Thermal degradation study by continuous thermal stability rig

Mahla Rashidian

Acknowledgment

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Declaration

This thesis is a presentation of my original research work. Wherever contributions of others are involved, every effort is made to indicate this clearly, with due reference to the literature, and acknowledgement of collaborative research and discussions.

The work was done under the guidance of Professor Hallvard F. Svendsen, at the Department of Chemical Engineering CO_2 capture group at the Norwegian University of Science of Technology (NTNU).

Mahla Rashidian

Abstract

This investigation was done at NTNU and together with Statoil research and development department in Rotvoll, Trondheim to facilitate a new continuous amine thermal degradation rig.

This study was an initial attempt to investigate continuous thermal stability rig as an alternative to thermal degradation study. The major purposes are: (1) to study MEA and MDEA thermal degradation by thermal stability rig apparatus which is designed by Statoil. (2) to demonstrate the result differences between the new and conventional experimental methods.

MEA and MDEA were selected in this study due to have more available literature data in amine based absorption process. The loaded liquid was circulated through the pipe from the cold stream to the hot stream. There is no analytical method was connected to the rig therefore a regular sample was taken every week and sent to SINTEF analytical lab to identify degradation products.

Residence time of solution in high temperature zone also was calculated as an important factor in thermal degradation investigation. Different authors have been provided to understand: the background, the experimental set up, the analytical method to describe the degradation products, data interpretation and the mechanism of the degradation.

Based on analytical results, it seems that only small portion of MEA and MDEA were degraded during 6 weeks experimental time. It showed that the elapsed time was not enough to observe degradation in a significant amount. Metal qualification tests showed low metal concentration in solutions and generally very little corrosiveness effect. However, few degradation products were reported in this study the most probably degradation mechanism is estimated similar to suggested degradation pathway by Davis (2009). More works are required in future to better interpret the new thermal stability rig.

Nomenclature

EI	Electronic Impact
GC	Gas chromatography
GC-MS	Gas Chromatography – Mass Spectrometry
HPLC	High-performance liquid chromatography
IC/MS	Ion chromatography-mass sepctrometry
ICP-MS	Inductively coupled plasma mass spectroscopy
LC-MS	Liquid Chromatography – Mass Spectrometry
LC-MS/MS	Liquid Chromatography-Mass Spectrometry/Mass Spectrometry

Compound abbreviation

AEEA/HEEDA	N-(2-hydroxyethyl)-ethylenediamine
BaCl$_2$	barium chloride
BHEOX	*N,N'*-Bis(2-hydroxyethyl)oxamide
BHEP	2,2'-(piperazine-1,4-diyl)diethanol
CO$_2$	Carbon dioxide
COS	Carbonyl sulfide
CS$_2$	Carbon disulfide
DEA	Diethanolamine
DHU	N,N'-di(hydroxyethyl)urea
DMMEA	2-(dimehylamino)ethanol
DMP	1,4-dimethylpiperazine
EG	ethylene glycol
EO	ethylene oxide
NaOH	sodium hydroxide

HCl	hydrochloric acid
H₂O	Water
H₂S	dihydrogensulfide
HEA	*N*-(2-hydroxyethyl)acetamide
HEIA	1-(2-hydroxyethyl)-2-imidazolidinone
HEF	*N*-(2-hydroxyethyl)formamide
HEP	N,N'-bis(2-hydroxyethyl)piperazine
HEO	3-(2-hydroxyethyl) oxazolidinone-2
HMP	1-(2-hydroxyethyl)-4-methylpiperazine
MEA	monoethanolamine
MEA-urea	N,N'di(hydroxyethyl)urea
MDEA	Methyldiethanolamine
OZD	2-oxazolidinone
TEA	Triethanolamine
TEG	Three Ethylene Glycol
THEED	N,N,N'-tris(2-hydroxyethyl)ethylenediamine
TMA	trimethylamine
TMBDA	tetramethylbutylenediamine
TriHEIA	1-(2-((2-hydroxyethyl)amino)ethyl)imidazolidin-2-one

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1. Introduction

This chapter is used to briefly discus of role of CO_2 on climate change and identify CO_2 capture process based on absorption/stripping and its environmental impact and explain specific motivation of this work.

1.1 Environmental impact

Warming of the climate system is accepted by the scientific community and anthropogenic CO_2 emissions are the main source of it. (IPCC, 2007) Fossil fuels are the dominate sources to generate heat and power (primary energy) which are covered 80% of total energy demand in the world. (IEA, 2008) In figure 1.1 the world energy demand can be seen versus different fuels from energy outlook report (IEA, 2011) It is estimated that energy demand will be increased by 40% up to 2030, and it means 77% increasing of coal usage (Eide-Haugmo,2011). CO_2 emission reduction depends on energy efficiency improvement and alternative fuels such as natural gas and renewal sources.

The most common technology to reduce released CO_2 from fossil fuel is carbon capture and storage (CCS).
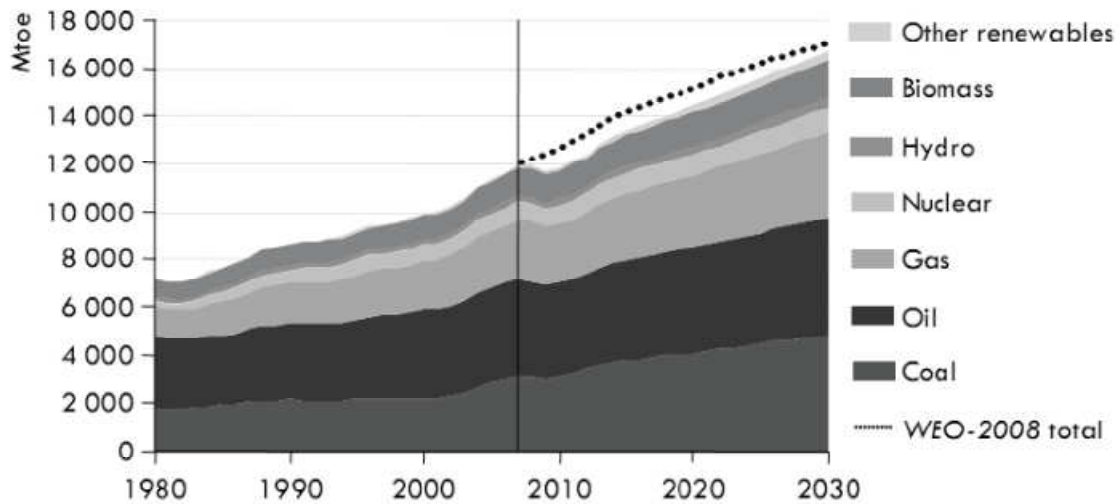
Figure 1.1 world energy demand versus different types of fuel (IEA, 2008)

In CO_2 capture process based on absorption, degradation is a main problem and it needs to be reduced to the smallest possible amount. Amine degradation is an irreversible conversion of an absorbent solution to unwanted products. Degradation is reduced solution concentration and consequently its absorption capacity. Degradation products

can also increase the viscosity, foaming and corrosion (Kohl and Nielsen, 1997). Degradation also causes higher regeneration energy demand in the system and creates undesirable environmentally emission as well. Different solvents were tested regard stability and reaction at high temperatures close to stripper condition.

1.2 CO$_2$ capture by Amine absorption/Stripping

Amine absorption with MEA is one of the most common technologies to CO$_2$ capture from flue gases and is more developed compare to other methods. Figure 1.2 illustrates an MEA absorption/stripping system.
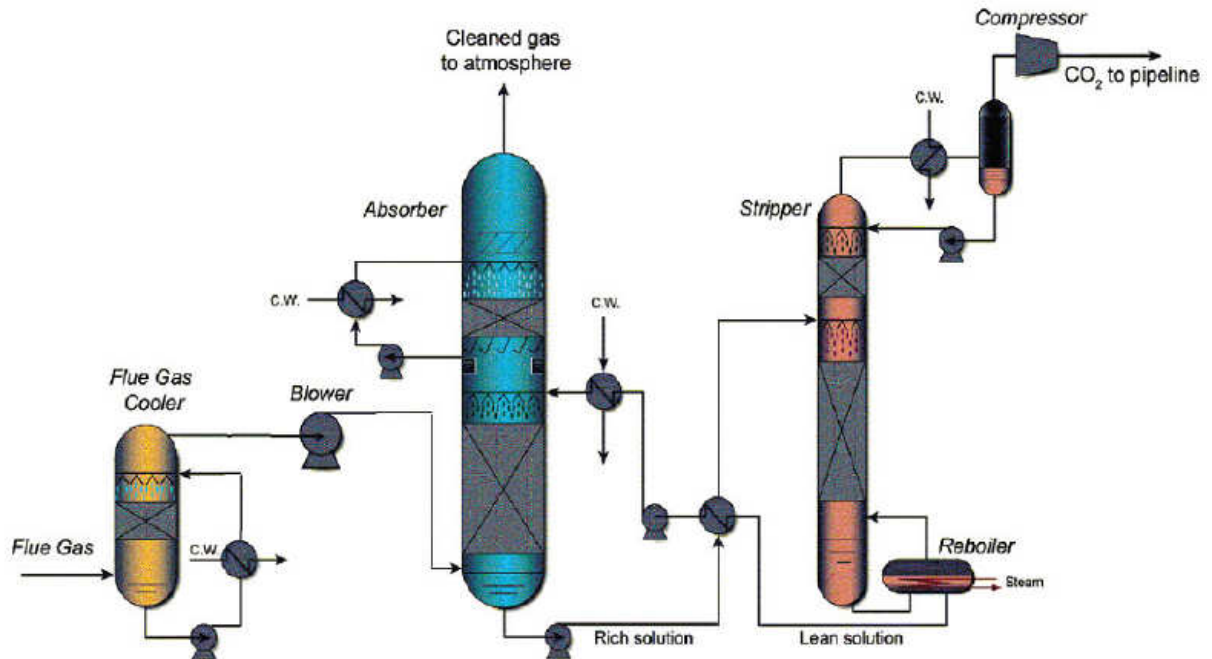
Figure 1.2 flow diagram of CO$_2$ capture from flue gas by chemical absorption (Tobiesen and Svendsen, 2006).

The flue gas, which contains approximately 10% CO$_2$, is cooled and entered into the bottom of the absorber. Then it is contacted counter currently with lean solution 15-40 wt% MEA in water and (0.2-0.4 mole CO$_2$/mole MEA) which enters from the top of absorber. Around 90% of CO2 is removed from flue gas. The treated flue gas exits from the top of absorber and then passing through water wash section to reduce amine into vapor phase as much as possible. The rich solution with (0.4-0.5 mole CO$_2$/mole MEA) exits from the stripper bottom and preheated counter-currently in an exchanger by lean amine solution the stripper. So the CO$_2$ is released by stripping the solution by swing temperature between 40°C to about 120°C with extra heating by steam in a reboiler. The hot lean amine exits from stripper bottom and cooled down by passing the cross-

exchanger before returning back to the absorber to further CO_2 removal. Since steam generation unit results in reducing the efficiency of CO_2 capture plant about 8-13% (IEA 2003), therefore Solution recovery in stripper is the largest economic factor in this CO_2 capture technology.

1.3 Background

There are three types of degradation, "oxidative degradation in the absorber, volatility losses in the effluent and thermal degradation in the cross exchanger, stripper and thermal reclaiming unit."(Davis, 2009)

Oxidative degradation occurs by oxidation and fragmentation of amine, and thereby forming heat-stable salts. Since there is no oxygen in natural gas treating process, this type of degradation is not normally the main degradation in such processes. Volatility losses can be controlled by add water wash section to the absorption process. Thermal degradation happens by carbamate polymerization and resulting in forming higher molecular weight products. Thermal degradation is highly depending on CO_2 present in solution. In CO_2 free solutions thermal degradation is negligible unless at Fhigh temperatures above 200°C , whereas oxidative degradation is depending on oxygen and metal ions.

Reclaimers can be used to remove thermal and oxidative degradation products, and ion exchange and electrolysis can be used to remove heat-stable salts. Based on Blake (1962) research, half of thermal degradation products are formed by reclaiming because of elevated temperatures around 150°C.

Thermal degradation for several amines with and without CO_2 has been studied such as MEA by (Polderman et al., 1955; Yazvikova et al., 1971; Yazvikova et al., 1975; Strasisar et al, 2003; Tazli, 2004; Davis,2009; Eide-Haugmo, 2011). MDEA (Chakma and Miesen, 1997a; Davis, 2009; Eide-Haugmo, 2011). Lepaumier et al., (2010;2009a,b;2008) studied over 16 compounds include ethanolamine and ethylenediamine for thermal degradation.

1.4   Present research objective and scope

Since the cost of amine degradation is an important part of operating costs and also environmental impacts of releasing used chemicals as absorbents in CO_2 capture process, therefore it is important to get better understanding of amine degradation, type and quantity of degradation products before installing a unit.

This study is a combination of literature review and experimental work. In experimental part, thermal stability of MEA and MDEA solutions with CO_2 are tested by thermal stability rig to identify and quantify thermal degradation products. Different analytical method such as Liquid Chromatography-Mass Spectrometry (LC-MS), Gas Chromatography-Mass Spectrometry (GC-MS) and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) are applied by SINTEF and Olav Hospital to identify and qualify degradation products. The main objective of the study is comparing the achieved results to previous findings literatures and find out advantages and disadvantages of thermal stability rig compare to previous method.

Specific goals are listed below:

> - Study of thermal degradation of MEA and MDEA with CO_2 at elevated temperature.
> - Understanding of the degradation reactions
> - Identification and quantification of thermal degradation product
> - Comparing the degradation products and amine loss of new experimental setup to conventional experimental methods which have been used previously.

2 Literature Review

To provide a good knowledge of this topic, a literature study was focused for MEA and MDEA. Different authors have been provided to understand: the background, the experimental set up, the analytical method to describe the degradation products, data interpretation and the mechanism of the degradation.

2.1 Monoethanolamine (MEA)

Monoethanolamine (MEA) is an organic base and has high ability to react with weak acids such as CO_2 at low temperatures and produce an amine carbamate. (Christensen, 1969). The process is reversible by heating up MEA in a stripper. At higher temperatures and CO_2 concentrations, MEA can form a degradation product called carbamate polymerization, and it is an irreversible degradation process which causes reducing acid gas absorption capacity, increasing viscosity of solution and also increasing corrosion and foaming.

2.1.1 Polderman et.al., (1955)

The first carbamate polymerization mechanism was suggested by Polderman et al. (1955). They used aqueous MEA solutions for natural gas treating plants and identified different degradation products. In suggested mechanism by Polderman, MEA reacts with CO2 to produce MEA carbamate which is a normal process in absorber and it is reversible in the stripper (reaction 1).
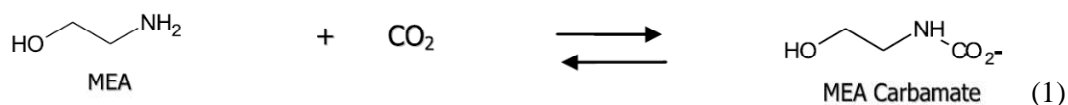
MEA carbamate in a condensation reaction can produce 2-oxazolidone (reaction 2) .
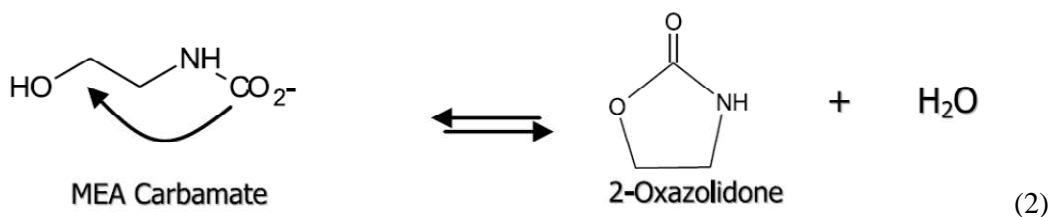
2-oxazolidone can also react with another MEA to form isolated degradation product, 1-(2-hydroxyethyl) imidazolidone (HEIA) as can be seen in below:

(3)
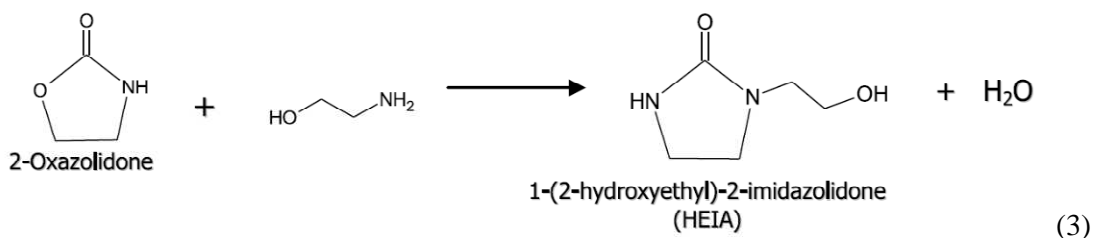
HEIA is a cyclic urea with low capacity to absorb CO_2 and result in reducing the overall capacity of the solution. HEIA hydrolyzing in reaction 4 is producing N-(2-hydroxyethyl) ethylenediamine (HEEDA) as a second degradation product.

(4)
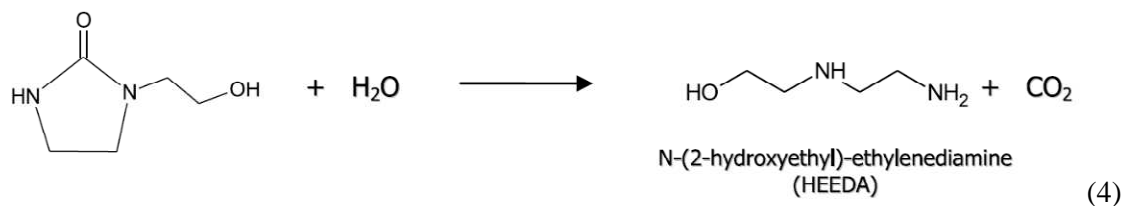
HEEDA reforms the absorption capacity of solution. It is a stronger base than MEA and makes regeneration process more difficult than ordinary situation without HEEDA. The last reaction is an equilibrium and it is influenced by solution temperature and CO_2 partial pressure.

HEIA and HEEDA were identified as two main degradation products of MEA carbamate polymerization. These degradation products can be removed from the solution by distillation of a slipstream. Polderman et al., (1955) reported HEEDA as a corrosiveness product, but not the main reason of corrosion.

2.1.2 Yazvikova et.al., (1971 and 1975)

Yazvikova (1971) studied formation of 2-oxazolidinone (OZD) and it was mentioned as a limiting stage in the overall conversion of MEA with CO_2. Reaction of MEA and oxazolidinone was fast. In a later study by Yazvikova (1975), oxazolidinone and MEA in absence of water at elevated temperatures about 200°C was discussed . He found out that all oxazolidinone consumed within 20 minutes and formed an equimolar amount of N,N'-di(hydroxyethyl)urea (DHU). DHU was converted to HEIA and HEEDA by further heating.

Therefore, two new stages of carbamate polymerization degradation were suggested by Yazvikova (1975); reaction of MEA and OZD to form N, N'-di (hydroxyethyl) urea and HEEDA and HEIA formation.

The results of this study were different compare to previous findings due to dehydrated samples. Water presence leads to MEA dilution and it takes part as a proton donor or acceptor in the reaction (Eide-Haugmo 2011).

2.1.3 Talzi and Ignashin (2002) and Talzi (2004)

They studied the reaction of MEA with CO_2, COS and CS_2 in gas treating process condition . The suggested degradation mechanism was almost the same as Polderman mechanism. The only difference was the path to urea and HEIA were parallel instead of series.

2.1.4 Strazisar et.al., (2003)

They focused on the degradation products of a flue gas treating. Different gas chromatography (GC) methods were applied to identify unknown degradation products which represented a mixture of oxidative and thermal degradation. The products mostly were from the thermal reclaimer bottom with very high amine concentration, heat and metal content that may not be a normal stripper condition. Also reported in this study, there was no HEEDA in the thermal reclaimer bottoms, which goes against the results of other papers on the same topic.

2.1.5 Davis et.al., (2009)

The recent study of MEA thermal degradation was done by Davis (2009) and Davis and Rochelle (2009). In this study, thermal degradation of MEA was tested under stripper operational conditions. The stainless steel reactors were filled with MEA solutions between 15 and 40 wt% and CO_2 loading from 0.2 to 0.5 (mole CO_2/mole MEA) then stored in forced convection oven at elevated temperatures (100-150°C). samples collected and different analytical methods had been done to identify degradation products .

The results of Davis (2009) work indicated that decreasing CO_2 loading has a first order effect on decreasing of degradation rate, and MEA concentration increasing has stronger effect than first order on degradation rate increasing.

In this study three main degradation products were reported; MEA-urea, AEEA/HEEDA and HEIA and other polymeric compounds. It was found that AEEA/HEEDA converted to HEIA in stoichiometric quantities. HEIA did not convert to AEEA/HEEDA and was a stable product. AEEA/HEEDA could degrade to more polymeric compounds in a same degradation pathway as MEA. According to Davis (2009) study results, a new thermal degradation pathway was suggested.

The new mechanism is similar to Polderman et al., (1955) suggested mechanism, but AEEA/HEEDA and HEIA formation reaction are switched and formation of MEA-urea and further reactions of AEEA/HEEDA are added to the new suggested mechanism. HEEDA can further react with CO_2 and form HEIA. It was investigated that AEEA/HEEDA can react to OZD and form a MEA-trimer and react further more to polymeric compounds either CO_2 and form cyclic urea (Eide-Haugmo, 2011).

The degradation product pathway for MEA 30 wt % with 0.4 (moles CO_2 / moles MEA) degraded at 135°C has been illustrated in figure 2.2.

From illustrated results in figure 2.1, HEIA is the main degradation product, AEEA/HEEDA is formed during first days and then converted to HEIA and other degradation products. Small amount of trimer is formed and after few days leveled off, whereas triHEIA is remaining in the solution.
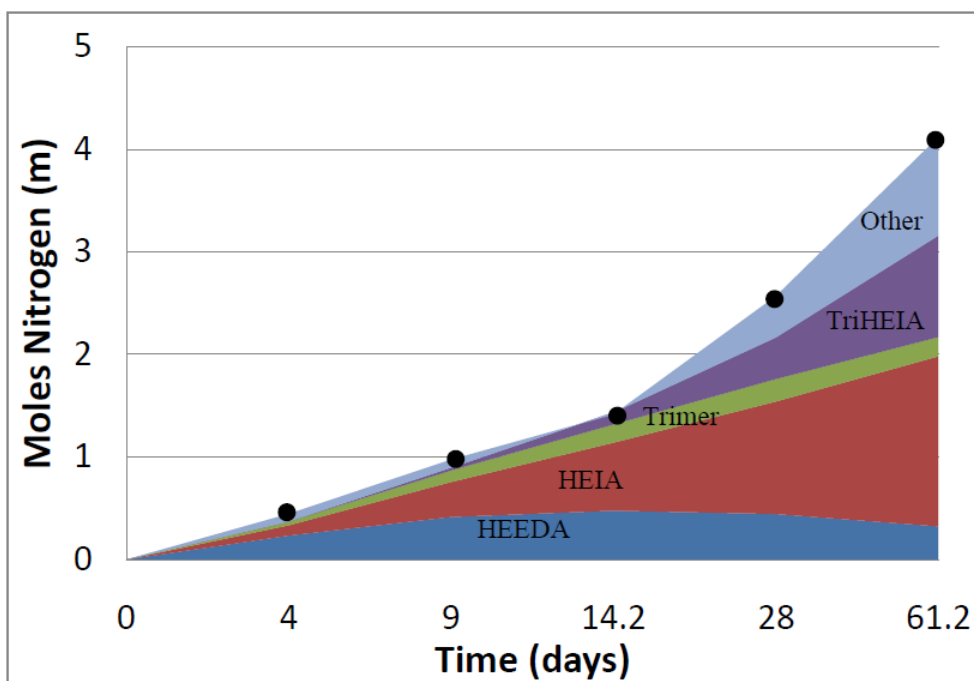
Figure 2.1 Breakdown of species in a degraded sample 7m MEA with a loading of 0.4 at 135° C, normalized by nitrogen content, Davis (2009)
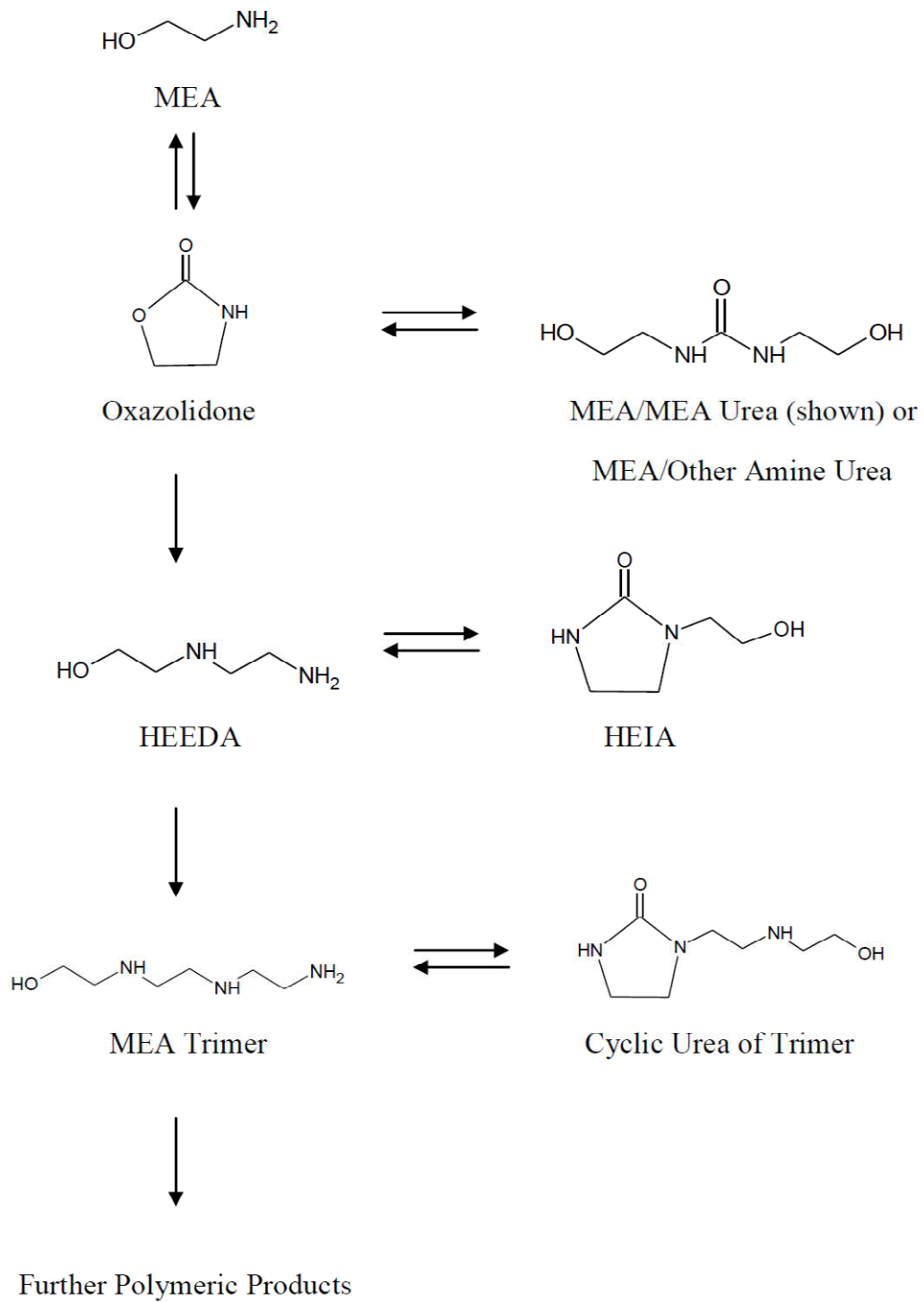
Figure 2.2 Suggested MEA degradation pathway by Davis (2009)

2.1.6 Eide-Haugmo (2011)

She studied MEA thermal degradation products and mechanism, and reported different degradation compounds. Remaining MEA in loaded and unloaded solutions as a function of time for thermal degradation were reported as can be seen in figures 2.3 and 2.4.
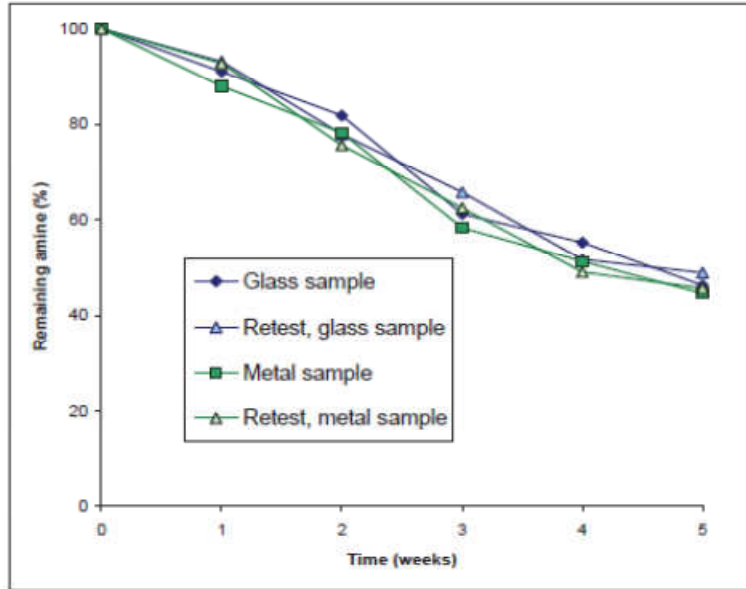
Figure 2.3 remaining amine as a function of time for thermal degradation of MEA with 0.5 CO_2 loading (Eide-Haugmo, 2011)
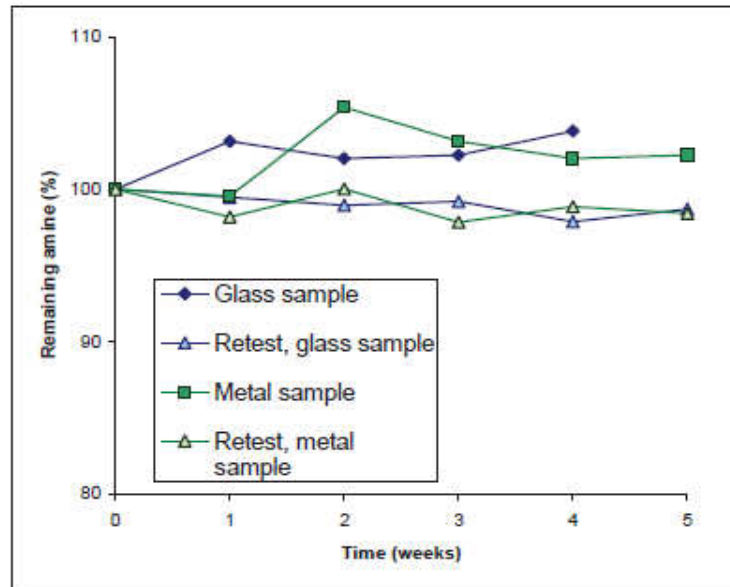
Figure 2.4 remaining amine as a function of time for thermal degradation of unloaded MEA solution. (Eide-Haugmo, 2011)

As can be observed from given results, in thermal degradation without CO_2 (unloaded) MEA is mostly stable and no significant degradation could be measured. While in thermal degradation with CO_2, MEA shows steady loss over the experiment time. Measured amine loss was around 12% per week and total amount after 5 weeks was approximately 55%. (Eide-Haugmo, 2011)

Degradation products structures were identified by GS-MS analysis method and results are shown in figure 2.5. There are four main identified degradation products; oxazolidion (OZD), AEEA/HEEDA, and two cyclic ureas/imidazolidiones (HEIA and AEHEIA). There was no standard to identify AEHEIA and founded compound could be imidazolidiones. (Eide-Haugmo, 2011)

Degradation products level during the 5 weeks are presented as percentage of MEA based on nitrogen balance in figure 2.6. oxazolidinone is produced in very low amount with almost constant concentration over time. This could be explained by OZD being an intermediate degradation product and reacts to form other degradation compounds. (Eide-Haugmo , 2011)

AEEA/HEEDA was formed in the first week and then decreasing slightly. It indicated that HEEA/HEEDA can be also an intermediate degradation product. The highest reported level of degradation product was HEIA which is a stable imidazolidine and will remain in solution.
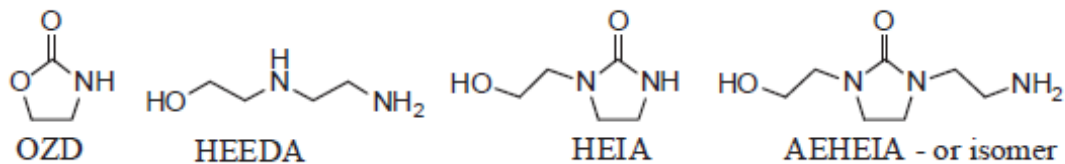
Figure 2.5 identified degradation products for thermal degradation of loaded MEA solution by GC-MS (Eide-Haugmo, 2011)
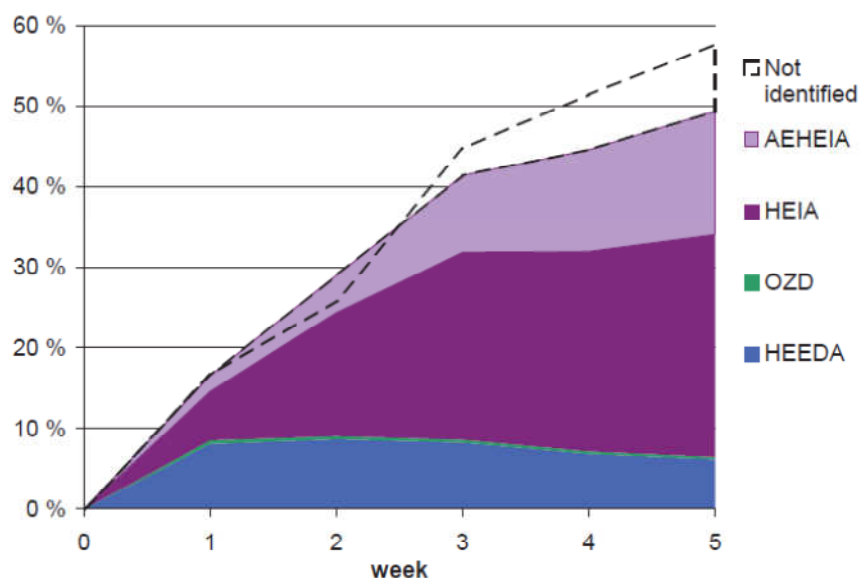
All identified degradation products for MEA in this study were confirmed by previous findings.

2.1.7 Laurance Reid Proceedings

There are some other literatures on MEA thermal degradation which mostly pay attention to natural gas treating processes and different engineering controls due to minimize thermal degradation and its drawbacks on the process.

Dingman et al. (1966) suggested low amine concentration around 15 wt% or less, rich CO_2 loading below 0.35 (moles CO_2/mole amine), initial loading around 0.1, and low pressure stripper to keep temperature as low as possible. The negative point of all this control measurements is increasing the energy consumption of the system.

Blake (1962 and 1963) suggested the design of thermal reclaiming units with pressure matching part to match unit pressure to the stripper. The distillate can be part of the boilup and match the desired amine/water ratio to distillate. It can help the water balance problem. This reclaiming system due to simple design and easy operation becomes a standard method in the industry.

2.2   Methyldiethanolamine (MDEA)

Methyldiethanolamine is mostly used for selective CO_2 and H_2S removal from gas stream in gas treating plants (Vidaurri and Khare, 1977; Blance and Elgue, 1981; Daviet et al., 1984; Haimour et al., 1987). Since MDEA is a tertiary amineand it doesn't have any hydrogen-nitrogen bound; therefore it's not react with CO_2 to form a carbamate. It represents that MDEA degradation by reacting with CO_2 is unlikely. (Chakma and Meisen, 1997)

To sum up, MDEA advantages are; high selectivity for hydrogen sulfide compare to carbon dioxide, higher energy efficiency, higher acid gas removal capacity, more resistance to degradation, smaller equipment size for new plants and the most important one is less corrosively compare to primary and secondary amines like MEA. (Lepaumier, 2009)

2.2.1   Meisen and Chakma (1988)

They worked on Methyldiethanolamine (MDEA) thermal degradation study. Degradation products of MDEA 4.28 M solution at 180° C over 144h under CO_2 partial pressure about 2.59 MPa reported as below:

Methanol, ethylene oxide (EO), trimethylamine (TMA), N, N-dimethylethanamine, ethylene glycol (EG), 2-(dimehylamino)ethanol (DMMEA), 4-methylmorpholine, 1,4-dimethylpiperazine (DMP), HEP, THEED, triethanolamine (TEA) and 1-(2hydroxyethyl)-4-methylpiperazine (HMP). The degradation compounds were identified by gas chromatography/mass spectrometry (GC-MS). Based on achieved results, MDEA degradation rate is very slow at lower temperatures around 120°C. (Chakma and Meisen, 1997)

2.2.1.1   Effect of temperature on MDEA degradation

As can be seen in semi-logarithmic plots of MDEA concentration versus time at different temperatures with initial concentration equal   to 4.28 mol/L (figures 2.7 and 2.8), MDEA degradation is strongly temperature dependent and it is negligible below 120°C.
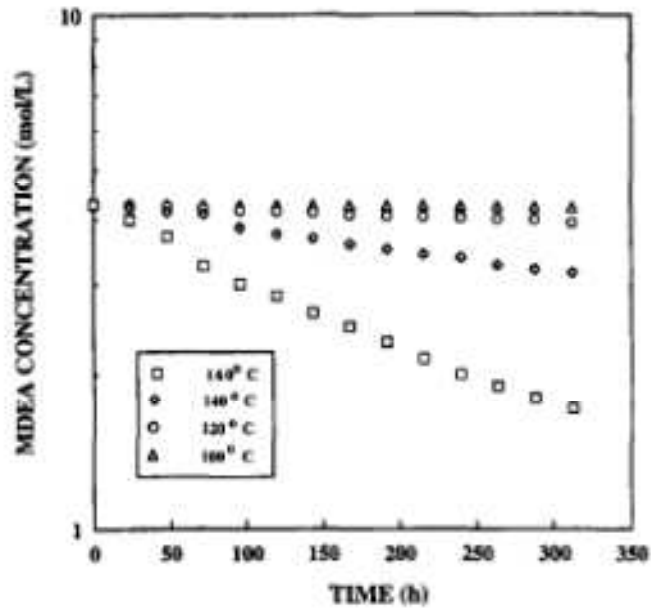
Figure 2.7 MDEA concentration as a function of time and temperature. (Initial MDEA concentration, 4.28 mol/L; CO_2 partial pressure, 2.59 MPa), (Meisen and Chakma, 1997)
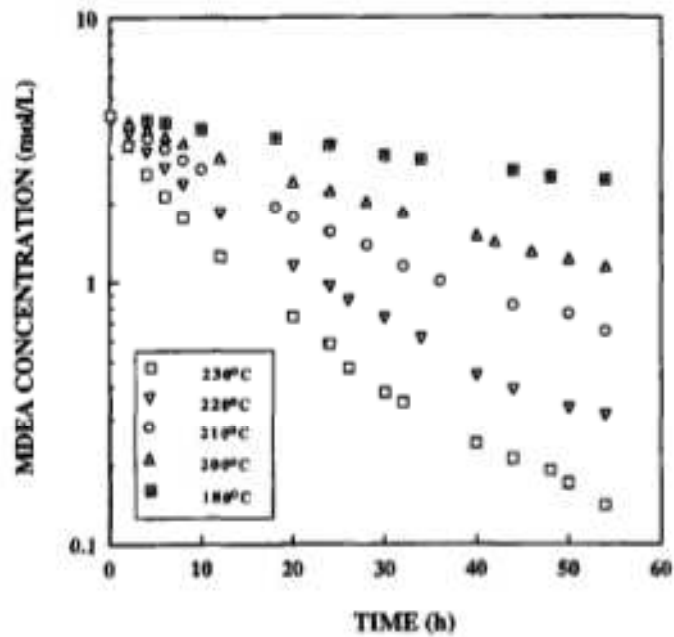
Figure 2.8 MDEA concentration as a function of time and temperature. (Initial MDEA concentration, 4.28 mol/L; CO_2 partial pressure, 2.59 MPa), (Meisen and Chakma, 1997)

2.2.1.2   Effect of initial MDEA concentration on degradation

In figure 2.7, results of MDEA concentration in range of 2.0 to 6.0 mol/L are plotted as a function of initial concentration of MDEA. The rate constant increases byincreasing the initial concentration up to 3.5 mol/L, and then it starts to decrease in higher initial MDEA concentration. The initial increase in degradation rate with concentration has explained by considering the CO_2 concentration increasing in solution as well as MDEA concentration has been increased, whereas at higher concentrations water is limiting and as a consequence, protonated MDEA is decreasing. Since the first step in MDEA degradation process is reaction between MDEA and protonated $MDEAH^+$, reduction of protonated concentration lead to decreases the overall MDEA degradation rate.
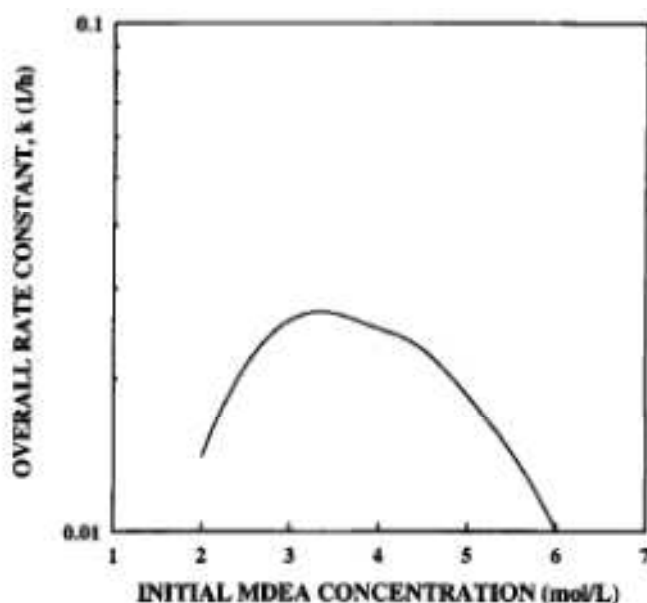
Figure 2.9 Overall MDEA degradation rate constant as a function of initial concentration. (temperature, 200°C; CO_2 partial pressure, 2.59 MPa), (Chakma and Meisen, 1997)

2.2.1.3   Effect of CO_2 partial pressure on degradation

As can be seen in figure 2.10, overall degradation rate is affected by CO_2 partial pressure. The degradation rate is increasing slightly (smoothly) by raising of CO_2 partial pressure and it could be because of increasing CO_2 solubility in MDEA solutions once the partial pressure is increased. (Chakma and Meisen, 1997)
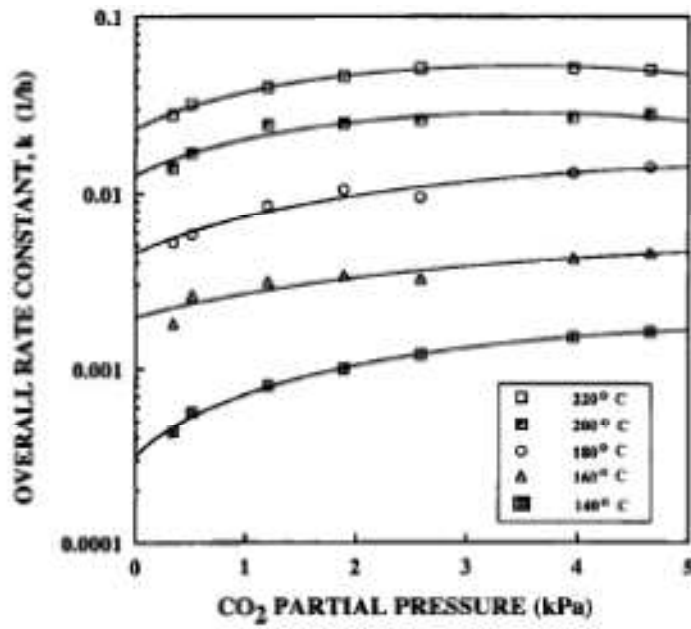
Figure 2.10 overall MDEA degradation rate constant as function of temperature and CO_2 partial pressure. (Initial MDEA concentration, 4.28 mol/L), (Chakma and Meisen, 1997)

Suggested MDEA degradation reaction mechanism by Chakma and Meisen are given as follow:

CH3 \\ N-C2H4-OH + CO2 + H2O ⇌ CH3 \\ H+ / N-C2H4-OH + HCO3−
CH3 /   CH3 /

DMAE

CH3 \\ N-C2H4-OH + CH3 \\ H+ / N-C2H4-OH ⟶ . . . . .
CH3 /   CH3 /

CH3 \\ CH3 / N+-C2H4-OH + CH3-N-C2H4-OH   **MAE**
CH3 /   H

↓ + CO2

COO−....H+
|
CH3 - N - C2H4-OH

MAE CARBAMATE

CH3 \\ N - CH3 + CH2 - CH2
CH3 /   O
                H

TMA

↓

CH2 - CH2
OH   OH

EG

HO-C2H4 \\ N-H + CH2 - CH2 ⟶ HO-C2H4 \\ N-C2H4 -OH
HO-C2H4 /   O   HO-C2H4 /

DEA   **EO**   **TEA**

HO-C2H4 \\ N-C2H4 - OH + HN \\ C2H4 -OH
HO-C2H4 /   / C2H4 -OH

⟶ HO-C2H4 \\ N-C2H4-N / C2H4 -OH + H+ + HCO3−
    HO-C2H4 /   \\ C2H4 -OH

THEED

17
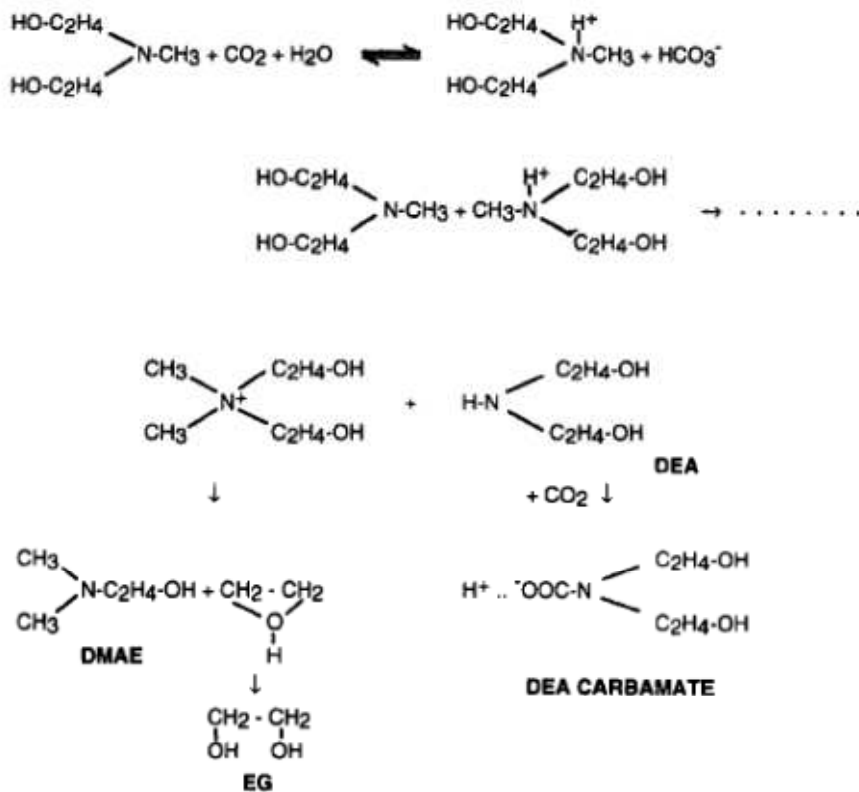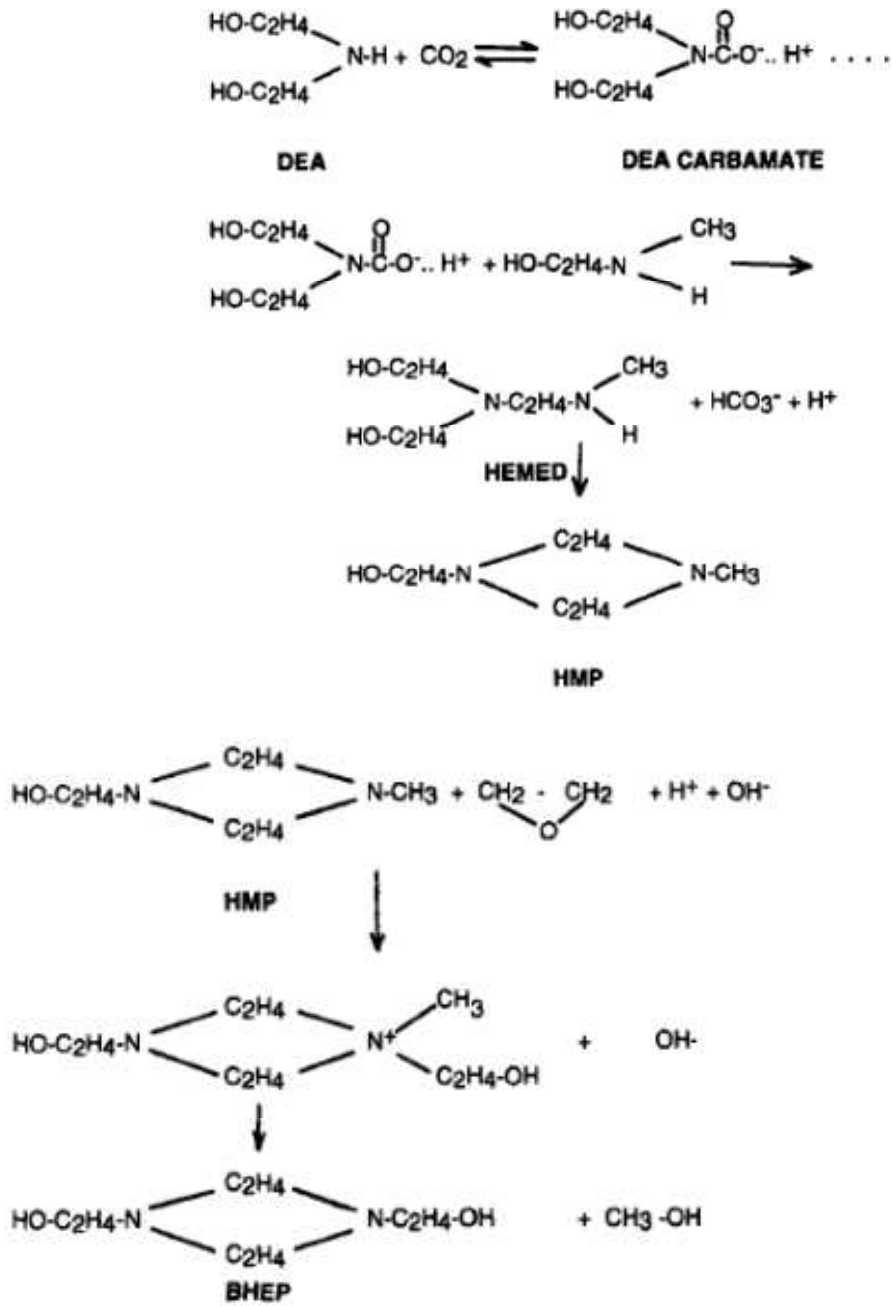
Figure 2.11 MDEA degradation mechanism suggested by Chakma and Miesen (1997)

MDEA degradation reactions can be listed as below: (Meisen and Chakma, 1997)

$$MDEA + CO_2 + H_2O \rightarrow MDEAH^+ \ldots \ldots \ldots$$

$$MDEA + MDEAH^+ \rightarrow DMAE + EO + DEA \ldots$$

$$DMAE + DMAEH^+ \rightarrow TMA + EO + MAE \ldots$$

$$MAE + CO_2 \rightarrow MAECOOH \ldots \ldots \ldots$$

$$EO + H_2O \rightarrow EG \ldots \ldots \ldots \ldots \ldots$$

$$DEA + CO_2 \rightarrow DEACOOH \ldots \ldots \ldots$$

$$DEACOOH + MAE \rightarrow HMP \ldots \ldots \ldots \ldots$$

$$DEA + EO \rightarrow TEA \ldots \ldots \ldots \ldots$$

$$HMP + EO \rightarrow BHEP \ldots \ldots \ldots \ldots$$

$$DEA + CO_2 \rightarrow HEOD \ldots \ldots \ldots \ldots$$

$$DEA + CO_2 \rightarrow THEED \ldots \ldots \ldots \ldots$$

$$THEED \rightarrow BHEP \ldots \ldots \ldots \ldots \ldots$$
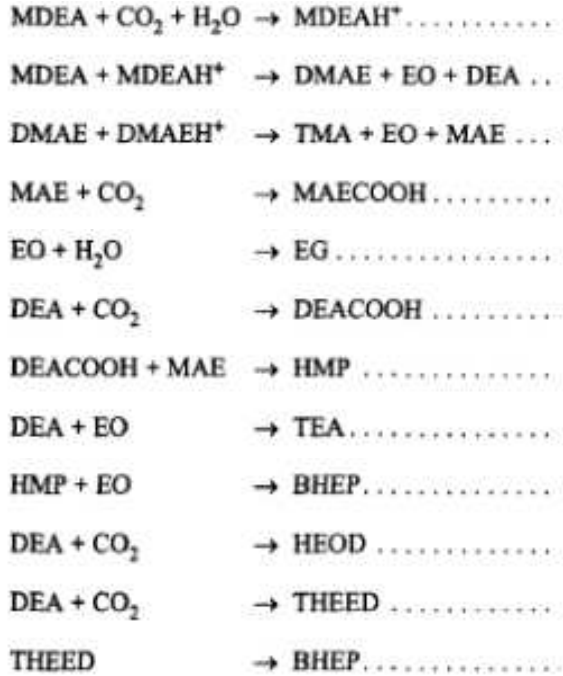
2.2.2   Bedell (2008)

He suggested different degradation pathways for MDEA under aerobic conditions; elimination reactions, hydrolysis, hemolytic cleavage and disproportionation. Data from hydrolysis of amino acid at high temperatures and extrapolated to stripper condition shows logical pathway of amine degradation. The most favorable MDEA degradation pathway under normal stripper condition would be an initial transethoxylation or disproportion. In this free radical mechanism one trimethanolamine molecule and one dimethylethanolamine can be formed by replacing an ethanol group of MDEA with a methyl group of another molecule. DEA formation by replacing a methyl group with hydrogen could also be explained by free radical mechanism. Whenever DEA or any other secondary amines formed, reactions could take place according to the degradation pathway of that particular amine by carbamate polymerization.

2.2.3   Davis (2009)

MDEA showed low rate of degradation that was in accordance with Meisen and Chakma results.
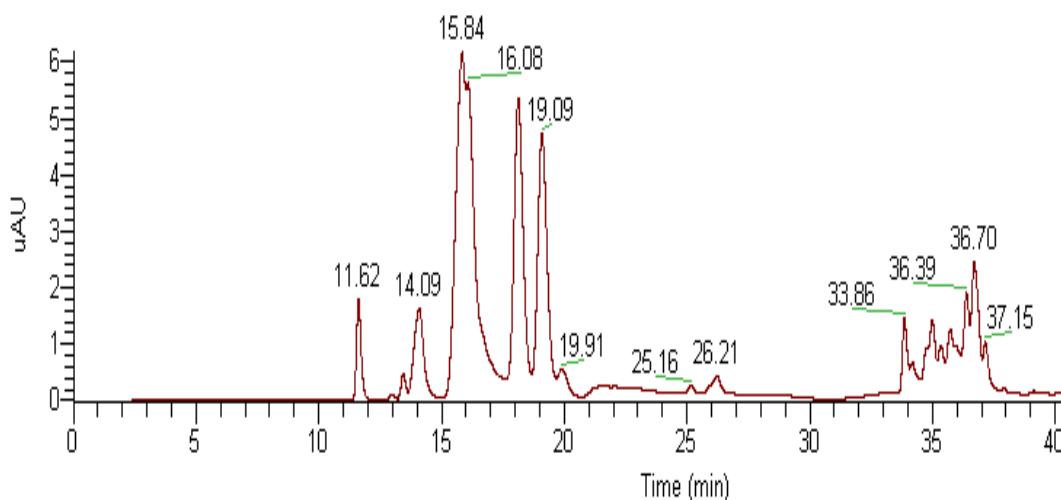
Figure 2.12 IC/MS chromatogram of 50 wt% MDEA aqueous solution on a CO₂ free basis with a loading of 0.4 moles of CO₂ per mole of alkalinity held at 135°C for 4 weeks (Davis 2009)

MDEA formed lots of degradation products at temperatures higher than 135°C. As can be seen in figure 2.12, the peak at 14 min with Mw 105 represents diethanolamine and peak at16 min, next to MDEA (15.84 min) is dimethylethanolamine. They both are MDEA degradation products and identified in previous works by Meisen and Chakma (1988). Also peaks at 16.1 and 19.1 min with Mw of 133 and 103 correspond to DEA dimer and THEED. The remaining peaks present a big range of degradation products which have not been identified as MDEA degradation products before.

2.2.4   Eide-Haugmo (2011)

She performed a far ranging study on amine degradation including MDEA. Four main MDEA degradation products were identified by GC-MS; a tertiary amine DMMEA, an oxazolidinone (HEO) and two piperazine products (HEP and BHEP). DMMEA, HEO and BHEP were identified previously by Meisen and Chakma, Lepaumier and Davis, whereas HEP was identified for the first time by Eide-Haugmo (2011).

2.3   Other studies

Many other amines have been studied and in this section some of them covered by Lepaumier, et.al., (2008).

2.3.1   Lepaumier et.al., (2008)

they have studied a large range of different amines degradation based on the chemical structure of the amine. 17 different molecules such as alkanoamines, diamines and triamines without an alcohol function were focused. Experiments were done in 100 mL stainless steel reactors with 4M amine, 2 Mpa of CO_2 and at 140°C for 15 days. After 15 days dimethylpiperazine (DMP) showed the lowest degradation about 3.7 % loss and HEEDA, the dimer of MEA showed the highest amount of degradation about 99 % loss during the same time. In figure 2.13, total degradation of different species are illustrated in similar way.
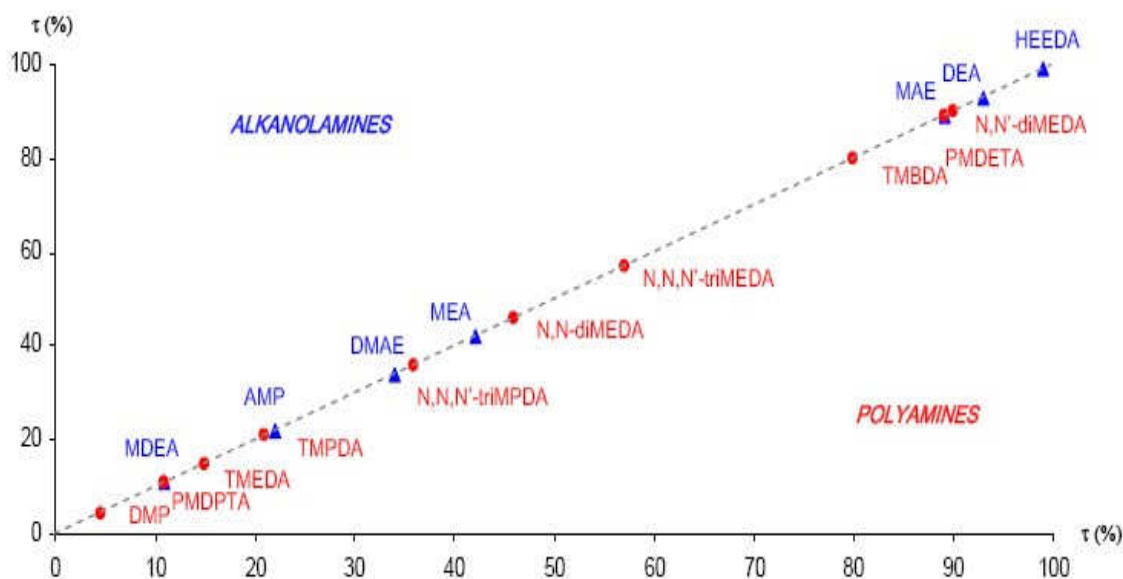
Figure 2.13 shows amine loss of all studied amines after 15 days at 140°C and 2Mpa CO_2 (Lepaumier 2008)

2.3.1.1   Alkanoamines

Based on achieved results, tertiary amines and hindered amines had minimum amine loss, whereas primary amines, secondary amines and diamines showed higher amine loss. The hindered amines such as AMP mainly converted to oxazolidone compounds. The tertiary amines had dimethyl/dealklation reactions, some addition reactions and

finally some unknown degradation products. The primary amines like MEA participated in imidazolidone and some more reactions. The secondary amines had ring closures and number of other reactions. The suggested alkanoamine degradation mechanism is shown in figure 2.14.
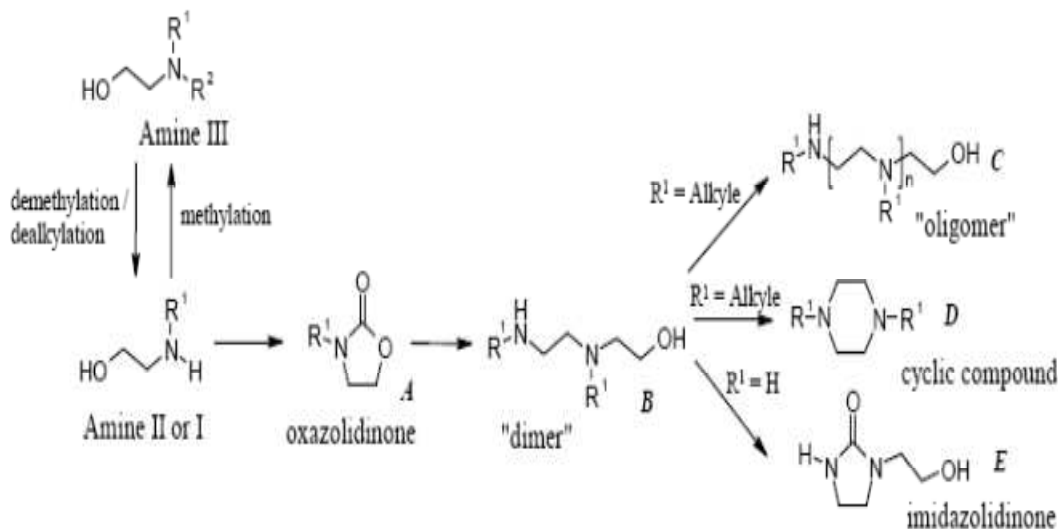
Figure 2.14 reaction pathway for alkanoamines based on amine functional groups (Lepaumier 2008)

MEA according to have hydrogen for R1 group would prefer to form imidazolidone (structure E in figure 2.14). MDEA would go through demethylation/dealkylation reactions before going through MEA or DEA thermal degradation pathway. DEA would follow structure C and D.

2.3.1.2 Polyamines

In this study polyamines are grouped in 4 classes; dimethylpiperazine (DMP), ethylendiamines, propylenediamines and tetramethylbutylenediamine (TMBDA). demethylation/dealkylation was formed in all groups. Ethylenediamines has two more reactions; imidazolidone and ring closure. TMBDA has complete ring closure reactions. The suggested polyamines degradation mechanism is shown in figure 2.15.
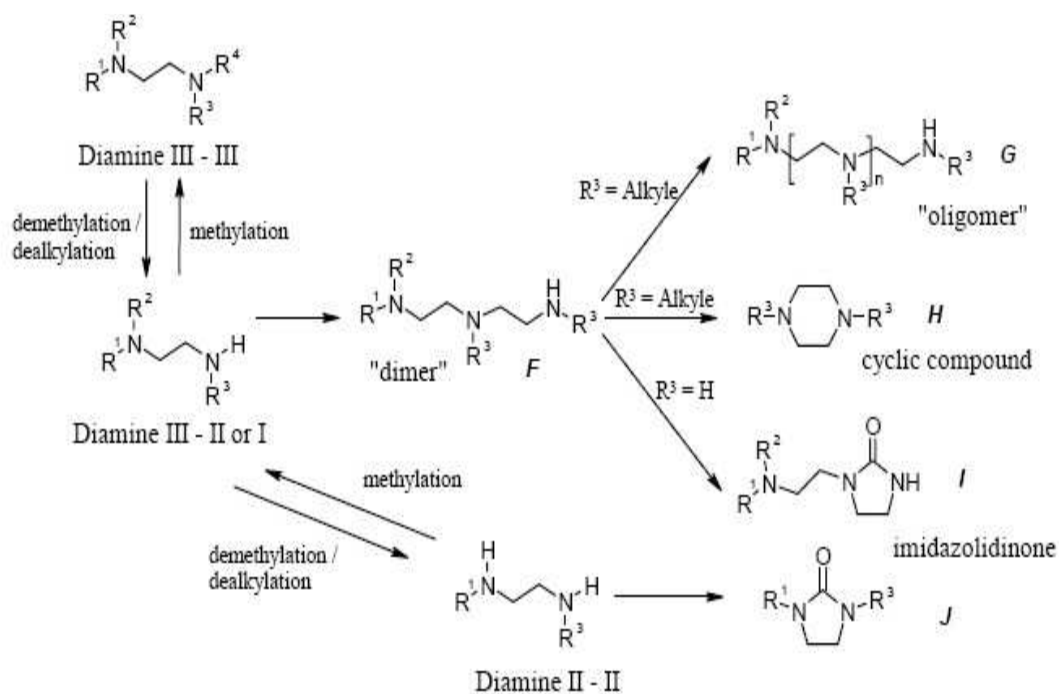
Figure 2.15 reaction pathway for polyamines based on amine functional groups (Lepaumier 2008)

As can be seen, polyamines degradation pathway is almost the same as alkanoamines and the only difference is an imidazolidone formation by an additional demethylation reaction from a diamine III-II to a diamine II-II.

3   Experimental apparatus and analytical methods

This chapter is used to provide information about the new thermal stability rig and experimental set up steps. Information about the solution preparation and different analytical methods which have been used to identify different degradation products are also given in this chapter.

3.1   Experimental apparatus

Amine thermal stability experiments were conventionally done in stainless steel cylinders which were stored in high temperature ovens at around 135°C during the experiments and samples were collected weekly (Eide-Haugmo, 2011 and Davis et. al., 2009). This method can be called a conventional static apparatus. No liquid movement or agitation during the experiment, the temperature can be assumed uniformly during the experiment. This method somehow was able successfully to study the thermal stability.

A new thermal stability rig was designed by Statoil which can be called as a continuous apparatus was run for the first time in the spring of 2013 at NTNU CO_2 capture lab. The experimental set-up consists of two heating baths to represent the absorber and stripper temperatures condition. The preloaded liquid was circulated through the pipe from the cold stream to the hot stream. There is no analytical method was connected to the rig therefore a regular sample was taken every week and sent to SINTEF/NTNU analytical lab to identify the degradation products.

In this experimental work the long coil equal 10 (m) was installed to increase the contact area of a heating source and liquid inside the coil. Overall length of the loop in the rig includes two coils and other connection piping in system is approximately 30 (m). all pipes, coils and solution vessel are stainless steel.

As can be seen in figures and P&ID , the rig includes a stainless steel vessel for loading solutions, two heating bath circulators, a flow meter to measure the liquid flow rate inside the coil (L/min) and a pump to recycle the solution through the system.

Since the maximum design pressure of the system is 6 bar a safety valve has been installed and it will response in case of pressures higher than 6 bar. An emergency button is installed in case of emergency which is connected to the main power of the system.

VX-001
300-400ML

P-001

Figure 3.1 stainless steel vessel for loading the solution
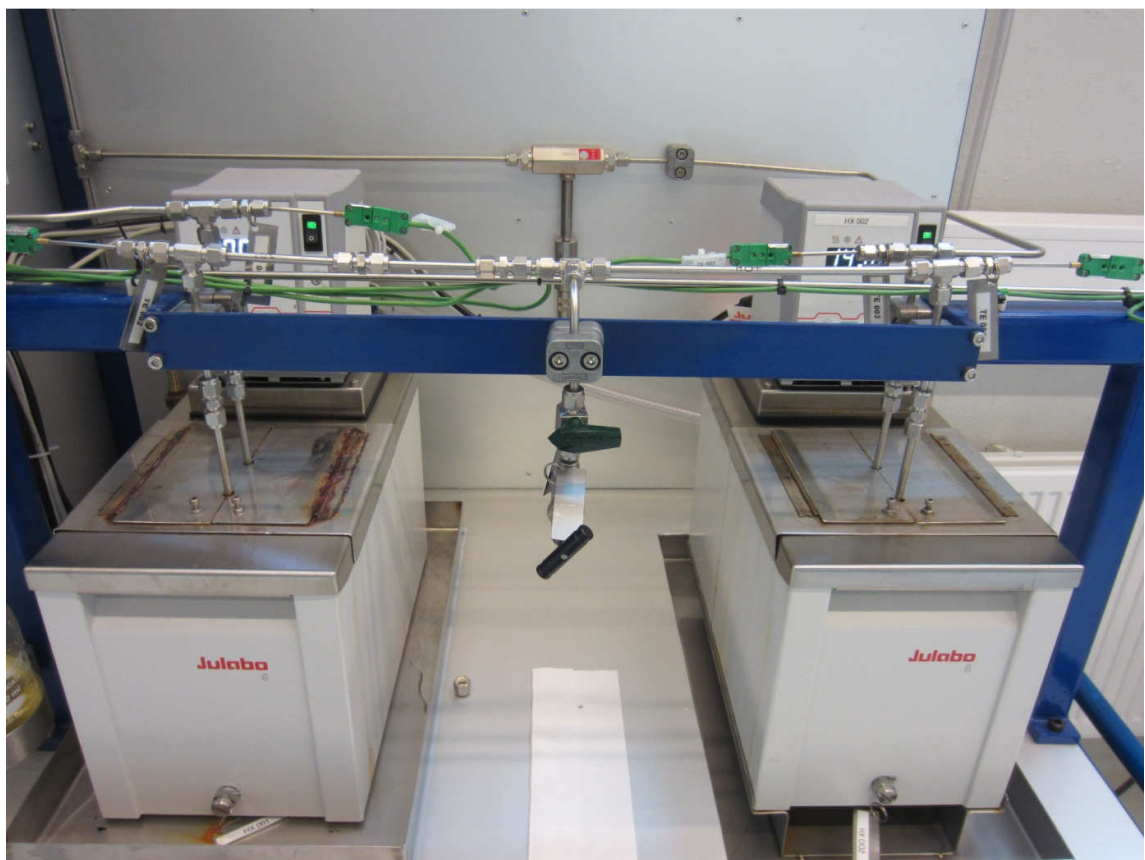
Figure 3.2 cold and hot bathes

3.2 Experimental steps/details

There are three main steps: start-up, shut-down and cleaning that are explained in below.

3.2.1 Start-up of the thermal stability rig

- Filling the cold bath with water
- Filling the hot bath with Three Ethylene Glycol (TEG) or Silicon oil
- Opening the cooling water valve to cool down the cold bath water and keep it around set point
- Feeding the prepared solution into the vessel by separation fennel to prevent spilling and HSE purposes. Solution has been sucked in by a syringe which is connected to the upper point of the vessel.
- Degassing of the vessel after each sucking should be done by disconnecting the syringe and removes the air manually from syringe.
- Pressurized the solution by nitrogen around 3 bar.
- Close the main source nitrogen valve on the wall and the main green one on the apparatus.
- Switch on the main power button and both heat circulators (Julabo).
- Lab-view program is turned on and opened after switching on the main power due to receive correct signal from apparatus.
- Turning on the pump, but before starting the pump system should be degassing from the higher drain point. The pump was set on 0.64 (L/min). the maximum design flow rate of pump is 0.8 (L/min).
- Setting the both hot and cold bath temperatures from lab-view program.
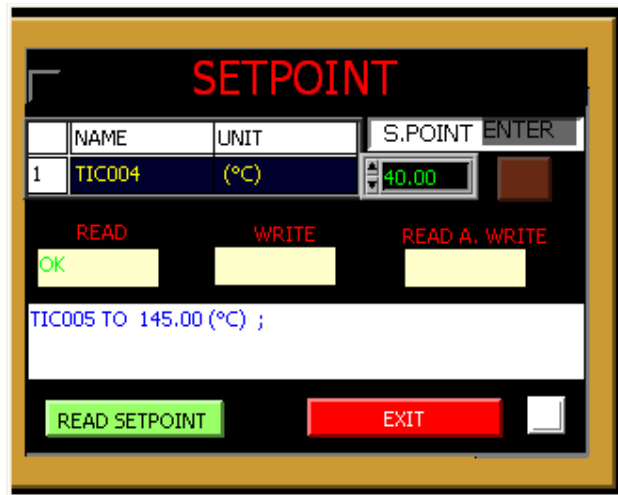
Figure 3.3 Set point window to set cold and hot bathes temperature

All temperatures and pressure were monitored from the lab-view program. Each set of experiment was run for minimum 5 weeks, and the only critical issue to consider was water level in Julabo and adjusting the cooling water to keep the cold bath temperature around 40°C.
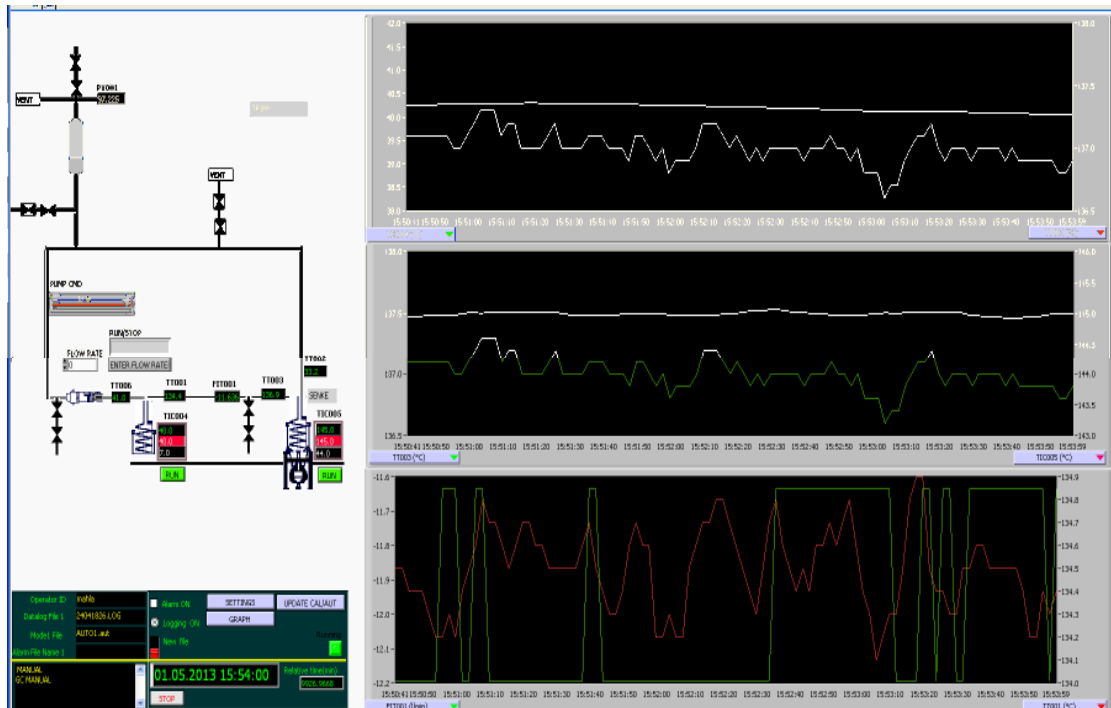
Figure 3.4 experiment monitoring window from lab view program

3.2.2 Shut-down thermal stability rig

- ➢ Turn off both heat circulators
- ➢ Turn off the pump
- ➢ Close the cooling water valve
- ➢ Switch off the main power of apparatus
- ➢ Close the main valve and the apparatus nitrogen valves
- ➢ Save the final log on lab-view profile
- ➢ Turn off the PC

3.2.3 Apparatus cleaning procedure

- ➢ Switch on the main power
- ➢ Turn on hot bath and set it to around 60°C
- ➢ Open nitrogen valve around 2 bar
- ➢ Turn on the pump
- ➢ Open the vessel drain valve (HV-002/HV-003) and try to empty the line as much as possible by closing the valve pressurized for a few seconds and opening again
- ➢ Open HV-004/HV-005 to drain the solution from pipe lines and try to make lines empty by the same procedure as HV-003
- ➢ Open HV-008/HV-009 to drain recycle line by doing the same procedure as previous steps
- ➢ Filling the feed vessel with deionized water and run the system for 15-20 minutes
- ➢ Drain water from the system by exactly the same steps as draining solutions which has listed above
- ➢ Turn off the pump
- ➢ Turn off heat circulators main power
- ➢ Running the nitrogen through the system, by opening and closing the same valves for 15 minutes the lines and vessel will be completely dry and ready to the next experimental set.

At higher temperatures (135°C), solution removing and apparatus drying will be much faster and easier. So it is highly recommended to clean the apparatus right after taking the last sample.

3.3 Solution preparation and dilution

Solutions were prepared based on weight percent. A certain amount of amine was blended with deionized water, then moved to loading reactor and put on the scale for adding CO_2. A glass tube with a silicon pipe fit was placed in solution which was

connected to a CO_2 cylinder and pressurized CO_2 was added to solution up to target amount. Adding CO_2 was done in a way that solution surface has rarely broken by bubbles to prevent water loss. CO_2 loading is an exothermic reaction and surface of solution has been kept below 40 C by controlling the loading rate and it was also a way to prevent water loss in the solution. More detail can be found in Hilliard (2008).
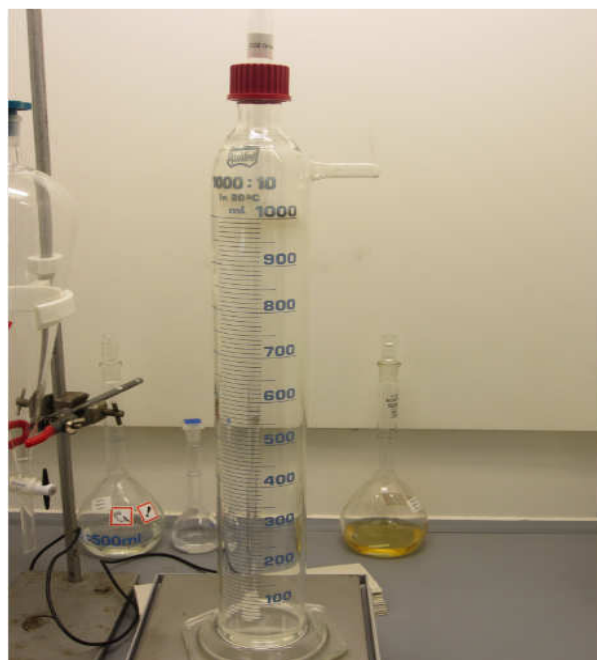
Figure 3.5 loading reactor

Figure 3.6 silicon pipe to connect CO_2

Figure 3.7 CO$_2$ cylinders for CO$_2$ loading system

In order to check the total amine concentration in the solution, the initial solution was titrated with H$_2$SO$_4$ 0.1M as it has been explained in analytical methods section in this report.

Dilution for analytical testing was done by gravimetrically method. Samples were diluted 10 times by weight. Final diluted samples were mixed with a GVlab vortex apparatus as seen in figure 3.8.

Figure 3.8 vortex for small amount of diluted samples

3.4 Analytical methods

Chromatographic and titration analyses were used to analyze the samples. Different methods are explained in this section.

3.4.1 LC-MS/MS

Liquid Chromatography - Mass Spectrometry (LC-MS) was done at SINTEF analytical lab and applied to measure the initial amine concentration (mol/L) and amine concentration in degraded products. The LC-MS system which has been used is Liquid Chromatography – Mass Spectrometry/Mass Spectrometry (LC-MS/MS), 6460 Triple Quadrupole Mass Spectrometer and 1290 infinity LC chromatograph and infinity auto sampler 1200 series G4226A from Agilent Technology (Eide-Haugmo, 2011). This method is explained in detail by Lepaumire et al., (2011).

3.4.2 GC-MS/MS

Gas Chromatography – Mass Spectrometry (GC-MS) was done at SINTEF analytical lab and used to identify and determined the degradation products. A Gas Chromatograph 7890A made of an Autosampler 7693 with a mass spectrometer. The mass spectrometer can be used in both Scan and SIM mode, and Electronic Impact (EI), Positive Chemical Ionization (PCI) and Negative Chemical Ionization (NCI). In this method when there was not any commercial available products for the degradation compounds, they were identified based on a library match and specifications are based on the similar structure chemicals. (Eide-Haugmo, 2011) This method is explained in detail by Lepaumire et al., (2011).

3.4.3 ICP-MS

Inductivity coupled plasma mass spectroscopy (ICP-MS) was used to metal quantification. The assessed metals were iron, vanadium, chromium, manganese, nickel and molybdenum. The used system was Element 2 from Thermo Fisher (Bermen, Germany). The analyses were done at St. Olav hospital.

3.5 Titration methods

There are two different titration analytical methods; total alkalinity and CO_2 content. They are presented in this section.

3.5.1   Total alkalinity titration method

Total alkalinity titration was used to measure the total alkalinity of solutions during the experiments in samples. 0.2 ml of sample was weighed and diluted in 50 ml water and titration the solution with H_2SO_4 0.1M until pH=2.5.

Figure 3.9 alkalinity titration system

3.5.2   CO$_2$ titration method

CO$_2$ titration method was used to measure CO_2 concentration in the samples. In this method approximately 0.5 grams of sample was weighed out to a solution of $BaCl_2$ barium chloride (1N, 25ml) and NaOH sodium hydroxide (0.1N, 50ml). To enhance following reaction to produce $BaCO_3(s)$ the solution was boiled around 4 minutes.

$$Ba^{2+} + CO_2 + 2OH^- = BaCO_3(s) + H_2O$$
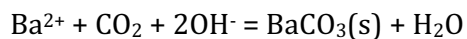
The solution was filtrated and then hydrochloric acid (0.1N, 40ml) was added gravimetrically to dissolve $BaCO_3$ and the excess HCl in the solution was then titrated with NaOH sodium hydroxide 0.1N to reach the end point at pH = 5.25.

$$BaCO_3 + 2HCl = BaCl_2 + CO_2 + H_2O$$

For each sample two parallels were titrated to be sure about the results. One blank sample was also made without adding amine samples, because of existing CO_2 in air that should be taken into account in calculations.
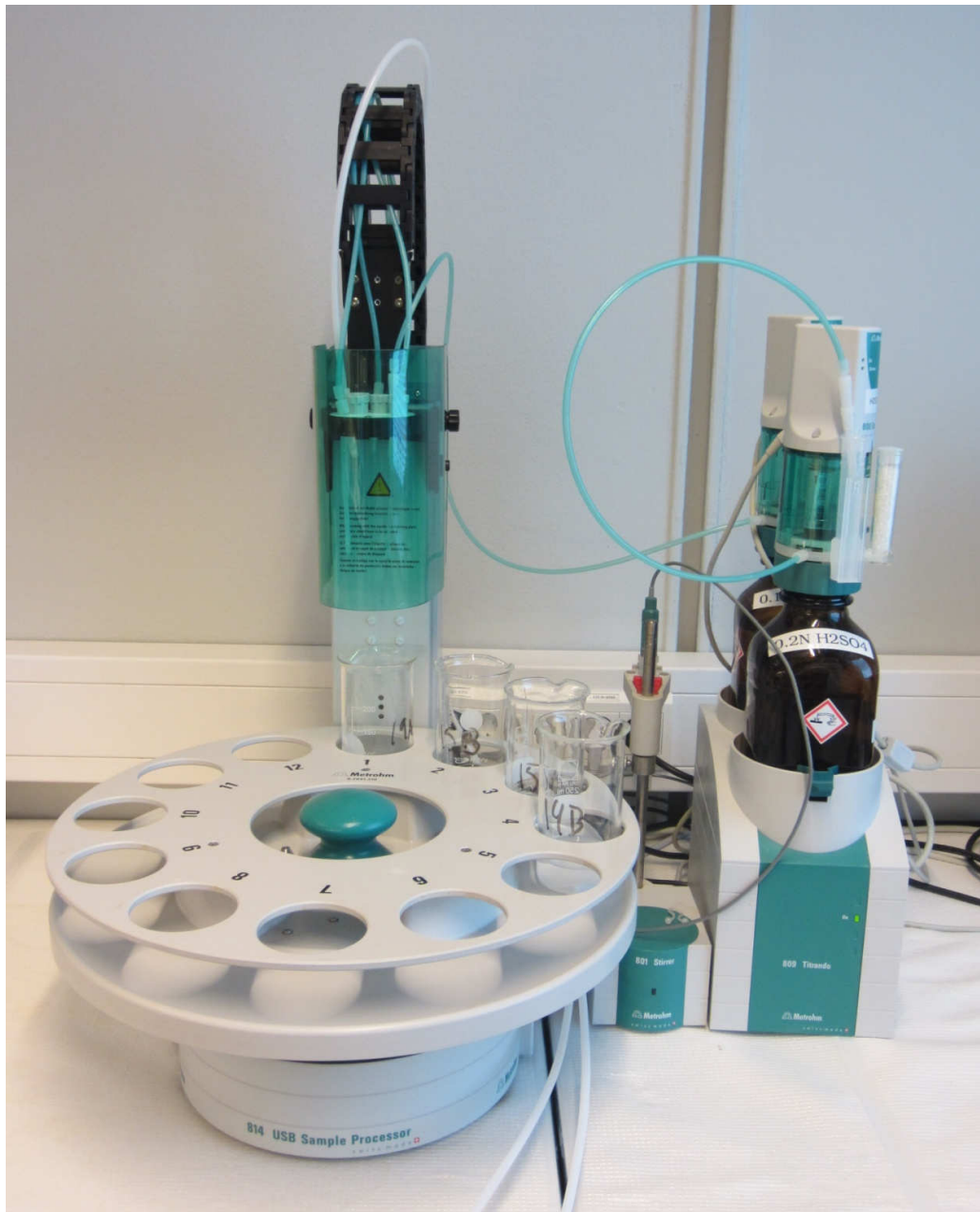
Figure 3.10 CO_2 titration system

4   Heat transfer calculation

In this section heat transfer coefficient and solution temperature profile calculation based on theory and assumptions are discussed.

The thermal stability rig was design as a continuous apparatus and the liquid was circulated from cold stream to the hot stream. The residence time of the solution was estimated by using the length of the coil and the mass flow of the liquid. The temperature ,of course, varies along the line. To estimate the temperature profile, a subsequent calculation was proposed:

4.1   Heat transfer coefficient

Heat transfer coefficient near the inlet due to zero thermal boundary layer thickness is the highest and reducing gradually to completely developed value. In fully developed region in a circular system the flow rate profile is steady while the temperature profile is changing along the line. (Cengel, 2002)

To simplify the calculation, following assumptions are made:

-   Coil is assumed as a straight tube (a helix)
-   Chamber temperature consider as surface temperature of the coil.
-   No heating loss.
-   Steady state

Considering the assumptions and according to following equations heat transfer coefficient at the inlet and outlet of coil are calculated.

$$Q = A_s . h . (T_S - T_\infty)$$

Where;

Q : Heat transfer rate [kJ/sec]

A_s : Surface area of tube [m^2]

h : Heat transfer coefficient [$W/m^2 . °C$]

T_S : Surface temperature of tube [°C]

T_∞ : Fluid temperature inside tube [°C]

Surface area is calculated as below:

$$A_s = \pi . D . L$$

D: Tube diameter [m]

L: Tube length [m]

And heat transfer rate is determined from following equation:

Q = ω . C_p . ΔT

Where;

ω: Mass flow rate of solution [kg/sec]

C_p : Solution heat capacity [kJ/kg. K]

ΔT: Fluid inside the tube (solution) temperature difference [°C]

After replacing all parameters by calculated numbers, heat transfer rate was calculated. Then from following equations heat transfer coefficients were determined.

Heat transfer coefficient at the beginning and the end of tube are equal to:

$$h_1 = \frac{Q}{A_s . (T_S - T_1)}$$

$$h_2 = \frac{Q}{A_s . (T_S - T_2)}$$

4.2 Temperature profile inside the tube versus length

Heat transfer coefficient difference in circulating region with constant flow rate profile is indicated temperature variation during the heat transfer process along the tube. To trace the actual temperature profile of fluids along the heat exchanger, long mean temperature difference needs to be calculated. It is an exact difference between cold and hot fluids and is always lower than arithmetic temperature difference. (Cengel, 2002)

To calculate temperature profile following equation is used:

Q = U . A_s . ΔT_{lm}

Where;

U : Overall heat transfer coefficient [kW/m^2]

$$\frac{1}{U} = \frac{1}{h_i} + \frac{1}{h_o}$$

Overall heat transfer coefficient (U), can be also estimated from equation 6 since all other parameters are known and calculated.

ΔT_{lm}: Logarithmic mean temperature difference [°C]

$$\Delta T_{lm} = \frac{\Delta T_1 - \Delta T_2}{\ln\frac{\Delta T_1}{\Delta T_2}}$$

ΔT_1 : Temperature difference between two fluids at the inlet [°C]

ΔT_2 : Temperature difference between two fluids at the outlet [°C]

Then profile temperature along the tube are modeled in excel. All calculations and results are available in Appendix C.

5   Thermal degradation

In this chapter achieved results by different analytical methods are discussed based on and comparison to previous findings for MEA and MDEA. Uncertainties and exist problems in this study are also reported in this section.

5.1   MEA thermal degradation

MEA thermal degradation at temperatures lower than 200°C happens by reaction between MEA and CO_2 to form MEA carbamate and protonated MEA.

This reaction occurs in absorber and is normally reversible in stripper. Under stripper operational condition the reaction may cross a dehydrolysis reaction and produce an oxazolidone as a first step of degradation. All reactions and mechanism were discussed in detail in chapter 2.

In this study MEA 30 wt% with 0.4 CO_2 loading (mol CO_2/ mol MEA) at 135°C under constant pressure around 2.5 bar was tested by thermal stability rig over 6 weeks. Samples were collected every week and different analytical methods were applied to measure percentage of MEA loss and identify degradation products .

The first applied analytical method was alkalinity titration (chapter 3), to determine the total alkalinity of solutions but it has not accuracy on the particular amine (MEA). The alkalinity titration results are shown in figure 5.1. As it is illustrated, the amount of total alkalinity in solutions was constant during the experiment time, however it does not necessarily mean constant MEA concentration since the degradation products are also having amine group from its original MEA structure.
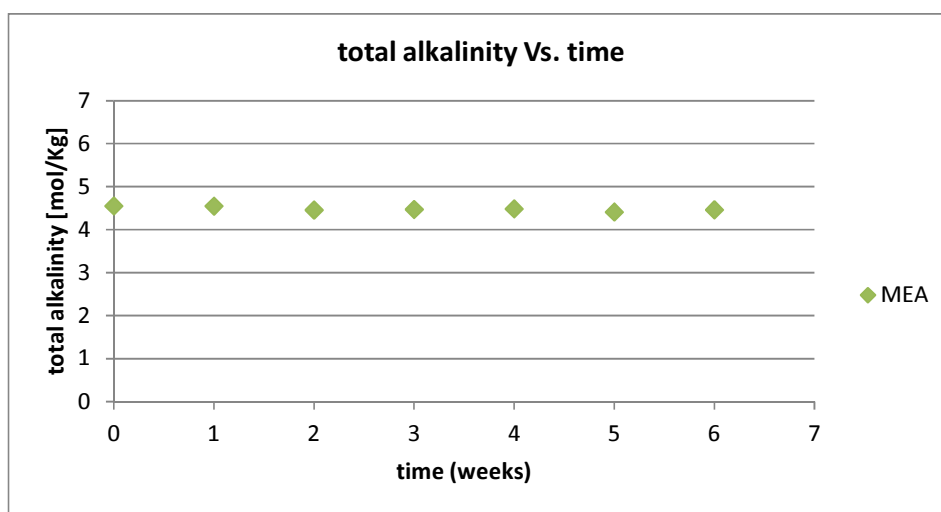
Figure 5.1 Total alkalinity measurement over the experimental times

Results of MEA concentration over 6 weeks by LC-MS analytical method can be seen in figure 5.2. MEA concentration was almost constant except week two and three that showed slightly increase which could be due to evaporation of water during handling the samples or some analytic method errors. A constant MEA concentration confirms no degradation during this study.

MEA concentration Vs. time
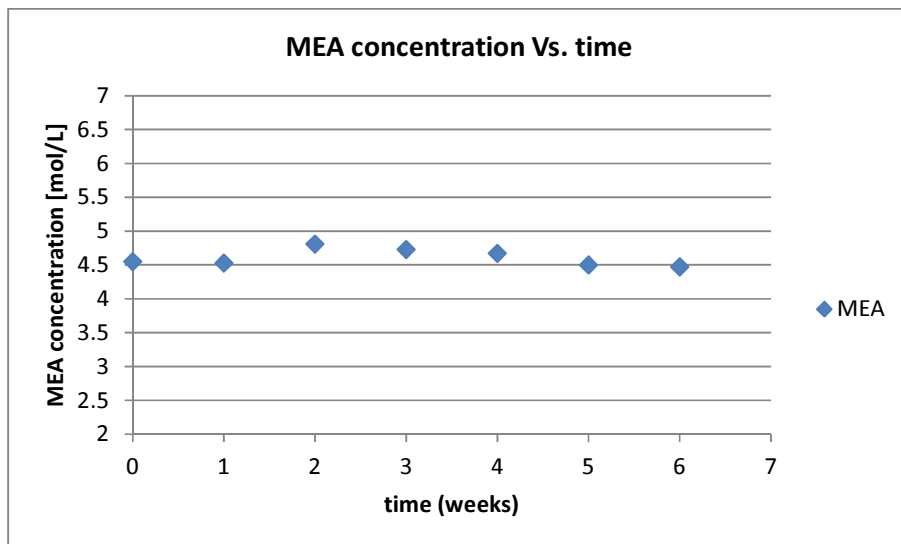
Figure 5.2 MEA concentration versus time based on LC-MS analytical method

All alkalinity titration results were converted to mol/L by applying density of MEA equal to 1.1 (kg/L). When the LC-MS and titration results were compared (Figure 5.3), it seems that there is agreement that only small portion of MEA was degraded. It gave an idea that the elapsed time was not enough to observe the MEA degradation in a significant amount.

MEA concentartion Vs. time
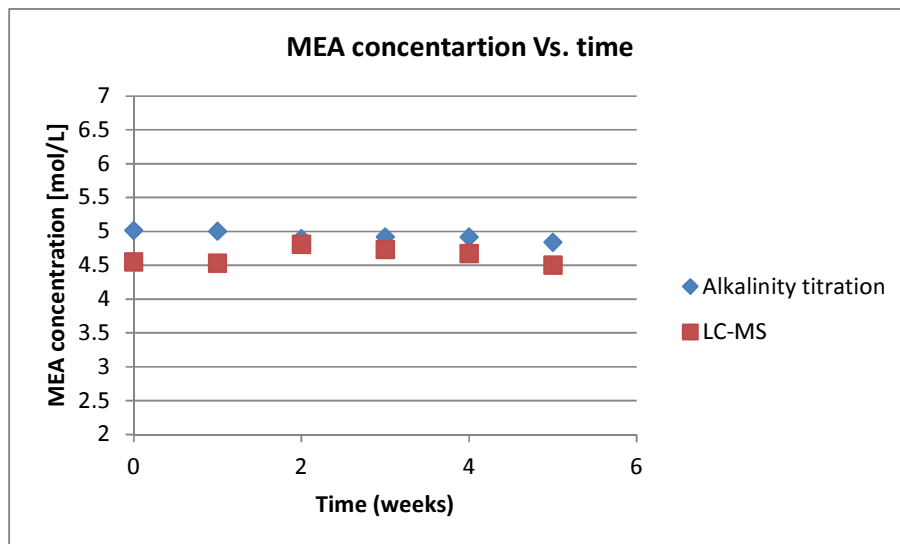
To see more detail, the identified degradation product done by LC-MS is presented in Figure 5.4. Different products can be distinguished, i.e.: an oxazolidinone (OZD), a dimer HEEDA, N-(2-hydroxyethyl)formimide (HEF), N-(2-hydroxyethyl)-glycine (HeGly), 4-(2-hydroxyethyl)-2-piperazinone (HEPO), HEI, HEHEAA and very small amount of HEA and BHEOX around less than 1 (μg/mL).

However this thermal degradation study is done in absence of oxygen, but due to high temperature condition there are list of byproducts similar to those with O_2 (Lepaumier, 2009). Identified byproducts in LC-MS were: HEF, HeGly, HEPO, HEI, HEA and BHEOX.
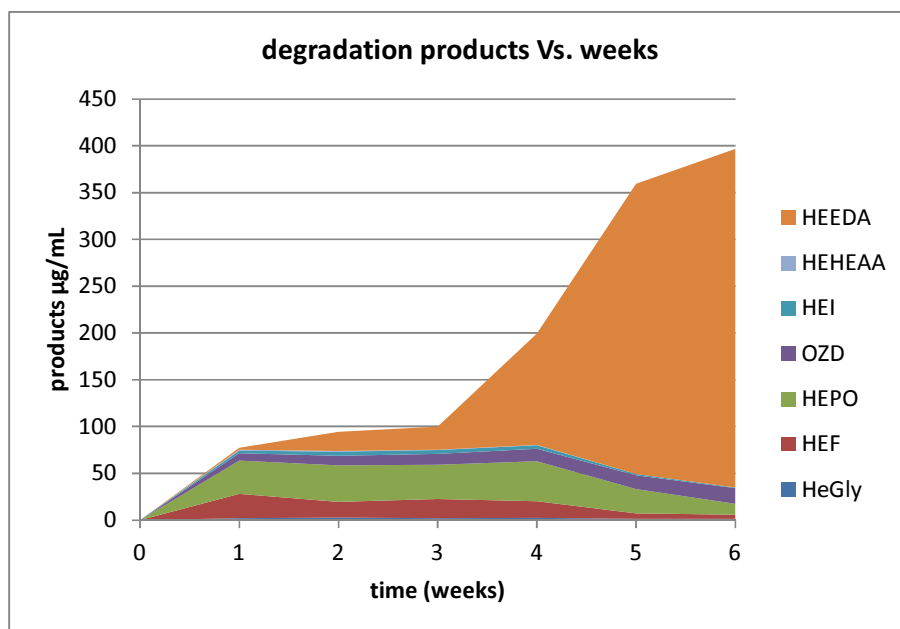
Figure 5.4 The determined degradation products by LC-MS over weeks

As it can be seen in figure 5.4, it can be explained :

Weeks 0-1 : HeGly, HEF, HEPO, HEI, OZD and HEEDA were formed. HeGly, HEF and HEI were produced in very small amount around 2.2 to 25.9 ($\mu g/mL$) and slightly leveled-off during the experiments. Reaction and mechanism of byproducts are discussed in detail by Lepamuier, et al., (2008, 2009a) on an oxidative degradation study.

During weeks 2-3 OZD slightly increased while HEEDA increased rapidly. In this case, the most probably mechanism based on the previous studies could be suggested (Davis, et al., 2009) (chapter 2). Based on this mechanism OZD is forming in significant amount during the first weeks and then start converting to HEEDA .

Weeks 3-4, HEEDA is increased significantly due to OZD reached the peak and consequently conversion to HEEDA increased.

Weeks 4-5 : HEEDA rose up rapidly during the fifth week as well whereas OZD declined significantly.

Week 5-6 : HEEDA moderately grew from 350 to 400 ($\mu g/mL$). The observed change in HEEDA trend can be explained by Davis mechanism that in case of longer experiment and more degradation in solution HEEDA is increasing for a while and then consuming to produce other degradation product i.e., HEIA.
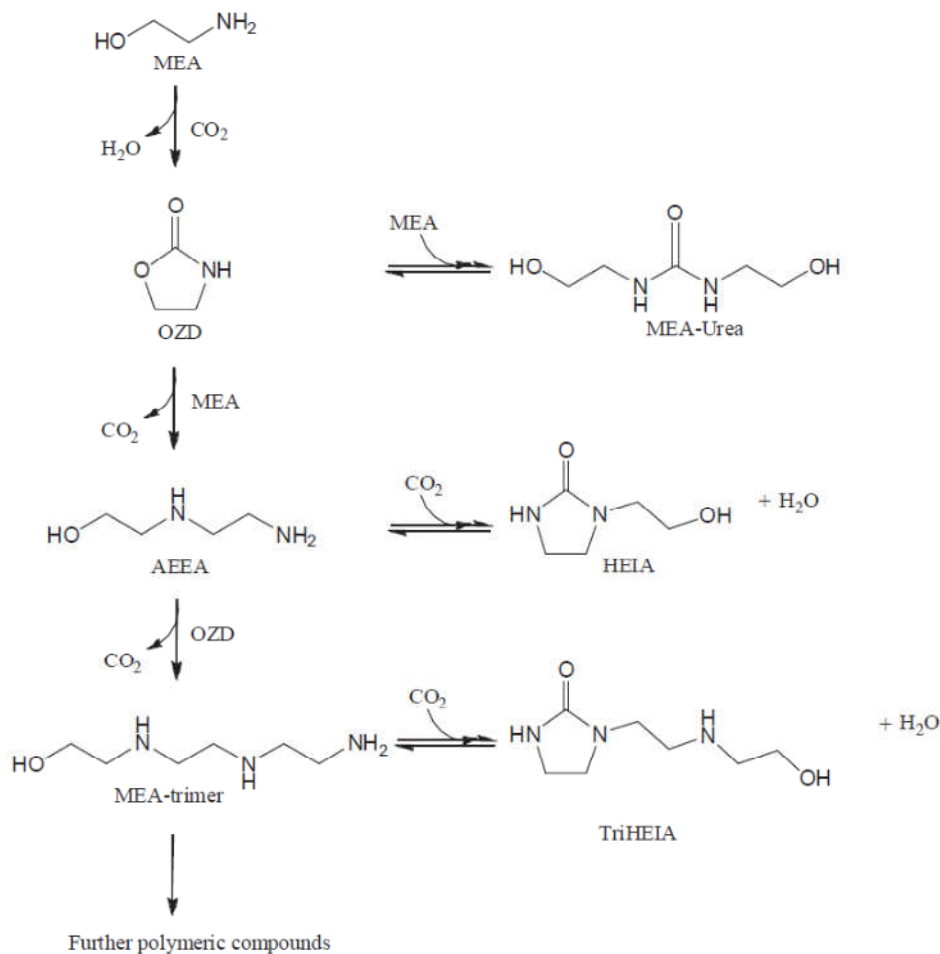
Figure 5.5 thermal degradation pathway suggested by Davis (Chapter 2)

OZD and HEEDA are MEA thermal degradation products which were confirmed by previous finding on MEA thermal degradation by Lepaumier (2008), Polderman (1955), Yazvikova et al. (1971), Davis (2009) and Eide-Haugmo (2011). (see chapter 2 for more detail)

5.1.1 Comparison between achieved results on MEA degradation and literature

To compare thermal degradation products in this experimental work with previous studies, facts about different analytical and experimental methods which is the main purpose of this study need to be taking into account.

It was previously explained in chapter 3, thermal stability rig is a continuous apparatus to test resistance of different amine solutions at high temperatures (close to stripper operational condition) in the industry by swing temperature in a cycle continuously. The heat transfer coefficient difference at the inlet and the outlet of the coil tube can be estimated from the modeling of temperature profile along the coil as demonstrated in

figure 5.6, (chapter 4), the calculated residence time of solution was around 100 –
135°C is approximately a week (168 h). (see Appendix C For more detail)
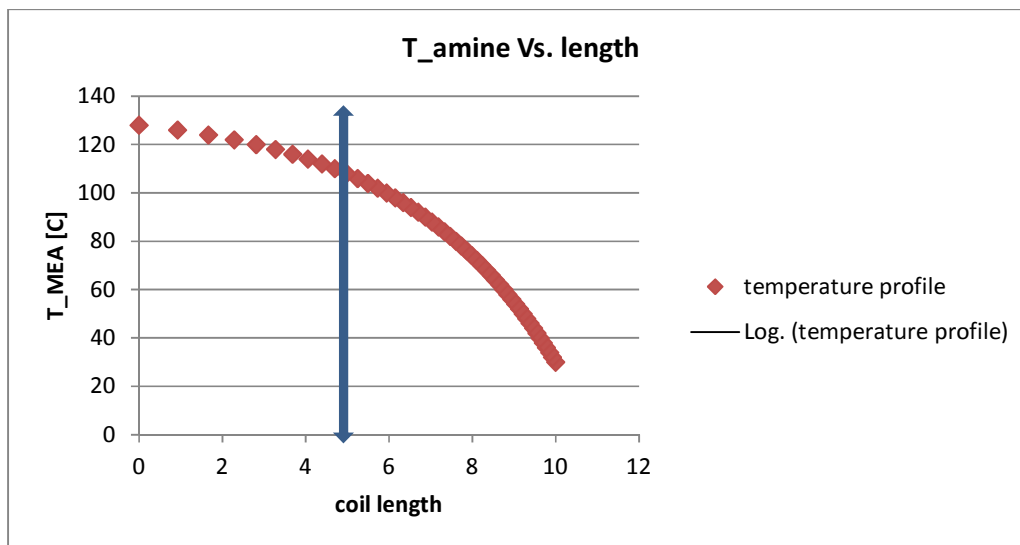
Figure 5.6 Amine temperature profile

It should also be considered that the degradation products in the previous studies were
identified by GC-MS analysis method (see chapter 3). In this study, GC-MS apparatus
due to some technical problems was out of work and expected to be fixed during the
first few months. But the apparatus was not under operation during the whole study, so
under my supervisor consideration GC-MS analysis was scoped out.

As can be seen in figure 5.7, OZD is formed during the first two weeks and then is
slightly raised up and HEEDA is formed from the second week and rapidly increasing in
solution. In accordance with the study by Lepaumier (2008), the identified OZD is in
small amount, and the results are also accordance to the suggested mechanism by Davis
(2009) and the limiting reaction stage suggested by Yazvikova et al. (1971). (see
chapter 2)

According to figures 5.8, Davis (2009) and 5.9, Eide-Haugmo (2011), the identified
products (HEEDA) is an intermediary product, which is reacting further after being
formed from the second week. By considering the experiments duration as solutions
residence time at high temperatures (around 135°C), achieved results in this
experimental work over 6 weeks are confirmed by previous findings in literatures
during the first week of experiments. Following figures show this comparison.
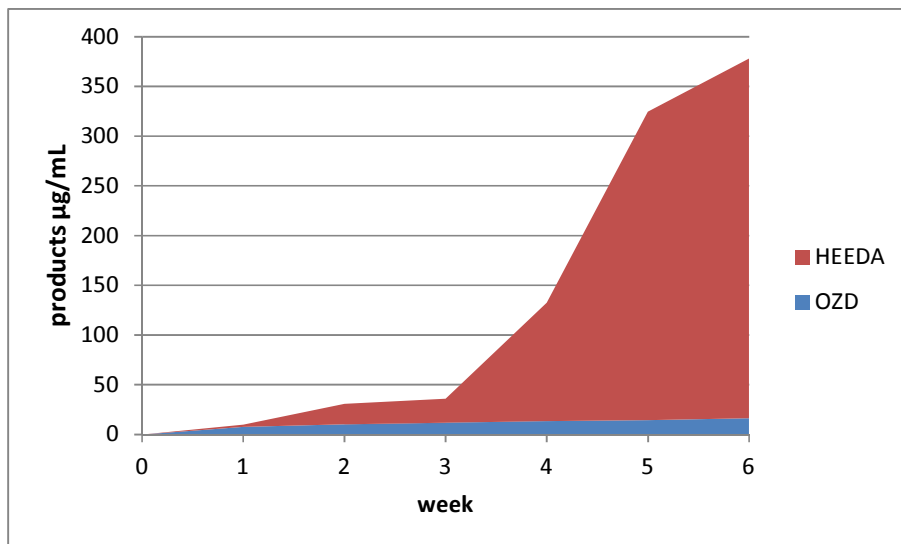
Figure 5.7 MEA main thermal degradation products over 6 weeks
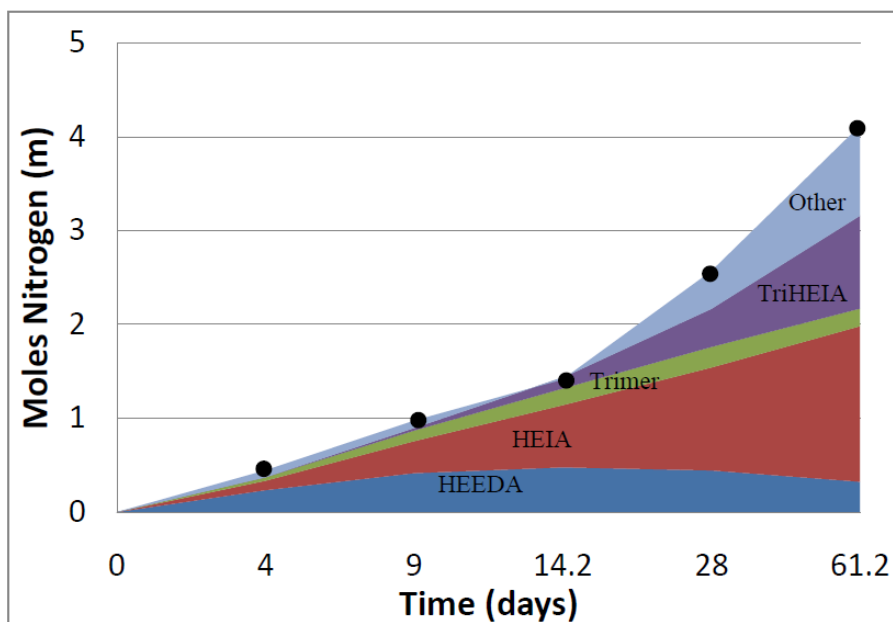
Figure 5.8 MEA thermal degradation reported by Davis (2009)
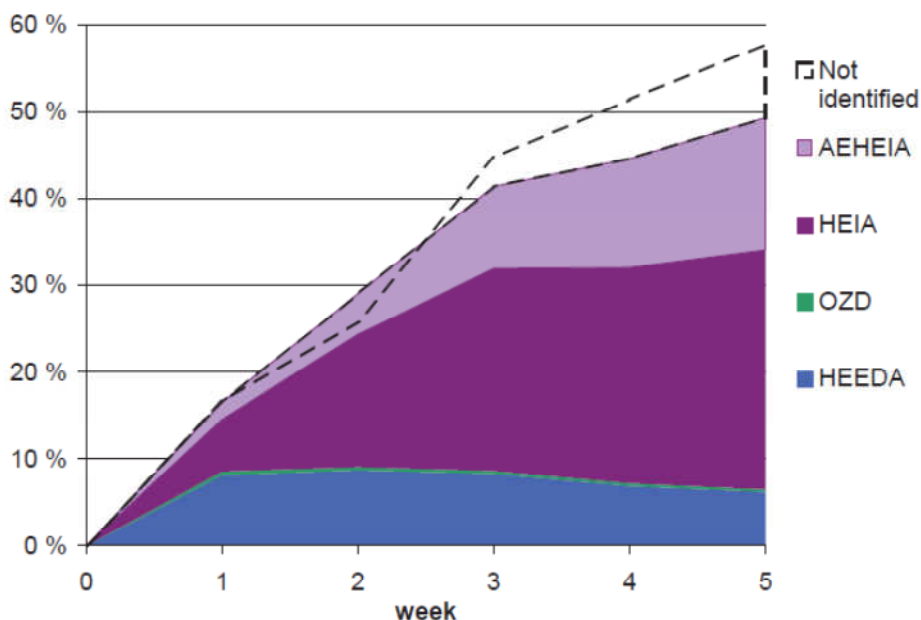
Figure 5.9 MEA thermal degradation products reported by Eide-Haugmo (2011)

According to the above figures, some more degradation products were identified by Davis (2009) and Eide-Haugmo (2011) that HEIA was found in the highest concentration. HEIA is a stable imidazolidinone that is accumulated in solution. It also was reported as a major degradation product by Lepaumier et al. (2009a). Investigating previous degradation pathways from literatures in presence of OZD and HEEDA, HEIA can be estimated as a next degradation product in this study. (chapter 2)

5.1.2   ICP-MS results

In order to test how the rate of thermal degradation is catalyze by metal, MEA samples were collected and sent to Olav hospital to test by ICP-MS analytical method which used to metal qualification. In ICP-MS test Fe, Ni, Cr, V and Molybdenum were quantified. Iron, nickel and chromium were found as metals leached from stainless steel equipment and vanadium sometimes used as a corrosion inhibitor in amine systems. The metal can present in the solution when the metal container exposed in the liquid at certain time and temperature.

Results generally showed that there is no significant amount of metal in solutions, and it could be because of the correlation between degradation of absorbent with metals dissolution and corrosion. A comparison of ICP-MS results in present work to Eide-Haugmo (2011) study are illustrated in the following figures.

Figure 5.10 Comparison of Metal concentration (Vanadium) from the ICP-MS results

(◆, Eide-Haugmo, I, 2011; ■, present works)

As it is illustrated in figure 5.10, Vanadium concentration in present work is much less than Eide-Haugmo (2011) results. Eide-Haugmo reported around 46% degraded MEA while no significant degradation reported in this study, then low metal concentration is acceptable.

Figure 5.11 Comparison of Metal concentration (Chromium) from the ICP-MS results

(◆, Eide-Haugmo, I, 2011; ■, present works)

As seen in figure 5.11, Chromium concentration in solution is higher than Vanadium. It could be formed as leached metal from stainless steel pipes as all pipelines are stainless steel in the loop. Chromium concentration in present work is less than Eide-Haugmo, (2011) due to very small amount of degradation compare to reported degradation by Eide-Haugmo, (2011)It generally means less corrosiveness effect in present work.
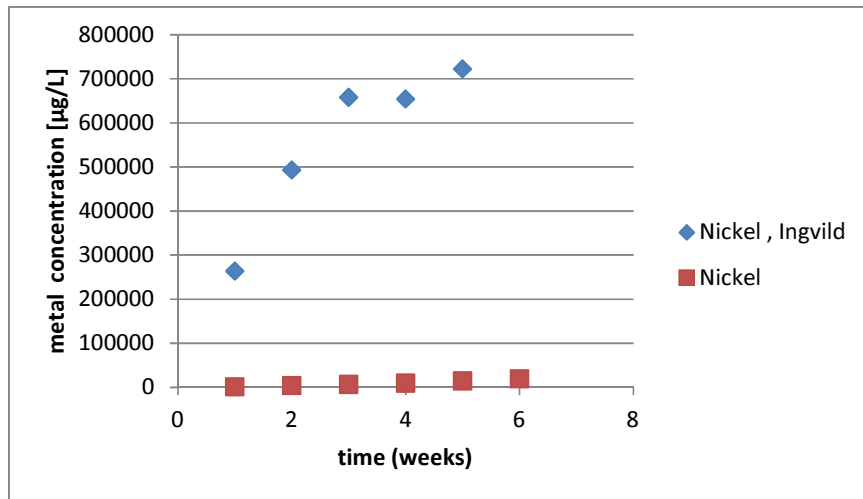
Figure 5.12 Comparison of Metal concentration (Nickel) from the ICP-MS results

(◆, Eide-Haugmo, I, 2011; ■, present works)

From figure 5.12 and 5.13 can be investigated that in case of Nickel and Iron the same explanation as Chromium could be used since three of them were found as found as metals leached from stainless steel equipment.

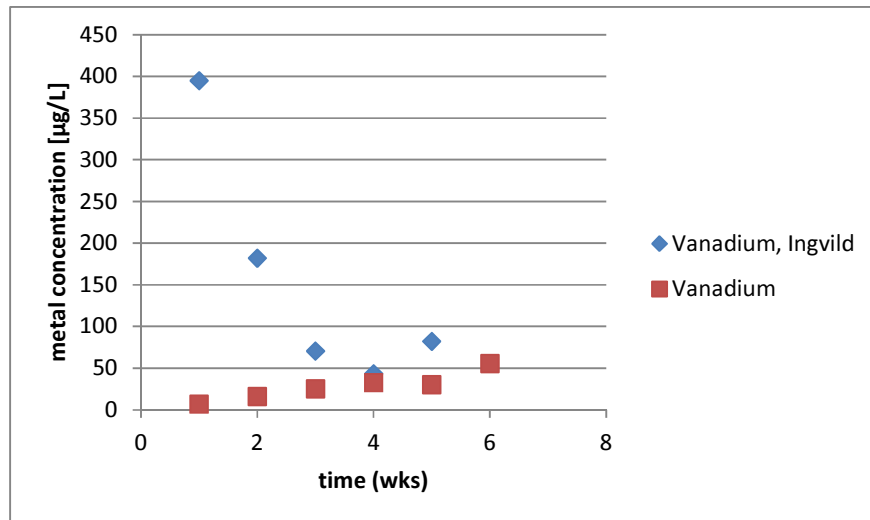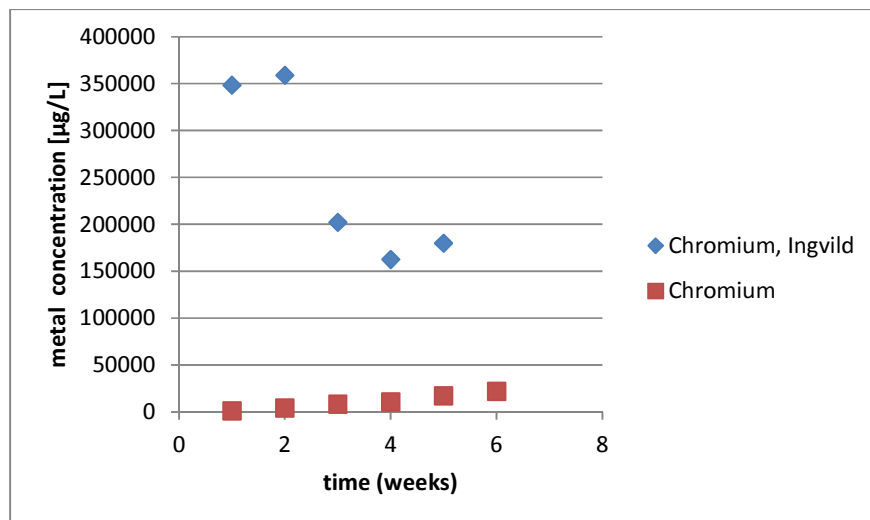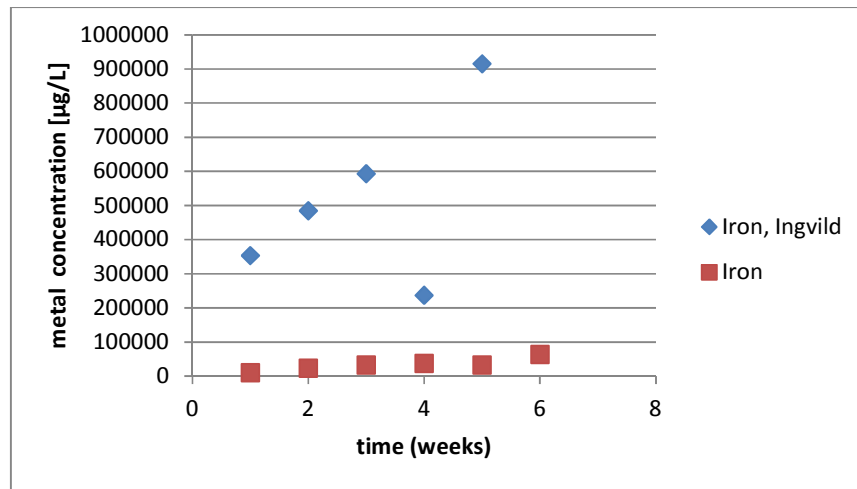**Figure 5.13 Comparison of Metal concentration (Iron) from the ICP-MS results**
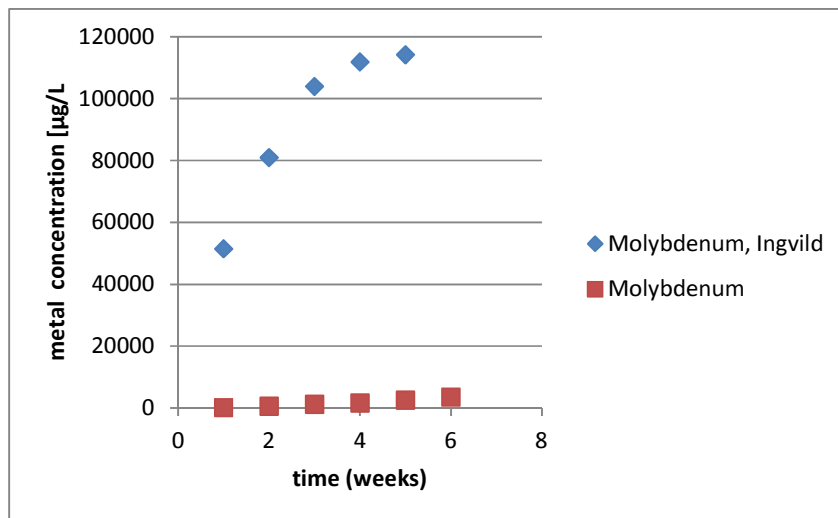
(◆,Eide-Haugmo, I, 2011; ■, present works)

Generally, the present comparison between metal qualification results of the present work and Eide-Haugmo (2011) says a negligible amount of MEA degradation in this study, as it was also observed in the alkalinity titration and LC-MS results in previous sections.

5.2   MDEA thermal degradation

MDEA is a tertiary amine with high selectivity for hydrogen sulfide removal with higher acid gas removal capacity compare to primary and secondary amines. It also has more resistance to degradation at high temperatures, high energy efficiency and due to have no hydrogen-nitrogen bound there is no reaction between MDEA and CO_2 to form a carbamate. Therefore degradation of MDEA below 120˚C is unlikely and negligible. (Chakma and Meisen, 1997)

In the present study, MDEA 50 wt% with 0.4 CO_2 loading (mol CO_2/ mol MEA) at 145˚C under steady pressure around 2.5 bars was run by thermal stability rig over 5 weeks. Samples were collected every week and different analytical methods were applied to measure amount of MDEA loss and identify degradation products.

As discussed in MEA thermal degradation section, firstly alkalinity titration (chapter 3) was done to measure the total alkalinity of solutions. Total alkalinity in solutions over 5 weeks is shown in figure 5.15, however it does not indicate any specific results related to amount of MDEA loss.

total alkalinity Vs. time
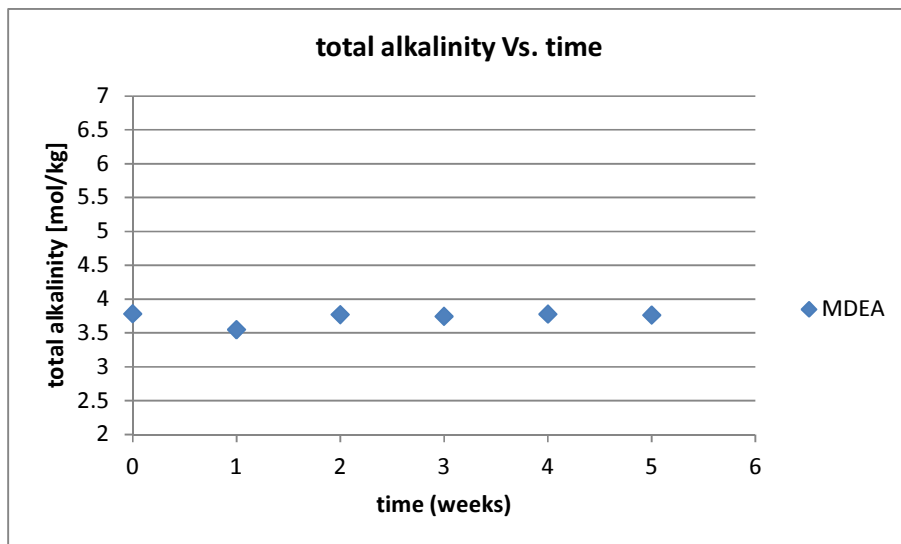
Figure 5.15 Total alkalinity measurement over time by alkalinity titration

LC-MS analysis (chapter 3) results are illustrated in figure 5.16. As can be seen, MDEA concentration over the experiment time is constant and it is showed no degradation in solutions.

MDEA concentration Vs. time
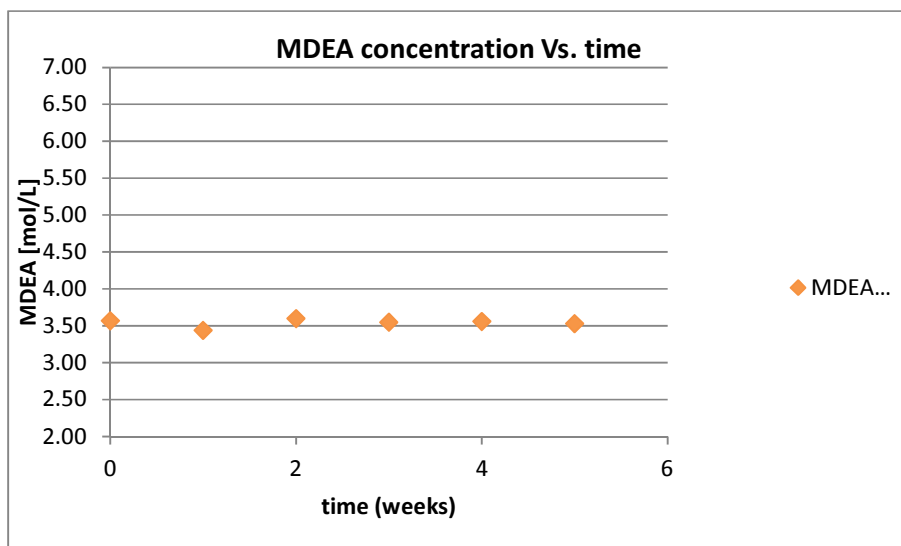
Figure 5.16 MDEA concentration over 5 weeks by LC-MS analysis

All alkalinity titration results were converted to (mol/L) by applying MDEA density equal to 1.04 (kg/L). When the LC-MS and titration result were compared (Figure 5.17), it seems that there is agreement that only small portion of MDEA was degraded. The same as MEA experiment It might be an idea that the elapsed time was not enough to MDEA degradation in significant amount.
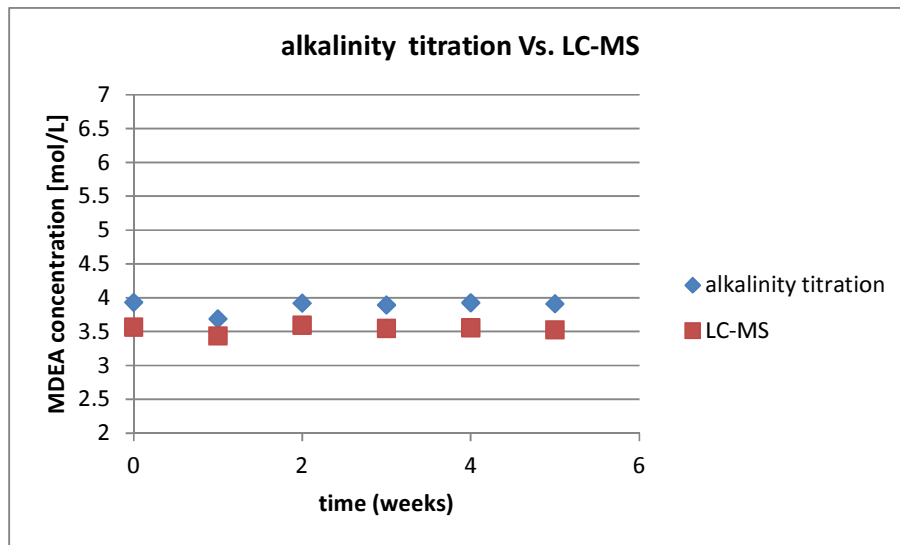
Figure 5.17 Comparison of alkalinity titration and LC-MS results

Since there was no analytical method and reference material to identify the main MDEA degradation products in the SINTEF analytical lab, hence no degradation products are reported by LC-MS in this work. But the negative LC-MS scan reported results with no peaks showed non-detectable amounts of degradation in solution.

DMEA and its fragments were found as primary degradation product in LC-MS scan. DMEA was also reported as a first identified degradation products by Chakma and Meisen (1988;1997). They reported four main products; DMEA, an oxazolidinone (HEO) and two piperazine compounds (HEP and BHEP). Lepaumier (2008) found DMEA and HEO and Davis (2009) reported DMEA in his work as well.

As it was mentioned in MEA thermal degradation section, the main idea of this thermal stability experiment is testing the resistance of solution to high temperatures around (100°C - 145°C) that is close to stripper operational condition in the industry. Based on heat transfer coefficient calculation and temperature profile along the coil length (Appendix C), residence time of solution at high temperatures was found around a week.
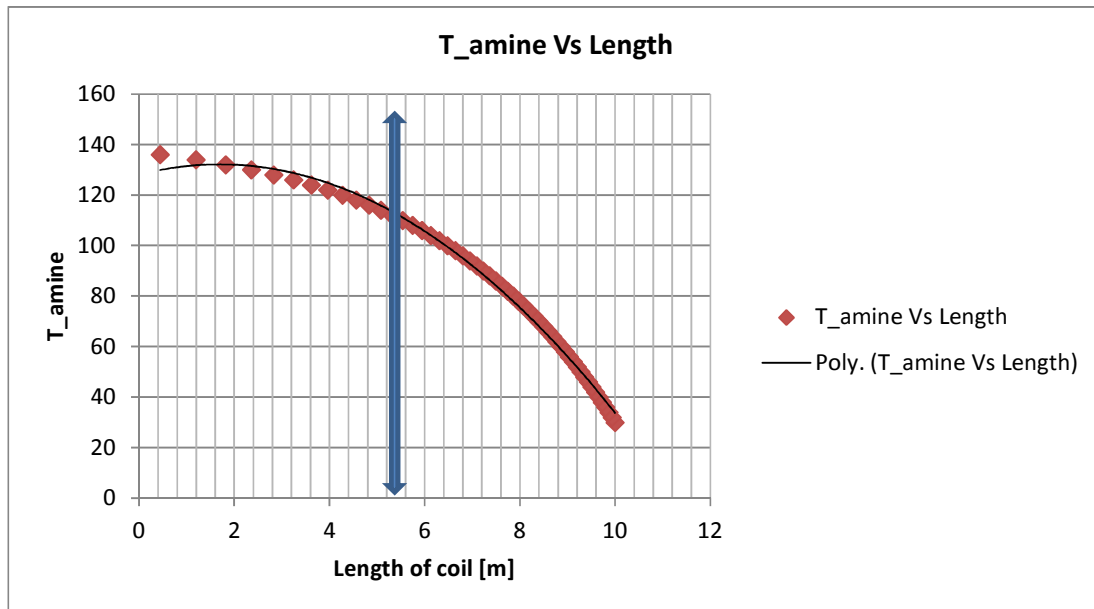
Figure 5.18 temperature profile along coli length

MDEA is a more stable amine than MEA with lower degradation rate. Considering MEA results in previous section and calculated residence time of solution in hot zone It can be investigated that MDEA thermal degradation study by new thermal stability rig needs also more time to observe significant amount of degradation.

5.2.1   ICP-MS results

Degradation of solution is interlinked with metal decomposition and corrosion. According to negligible amount of MDEA degradation in this study, small amount of metal in solution as is acceptable. In following figures a comparison between metal concentration in MEA and MDEA solutions of the present work is illustrated. It showed as expected amount of metal in MDEA is more less than MEA . As can be seen nickel and chromium are the highest concentrations in solutions because of metal leaching in side of stainless steel equipments. The second high concentration is iron. Based on results in this study, in general can be concluded that there is no significant corrosive effect in tested solutions.
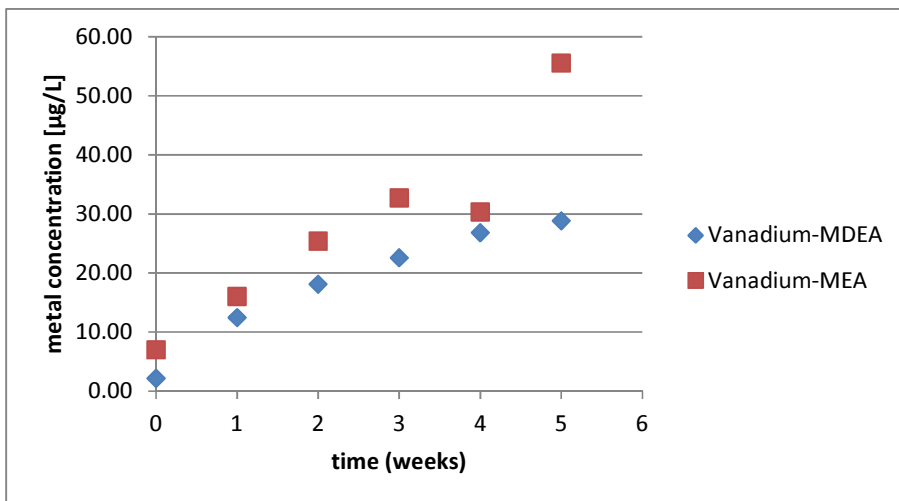
Figure 5.19 Comparison between metal concentration (Vanadium) in MEA and MDEA solutions
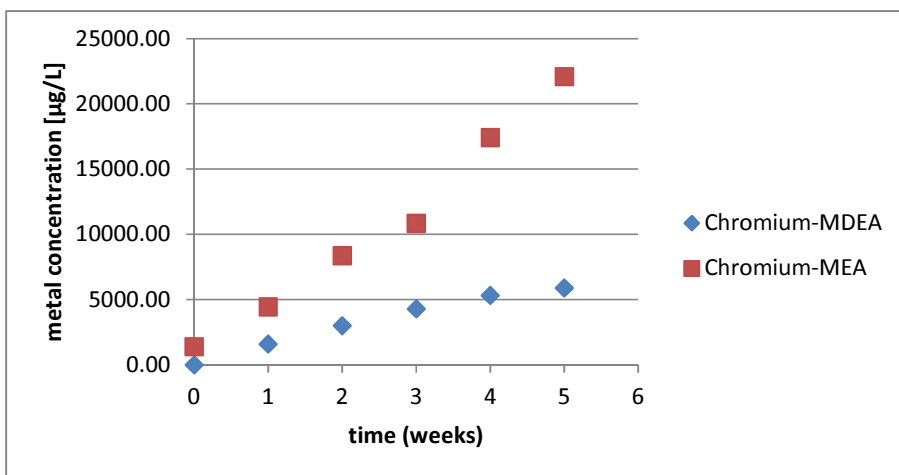
Figure 5.20 Comparison between metal concentration (Chromium) in MEA and MDEA solutions
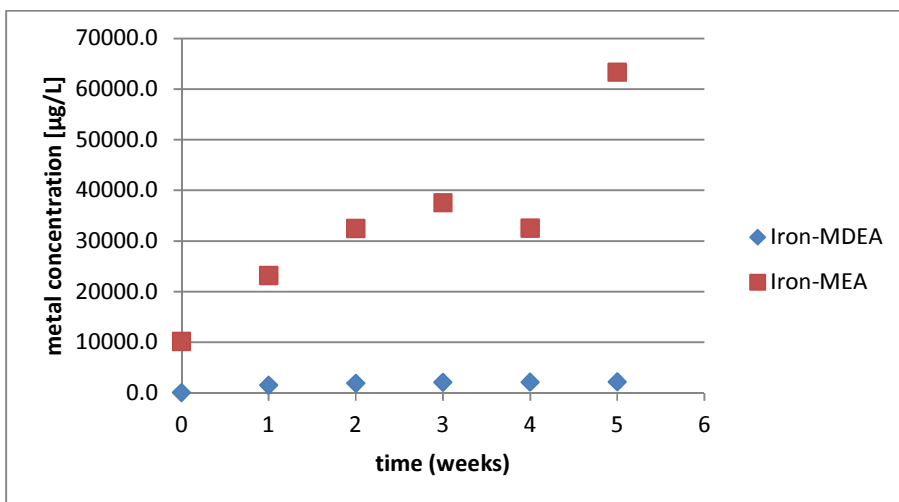
Figure 5.21 Comparison between metal concentration (Iron) in MEA and MDEA solutions
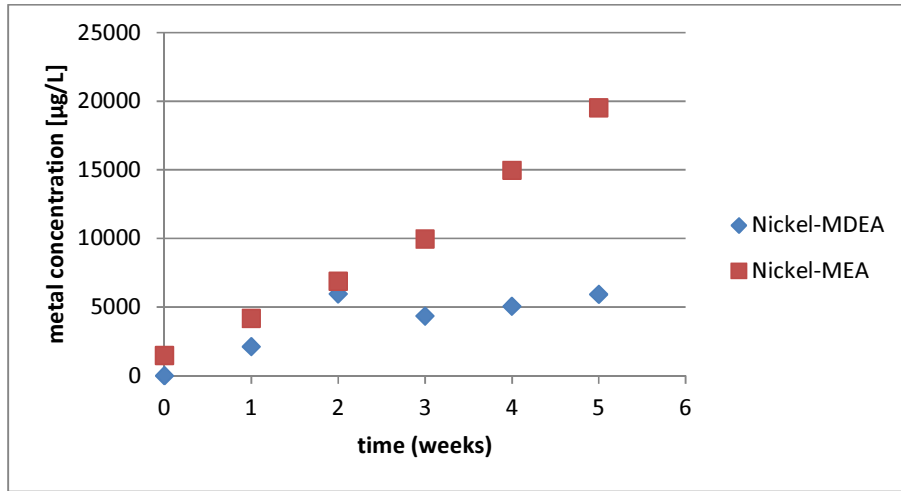
Figure 5.22 Comparison between metal concentration (Nickel) in MEA and MDEA solutions
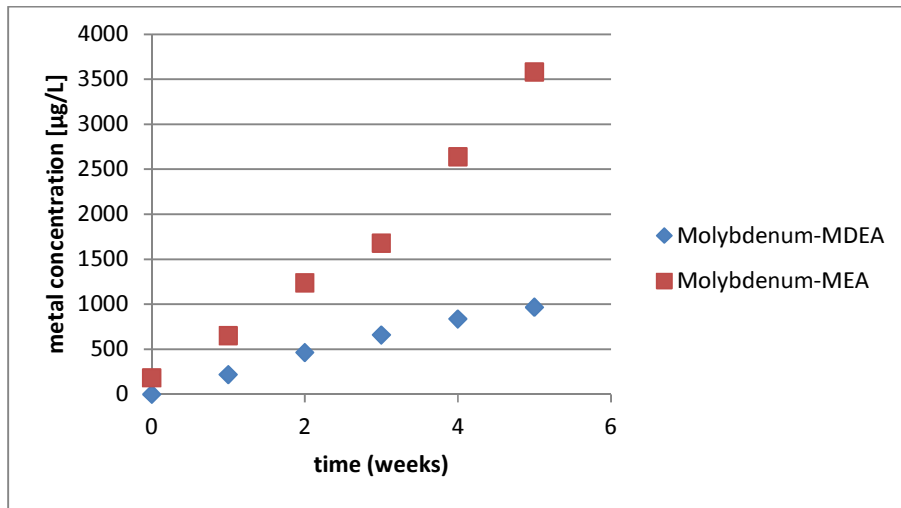
Figure 5.23 Comparison between metal concentration (Molybdenum) in MEA and MDEA solutions

5.3 Uncertainties and problems

There were some problems with the temperature measurement system. Thermometers were installed with a little distance from coil outlets and it resulted approximately in ± 1°C. The actual solution temperature in hot bath because of thermal conductivity and heating loss was always lower than the set temperature .

In all calculations flow rate was considered as a constant parameter, while it was fluctuating a bit due to change temperature and pressure during the process. Flow meter was no available signal to trace.

To make direct comparison with reported results in literatures easier, amine solutions were tested at the same temperature, concentration based on weight and the same concentration of CO_2 as previous studies, but still due to operating and scaling errors there are some differences.

In addition, after taking out each sample and pressurizing the system again because of manually setting during the experiment, the actual pressure above each sample could be different at the experimental condition. But that pressure variation is not believed to have a significant effect .

However the system has been degassing after solution loading, still some air remained in the pipes. Air also could be dissolved in solution during the solution preparing and taking out the samples . So the high temperature condition in the thermal stability experiment and the presence of air can be the reason of oxidative products as byproducts in this study.

6   Conclusion and recommendation

This chapter is used to summarized the key findings from this experimental work about MEA and MDEA thermal degradation. The findings from Comparison between present and previous results has been investigated to conclude that thermal stability rig could be an alternative to amine thermal degradation study. recommendations on thermal degradation studies by the new rig for future works are also made in this chapter.

6.1   Conclusion and recommendation

This thesis has investigated thermal degradation of amine solutions under stripper operational condition. MEA and MDEA have been tested as benchmark solutions at CO_2 capture in amine based absorption process . MEA with 30 wt% concentration and 0.4 CO_2 concentration in (mol CO_2/mol MEA) at approximately 135°C under constant pressure around 2.5 bar, and MDEA with 50 wt% concentration and 0.4 CO_2 concentration in (mol CO_2/mol MDEA) at approximately 145°C under constant pressure around 2.5 bar are tested to assess thermal resistance of solutions by thermal stability rig apparatus which is a new continuous experimental set up over several weeks . To make direct comparison of achieved results with previous findings in literature , the solutions are prepared under the same condition as previous studies on MEA and MDEA thermal degradation.

The purpose of the recent study was to answer " Could thermal stability rig be a beneficial alternative method to thermal degradation study?" it has been assessed by using different analytical methods to identify degradation compounds and comparing the amount and mechanism of degradation products to previous studies.

The results of LC-MS in this study indicated few numbers of degradation compounds in very small amount and no new identified compounds comparing with literature. These findings have shown that generally there is no significant degradation for MEA and MDEA due to the short residence time in the hot zone at elevated temperature. Considering the results and coil heat transfer calculations in this study, gave an idea that observing significant degradation by new thermal stability rig required more experimental time.

Different MEA degradation products can be distinguished in LC-MS, i.e.: DEA, an oxazolidinone (OZD), a dimer HEEDA, N-(2-hydroxyethyl)formimide (HEF), N-(2-hydroxyethyl)-glycine (HeGly), 4-(2-hydroxyethyl)-2-piperazinone (HEPO), HEI, HEHEAA and very small amount of HEA and BHEOX. OZD and HEEDA confirmed by previous findings as main degradation products and Davis (2009) thermal degradation pathway is suggested as a most probably degradation pathway. The rest are byproducts which were formed under elevated temperatures following general degradation mechanism suggested by Lepaumier (2008,2009a). Based on LC-MS scan result, only

DMEA was found as a primary MDEA degradation product. ICP-MS analysis results of both MEA and MDEA solutions revealed that there is no significant corrosive effect in solutions in this study.

The findings suggested that generally thermal stability rig was suitable to do the thermal degradation study, however a conventional method has some advantages in comparison with it, such as possibility of testing a big range of amines at the same time under the same conditions and identifying the wide range of thermal degradation products and mechanism in shorter time. But still more works are required in order to better understanding of the new thermal stability rig and its advantages .

Some important limitations in this study need to be considered. Since it has been understood from the results the thermal stability rig is a time consuming apparatus, time become a main limitation factor in this study. Based on previous studies, the GC-MS analytical method has been used to find and identify degradation products lack of this method was a barrier to investigate all degradation products in the present work.

Future research can investigate thermal degradation by the new thermal stability rig over longer period of time to observe significant degradation in solutions. Use GC-MS analysis to indentify and qualify all degradation products and suggest degradation mechanism . Then more accurate comparison might be made based on available data to better understanding of advantages and disadvantages of the new thermal stability rig.

7 Appendix

A. Ethanolamine (MEA)

A.1 thermal degradation data

Week	loading	HeGly	HEF	BHEOX	HEA	HEPO	OZD	HEI	Unit
1	0.4	2.2	25.9	<1	<1	35.8	7.8	2.7	µg/mL
2	0.4	2.9	16.9	<1	<1	38.9	10.3	4.5	µg/mL
3	0.4	2.3	20.3	<1	<1	36.8	11.7	4.1	µg/mL
4	0.4	2.5	17.9	<1	<1	42.5	13.4	3.8	µg/mL
5	0.4	1.6	5.6	<1	<1	26.2	14.6	1.2	µg/mL
6	0.4	1.6	4.4	<1	<1	11.7	16.4	0.8	µg/mL

Table A. 1 Mix degradation results by LC-MS analytical method

Week	loading	HEHEAA	HEEDA	Unit
1	0.4	1.095	2	µg/mL
2	0.4	0.471	21	µg/mL
3	0.4	0.346	24	µg/mL
4	0.4	0.412	119	µg/mL
5	0.4	0.223	310	µg/mL
6	0.4	0.175	362	µg/mL

Table A. 2 Mix degradation results by LC-MS analytical metho

week	Loading	MEA	Unit	DEA	Unit
1	0.4	4.53	mol/L	133	µmol/L
2	0.4	4.81	mol/L	220	µmol/L
3	0.4	4.73	mol/L	461	µmol/L
4	0.4	4.68	mol/L	619	µmol/L
5	0.4	4.50	mol/L	529	µmol/L
6	0.4	4.48	mol/L	299	µmol/L

Table A. 3 MEA and DEA concentration over elapsed time

Week	loading	Vanadium	Chromium	Manganese	Iron	Nickel	Molybdenum	Unit
1	0.4	7.03	1402	387	10187	1482	184	µg/L
2	0.4	16.1	4456	717	23199	4187	653	µg/L
3	0.4	25.4	8370	1134	32476	6888	1238	µg/L
4	0.4	32.8	10847	1426	37575	9959	1679	µg/L
5	0.4	30.3	17433	1935	32550	14964	2638	µg/L
6	0.4	55.6	22099	2683	63363	19523	3581	µg/L

Table A. 4 Metal qualification results by ICP-MS analytical method

B. N-methyl diethanolamine (MDEA)

B.1 Thermal degradation data

Week	Loading	MDEA	Unit
0	0.4	3.57	mol/L
1	0.4	3.44	mol/L
2	0.4	3.60	mol/L
3	0.4	3.55	mol/L
4	0.4	3.56	mol/L
5	0.4	3.53	mol/L

Table B.1 MDEA concentration over elapsed time

week	loading	Vanadium	Chromium	Manganese	Iron	Nickel	Molybdenum	Unit
1	0.4	2.18	4.74	3.80	92.2	< loq	< loq	µg/L
2	0.4	12.5	1608	31.8	1556	2120	220	µg/L
3	0.4	18.1	3014	19.8	1921	5963	465	µg/L
4	0.4	22.6	4298	15.2	2123	4352	660	µg/L
5	0.4	26.9	5334	15.2	2142	5057	837	µg/L
6	0.4	28.8	5900	15.1	2210	5928	967	µg/L

Table B. 2 MDEA metal qualification results by ICP-MS analytical method

C. Calculations

$$Q = \omega \cdot C_p \cdot \Delta T$$

$$A_s = \pi \cdot D \cdot L$$

$$Q = A_s \cdot h \cdot (T_S - T_\infty)$$
Where;

Q : Heat transfer rate [kJ/sec]

A_s : Surface area of tube [m^2]

h : Heat transfer coefficient [$W/m^2 \cdot °C$]

T_S : Surface temperature of tube [°C]

T_∞ : Fluid temperature inside tube [°C]

Surface area is calculated as below:

D: Tube diameter [m]

L: Tube length [m]

And heat transfer rate is determined from following equation:

$$Q = \omega \cdot C_p \cdot \Delta T$$

Where;

ω: Mass flow rate of solution [kg/sec]

C_p : Solution heat capacity [kJ/kg. K]

ΔT: Fluid inside the tube (solution) temperature difference [°C]

Heat transfer coefficient at the beginning and the end of tube are equal to:

$$h_1 = \frac{Q}{A_s \cdot (T_S - T_1)}$$

$$h_2 = \frac{Q}{A_s \cdot (T_S - T_2)}$$

To calculate temperature profile following equation is used:

$Q = U \cdot A_s \cdot \Delta T_{lm}$

Where;

U : Overall heat transfer coefficient [kW/m^2]

$$\frac{1}{U} = \frac{1}{h_i} + \frac{1}{h_o}$$

Overall heat transfer coefficient (U), can be also estimated from equation 6 since all other parameters are known and calculated.

ΔT_{lm}: Logarithmic mean temperature difference [°C]

$$\Delta T_{lm} = \frac{\Delta T_1 - \Delta T_2}{\ln \frac{\Delta T_1}{\Delta T_2}}$$

ΔT_1 : Temperature difference between two fluids at the inlet [°C]

ΔT_2 : Temperature difference between two fluids at the outlet [°C]

MEA solution in excel based on above equations:

V_dot p[L/min]	0.64
Density_MEA [kg/L]	0.9167
Cp_MEA30wt%[kJ/kg.K]	3.418
T_MEA_out [˚C]	128
T_MEA_in [˚C]	30
T_chamber [˚C]	135
L_coil [m]	10
d_coil [m]	0.006
m_dot [kg/s]	0.009778
Q_dot [kJ/s]	3.275323
Delta_T1	7
Delta_T2	105
Delta_T_lm	36.1884
As [m2]	0.1884
U_overal [KW/m2]	0.480401
h-inlet [kJ/m2.s.K]	0.165571
h-outlet [kJ/m2.s.K]	2.483563

MDEA solution in excel based on above equations :

V_dot p[L/min]	0.64
Density_MDEA [kg/L]	1.04
Cp_MDEA50wt%[kJ/kg.K]	3.6952
T_MDEA_out [˚C]	137
T_MDEA_in [˚C]	30
T_chamber [˚C]	145
L_coil [m]	10
d_coil [m]	0.006
m_dot [kg/s]	0.011093
Q_dot [kJ/s]	4.386153
Delta_T1	8
Delta_T2	115
Delta_T_lm	40.1427
As [m2]	0.1884
U_overal [KW/m2]	0.579958
h-inlet [kJ/m2.s.K]	0.202444
h-outlet [kJ/m2.s.K]	2.910133

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