62	11	34	65	26	33	54	150	1264	1239

The HSSs contents for the reclaimed products, the feed and two waste fluids are summarized and shown in Table 4.8. Seen from Table 4.8, the contents of sulfate, chloride and nitrate are relatively low in the feed, below 100 ppm. The sulfate content has been reduced by more than half. As to the HSSs of chloride and nitrate, their contents in the reclaimed products are around 6 and 13 ppm respectively, lower than those in the feed.

Compared with the contents of sulfate, chloride and nitrate, the contents of glycolate, formate and acetate are much higher in the degraded feed. The formate content in the feed is 580 ppm; however, this value has been largely reduced in the product. The glycolate content has been decreased from 325 ppm in the feed to around 200 ppm in the products. On the other hand, the acetate content goes down from 150 ppm in the feed to around 50 ppm in the reclaimed products.

To better evaluate the removal efficiency of the reclaimer, Figure 4.8 is presented, in which the average values for the product and the waste are employed. Although HSSs of sulfate, chloride, nitrate, glycolate, formate, and acetate still exist in the reclaimed products, their contents in the products are much lower, compared with their contents in the feed, as can be seen in Figure 4.8.

For most of the degradation products, their contents are much higher in the waste than in the feed. However, there are more glycolate and sulfate in the feed than in the waste. The reason might be that these two kinds of HSSs accumulate more easily in the lower layer of the liquid inside the evaporator while upper layer is more easily to be collected.

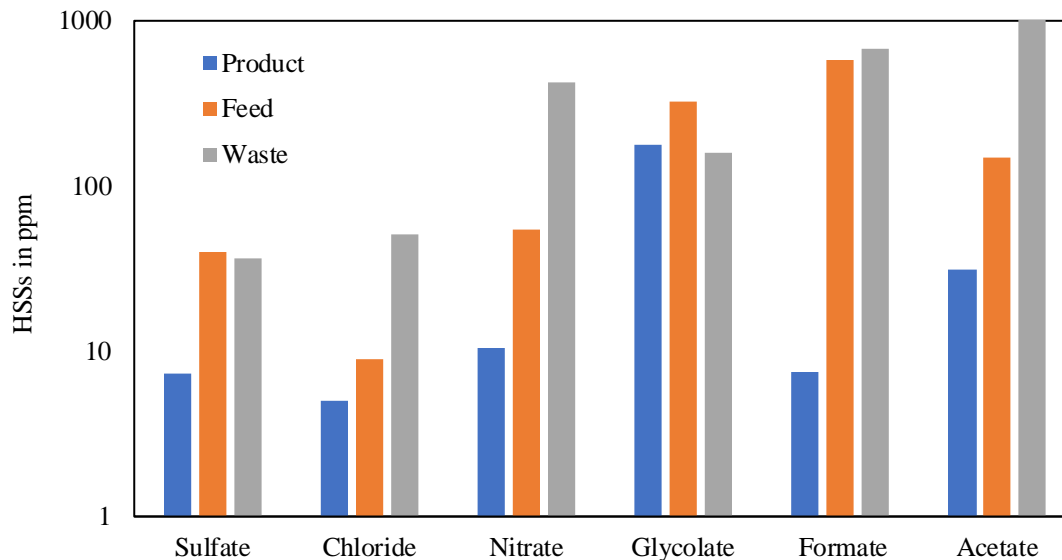


Figure 4.8 Change of HSSs contents in the product, the feed and the waste.

The GC chromatograms of the feed and the reclaimed product are shown in Figure 4.9 and 4.10. In both Figure 4.9 and 4.10, there are two large peaks, which represent water and MEA respectively. There are a lot of small peaks in Figure 4.9, which represent different degradation products except HSSs as HSSs cannot be detected by this column. However, these small peaks do not exist in the Figure 4.10, which proves that these degradation products have been eliminated after reclamation.

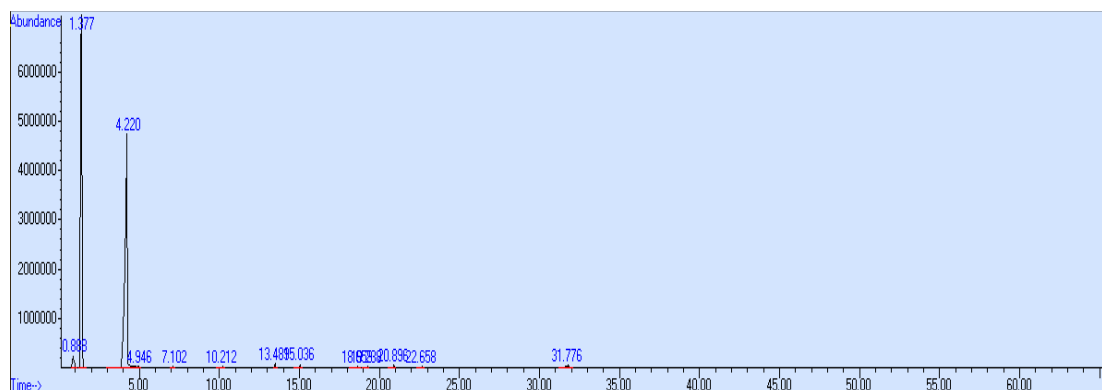


Figure 4.9 GC chromatogram of the feed

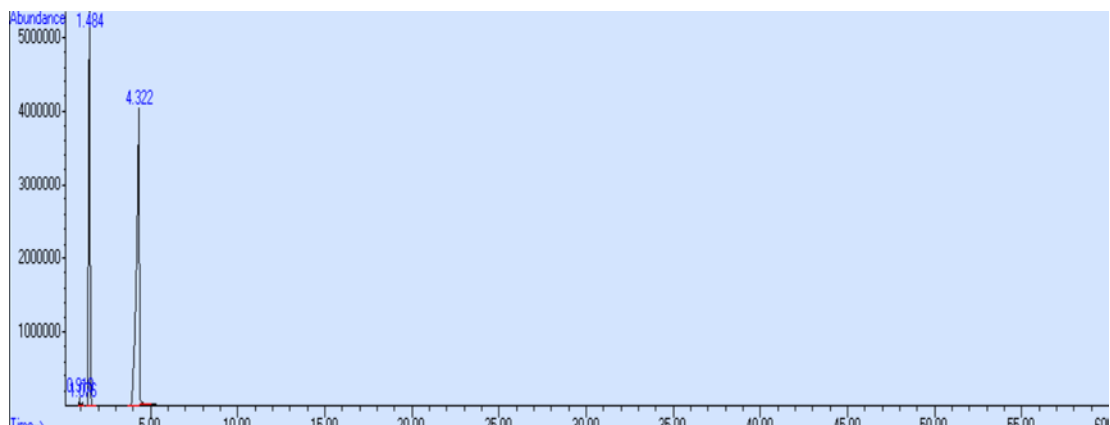


Figure 4.10 GC chromatograph of the product

4.5 Conclusions

In this work, a novel thermal reclaimer was introduced and the degraded solvents of monoethanolamine (MEA) and monoethylene glycol (MEG) obtained from the working plant were used as feeds of the reclaimer. The degraded feed, reclaimed products and wastes for each degraded solvent were carefully analyzed and compared to see the removal efficiency of this reclaimer. The required working temperature and pressure for MEA and MEG are 413.15 K and 38 KPa, and 445.15 K and 20 KPa, respectively. The result shows that this reclaimer is able to remove most of the undesirable degradation products and impurities from the degraded solvent and restore each solvent to almost its original purity. The concentrated waste was collected periodically while the reclaimer was in continuous operation. Concentrating the waste can contribute to the reduction of the waste quantity collected for disposal.

Chapter 5: Conclusions and Suggestions for Future Work

5.1 Conclusions

Densities, viscosities, refractive indices and electrical conductivities of both artificial degraded and industrial degraded MEA solutions were measured at standard temperature of 298.15 K or 293.15 K. Several conclusions can be drawn:

(1) The physical properties of density, viscosity, refractive index and electrical conductivity show a significant dependence on solvent mass fraction, degradation products content and CO₂ loading. They change linearly with increasing solvent mass fraction, degradation products content and CO₂ loading.

(2) Empirical correlations have been developed so that the degradation level could be roughly estimated with a simple property measurement by the CO₂ plant operators, which could avoid using complex equipment and lengthy laboratory techniques. The data and the correlations could also be useful for the CO₂ capture plant designers to consider the impact of degradation products on the physical properties of the solvent.

A new reclaiming process was developed to continuously separate degradation products and other types of impurities from MEA and MEG solvents. Several conclusions can be drawn:

(1) The degraded feed, reclaimed product and waste for each kind of degraded solvent were carefully analyzed and compared to see the removal efficiency of this reclaimer. The result shows that the new reclaimer can remove most of the undesirable degradation products and impurities from the degraded MEA and MEG solvents and restore each solvent to almost its original purity.

(2) The required working temperature and pressure for the reclamation of MEA and MEG solvents are 413.15 K and 38 KPa, and 445.15 K and 20 KPa, respectively.

(3) The concentrated waste was collected periodically. Concentrating the waste can contribute to the reduction of the waste quantity collected for disposal.

5.2 Suggestions for Future Work

Based on the results and findings in this study, several recommendations for future research are as follows:

(1) For physical properties of density, viscosity, refractive index and electrical conductivity, two empirical correlations have been developed for each physical property. The average absolute percentage deviation (AAD) of the correlations of density and refractive index is quite low, which proves the reliability of the correlations. However, for the correlations of viscosity and electrical conductivity, AAD values are high. Consequently, it is essential to conduct more measurements in future work to develop more reliable empirical correlations for viscosity and electrical conductivity.

(2) Densities, viscosities, refractive indices and electrical conductivities of both artificial degraded and industrial degraded MEG solvents can also be measured at standard temperature of 298.15 K or 293.15 K to see the impact of the solvent concentration and degradation products content on the physical properties of MEG solvent.

(3) In the future work, any single, mixed or formulated degraded solvent can also be reclaimed in this reclaimer to see whether this reclaimer can still work efficiently with any other degraded solvents.

(4) More GC-MS work should be involved in the future to determine the degradation product represented by each small peak.

(5) Solvent pre-treatment using ion-neutralization methods will be carefully studied in the future. Neutralization will be done by two methods, inline mixing and mixing tank, in order to optimize the best mixing arrangement for ionic species in real industrial applications. The bench scale glassware of CSTR and PFR will be designed and manufactured for this study.

(6) The solvent post-treatment using activated carbon will be applied to the recovered solvent in the future. The activated carbon isothermal and dynamic experimental investigation will be applied to determine the suitability and removal efficiency in removing any degradation products left after the thermal reclamation. The test will be first carried out in isothermal conditions as batch till

equilibrium stage to determine total efficiency, selectivity and capacity depending on temperature and pH-value of the solvent and on the characteristics (surface area, porosity, pore size) of different types of activated carbon material. Subsequently, the test will be performed in continuous flow conditions to enhance the process parameters, such as throughput, kinetics, and conversion.

(7) A modeling and simulation program including the new reclaimer unit can be developed in the future work. It will incorporate all the new performance parameters and findings obtained from the bench reclaimer unit. The new developed correlation equations of density and viscosity can also be integrated into the model.

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Appendix A

The following three tables list the determination processes of solvent concentration, heat stable salts (HSSs) content and CO₂ loading for one MEA sample.

Table A.1 Solvent Concentration Determination

	Measurement 1	Measurement 2	Measurement 3
Solvent volume, ml	1.0	1.0	1.0
pH of Water added prior titration	6.71	6.70	6.71
pH with solvent prior titration	10.79	10.76	10.79
Reference Burette Reading (V ₀), ml	0.85	0.50	1.7
Final Burette Reading (V ₁), ml	26.65	26.25	27.50
Acid Consumed (V ₁ -V ₀), ml	25.80	25.75	25.80
Solvent Concentration, N	2.580	2.575	2.580
Solvent Concentration, wt%	15.635	15.605	15.635
Average Solvent Concentration, wt%		15.625	

Table A.2 Heat Stable Salts (HSSs) Content Determination

	Measurement 1	Measurement 2	Measurement 3
Solvent volume, ml	1.0	1.0	1.0
pH of Water added prior titration	6.70	6.72	6.71
Reference Burette Reading (V_0), ml	1.10	2.75	4.60
Burette Reading (V_1), ml	2.70	4.40	6.30
pH of water after pre-conditioning	11.43	11.41	11.41
pH with solvent prior titration	11.49	11.47	11.47
Burette Reading (V_2), ml	2.75	4.50	6.40
pH with solvent after titration	11.50	11.50	11.50
Base Consumed (V_2-V_1), ml	0.05	0.10	0.10
HSS, eq/lit	0.005	0.010	0.010
HSS, wt% as solvent	0.030	0.060	0.060
Average HSS, wt% as Solvent		0.050	

Table A.3 CO₂ Loading Determination

	Measurement 1	Measurement 2	Measurement 3
Solvent volume, ml	1.0	1.0	1.0
pH of Water added prior titration	6.70	6.72	6.71
Reference Burette Reading (V ₀), ml	6.50	8.60	10.50
Burette Reading (V ₁), ml	8.40	10.30	12.20
pH of water after pre-conditioning	11.43	11.41	11.41
pH with solvent prior titration	11.46	11.45	11.45
Burette Reading (V ₂), ml	8.60	10.50	12.40
Base Consumed (V ₂ -V ₁), ml	0.20	0.20	0.20
(CO ₂ + HSS), eq/lit	0.020	0.020	0.020
[(CO ₂ + HSS) - (HSS)], eq/lit	0.012	0.012	0.012
CO ₂ Loading, CO ₂ mol/Solvent mol	0.005	0.005	0.005
Average CO ₂ Loading, mol/mol		0.005	