THERMAL AND OXIDATIVE DEGRADATION OF MORPHOLINE AND BLEND OF PIPERAZINE AND DIETHANOLAMINE FOR CO_2 CAPTURE

SHAUKAT ALI

FACULTY OF ENGINEERING
UNIVERSITY OF MALAYA
KUALA LUMPUR

2016

THERMAL AND OXIDATIVE DEGRADATION OF MORPHOLINE AND BLEND OF PIPERAZINE AND DIETHANOLAMINE FOR CO_2 CAPTURE

SHAUKAT ALI

THESIS SUBMITTED IN FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

FACULTY OF ENGINEERING
UNIVERSITY OF MALAYA
KUALA LUMPUR

2016

UNIVERSITY OF MALAYA
ORIGINAL LITERARY WORK DECLARATION

Name of Candidate: Shaukat Ali

Matric No: KHA130035

Name of Degree: Doctor of Philosophy

Title of Thesis: Thermal and oxidative degradation of morpholine and blend of piperazine and diethanolamine for CO_2 capture

Field of Study: Purification & Separation Processes

I do solemnly and sincerely declare that:

(1) I am the sole author/writer of this Work;
(2) This Work is original;
(3) Any use of any work in which copyright exists was done by way of fair dealing and for permitted purposes and any excerpt or extract from, or reference to or reproduction of any copyright work has been disclosed expressly and sufficiently and the title of the Work and its authorship have been acknowledged in this Work;
(4) I do not have any actual knowledge nor do I ought reasonably to know that the making of this work constitutes an infringement of any copyright work;
(5) I hereby assign all and every rights in the copyright to this Work to the University of Malaya ("UM"), who henceforth shall be owner of the copyright in this Work and that any reproduction or use in any form or by any means whatsoever is prohibited without the written consent of UM having been first had and obtained;
(6) I am fully aware that if in the course of making this Work I have infringed any copyright whether intentionally or otherwise, I may be subject to legal action or any other action as may be determined by UM.

Candidate's Signature Date:

Subscribed and solemnly declared before,

Witness's Signature Date:

Name:

Designation:

ABSTRACT

Amine-based post-combustion carbon capture (PCC) technology is one of the mature options to contribute to the mitigation of CO_2 emissions. The benchmark amine for this technology is monoethanolamine (MEA). MEA undergoes irreversible reactions, resulting loss of its concentration under process operating conditions. Degradation of solvent may cause environmental concerns, increased costs and process operation problems. Current effort is made to look into the thermal and oxidative degradation of (30.34 wt.%) morpholine (MOR) and (31.5 wt.%) blend of piperazine (PZ) and diethanolamine (DEA). Thermal degradation experiments were conducted using 316 stainless steel cylinders closed with Swagelok endcaps, which were kept in convection ovens. Degraded samples were analyzed by using Gas Chromatography (GC) with Flame Ionization Detector (FID) for final concentration of parent amines and GC with Mass Spectrometry (MS) was used for identification of degradation products. Thermal degradation of MOR was investigated with CO_2 loadings of 0.0-0.48 mol CO_2/mol alkalinity at 135-190 °C. Whereas, thermal degradation of PZ/DEA (0.8 m/3.2 m) was investigated at 135 °C with CO_2 loading of 0.0 to 0.40 mol CO_2/mol alkalinity. Oxidative degradation experiments of the both systems were conducted in a low gas flow, 1-liter stirred tank semi-batch jacketed glass reactor. In oxidative degradation, O_2 partial pressure was varied from 50 to 90 kPa and three temperatures 40, 50 and 60 °C were used for both systems. Results of thermal degradation of MOR showed that MOR is stable up to 150 °C. However, it degrades significantly at 175 °C and higher temperatures. CO_2 loading had also a direct effect on loss of MOR. A kinetic model is proposed for rate of degradation of MOR, statistically, which fits experimental data well. In comparison with other amines like MEA, DEA, methyldiethanolamine (MDEA) and PZ, the MOR is the most stable amine at elevated temperatures. Oxidation of MOR increases by increasing both temperature as well as O_2 partial pressure. A kinetic model has been proposed for the oxidation of MOR. Predicted results of model are compared with those of obtained through experiments, which statistically show that the model is well representative of MOR oxidation. In thermal degradation of blended system, loss of PZ was higher than other investigated blends of PZ like PZ/MDEA, PZ/aminomethylpropanol (AMP), and PZ/MEA under similar experimental conditions. CO_2 loading increased the rate of degradation of both PZ and DEA. Concentration of PZ approached to zero within 300 hours of experiment at high CO_2 loading. Empirical rate equations are proposed for their thermal degradation of both PZ and DEA. Model of PZ is well representative of the experimental data, whereas model of DEA lacked the fitting of experimental data. Oxidative degradation experimental results of blend indicate that loss of PZ is very high in presence of DEA and it increases as O_2 partial pressure and temperature are on rise. Degradation rate models for PZ and DEA are found to fit experimental data very well. Coefficients of the models indicate that loss of PZ and DEA are a function of Oxygen concentration and temperature.

ABSTRAK

Teknologi memerangkap karbon selepas pembakaran (PCC) berasaskan amina adalah salah satu pilihan yang matang untuk menyumbang kepada pengurangan pelepasan CO_2. Penanda aras bagi amina dalam teknologi ini adalah monoetanolamina (MEA). MEA melalui tindak balas tak boleh balik, menyebabkan kepekatannya hilang semasa proses pengendalian. Degradasi pelarut ini akan memberi kesan buruk kepada alam sekitar, meningkatkan kos dan menyebabkan masalah dalam proses kendalian. Dalam kajian ini, usaha dijalankan untuk mengkaji degradasi terma dan oksidatif (30.34 wt.%) Morfolina (MOR) dan (31.5 wt.%) campuran Piperazina/Dietanolamina (DEA). Uji kaji degradasi terma telah dijalankan menggunakan 316 silinder keluli tahan karat yang ditutup dengan tukup hujung “Swagelok”, dan telah disimpan dalam ketuhar perolakan. Sampel yang telah degradasi dianalisis menggunakan Gas Chromatography (GC) yang dilengkapi Flame Ionization Detector (FID) bagi mengukur kepekatan akhir amina. GC yang dilengkapi dengan Mass Spectrometry (MS) telah digunakan untuk mengenal pasti produk degradasi. Degradasi terma MOR dikaji dengan beban CO_2 antara 0.0-0.48 mol CO_2/mol kealkalian pada 135-190 °C. Manakala, degradasi terma PZ/DEA (0.8 m/3.2 m) telah dikaji pada 135 °C. Beban CO_2 campuran telah dikaji antara daripada 0.0 ke 0.40 mol CO_2/mol kealkalian. Uji kaji degradasi oksidatif untuk kedua-dua sistem MOR dan campuran PZ/DEA telah dijalankan dalam aliran gas yang rendah, tangki teraduk 1-liter yang merupakan reaktor kaca separuh-kelompok berjaket. Dalam uji kaji degradasi oksidatif, tekanan separa O_2 telah dikaji pada 50-90 kPa dan tiga suhu berbeza iaitu 40, 50 dan 60 °C telah digunakan untuk kedua-dua sistem ini. Hasil uji kaji degradasi terma MOR menunjukkan bahawa Morfolina adalah stabil sehingga suhu 150 °C. Walau bagaimanapun, ia telah terdegradasi dengan ketara pada 175°C dan suhu yang lebih tinggi. Beban CO_2 juga mempunyai kesan langsung ke atas kehilangan MOR. Satu

model kinetik telah dicadangkan untuk kadar degradasi MOR, berdasarkan anailisa statistik, model ini bersesuaian untuk mewakili data uji kaji. Berbanding dengan amina lain seperti MEA, DEA, metildietanolamina (MDEA) dan PZ, Morfolina adalah amina yang paling stabil pada suhu tinggi. Pengoksidaan MOR meningkat dengan peningkatan suhu serta tekanan separa O_2. Satu model kinetik telah dicadangkan untuk pengoksidaan MOR. Hasil keputusan yang diramalkan oleh model ini dibandingkan dengan keputusan yang diperolehi melalui uji kaji makmal. Berdasarkan analisis statistik, model ini adalah berpadanan untuk mewakili pengoksidaan MOR. Dalam kajian degradasi terma bagi sistem campuran, kehilangan PZ adalah lebih tinggi daripada campuran PZ lain seperti PZ/MDEA, PZ/aminometil propanol (AMP), dan PZ/MEA pada keadaan kendalian uji kaji `yang serupa. Beban CO_2 meningkatkan kadar degradasi kedua-dua PZ dan DEA. Kepekatan PZ menghampiri sifar dalam tempoh 300 jam eksperimen pada beban CO_2 yang tinggi. Persamaan kadar empirik dicadangkan untuk degradasi terma bagi kedua-dua PZ dan DEA. Model PZ adalah bersesuaian untuk mewakili data eksperimen, manakala model DEA kurang padan dengan data eksperimen. Keputusan eksperimen untuk kesan degradasi oksidatif bagi campuran menunjukkan bahawa kehilangan PZ adalah sangat tinggi dengan kehadiran DEA dan kehilangannya meningkat dengan peningkatan tekanan separa O_2 dan suhu. Model kadar degradasi untuk PZ dan DEA didapati sangat padan dengan data eksperimen. Pekali model menunjukkan bahawa kehilangan PZ dan DEA adalah berkaitan dengan kepekatan oksigen dan suhu.

ACKNOWLEDGEMENTS

First and the foremost, I am grateful to Almighty Allah (S.W.T) for rewarding me courage to complete my thesis within time. Without his will, it would not have been possible to achieve anything.

Involvement, ingenuity, support and motivation that I received from Dr. Brahim Si Ali is laudable. I would like to thank him for taking me under his supervision, which enabled me to achieve this thesis. In campus or off campus he always stood with me to support most of the times. More than a researcher, I found him a best teacher who used to discuss not only research but also fundamentals of engineering, to proceed to achieve the objectives of the research. I am also thankful to my co-supervisor Dr. Badrul M Jan. He remained very much cooperative throughout my research at department of Chemical Engineering, University of Malaya.

Without cooperation of lab-mates, this research would not have been possible. I am thankful to Brother Idris Mohamed Saeed for his cooperation during my research. I especially thank to Mrs Lubna Ghalib for being helpful and cooperative during the thesis write-up. I am also grateful to Ms Hawa Imam Maroof and Ms Fariha Husna for their help in translating abstract into Bahasa Melayu. Encouragement from my fellows Mushtaq Ahmed, Anam Asghar and Mohamed Ajeel is praiseworthy.

Lab assistants and technicians were invaluable during my research. Big thanks goes to Fazizah Abdullah for her generosity, cooperation and training in using Auto-titrator and trials of HPLC. Norhaya Abdur Raheem was as cool as always, she trained and helped me, how to use the GC-FID. She was always available whenever I need the most in troubleshooting the equipment. Research officer, Lee Ching Shya was always supportive to me, I am very thankful to her for being cooperative in handling the GC, especially during method development. I am thankful to most of the workshop members, Mr. Jalaludin, Mr. Kamarul, Mr. Qamaru din, Mr. Azzaruddin and others for their help in cutting stainless steel cylinders and in moving gas cylinders and all other aspects where they helped me.

Managing research activities is always difficult while being family men. I am thankful to my wife who always remained patient and helpful, even when I used to return home at 2-3 am late night. I am also thankful to my parents for their support and prayers.

Finally, yet importantly, this research would not have been possible without financial assistance of High Impact Research (HIR), University of Malaya. We are thankful to University of Malaya to grant us the project (UM/625/1/123) to carry out this research.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS AND ABBREVIATIONS

Abbr.	Abbreviation
AEA	Aminoethylacetamide
AEEA	N-(2-aminoethyl) ethanolamine
AEM	4-(2-Aminoethyl)morpholine
AEP	N-(2-Aminoethyl)piperazine
AHZ	Acetohydrazide
AHZ	Acetohydrazide
AMP	Aminomethylpropanol
AMPD	2-Amino-2-methyl-1,3-propanediol
APP	1-(3-Aminopropyl)-2-pyrrolidone
BAE	Bis(amino ethyl)ether
BEA	Benzenemethanamine
BHEP	1,4-Bis(2-hydroxyethyl)piperazine
Bicine	(Bis(2-hydroxyethyl)amino)acetic Acid
BM	4-ButylMorpholine
BM	Butylmorpholine
DAB	1,4-diaminobutane
DEA	Diethanolamine
DETA	Diethylenetriamine
DMPZ	2-dimethylpiperazine
DGA	Diglycolamine
DMAE	N,N-dimethylaminoethanol
DMH	N,N-Dimethylhydrazine
DMM	2,2-Dimethylmorpholine

DMP	N,N’-dimethylpiperazine
DMPD	2,5-Dimethyl-4-piperidinol
EDA	Ethylene diamine
EDA	Ethylenediamine*
EO	Ethylene oxide
EO	Ethylene Oxide*
FID	Flame ionization detector
FM	N-Formylmorpholine
FPZ	Formylpiperazine
GC	Gas chromatography
HEEDA	N-(2-hydroxyethyl)ethylene diamine
HEOD	3-(2-Hydroxyethyl)-2-oxazolidinone
HMDA	Hexamethylenediamine
HMI	Hexamethyleneimine
HOBID	5-(4-Hydroxybutyl)-2,4-imidazolidinedione
HomoPZ	Homopiperazine
HPLC	High performance liquid chromatography
IAA	N-(1H-Imidazol-2-yl)acetamide
IC	Ion chromatography
k_1	First order rate constant
MAA	4-Morpholinylacetaldehyde
MAE	N-methylaminoethanol
MDEA	Methyldiethanolamine
MPZ	1-methylpiperazine

ME	2-Morpholinoethanol
MEA	Monoethanolamine
MEDA	N-[2-(4-morpholinyl)ethyl]ethanediamide
MEST	Maximum estimated stripper temperature
MM	4-Methyl-2-morpholinone
MMEA	2-(methyl amino)ethanolamine
MOR	Morpholine
MS	Mass Spectrometry
NEM	N-Ethylmorpholine
OA	Oxamide
OZD	Oxazolidone
PA	Propionamide
PCC	Post-combustion Carbon Capture
PD	Piperidine
PDA	Propanediamine
PMDETA	N,N,N’,N’,N’’-pentamethyldiethylenetriamine
PPA	Phenylpropanolamine
PPA	Phenylpropanolamine
Pyr	Pyrrolidine
PZ	Piperazine
PZE	2-Piperazin-1-ylethanol
R^2	Coefficient of determination
TAEA	Tris(2-aminoethyl)amine
TEA	Triethanolamine
TEDA	Triethylenediamine

TEPA	Tetraethylenepentamine
TEPA	Tetraethylenepentamine
THEED	N,N,N',N'-Tetrakis(2-hydroxyethyl)ethylenediamine

CHAPTER 1: INTRODUCTION

1.1 Research background

Demand of CO_2 capture has accelerated research for CO_2 capture technologies in order to minimize global CO_2 emissions. To date, numerous technologies have been introduced for CO_2 capture, however, maturity of carbon capture technologies surrounds post-combustion CO_2 capture, Oxyfuel combustion, and calcium looping technologies (MacDowell et al., 2010; T. Wang, Hovland, & Jens, 2015). Post-combustion CO_2 capture involves, CO_2 absorption through alkaline amine solvents (Gary T Rochelle, 2009). Although, history of absorption of sour gases from natural gas through aqueous amine solvents date back to 1930s (Robert, 1930). However, at present, this technology has emerged as competitive over others due to its retrofit benefits and maturity.

One of the difficult task in technology design or upgradation is the amine solvent selection. There are a number of criteria for a feasible solvent. One of an essential property for an efficient solvent considered is the capacity and absorption rate of CO_2 (Puxty et al., 2009). Higher the CO_2 solubility and CO_2 absorption rate, better the solvent. Furthermore, stability of the solvent is also not overlooked due to its emerging drawbacks. A number of new amines are under investigation for the sake of a promising amine or an amine system that should have good CO_2 capture properties and higher stability (Hilliard, 2008b; Idem et al., 2005; Namjoshi, Li, Du, & Rochelle, 2013). PZ is a newly established solvent, which has shown promising CO_2 capture properties and higher stability under process operating conditions compared to others (Dugas & Rochelle, 2009; Stephanie Anne Freeman, 2011; Stephanie A. Freeman & Rochelle, 2011; Stephanie Anne Freeman & Rochelle, 2012b; L. Li et al., 2013; Namjoshi et al., 2013; G. Rochelle et al., 2011).

Even though PZ is marked a stable solvent but it has limited CO_2 solubility, due to which precipitation occurs with both higher and lower CO_2 loadings (L. Li et al., 2013). To avoid precipitation, PZ may be used in a blended form with other amines (F. Closmann, Nguyen, & Rochelle, 2009; F. B. Closmann, 2011; Stephanie A Freeman et al., 2013). DEA is a suitable solvent for CO_2 capture as it is less corrosive and less volatile (Gunasekaran, 2012; Monoj K. Mondal, 2009; Monoj K Mondal, 2010). PZ in combination with DEA has shown competitive CO_2 capture properties like CO_2 solubility and CO_2 absorption rate (Ghalib, Ali, Ashri, & Mazari, 2016; Monoj K. Mondal, 2009; Monoj K Mondal, 2010).

1.2 Problem statement

Stability of solvent is a critical property for its choice as these amines undergo irreversible reactions. Common amines investigated through detailed studies for this technology are monoethanolamine (MEA), methyldiethanolamine (MDEA), DEA, PZ and AMP (Dumée, Scholes, Stevens, & Kentish, 2012; George S Goff & Gary T Rochelle, 2004; C. Gouedard, D. Picq, F. Launay, & P. L. Carrette, 2012; MacDowell et al., 2010; Gary T Rochelle, 2009; Strazisar, Anderson, & White, 2003). Amines experience irreversible reactions resulting loss in concentration of solvent by reacting with acid gases (CO_2, H_2S, COS, CO, SOx and NOx). Reaction of acid gases and amine is more intensive at elevated temperatures and in the presence of oxygen (Stephanie A. Freeman, Davis, & Rochelle, 2010; Goff & Rochelle, 2006; H. Lepaumier, D. Picq, & P. L. Carrette, 2009; M. Wang, Lawal, Stephenson, Sidders, & Ramshaw, 2011). MEA is the benchmark amine solvent for the technology to date, however, research is ongoing in order to find a more suitable solvent for this technology (Shaukat A Mazari, Brahim Si Ali, Badrul M Jan, & Idris Mohamed Saeed, 2014). Amine solvent makeup cost and environmental concerns due to degradation of the solvent are driving forces behind the search for alternative amine solvents (Rao & Rubin, 2002). It is unlikely that any major innovation in design of either process or columns maybe discovered to minimize the cost of post-combustion carbon capture due to its maturity. However, economical approach through solvent management is a possibility (De Brito, 1994).

PZ in combination with DEA has shown competitive CO_2 capture properties like CO_2 solubility and CO_2 absorption rate (Ghalib et al., 2016; Monoj K. Mondal, 2009; Monoj K Mondal, 2010). M. K Mondal (2009; 2010) reported that DEA/PZ blend has higher CO_2 loading capacity than other blends like DEA/AMP, DEA/MDEA, TIPA/PZ and has competitive CO_2 solubility at lower temperature and higher CO_2 partial pressure. Furthermore, Adeosun A., (2013) found that 10 wt.% DEA/20 wt.% PZ blend has the highest CO_2 absorption rate than 10 wt.% MEA/20 wt.% PZ 10 wt.% AMP/20 wt.% PZ and 10 wt. % MDEA/20 wt.% PZ. In addition to PZ, MOR has also been screened out as thermally stable solvent (Stephanie A. Freeman, Davis, et al., 2010; Stephanie A. Freeman & Rochelle, 2011; Stephanie Anne Freeman & Rochelle, 2012b). MOR has also comparatively good tendency to react with CO_2, resulting a higher rate of CO_2 absorption than MEA (Liu, Jinka, Remias, & Liu, 2013; Matin, Remias, Neathery, & Liu, 2013). However, thermal and oxidative stability of both systems PZ/DEA blend and MOR has not been investigated yet. At present most of the studies are focused on the degradation chemistry of amines except few who focused on the degradation kinetics and the modeling of degradation rate.

1.3 Objectives of the research

Broadly, the degradation kinetics of MOR and blend of PZ and DEA are focused in this study. In precise the following objectives has to be achieved in the current investigation;

1. Identification of degradation products of MOR and blend of PZ and DEA

2. Determination of loss of amine, degradation rates and rate constants
3. Formulation of rate equations to predict the rate of reactions.

1.4 Scope and layout of the thesis

The study comprises of two degradation methods and two amine systems. Thermal and oxidative degradation are the methods, whereas MOR and the blend of PZ and DEA are the systems. Hence, a following set of core areas are covered in this thesis:

1. Thermal degradation of MOR
2. Oxidative degradation of MOR
3. Thermal degradation of PZ and DEA blend
4. Oxidative degradation of PZ and DEA blend

In each set of core areas, all the mentioned objectives are achieved. In general, layout of the thesis is as following:

Chapter 1. Introduction

In this chapter background of research, problem statement, objectives of work, scope of the work and layout of the thesis is described.

Chapter 2. Literature review

A detailed literature review has been conducted on the importance of amine solvents and causes of their degradation. Detailed thermal and oxidative degradation methods are discussed.

Chapter 3. Materials and methods

This chapter provides details of experimental setup and methods used for the experiments and analyses.

Chapter 4. Results and discussions

Results and discussions of all of the objectives and systems are embedded in this single chapter. Results are depicted and debated as sub chapters as following:

4.1 Thermal degradation of MOR

4.2 Oxidative degradation of MOR

4.3 Thermal degradation of PZ and DEA blend

4.4 Oxidative degradation of PZ and DEA blend

Chapter 5. Conclusions and recommendations

Details on findings in each objective through each system and method are provided in this chapter. Furthermore, suggestions are also given for the future work, which are very important and related to this work.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

This chapter introduces carbon dioxide emissions and their raising concerns. Technological development for CO_2 capture is discussed and an emphasis has been given to amine-based post-combustion CO_2 capture. To avoid economical burdens, process operation complications, and environmental concerns, this study is enrooted to the development of an amine system. For an amine development for CO_2 capture, stability is one of the major challenges. The literature is reviewed on the thermal and oxidative degradation of amines. Not all but literature on focused amines like MEA, DEA and PZ is discussed precisely. Whereas, studies on other amines are provided in miscellaneous section. PZ and DEA are directly involved in our study; hence, it was mandatory to discuss them in details and discussion of MEA is based on its maturity, as this is one of the benchmark solvents. Unfortunately, there is not much literature on the degradation of PZ/DEA blend system and MOR; hence, it was not possible to bring them in any exhaustive debate in the literature. However, there were few screening studies on thermal degradation of MOR from Rochelle group, which are highlighted in the discussion.

2.2 Carbon dioxide emissions and environment

Global warming is a well-known, worldwide concern, most probably caused by increasing concentrations of CO_2 and other greenhouse gases in the earth's atmosphere, due to human activities. Power sector, mainly relies on coal, gas and heavy oil. Coal is widely known as one of the most intensives of the fossil fuels, which is amplifying its share in the global warming. The report of international energy agency revealed that the highest rate of CO_2 emissions of 71.5% has been observed in electricity and heat sector for last two decades, from 1990 to 2010 (IEA, 2012). Global CO_2 emissions can raise up to 29% by the year 2035, which are nearly double to that of, which were in 1990 (BP, 2014). Another report claimed that the global energy-related CO_2 emissions has been predicted to increase up to 46% by 2040, approaching 45 billion metric tons (Sieminski, 2013). As a result, ecosystems may fail and about 15-40% of all of the species may get destroyed (Shao & Stangeland, 2009). However, a decrease of 50% of worldwide CO_2 emissions is necessary to limit the long-term global average temperature rise to between 2 and 2.4 °C by the year 2050 (IPCC, 2013).

2.3 Technologies of choice for CO_2 capture

CO_2 capture technologies are a valuable way to achieve an important reduction in CO_2 emissions. There are a number of technologies, which are being evaluated for the capture of industrial CO_2 emissions. Generally, three technology choices are widely known as viable for large scale development in coming times, like post-combustion CO_2 capture using amine solvents, Oxyfuel combustion and calcium looping technologies (MacDowell et al., 2010). Amine scrubbing may be a more feasible technology for CO_2 capture from coal-fired power plants due to its retrofit approach for capturing CO_2 from existing power plants (Rao & Rubin, 2002). The estimated energy requisite for an advanced amine scrubbing process may be up to 2.6 MJ/tons CO_2, with an overall thermodynamic efficiency of 50% (Rochelle et al., 2011).

2.4 Post-combustion CO_2 technology overview

CO_2 absorption by chemical technology refers to the counter-current, gas-liquid contact, in a separating column known as absorber. Stripper in parallel is configured with absorber for the regeneration of the solvent, which is later recycled to the absorber. Additional amine is added to the absorber as solvent make up, because of the degradation of solvent. A detailed flow diagram of amine-based absorption/stripping technology is illustrated in Figure 2.1.

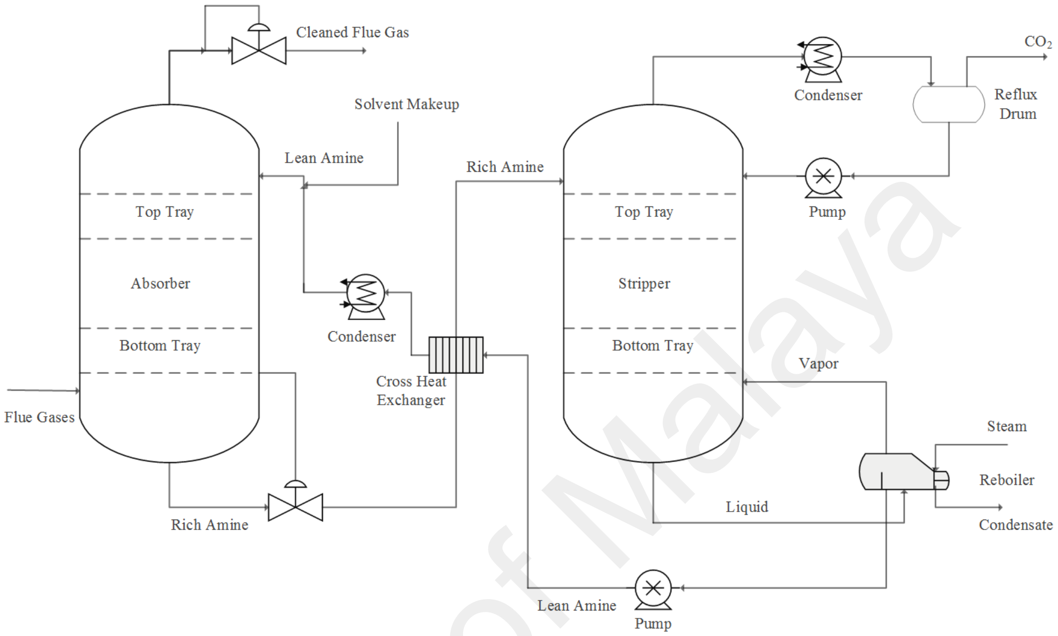


Figure 2.1: Schematic of basic chemical absorption/stripping process for amine-based CO_2 capture

2.5 Solvent management

2.5.1 Solvent selection

Solvent selection is a critical stage for the amine-based CO_2 capture technology. Solvent selection cannot be underestimated due to two main reasons; economics and environment. Studies have brought to light that the solvent makeup accounts around up to 10% of the total operating cost of the CO_2 capture technology using monoethanolamine (MEA) as a standard solvent (Rao and Rubbin 2002). Common amines tested are like MEA, MDEA, DEA and AMP. However, most of the amines are found to degrade under process operating conditions producing hazardous compounds. A continuous research is underway to develop an amine system (single or blend) that should be stable under process operating conditions and should have higher CO_2 capture capacity with favorable thermodynamic properties (Aronu, Svendsen, Hoff, & Juliussen, 2009; Ma’mun, Svendsen, Hoff, & Juliussen, 2007; Mangalapally et al., 2009; Notz, Asprion, Clausen, & Hasse, 2007). A number of amines have been tested to date; Table 2.1 provides a detailed list of common amines tested for CO_2 capture.

Table 2.1: Common amines tested for stability under different conditions

Amine	Abbr.	T (˚C)	CO_2 loading (mol CO_2/mol alkalinity)	Reference
Monoethanolamine	MEA	100-150	0.2-0.5	(Bello & Idem, 2005b; da Silva et al., 2012; H. Lepaumier, D. Picq, & P.-L. Carrette, 2009a; Strazisar et al., 2003; Supap et al., 2001)
Diethanolamine	DEA	120-180	0.0-2.0 MPa	(Hsu & Kim, 1985; Jamal & Meisen, 2001; C. Kim & G. Sartori, 1984; Helene Lepaumier et al., 2009a; Paitoon & Raphael, 2013; Tontiwachwuthikul et al., 2011)
Piperazine	PZ	135-175	0.0-0.47	(Stephanie A. Freeman, Dugas, Van Wagener, Nguyen, & Rochelle, 2009; Stephanie A. Freeman, Dugas, Van Wagener, Nguyen, & Rochelle, 2010; G. Rochelle et al., 2011)
Morpholine	MOR	175	0.30	(Alper, 1990; Stephanie A. Freeman & Rochelle, 2011; Liu et al., 2013)
1-methylpiperazine	1-MPZ	150	0.30	(Stephanie A Freeman et al., 2013; Stephanie A. Freeman & Rochelle, 2011)
2-methylpiperazine	2-DMPZ	150	0.30	(Stephanie A Freeman et al., 2013; Stephanie A. Freeman & Rochelle, 2011)
Piperidine	PD	175	0.30	(Stephanie A. Freeman & Rochelle, 2011)
Pyrrolidine	Pyr	150	0.30	(Stephanie A. Freeman & Rochelle, 2011)
Hexamethylenediamine	HMDA	175	0.30	(Stephanie A. Freeman & Rochelle, 2011)

Table 2.1 (Continued): Common amines tested for stability under different conditions

Amine	**Abbr.**	**T (˚C)**	**CO_2 loading (mol CO_2/mol alkalinity)**	**Reference**
N-(2-aminoethyl)ethanolamine	AEEA	150	0.2-0.4	(Bindwal, Vaidya, & Kenig, 2011; Ma'mun et al., 2007)
Aminomethylpropanol	AMP	135-150	0.0-0.5	(Helene Lepaumier et al., 2009a; Han Li, Le Li, Thu Nguyen, Gary T Rochelle, & Jian Chen, 2013a; Tielin Wang & Klaus- J. Jens, 2012; T. Wang & Jens, 2014)
Tetraethylenepentamine	TEPA			(Aronu et al., 2009)
1,4-diaminobutane	DAB	175	0.30	(Namjoshi et al., 2013)
Bis(amino ethyl)ether	BAE	175	0.30	(Namjoshi et al., 2013)
N,N-dimethylaminoethanol	DMAE	140	2 M Pa	(Helene Lepaumier et al., 2009a)
N,N'-dimethylpiperazine	DMP	140	2 MPa	(Helene Lepaumier et al., 2009a)
N-(2-hydroxyethyl)ethylene diamine	HEEDA	135	0.25	(Helene Lepaumier et al., 2009a)
N-methylaminoethanol	MAE	140	2 MPa	(Helene Lepaumier et al., 2009a)
Hexamethyleneimine	HMI	175	0.30	(Stephanie A. Freeman & Rochelle, 2011)

Table 2.1 (Continued): Common amines tested for stability under different conditions

Amine	**Abbr.**	**T (˚C)**	**CO_2 loading (mol CO_2/mol alkalinity)**	**Reference**
N,N,N',N',N''-pentamethyldiethylenetriamine	PMDETA	140	2 MPa	(Helene Lepaumier et al., 2009a)
2-(methylamino)ethanolamine	MMEA	135	0.50	(Ma'mun et al., 2007)
Ethylenediamine	EDA	100-135	0.40	(Zhou, Chen, Nguyen, Voice, & Rochelle, 2010)
Diethylenetriamine	DETA	135	0.17	(Stephanie A. Freeman & Rochelle, 2011)
N-(2-aminoethyl)piperazine	AEP	135	0.40	(Du et al., 2013)
Homopiperazine	HomoPZ	175	0.30	(Stephanie A. Freeman & Rochelle, 2011)
Ddiglycolamine	DGA	135	0.40	(Al-Juaied & Rochelle, 2006; Alper, 1990)
Methyldiethanolamine	MDEA	100-180	0.0-0.50	(Amitabha Chakma & Meisen, 1988; A Chakma & Meisen, 1997; F. Closmann & Rochelle, 2011; F. B. Closmann, 2011; Namjoshi et al., 2013)

Many of the tested amines have good CO_2 capture capacity and rate of absorption of CO_2 under absorber operating conditions; however, search for the best is still ongoing. Some new solvents (systems) have shown better CO_2 capture capacity with feasible physical characteristics and thermal stability, like PZ and MOR under process operating conditions (Bishnoi & Rochelle, 2000; Stephanie Anne Freeman, 2011; Stephanie A. Freeman, Davis, et al., 2010; Liu et al., 2013; Matin et al., 2013; Nielsen, Li, & Rochelle, 2013). PZ is well known for its limited CO_2 solubility as being a diamine. It has been speculated that the limited CO_2 solubility of PZ may be addressed through their blending with other amines (Ali, Al-Rashed, & Merchant, 2010; Bishnoi & Rochelle, 2002; Derks, Hogendoorn, & Versteeg, 2010; Dubois & Thomas, 2009; Zhang, Wang, Zhang, Yang, & Xu, 2003).

2.5.2 Thermal degradation of amines

Stripper operates at temperatures above 120 ˚C, depending up on the amine and its maximum estimated stripper temperature (MEST), where there are maximum chances of thermal degradation, and it may occur in cross heat exchanger and the reclaimer too. Due to the degradation products, capacity of the solvent to capture CO_2 decreases. To maintain CO_2 capture level, ultimately, the solution is discarded and fresh solvent is added as makeup. A number of studies on thermal degradation of amines have been conducted under various conditions to investigate the stability of the solvents (Bougie & Iliuta, 2014; J. Davis & Rochelle, 2009; Stephanie A. Freeman & Rochelle, 2011; C. Gouedard, D. Picq, F. Launay, & P.-L. Carrette, 2012; Gary T. Rochelle, 2012; Kali-Stella Zoannou, Devin J. Sapsford, & Anthony J. Griffiths, 2013a). Davis, Freeman, Closmann, Lepaumier and Eide-Haugmo (F. Closmann & Rochelle, 2011; J. D. Davis, 2009; Eide-Haugmo et al., 2011; Stephanie Anne Freeman, 2011; Helene Lepaumier et al., 2009a) are main contributors in thermal degradation of various amines in recent past.

2.5.2.1 Monoethanolamine

Several researchers have studied thermal degradation of MEA exhaustively (J. Davis & Rochelle, 2009; Hatchell, Namjoshi, Fischer, & Rochelle, 2014; Polderman, Dillon, & Steele, 1955; Zhou, Wang, & Chen, 2012; Kali-Stella Zoannou, Devin J Sapsford, & Anthony J Griffiths, 2013b). Hélène Lepaumier et al., (2011) executed an investigation to compare thermal degradation results of pilot plant (Esbjerg plant) to those of obtained through experiments at lab scale. Lab scale experiments were conducted depicting the pilot plant stripper conditions (30% w/v aqueous MEA solution with initial CO_2 molar loading of 0.5 at 135 ºC). After an experimental span of 5 weeks, a loss of 57.6% occurred in the initial concentration of MEA under lab scale. The rate was linear until 4 weeks, however, it declined in week 5. Whereas, thermal degradation at pilot plant scale was limited. Vevelstad, Grimstvedt, Knuutila, & Svendsen, (2013), conducted thermal degradation study of already oxidized amine solutions with CO_2 in closed cylinders at a temperature of 135 °C in both closed and open batch reactors. Amine loss after five weeks was 50-56% for most of the MEA solutions. The results enlightened that there is no effect of oxidative degradation on the thermal degradation of MEA. Huang et al., (2013) established that the flue gas contaminants enhanced the thermal degradation of amine (MEA). Results showed that the MEA degrade significantly in presence of nitrite (5000 ppm). However, the acidic impurities seemed not to influence the rate of thermal degradation of MEA. Though, it may affect the product distribution (Zhou, Wang, & Chen, 2011).

Zoannou et al., (2013) performed thermal degradation of 30 % MEA at two different CO_2 loadings, 0.19 and 0.37 mol of CO_2/mol of MEA at 160 ºC for 8 weeks in a high-pressure vessel. The results showed that after 8 weeks MEA concentration reduced by 95%.

J. D. Davis, (2009), conducted thermal degradation study of about 18 amines in stainless steel thermal cylinders closed with Swagelok endcaps. Cylinders were kept in convection ovens, up to 150 °C for the duration of 1-6 weeks. Davis mainly focused the degradation of MEA. He found that besides temperature, increasing the concentration of amine or CO_2 loading increased the thermal degradation. In screening experiments of various amines, degradation rate investigation was based on 7 m alkalinity with 0.4 mole CO_2 per mole alkalinity (mol CO_2/mol alk) at 135 °C for 28 days. The amines degradation rate was ranked as follows: cyclic amines with no side chains < long chain alkanolamines < alkanolamines with steric hindrance < tertiary amines < MEA < straight chain di- and triamines. Furthermore, study exhibited that the PZ and MOR were found to be stable solvents, however they degraded significantly when blended with MEA.

Lepaumier et al. (2009; 2010;), conducted thermal degradation study of 17 different amines including: alkanolamines, diamines, and triamines without alcohol function with a concentration of 4.0 mole/kg. Experiments were conducted in 100 ml stainless steel batch reactors, with and without CO_2 and O_2 presence at 140 °C for a period of 15 days. CO_2 loading increased the rate of degradation of amines. Study provided some of the conclusions as: the stability of the ethanolamines is in an order of, III> hindered I>I>II (I, II, III represents primary, secondary and tertiary amine respectively). Thermal stability of ethylene diamines is as: III-III > III-I > III-II > II-II. Author found that MEA loss in presence of CO_2 was 42% of its initial concentration.

2.5.2.2 Piperazine

Thermal degradation studies for PZ have been carried out comprehensively by Rochelle group (Chen & Rochelle, 2011; Stephanie Anne Freeman, 2011; Stephanie A. Freeman, Davis, et al., 2010; Stephanie Anne Freeman & Rochelle, 2012b; L. Li et al., 2013; Namjoshi et al., 2013), under different conditions. J. D. Davis, (2009), conducted experiments on 5 m and 8 m PZ, whilst amine screening tests and concluded that PZ did not degrade at up to 135 °C. Freeman et al. (2009; 2010 2011; 2012a; 2012b) carried out thermal degradation experiments using 5 inches (in.) long 316 stainless steel (316SS) cylinders with Swagelok endcaps and kept cylinders in mechanical convection ovens for thermal degradation. Thermal degradation was investigated for 4, 8, 12 and 20 m PZ for up to 72 weeks with CO_2 loadings ranging from 0.0 to 0.47 mol CO_2/mol alkalinity at 135-175 °C. Thermal degradation of PZ followed first and second order kinetics (Stephanie Anne Freeman & Rochelle, 2012b). The rate constants of first and second order kinetics are presented in Table 2.2 and Table 2.3 respectively.

Table 2.2: Summary of results of k_1 for PZ, with respect to temperature, PZ Concentration and CO_2 loading (Stephanie Anne Freeman, 2011)

Temperature (°C)	**Concentration (m)**	**CO_2 loading (mol CO_2/ mol alkalinity)**	**k_1, 10^{-9} (s^{-1})**
135	8	0.30	1.0
	8	0.40	0.5
	10	0.30	4.8
	10	0.40	-
150	8	0.30	6.1
	8	0.40	7.9
	10	0.30	8.9
	10	0.40	6.0
	15	0.30	-
	20	0.30	24.2
165	4	0.30	35.5
	8	0.00	0.8
	8	0.10	18.4
	8	0.30	31.4
	8	0.40	40.9
	12	0.30	50.3
175	4	0.30	114
	8	0.00	7
	8	0.10	65.8
	8	0.20	78.8
	8	0.30	132
	8	0.40	171
	8	0.47	23.8
	12	0.30	156
	20	0.10	44.7
	20	0.30	168

Table 2.3: Summary of results of k_2 for PZ, at different temperatures, PZ concentrations and CO_2 loading (Stephanie Anne Freeman & Rochelle, 2012b)

Temperature (°C)	**PZ Concentration (m)**	**CO_2 loading (mol CO_2/mol alkalinity)**	**k_2, 10^{-13} (mmol/kg-s)**
135	8	0.30	2.39
150	8	0.30	14.9
165	8	0.30	128
175	4	0.30	1120
175	8	00	148
175	8	0.10	195
175	8	0.20	277
175	8	0.30	565
175	8	0.40	617
175	8	0.47	134
175	12	0.30	617
175	20	0.30	821

Thermal degradation of PZ increased with the increase in all the three parameters: temperature, PZ concentration and CO_2 loading. Degradation of 8 m PZ increased linearly from 0 0 to 0.3 moles CO_2 per mole alkalinity at 150 to 175 °C. However, it decreased when CO_2 loading was above 0.4 mole CO_2/mol alkalinity under the same conditions. At the meantime the maximum degradation noticed at 175 °C was with 0.3 to 0.4 mol CO_2/mol alkalinity (Stephanie Anne Freeman, 2011). Based on one of the modeling studies (Stephanie Anne Freeman & Rochelle, 2012a) of 8 m PZ at 175 °C, it was found that the concentrations of free PZ and $PZCOO^-$ were low above 0.4 mol CO_2/mol alkalinity while the concentration of HCO_3^- reached to a significant level. The presence of CO_2 in form of HCO_3^- neutralized the catalytic influence of CO_2 when existing in the form of other species, at lower CO_2 loading.

Freeman et al. (2009) reported a comparative thermal degradation study for PZ and MEA. At 175 °C, PZ seemed to lose up to 32% of its initial concentration in 4 weeks. A weekly loss of 5.3% and 11%, 0.25% and 0.8%, was noticed for 7 m MEA with 0.4 mol CO_2/mol alkalinity and 10 m PZ with 0.3-mol CO_2/mol alkalinity at 135 and 150 °C respectively. Furthermore, 8% weekly loss was reported for 8 m PZ with a CO_2 loading of 0.3 mol CO_2/mol alkalinity at 175 °C. Results of PZ and MEA under conditions indicated in

Figure 2.2 are assumed for four weeks, based on weekly loss.

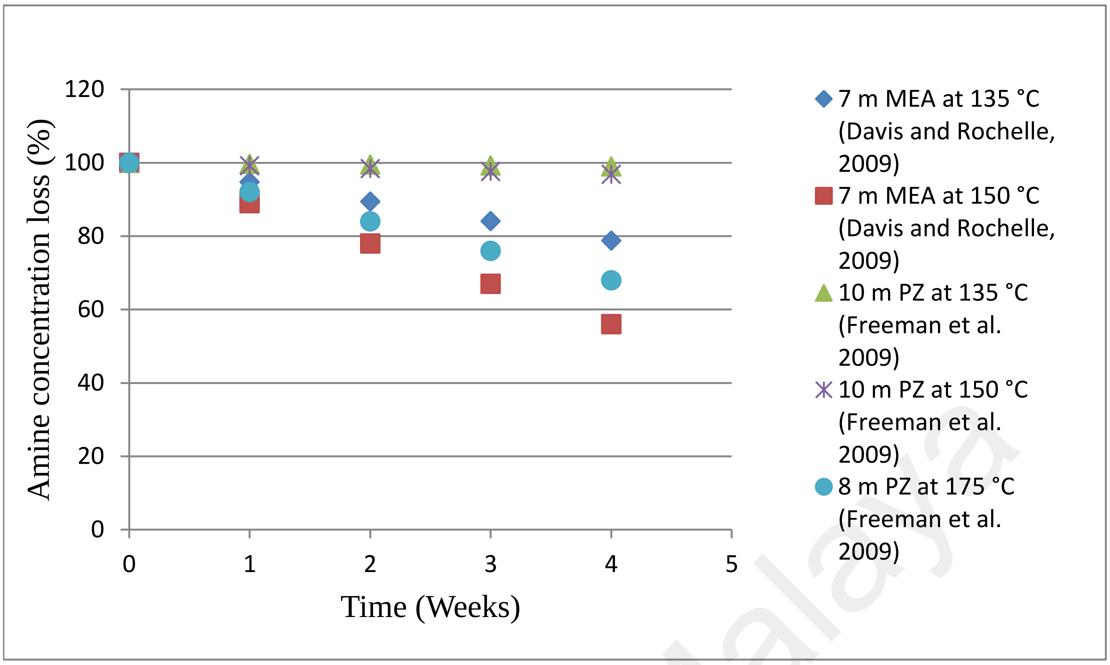


Figure 2.2: The percentage loss of 7 m MEA with 0.4 mol CO_2/mol alkalinity degraded at 135 and 150 °C, 10 m PZ with 0.3 mol CO_2/mol alkalinity at 135 and 150 °C and 8 m PZ with 0.3 mol CO_2/mol alkalinity at 175 °C

2.5.2.3 Diethanolamine

Kennard and Meisen (1980) used 30 wt.% DEA solutions at a CO_2 partial pressure of 600 psia and heated in a pressure vessel at 175-205 °C. The elevated temperature and pressure were used to accelerate thermal degradation so an experiment could be completed in a matter of hours rather than weeks. Gas chromatography was used to measure the appearance of degradation products. They reported THEED as a new degradation product along with the previously discovered HEO and HEP, but did not report a reaction mechanism for its formation. They noted that DEA degradation was not first order over the entire temperature range, particularly above 185 °C. At higher temperatures, the degradation rate slowed significantly after 5 hours and the resulting Arrhenius plot over the complete temperature range was not a straight line indicating that DEA thermal degradation is not a first order reaction. The initial DEA concentration was then varied and it was shown that DEA degradation increased with increasing solution concentration.

At a constant CO2 partial pressure of 4137 kPa, the Arrhenius plot for different DEA concentrations is given below in Figure 2.3.

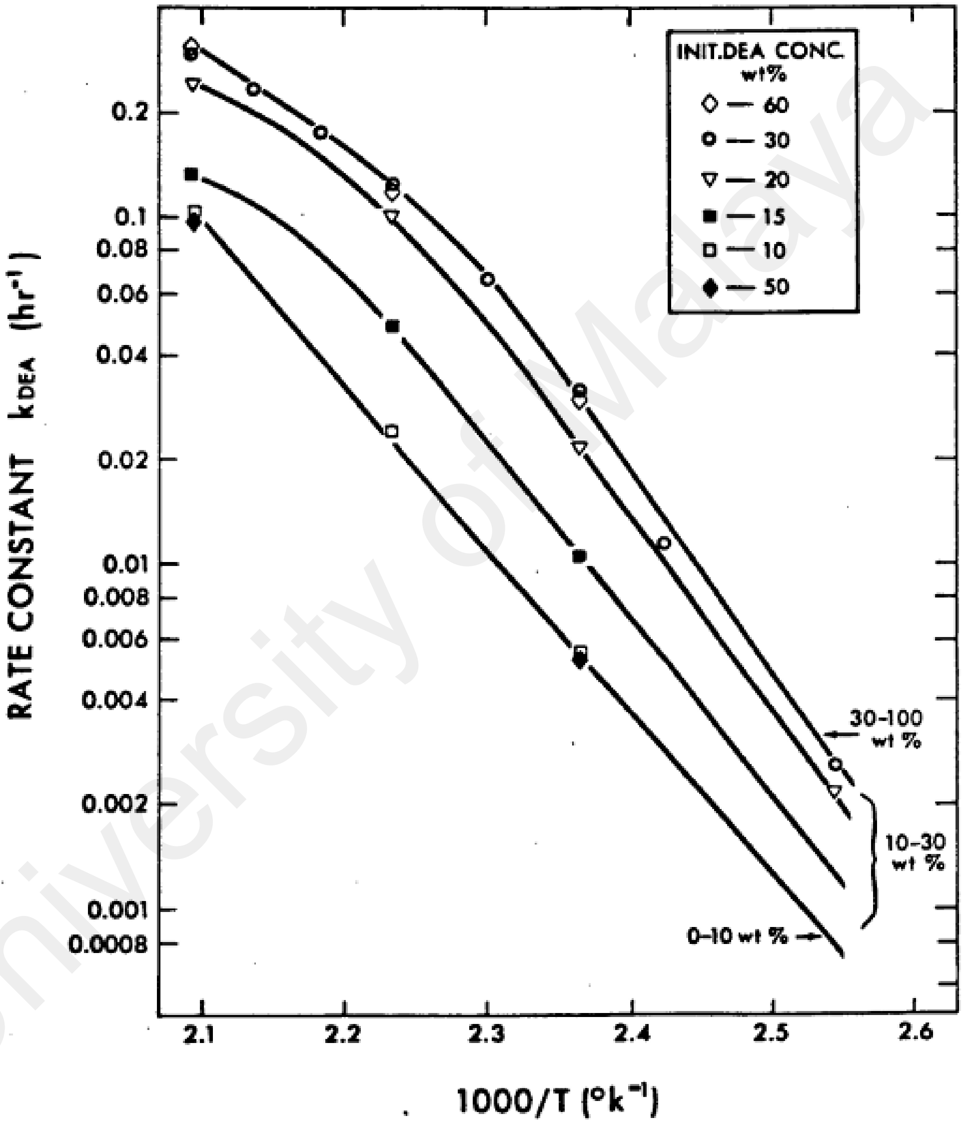


Figure 2.3: Arrhenius plot for various DEA concentrations at 4137 kPa CO_2 (M. L. Kennard & Meisen, 1985)

At low DEA concentrations (0-10 wt.%), the value of first order rate constant for DEA disappearance is constant. From 10-30 wt.% the rate constant increased rapidly and from

30-100 wt.% the rate constant reached to the maximum and slightly decreased as it approached to 100 wt.%. The activation energy of the curves at low temperature is about 23 kcal/mol.

The CO2 partial pressure was varied from 1500 – 6900 kPa at 195 °C for 30 wt.% DEA solution. Figure 2.4 shows the DEA concentration as a function of time and CO2 partial pressure.

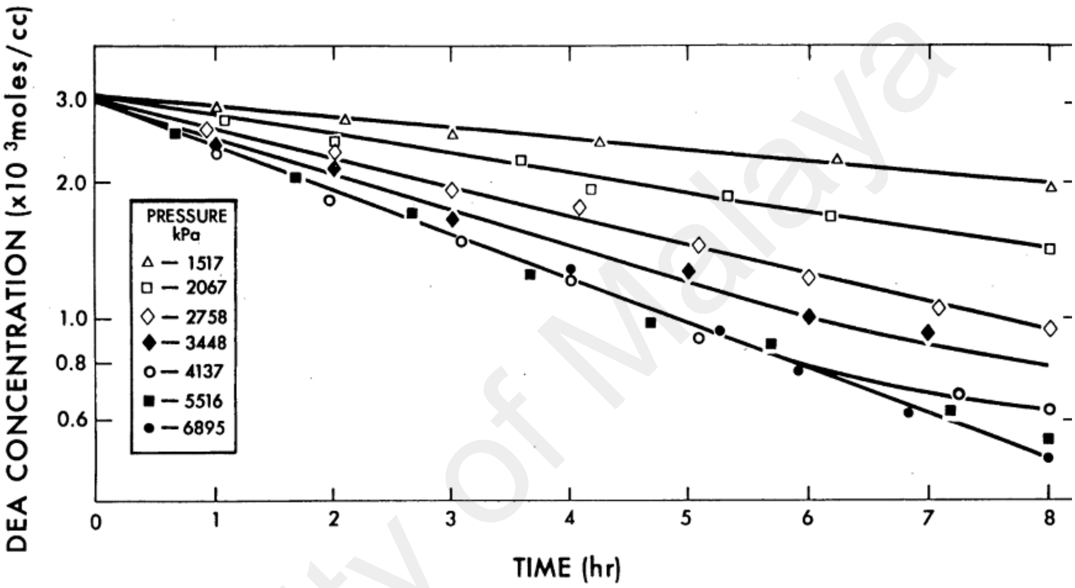


Figure 2.4: DEA concentration as a function of time and CO_2 partial pressure from a 30 wt.% DEA held at 195 °C (M. L. Kennard & Meisen, 1985)

The degradation of DEA increased on the rise of CO_2 concentration from 1500 to 4100 kPa, which corresponds to a loading of 0.5 moles CO_2 per mole DEA. Above 4100 kPa the degradation rate did not increase with increasing CO_2 concentrations.

2.5.2.4 Miscellaneous studies

Eide-Haugmo et al., (2011) used methods of Lepaumier and Davis to degrade various amines at 135 °C, without and with CO_2 loading of 0.5 mol CO_2/mol amine. Results exhibited that the thermal degradation is directly affected by the CO_2 loading. In the presence of CO_2, hindered amine AMP had the highest stability and the secondary amines degraded faster. Bougie & Iliuta, (2014), thermally degraded five single amines namely:

2-amino-2-hydroxymethyl-1,3-propanediol (AHPD), PZ, 2-amino-1,3-propanediol (Serinol), AMP and MEA up to 130 °C for fourteen days in thermal cylinders. The initial concentrations of the amines were as following: 30 wt.% for MEA (4.95 M), AMP (3.35 M), and Serinol (3.46 M), 23 wt.% for AHPD (1.98 M) and 7 wt.% for PZ (0.76 M). The highest amine concentration loss was noticed for serinol, followed by MEA and PZ .The lowest amine concentration loss was observed for AMP and AHPD. However, the loss of PZ does not match with the literature as it is illustrated as a highly a stable amine compared to AMP (Davis, 2009; Freeman, 2011).

Dawodu and Meisen focused on degradation of MDEA and MDEA blended systems, specifically MDEA + MEA and MDEA + DEA at a constant CO_2 partial pressure of 2.58 MPa and temperatures ranging from 120 to 180 °C (Dawodu & Meisen, 1996). Degradation products were identified using GC and GC/MS techniques. DEA degraded the fastest followed by MEA and finally MDEA in the blended systems. MDEA was found to degrade at a rate over an order of magnitude slower than MEA and DEA. This was to be expected considering it is a tertiary amine and cannot form carbamate like the secondary amine DEA or the primary amine MEA thereby eliminating the possibility to form an oxazolidone intermediate. The rate constant for DEA disappearance was over twice as large as the one for MEA. DEA has the lowest activation energy of the amines studied followed by MEA and MDEA. This means that adjusting the temperature of the system would have the greatest effect on MDEA of the three amines studied.

Holub, Critchfield, & Su, (1998) describe degradation of alkanolamine solutions in CO_2 service. In laboratory tests with MMEA/MDEA and DEA/MDEA blends, the amount of MMEA degradation was comparable to DEA degradation. This would suggest that MMEA would also degrade much faster than MEA since DEA has a higher degradation rate than MEA under laboratory conditions. Thermal degradation rates of different amines are listed in Table 2.4.

Table 2.4: Thermal degradation rates of different amines

Solvent	Conc: (m)	Loading (mol CO_2/mol alkalinity	k_1, 10^{-7}, (s^{-1})					Reference
			100 °C	120 °C	135 °C	150 °C	175 °C	
MEA	7	0.20		0.28	0.90		3.97	(J. D. Davis, 2009)
MEA	7	0.40	0.02	0.29	1.34	8.28		(J. D. Davis, 2009)
DEA	4.0	0.50			9.91			(Eide-Haugmo et al., 2011)
DGA	7	0.40			0.39			(J. D. Davis, 2009)
PZ	8	0.47					0.24	(Stephanie Anne Freeman, 2011)
PZ	8	0.30			0.01	0.61	1.32	(Stephanie Anne Freeman, 2011)
PZ	8.0	0.20					0.79	(Stephanie Anne Freeman, 2011)
PZ	8.0	0.10					0.66	(Stephanie Anne Freeman, 2011)
HEEDA	3.5	0.40			16.0			(Stephanie Anne Freeman, 2011)
AMP	7.0	0.40			0.21	0.86		(Stephanie Anne Freeman, 2011)

Table 2.4 (Continued): Thermal degradation rates of different amines

Solvent	**Conc: (m)**	**Loading (mol CO_2/mol alkalinity**	**k_1, 10^{-7}, (s^{-1})**					**Reference**
			100 °C	**120 °C**	**135 °C**	**150 °C**	**175 °C**	
PZ	8.0	0.00				0.001	0.07	(Stephanie Anne Freeman, 2011)
1-MPZ	8.0	0.30				0.36		(Stephanie Anne Freeman, 2011)
2-MPZ	8.0	0.30				0.25		(Stephanie Anne Freeman, 2011)
MDEA	7.0	0.20			0.42	4.38		(F. B. Closmann, 2011)
Mor	8.0	0.30					0.5	(Stephanie Anne Freeman, 2011)
Pyr	8.0	0.30					14.0	(Stephanie Anne Freeman, 2011)
HomoPZ	8.0	0.30					18.5	(Stephanie Anne Freeman, 2011)
(PD	8.0	0.30					0.84	(Stephanie Anne Freeman, 2011)
HEP	7.0	0.40			0.46			(Stephanie Anne Freeman, 2011)
DETA	7.0	0.40			9.91			(Stephanie Anne Freeman, 2011)

Table 2.4 (Continued): Thermal degradation rates of different amines

Solvent	Conc: (m)	Loading (mol CO_2/mol alkalinity	k_1, 10^{-7}, (s^{-1})					Reference
			100 °C	120 °C	135 °C	150 °C	175 °C	
t2,5-DimethylPZ	2.0	0.30				0.09		(Stephanie Anne Freeman, 2011)
HMDA	8.0	0.30					1.9	(Namjoshi et al., 2013)
BAE	8.0	0.40					2.0	(Namjoshi et al., 2013)
DAB	8.0	0.40					27.2	(Namjoshi et al., 2013)
PDA	5.0	0.40				4.08		(Daniel Hatchell 2014)
Putrescine	5.0	0.40				2.69		(Daniel Hatchell 2014)
EDA	5.0	0.40				7.97		(Daniel Hatchell 2014)
HMI	8.0	0.30					59.30	(Stephanie Anne Freeman, 2011)
AEP	2.3	0.40			1.91			(J. D. Davis, 2009)

Data from Table 2.4 shows that the highly stable amines tested to date are MOR, PD, PZ, BAE and, HMDA. Only PZ has been studied in significant details up to now, however, other amines are not developed yet. Studies on PZ revealed that it is a stable solvent up to 150 °C with favorable CO_2 capture properties. However, it has lower CO_2 solubility, which is the hurdle for this solvent to be used as a single solvent for commercial means. Aforementioned amines are also ring structured or diamines, which makes them more favorable for CO_2 capture.

Du et al. (2013) investigated thermal degradation of PZ with N-(2-aminoethyl) piperazine (AEP). Degradation experiments of the 5 m PZ/2 m AEP were conducted in stainless steel cylinders. Solutions were loaded with CO_2 (0.2 to 0.3 mol CO_2/mol alkalinity), and the experimentation time was up to 20 weeks, at 150 and 175 °C. Amine loss for PZ was up to 10% and was 30% for AEP for 20 weeks at 150 °C. The blend did not sustain high temperature like 175 °C, where it lost most of its initial concentration for the same duration. Author reported that loss of the blend followed first order kinetics with rate constants of 1.52×10^{-8} s^{-1} and 20.1×10^{-8} s^{-1} at 150 °C and 175 °C respectively.

In the degraded blend of 7 m MEA/2 m PZ, Davis (2009) identified N-(2-hydroxyethyl) ethylenediamine (HEEDA), N-(2-hydroxyethyl) imidazolidone (HEI), N-(2-aminoethyl) piperazine (AEP), and ethylenediamine (EDA) as the dominant degradation products using cation IC-MS. HEEDA and HEI are present in MEA degradation, while AEP and EDA are new products due to the presence of PZ in the blend. The suggested mechanism for producing AEP is the reaction of PZ with oxazolidone produced during the first step of the carbamate polymerization mechanism of MEA. Given the relative concentrations of AEP and HEEDA, author estimated that PZ reacts up to five times faster to form AEP than MEA reacting with oxazolidone to produce HEEDA, indicating the strength of PZ as a reacting nucleophile. Even in a blend with MEA, the degradation results indicate some of the characteristics of PZ thermal degradation.

AMP/PZ blend provides higher CO_2 loading compared to AMP and PZ individually without precipitation as noticed in PZ alone at higher CO_2 loading (Brúder, Grimstvedt, Mejdell, & Svendsen, 2011; Samanta & Bandyopadhyay, 2009). However, the blend has higher volatility at lean conditions (Li et al., 2013). Thermal degradation of 5 m PZ/2.3 m AMP blend was investigated by H. Li (2013), at 135 and 150 °C with a CO_2 loading of 0.4 mol CO_2/mol alkalinity for up to 6 weeks. Two sets of experiments were run for AMP/PZ, and results are organized in percentage range, from lower to higher. In 6 weeks, 9 to 13% loss for PZ and 19 to 22% for AMP was noticed at 135 °C. However, degradation loss was higher at 150 °C, which accounted for 20 to 28% for PZ and 56 to 60% for AMP. The combination of AMP and PZ promoted the rate of degradation when blended together as higher degradation was noticed in the blended form than AMP or PZ alone. Degradation of PZ increased up to 10 folds in the blend of AMP/PZ while AMP degraded 3 times faster as exhibited in Table 2.5. Furthermore, results revealed that the blend degraded slowly compared to MEA at 150 °C.

Table 2.5: Thermal degradation first order rate constants (k_1) comparison between PZ and AMP individually and in blend (5 m PZ/ 2.3 AMP) with a CO_2 loading of 0.4 mol CO_2/mol alkalinity. Values are in 10^{-9}

Temperature (°C)	PZ	AMP	PZ in (PZ/AMP)	AMP in (PZ/AMP)	PZ+AMP
135	0.5	21	39	63	47
150	8.0	86	90	256	133

Closmann et al., (2009; 2011; 2013) investigated the blend of MDEA/PZ to replace 30% MEA. Experiments for 7 m MDEA/2 m PZ were conducted at temperatures from 100 to

150 °C with CO_2 loading from 0 to 0.43 mol CO_2/mol alkalinity. Thermal degradation experiments were performed in stainless steel cylinders, which were then placed in a temperature-controlled oven for up to nine weeks. In addition, some experiments were also run by adding 1 mM Fe^{2+}, to examine its catalytic effect on thermal degradation of the blend. Degradation kinetics results of 7 m MDEA/2 m PZ exhibited that the blend is stable up to 135 °C as reported in Table 2.6.

Table 2.6: Summary of thermal degradation of MDEA and PZ with uncertainties at 100, 120, and 135 °C with a CO_2 loading from 0.1 to 0.2 mol CO_2/mol alkalinity (F. Closmann et al., 2009)

Solvent	**Temperature (°C)**	**Time (Weeks)**	**MDEA degradation rate (mmolal/day)**		**PZ degradation rate (mmolal/day)**	
CO_2 loading (mol CO_2/mol alkalinity)			α= 0.1	α = 0.2	α= 0.1	α= 0.2
7 m MDEA	100	9	-6 ± 6	-18 ± 52	NA	NA
	120	9	-0.3 ± 11	-31 ± 16	NA	NA
7 m MDEA/2 m PZ	100	8	-3 ± 13	-19 ± 4	-2 ± 4	-6 ± 1
	120	8	-11 ± 11	-7 ± 20	-7 ± 3	-9 ± 5
7 m MDEA/2 m PZ 1 mM Fe^{2+}	100	6	NA	-3 ± 13	NA	-2 ± 5
	120	7	NA	-18 ± 20	NA	-11 ± 10
7 m MDEA/ 2 m PZ	135	6	-9 ± 8	-30 ± 15	-31 ± 3	-44 ± 2

Magnitude of errors as reported in Table 2.6 illustrate that either degradation of PZ and MDEA was almost zero or immeasurable. However, degradation rate increased by increasing temperature as well as CO_2 loading. Higher degradation was noticed from 120 to 135 °C.

2.5.3 Oxidative degradation of amines in CO_2 capture

Oxidative degradation of amines is highly undesirable for amine-based CO_2 capture process as this causes growing economic burden and operating problems like fouling, corrosion and foaming (Amitabha Chakma & Meisen, 1986). Driving force for the rate of oxidative degradation is the presence of O_2 partial pressure, concentration of amine, and temperature. Furthermore, George S. Goff & Gary T. Rochelle (2004) reported that oxidative degradation is accelerated by the presence of oxygen, and free metal ions. However, amine degradation is more sensitive to O_2 than the amine concentration (Supap et al., 2001; Vevelstad et al. 2013), CO_2 loading has also a significant impact on the oxidative degradation of amine (Chi & Rochelle, 2002). The presence of acidic gases meanwhile cannot be ignored as they have tendency to catalyze the oxidation of amine as SO_2 is observed to increase the rate of oxidation of MEA on an increase of its concentration (Uyanga & Idem, 2007). Oxidation of amines is more dependent on O_2 concentration than that of CO_2 (McDonald et al., 2014). Oxidative degradation in post-combustion CO_2 capture is widely studied by several scholars (Didas, Zhu, Brunelli, Sholl, & Jones, 2014; Fredriksen & Jens, 2013; Kindrick, Atwood, & Arnold, 1950; H. Lepaumier, D. Picq, & P.-L. Carrette, 2009b; Andrew J. Sexton & Rochelle, 2010; Voice & Rochelle, 2011; T. Wang & Jens, 2013).

2.5.3.1 Monoethanolamine

Bello & Idem (2005a), studied oxidative degradation of 5 and 7 m MEA at 55-120 °C with CO_2 loading of 0-0.44 mol CO_2/mol MEA with and without corrosion inhibitor sodium meta-vanadate ($NaVO_3$). The experiments were conducted in a rotary-type autoclave with an O_2 pressure of 250 and 350 kPa. Results of the study brought to light that the presence of the corrosion inhibitor $NaVO_3$, amine concentration, temperature and presence of O_2 increased the rate of the degradation of MEA; however, increase in CO_2 loading decreased the solvent degradation rate. The degradation of MEA-H_2O-O_2 and MEA-CO_2-O_2 systems also increases with increase in the temperature and O_2 partial pressure but decreases with increasing amine concentration (Bello & Idem, 2005b). Lepaumier et al., (2011) compared lab scale experimental results with those obtained from pilot plant (Esbjerg plant). Lab scale experiments were performed under typical oxidative degradation conditions in presence of CO_2 w/v aqueous MEA solution with initial CO_2 and air at absorber conditions (30% molar MEA loading of 0.4, sparged with air and CO_2 at 55 °C). MEA was found to lose 5.8% of its initial concentration in 9 days.

Elnan, (2012) studied oxidative degradation of amines, experiments were conducted using open batch reactor at different oxygen concentrations ranging from 21 to 98% and at temperatures 55 and 75 ^{o}C. The results showed that rise in temperature contributed more in MEA loss than increase in oxygen concentration. Furthermore, when MDEA was blended with MEA, it showed a decrease in the rate of degradation of MEA at elevated temperatures (≥ 100 °C) (Lawal, O. Bello, & Idem, 2005). Whereas, degradation rate increased by increasing temperature and O_2 partial and CO_2 loading depicted an opposed impact on the degradation of system (Lawal & Idem, 2006). Vevelstad et al. (2013) conducted oxidative degradation experiments of MEA (30 wt.%) with a CO_2 loading of

0.14 mol CO_2/mol alkalinity under oxygen concentration of 21-98% at 55-75 °C. Experiments were conducted in an open batch reactor. Authors found that rise in temperature from 55 to 75 °C imparted a higher effect on the degradation of MEA than the oxygen concentration change from 21 to 91%.

2.5.3.2 Piperazine

S.A. Freeman (2010; 2011) conducted bench scale oxidative degradation experiments of PZ in two low gas flow (LGF) (100 ml/min) Teflon oxidation reactor (TOR) and original oxidation reactor (OOR). Experiments of 8 to 10 m PZ, CO_2 loaded with 0.2-0.4 mol CO_2/mol alkalinity at temperatures 55-70 °C allowing 2% CO_2, and 98% O_2 as input parameters for 3-5 weeks. In oxidation, metal salts like iron (1 mM Fe^{2+}) stainless steel (0.4 mM Fe^{2+}, 0.1 mM Cr^{3+} and 0.05 mM Ni^{2+}) and copper (4 mM Cu^{2+}) were used (Stephanie Anne Freeman, 2011). Oxidation of PZ in presence of metal ions and O_2 followed first order kinetics. Oxidation of PZ seemed to increase with the increase in partial pressure of O_2 as well as temperature. An increase of 245% in O_2 partial pressure from 40 to 98 kPa enhanced PZ loss by 240% at 55 °C. The increase in temperature from 55 to 70 °C has increased oxidation by 230%. The increase in CO_2 loading from 0.2 to 0.3 mol CO_2/mol alkalinity increased oxidation, even so, the effect was not well understood. 8 m PZ loss in presence of 1.0 mM Fe^{2+} was observed to be 8% of the original amine in 450 hours. Higher degradation of 10 m PZ, accounted for 28% of the original amine in 220 hours when 4.0 mM Cu^{2+} was added as a catalyst. In the absence of any catalyst, a loss of 2 to 7% of PZ was noticed for 350 hours. Results exhibited that adding Cu^{2+} as a catalyst for the oxidation of PZ, increased the rate of degradation.

Nielsen et al., (2013) studied degradation of PZ in two pilot plants: Separation Research Program (SRP) and Pilot Plant 2 (PP2). The former used highly oxygenated synthetic flue gas containing ambient level NOx, while the latter used a slipstream of real flue gas taken from a coal-fired power plant. All the experiments were conducted with 8 m PZ with a CO_2 loading of 0.3 mol CO_2/mol alkalinity. Four campaigns were run in SRP, the first two campaigns were run at 135 °C for 1000 hours and the rest of the two campaigns tested a two-stage flash configuration at 150 °C for 1300 hours. Real flue gas stream was treated with selective catalytic reduction and limestone slurry to minimize the concentrations of SOx and NOx prior to PP2 entrance. Dominant degradation products of SRP and PP2 were found to be FPZ, EDA and formate. In SRP campaigns, little degradation occurred after 1350 hours of operation. However, oxidative degradation was the dominant part of the campaigns, mainly in PP2.

Oxidative degradation of an equimolar diamine blend of 4 m 2-methylpiperazine (2-MPZ) with 4 m PZ was examined by Sherman et al., (2013). Oxidative degradation of 2-MPZ/PZ blend was analyzed using LGF reactor with 98% O_2 and 2% CO_2 at 70 °C. Different metals, like iron (Fe), nickel (Ni), Chromium (Cr) were also added to know the catalytic effect of corrosion products on the rate of oxidation. In presence of Cr and Ni, amine loss was noticed as less than 0.3 mmol/(kg·hr) and total formate generation was measured to be 0.019 mmol/(kg·hr). Closmann et al., (2009) and Closmann, F. B. (2011) conducted oxidative degradation experiments of MDEA/PZ using an enclosed jacketed glass reactor. Nearly 350 mL solvent was degraded for fourteen days at 55 °C with a CO_2 loading ranging from 0.1 to 0.3 mol CO_2/mol alkalinity, allowing 2% CO_2 and 98% O_2 as input gases. MDEA individually formed Formate and amide faster compared to MDEA/PZ blend.

2.5.3.3 Diethanolamine

Diethanolamine is comparatively a less studied amine under oxidation conditions in recent past. Kindrick et al., (1950) studies show that DEA degradation kinetics is higher than MEA and MDEA. Rooney, P. Dupart, & Bacon, (1998) claimed that under similar experimental conditions of unloaded amine solutions, the oxidation is in order of 30% DEA > 50% MDEA > 30% MDEA > 50% DGA® > 20% MEA. Whereas, in presence of CO_2, the trend changes like 30% DEA > 50% DGA® > 20% MEA > 50% MDEA > 30% MDEA. Lepaumier et al., (2009b) studied oxidative degradation of various amines including DEA. Degradation experiments were conducted at 140 °C under air pressure (2 MPa) in stainless steel reactors for 15 days. Authors found that DEA was the most vulnerable amine among others, which lost 22% of its initial concentration in 15 days at 140 C, followed by MEA, which lost 21%. Wang & Jens. (2012; 2013; 2014) investigated the oxidation of PZ, MEA, DEA, AMP and MDEA. Authors observed that under 350 kPa O_2 and 120 °C the DEA loss became the second maximum among AMP, MDEA and MEA in 384 hours, which was 57.3 % after MEA (66.4%).

2.5.3.4 Miscellaneous studies

U.S. Army Chemical Research and Development Laboratories have proposed fragmentation of amines through electron abstraction. Oxidative degradation experiments, mainly focusing on tertiary amines, were conducted in the presence of chlorine dioxide (ClO_2) and other oxidants (Dennis Jr, Hull, & Rosenblatt, 1967; Hull, Davis, Rosenblatt, Williams, & Weglein, 1967; D. Rosenblatt et al., 1967; D. H. Rosenblatt, Hayes Jr, Harrison, Streaty, & Moore, 1963). Authors reported that the rate-limiting step is the electron abstraction, instead of hydrogen abstraction. Sacher, P. , & Brauch, S. (2001) investigated oxidation of primary and secondary amines in the presence of ClO_2 and chlorine while studying the application of chlorine based water treatment process for pharmaceutical agents. Study reported that the rate of oxidation of amines in presence of ClO_2 mainly depends on their structure. A generalized order of rate of degradation is suggested as: tertiary amines>secondary amines>primary amines. In addition, PZ has been reported as highly degradable in the presence of ClO_2 compared to other tested primary and secondary amines; however, it is resistant to chlorine. In another study, Wattanaphan P. (2012) conducted oxidation experiments in presence of sodium chloride (NaCl), ferrous chloride ($FeCl_2$), and hydrochloric acid (HCl) to investigate the effect of chlorides present in flue gas on the degradation of MEA. Study speculated that chloride ion (Cl^-) while reacting with protonated MEA($R\text{-}NH_3^+$) decreases the rate of degradation of MEA.

Wang & Jens, (2012; 2013; 2014) conducted a comprehensive study on oxidative degradation of AMP and blends of AMP with other amines. Experiments of 3-5 mol/kg AMP loaded and unloaded with CO_2 were conducted at temperatures 100-140 °C and O_2 partial pressure ranging from 250-350 kPa. They found that AMP degradation is influenced by varying the parameters such as temperature, amine concentration, CO_2 loading, and O_2 partial pressure. Degradation rate was slightly higher for 5 mole/kg AMP than 3 mole/kg AMP as well as for CO_2 loaded AMP samples than unloaded. Degradation rate increased by the increase in temperature, however, oxidation was highly O_2 partial pressure dependent. In the comparative study with each 5 mole/kg MEA, DEA and MDEA at 120 °C and 350 kPa O_2, the oxidation of AMP was lower than MEA and DEA but equivalent to MDEA. Further, the blend of AMP/PZ was tested at temperatures 80-120 °C with an O_2 partial pressure of 250 kPa for 13 days. Degradation of the blend increased with increase in temperature as well as with PZ concentration from 0.0 to 0.15 mole/kg as AMP concentration was fixed at 3.5 mole/kg. It is observed from the results that the loss of AMP/PZ is near to that in the single AMP system; however, PZ loss rate is greater than that of the single PZ system. This shows the catalytic effect of AMP to degrade PZ. AMP/MEA blends were examined at temperatures up to 100-140 °C with different concentrations of AMP and MEA and O_2 partial pressure of 250-350 kPa. Rate of degradation of the blends increased with the increase in temperature as well as O_2

partial pressure. However, the degradation rate of MEA was found higher than that of AMP in the blend.

CHAPTER 3: EXPERIMENTAL SETUP AND ANALYTICAL METHODS

3.1 Experimental apparatus and methods

3.1.1 Sample preparation and CO_2 loading

Aqueous solutions of amines were prepared gravimetrically in molal concentrations through using double distilled water. The water utilized for producing aqueous solutions was double distilled using a Millipore Direct-Q UV system at a standard of 18 megaohm*cm (at 25 °C) (referred to as DDI). The calculated amounts of amines were poured in a 2-Liter glass flask and then 1 kg water was transferred. With the cap, slightly a jar, the bottle was heated at 50 °C with magnetic stirring until the amines were completely dissolved into a solution. Heating was only used for the solutions involving presence of PZ. For MOR solutions, no heat was required as the reaction between MOR and water was exothermic. Once, required concentration of solution was prepared, it was titrated in order to know the total concentration and alkalinity of the solution based on Hilliard (2008) methods.

Two methods of CO_2 loading have been opted in this thesis for thermal degradation systems. One was the fix loading like 0.10-0.40 mole CO_2/mol alkalinity and other was CO_2 loading until saturation. The CO_2 loading until saturation was only performed for the MOR solutions. For the fix CO_2 loading, the CO_2 was also loaded gravimetrically, the basic methods of Hilliard (2008) were deployed. In the fix, CO_2 loading the pure stream of CO_2 was saturated before bubbling it into the solution using the saturator at the predetermined temperature. CO_2 was bubbled through the solution through a submerged fritted disk in the solution as shown in Figure 3.1. The CO_2 loading apparatus was placed on top of the scale (+0.001 g). CO_2 was bubbled slowly, until the required weight was achieved.

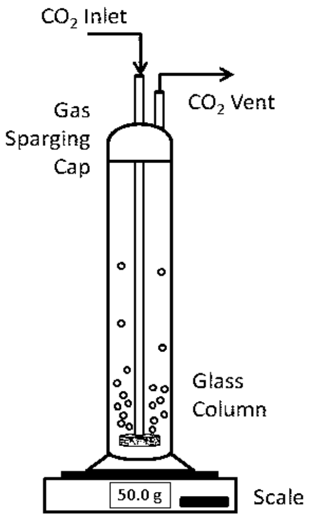


Figure 3.1: Schematic diagram of CO_2 loading apparatus

For CO_2 loading until amine saturation method, setup consisted of a stirred tank reactor, pure CO_2 gas cylinder, stirring plate, magnetic stirrer, Metrohm titrator system, pH probe, and computer. Pure CO_2 stream, line was connected to the saturator placed in the water bath. From saturator, line goes to the reactor. A pH probe was fixed in the reactor to monitor the CO_2 loading with time, which was connected to a Metrohm system. On the PC controlled system, a pH versus time graph was generated. The purpose of setup was designed to determine the equilibrium between CO_2 and amine solution. The pure CO_2 stream was saturated in a saturator placed in water bath and was allowed to enter the reactor from top of the reactor. Gas was bubbled through amine solution until equilibrium was achieved. The inlet gas flow was turned off once pH became consistent with time. Details of setup for CO_2 loading until amine saturation are provided in Figure 3.2.

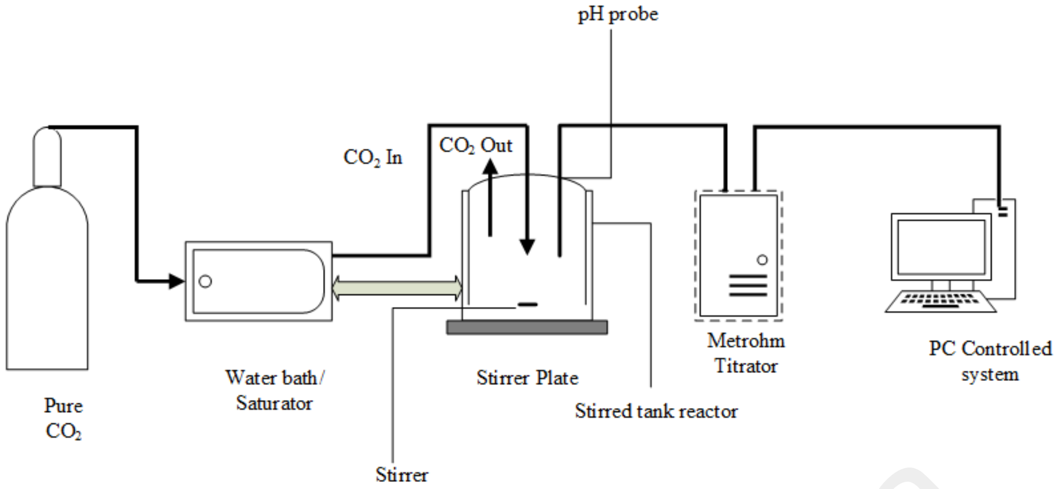


Figure 3.2: Schematic diagram of CO_2 loading setup for amine saturation method

3.1.2 Amine titration

Titration was used for two purposes; to determine the concentration/alkalinity of the solution and amount of CO_2 loading, which is commonly used method (S A Freeman, 2011; M. Hilliard, 2008; T. Wang, 2013). To investigate the amine concentration, a 0.5-1.0 g sample was taken from the prepared solution and was diluted up to 100-200 times with DDI water before titration using a 250 ml beaker. To prepare the auto-titrator, the dosing probe was placed in the probe holder and lowered into an empty waste beaker then manually 60 ml of sulfuric acid (H_2SO_4) solution was withdrawn from the titrant to clean the line. The beaker was then placed on the stirrer plate and a small magnetic stirrer was put into it for proper mixing during titration. After settling the beaker, auto-titrator probe was washed with DDI water, cleaned with tissue paper and then was inserted into the beaker. The probe sensor was fully submerged in solution but kept well above from the magnetic stirrer so that it should not damage the probe. A method, which was formulated before starting the actual sample titration based on some trials, was used. Stop conditions were programmed, in the method and other options like pH, number of end-points (EPs) were left off.

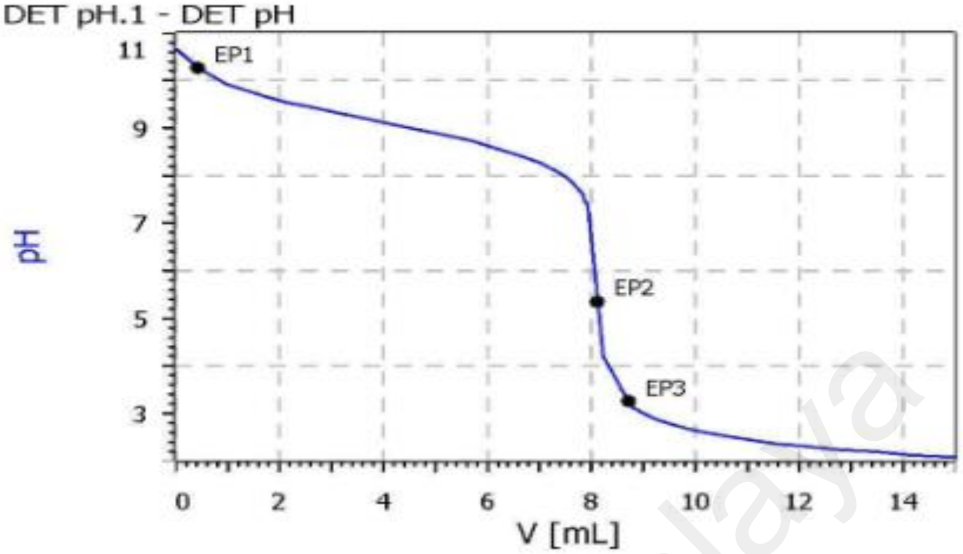


Figure 3.3: Typical titration graph for the determination of total alkalinity of amines

Total alkalinity test was performed by using 0.1 M/0.2 N H_2SO_4. Once titration stopped, the volume at last end-point was used to calculate the total alkalinity. Figure 3.3 is provided as an example, which is showing the titration path of PZ and DEA blend against sulfuric acid with respect to time. As mentioned, endpoint (EP) method is used for the titration. Figure shows three endpoints; every endpoint shows a chemical reaction equilibrium. Where EP2 and EP3 are showing equilibrium of DEA and PZ respectively. Equation (3.1) was used in calculations of total alkalinity.

$$Total\ Alkalinity\left(\frac{mole}{kg - solution}\right) = \frac{V_{H_2SO4}(ml)}{Sample(g)} \tag{3.1}$$

3.1.3 CO_2 loading verification

Once CO_2 was loaded in amine solution, they were titrated for CO_2 loading verification. For each CO_2 loading, two samples of almost 0.5 g were taken, and were mixed with 25 ml of $BaCl_2$ (0.5 M) and 50 ml NaOH (0.1 M) in a 250 ml Erlenmeyer flask. Samples were heated in the oven at 80 °C for 30-40 min, then cooled, and filtered by using 0.45 µm pore size filters with the help of vacuum. $BaCl_2$ and NaOH reacted as under to form the crystals of $BaCO_3$ following equation (3.2).

$$BaCl_2(l) + 2NaOH(l) + CO_2(g) \rightarrow BaCO_3(s) + H_2O(l) + 2NaCl(s) \quad (3.2)$$

Crystals were washed with 50-55 ml deionized water, and then 0.1 M HCl was added until the crystals disappeared. Meanwhile weight of HCl was monitored precisely. Samples were heated once again for 10 min in oven 80 °C to remove the traces of unreacted CO_2. Hot acidified samples were cooled to room temperature then titrated with 0.1 M NaOH. In parallel, a blank sample of 0.1 N NaOH and and 0.1 N HCl was also titrated. End-point method was used for the titration and last end-point volume was used for calculations. All the titration tasks were performed using 785 DMP Titrino autotitrator installed with Tiamo. The titration reaction of $BaCO_3$, and HCl was believe to occur as under (3.3):

$$BaCO_3(s) + 2HCl(l) \rightarrow BaCl_2(l) + CO_2(g) + H_2O(l) \quad (3.3)$$

The following set of equations (3.4 to 3.8); were used for the calculation of CO_2 loading.

$$n_{CO_2} - sample = \frac{V_{HCl(l)} \times V_{NaOH(l)} - V_{NaOH(l)} \times N_{NaOH(l)}}{2} \quad (3.4)$$

$$nCO_2 - blank = \frac{V_{HCL(l)} \times N_{HCL(l)} - V_{NaOH(l)} \times N_{NaOH(l)}}{2} \quad (3.5)$$

$$n_{CO_2} = n_{CO_2-sample} - n_{CO_2-blank} \tag{3.6}$$

$$n_{amine} = C_{amine} \times m_{sample} \tag{3.7}$$

$$\alpha_{CO_2} = \frac{n_{CO_2}}{n_{amine}} \tag{3.8}$$

Where, n_{CO_2} is the number of moles CO_2/kg solution, C_{amine} is the alkalinity of the amine, m_{sample} is mass of the sample, α_{CO_2} is the CO_2 loading/mol alkalinity.

Titration results of CO_2 loading verification were very close to the theoretical values and the CO_2 loading error was found to be within ±5%.

3.1.4 Thermal degradation

3.1.4.1 Apparatus description and experimental procedure

Experiments were conducted using half-inch diameter 316 stainless steel cylinders, enclosed with Swagelok endcaps, method developed by Rochelle group (J. D. Davis, 2009; S A Freeman, 2011). 316 stainless steel tubes were cut into 10 cm segments, and fitted on each end, with Swagelok endcaps. The Swagelok endcaps using ferrules can provide an airtight seal up 200 psi of pressure. Tubes were fitted with endcaps on per factory recommendations. 8 ml sample was filled in each cylinder under in presence of nitrogen gas, to avoid entrance of oxygen. Once samples were filled and cylinders were caped properly, they were then tightened up to 1.25 rotations as per factory guidelines. Each cylinder was weighed, labeled and then placed in the oven.

Figure 3.4: Typical stainless steel cylinder and oven for thermal degradation experiments

A set of two forced convection ovens from Memmert with programmable temperature were used for degradation. The picture of thermal degradation setup involving stainless steel cylinders and oven is depicted in Figure 3.4. Amine solutions were formed with different CO_2 loadings and were put in ovens for a fixed time, and each sample container was taken out from the oven with weekly intervals. Each coded cylinder was cooled on the bench top up to room temperature to quench the effect of temperature over degradation of the solvent. Samples were taken out of cylinders within 1-5 days, depending up on the availability of analytical equipment. One side endcap of the thermal cylinder was loosed in workshop to take sample. Samples were transferred into glass vails, in the lab under the blanket of nitrogen to avoid any oxygen content during shifting samples. Thermal cylinders, which lost weight more than 10%, were neglected and not used for the analysis. However, a few cases were found in which solution evaporated, mainly at high temperatures like 150 to 190 °C. These were the cylinders, which were reused and no new cylinder were found to fail at any temperature.

3.1.4.2 Limitations of the experimental setup

There were some limitations in the setup, which negligibly might affect the experimentation results. The first is that it was not possible to hold the gaseous degradation products while opening the thermal cylinders, compounds like ammonia, ethylene oxide etc. Therefore, focus has only been given to the liquid phase degradation products and mother solution. The second limitation was to know the effect of stainless steel composition on thermal degradation of both systems. The 316 stainless steel cylinders were not lined with glass. Third limitation was that by using this setup vigorous agitation was not possible. However, content of the solution may play the role of an agitator to some extent.

3.1.4.3 Sample Analyses

Due to limitations of the experimental setup, the focus was to analyze the liquid phase samples. Samples were analyzed for the identification of degradation products and concentration of parent amines. Gas chromatography was used for the identification of degradation products and quantification of parent amine concentration.

3.1.5 Oxidative degradation

3.1.5.1 Apparatus depiction and experimental procedure

The oxidative degradation experiments were conducted in 1.0 Liter jacketed glass (borosilicate 3.3 @ Pyrex) reactor, a low gas flow reactor. Reactor was equipped with 316 stainless steel top plate, stainless steel impeller, top plate lip seal (top and bottom), stainless steel shaft bearing with stirrer shaft, stainless steel glass vessel holder. The reactor was designed with bottom sample outlet PTFE valve. A digital temperature thermometer was fitted to the reactor control panel through the device. Overhead stirrer motor was capable of agitation speeds of up to 1400 rpm with overheat protection. Digital display and digital PID control of rpm is built in the central position of top plate. A stainless steel condenser (comes with built in coil) with inlet, outlet and exhaust point, which was connected to a water chiller to avoid the solution vaporization at high temperature. A stainless steel ring Spurger comes with top headlock, top plate Vinton circular ring, top head stainless steel plug circular ring were equipped with the reactor for proper distribution of reaction gases during degradation reaction. The heat supplied to the reactor was controlled by a temperature indicator controller system equipped with a J-type thermocouple. Temperature was measured by a J-type thermocouple and controlled by RSC LAUDA R22 type water bath. The feed gases were forced through the reactor from top by using a set of Brooks gas mass flow meters' model 5850C for reaction gases and controlled by a 4 channel Brooks mass flow controller model 0154E. Figure 3.5 is showing the oxidative degradation experimental rig.

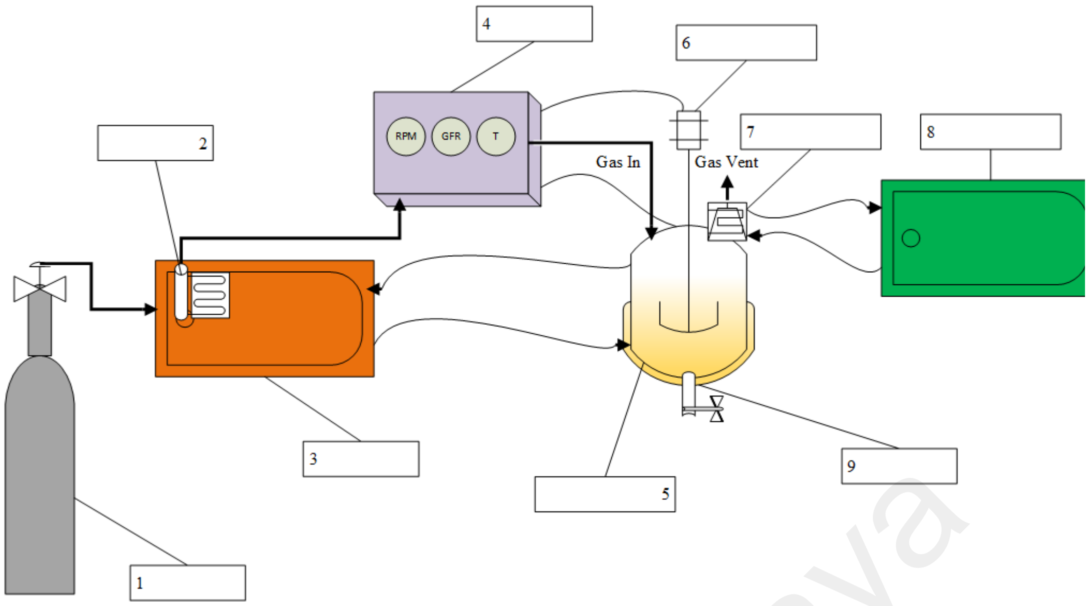


Figure 3.5: Oxidative degradation experimental setup. Following are the main components of setup: 1- Gas cylinder, 2- Saturator, 3- Water Bath/Heating Bath, 4- Control Box, 5- Low Pressure Jacketed Glass Reactor, 6- Impeller Motor, 7- Condenser, 8- Chiller, 9- Sampling Port

Initially reactor was started on cold run for two days to check the stability of parameters. Once, it was found that most of the parameters are stable then actual solution was inserted. The volume of the reactor is 1.0 liter; we used 750 ml in each experiment so that 1/4th of the reactor volume should be vacant for condensation of the vapors. Before purging designed gas into the reactor all control modules were turned on and conditions were achieved. Reaction gas was saturated using the gas saturated before introducing it into the reactor; and the saturator temperature was same as that of reaction temperature. Normally, after every 12-hour water was refilled in water bath to make-up for evaporation. Two heating/cooling baths were used in the setup. Heating bath was programmed few degrees above the required temperature in order to achieve the required temperature in the reactor. Cooling bath temperature was kept constant (4 °C) throughout the span of experimental phase. The picture of oxidative degradation experimental rig is given in Figure 3.6.

Figure 3.6: Lab rig for oxidative degradation experiments

3.1.5.2 Sample handling analyses

Reactor was monitored continually during the span of experimental phase; all the parameters like temperature, gas flow rate, agitator speed, refilling saturator and leakages were in focus. Initially, samples were taken in short time intervals like 3-4 hours. Later, samples were taken after 8-12 hours. Every time sample amount was 5 ml or less so that a mass balances should be maintained for the experimental duration. No parameter was changed during the sampling as the sampling valve was from bottom of the reactor. The samples taken were cooled at room temperature for 10 min and later were stored in the refrigerator. Solution level was always marked and at the end of experiment, a small change was observed mainly because of taking samples. We observed that the maximum solution volume change is 70-80 ml after taking 12-15 samples after 4-6 days.

3.2 Analytical apparatus and methods

In both thermal and oxidative degradation, the liquid phase samples were of interest for analyses. Analyses were conducted for identification of degradation products and quantification of parent amines concentration. In the current study, two different analytical systems are used for the analyses. Gas Chromatography Mass Spectrometry (GC-MS) is used for identification of degradation products, while, GC-FID is used for the quantification of parent amine concentration. In this investigation, only liquid phase samples were analyzed, due to the limitations of the offline system gas phase samples were not possible to be analyzed as no online system was used.

3.2.1 Gas chromatography mass spectrometry (GC-MS)

Gas chromatography (GC) coupled with Mass Spectrometer (MS) using Shimadzu GC-MS-QP2010, with ultra-auto sampler AOC 20I+S in which RTX-5MS with the dimensions of 30 m, 0.25 mm ID, 0.25 µm was used for detection of the compounds. Method developed by Helene Lepaumier et al., (2009a) was followed for the detection of the degradation products. Samples were diluted with absolute ethyl alcohol for analyses, purchased from Merck Millipore. Dilution ranged from 50-100 times depending on the concentration of the amine to avoid column overload and to improve separation of the components. An auto injector was used to automatically introduce samples into the GC column to give better reproducibility. Computer fitting of the mass spectrum to the mass spectra database was part of the strategy used to identify the degradation products of samples. This was followed by the database of GC-MS library in order to confirm the identification of the components in the samples. The products were identified by matching their mass spectra with commercial mass spectra of the National Institute of Standards and Technology (NIST) database. Details of GC-MS method used in this thesis are provided in Table 3.1.

Table 3.1: Dimensions of column and operating conditions of GC-MS used for identification of degradation products

SNo.	Parameter	Value
	Length, Internal Diameter, Thickness	30 m, 0.25 mm, 0.25 um
1	Initial Temperature	35 °C
2	Initial hold up time	5 min
3	Oven Ramp (1)	3 °C/min
4	Oven Ramp (2)	8 °C/min
5	Final Temperature	230 °C
5	Final Hold up time	30 min
6	Flow rate	0.9 ml/min
7	Injector Temperature	280 °C

3.2.2 Gas chromatography-flame ionization detector (GC-FID)

Gas chromatography (GC) coupled with Flame Ionization Detector (FID) was used with Agilent 7890A with an auto-sampler G4513A using a nonpolar column, CP-Sil 8 CB, with dimensions of 15 m, 530 μm, and 1 μm Length, internal diameter, and thickness respectively for the quantification of the parent amine as concentration. Samples were diluted with absolute ethyl alcohol for analysis, purchased from Merck Millipore. Dilution ranged from 100-150 times depending upon the concentration of the amine. Initially, two samples were made from each sample/cylinder and were analyzed. Once consistency was found in the result after more than 50 samples, then a single sample was analyzed for each cylinder/sample, a method developed based on trial and error was used in this thesis is tabulated as in Table 3.2.

Table 3.2: GC-FID method for quantification of the parent amine and degradation products concentration.

Parameter	Value
Initial temperature	50 °C
Oven ramp 1	4 °C/min
Intermediate temperature	86 °C
Oven ramp 2	10 °C/min
Final temperature	246 °C
Flow rate	1.6 ml/min
Injector temperature	150 °C
Detector temperature	250 °C
Final holdup time (min)	10 min

CHAPTER 4: RESULTS AND DISCUSSIONS

4.1 Introduction

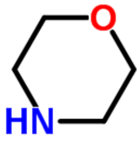
Most of the results achieved from objectives are displayed, depicted and debated in this chapter. Furthermore, with each sub chapter materials and methods is given. It was tried not to have any repetition with chapter 3. Materials and method was put in this chapter to avoid any misunderstanding.

4.2 Thermal degradation of morpholine

4.2.1 Background

Amine-based absorption and stripping process is a reasonable methodology for removing CO_2 from coal-fired power plant flue gas (Kenarsari et al., 2013; MacDowell et al., 2010b; Rao & Rubin, 2002). For this process, solvent choice is considered as an essential need as it accepts a noteworthy part in the execution of CO_2 capture and additionally financial aspects (G. Rochelle et al., 2011; Gary T Rochelle, 2009). However, the practicality of a solvent relies upon a few parameters, in particular; CO_2 capture limit, CO_2 solubility, CO_2 absorption rate, degradation resistance and ecological effect. Thermal degradation confrontation of solvent is very important as the stripper temperatures go above 120 °C, which causes a rise in steam requirement and eventually lowers CO_2 capture capacity (J. Davis & Rochelle, 2009; J. D. Davis, 2009). It is known for the ring structure amines to have better CO_2 absorption rate than other amines because of higher carbamate formation (Bishnoi & Rochelle, 2000). Morpholine has good tendency to react with CO_2, resulting a higher rate of CO_2 absorption than MEA (Liu et al., 2013; Matin et al., 2013). It is shown in literature that 3 M MOR has better CO_2 solubility at temperatures like 40 and 60 °C than 2 or 4.5 M (Khosravi, Feyzi, Dehghani, & Kaviani, 2015). In our previous work (Shaukat A. Mazari, Brahim Si Ali, Badrul M. Jan, & Idris Mohamed

Saeed, 2014; Mazari, Ali, Jan, Saeed, & Nizamuddin, 2015), we reported that MOR is screened out as one of the thermally stable solvents. Morpholine is a ring structure secondary amine as shown in scheme 1.



Scheme 1: Structure of morpholine

This sub-chapter focuses on thermal degradation of MOR under different CO_2 loadings and temperatures. Solvent concentration was chosen based on the 30% benchmark MEA concentration. Hence, we have taken 3.48 M (5 m) as study concentration so that a balance should be maintained between MEA benchmark and MOR solubility results. CO_2 loading was varied from lean to rich. Thermal degradation products of MOR are identified; thermal degradation of MOR is quantified and predicted using a kinetic empirical model. In addition, results of MOR loss were compared against loss of other amines.

4.2.2 Materials and experimental matrix

Detailed methodology is provided in section 3. MOR (99%) for synthesis was purchased from Merck. A five molal (5 m) solution of MOR was prepared in a 2-liter volumetric flask. Required amount of MOR was poured into the flask; later 1 kg of water was added. Solution was titrated with (0.2 N) H_2SO_4 for the verification of amine concentration and test was repeated thrice for confirmation. After confirmation of the concentration/alkalinity, solution was loaded with different concentrations of CO_2. Each batch of CO_2 loaded and unloaded solution was then degraded at 135 °C to 190 °C for twelve weeks. A detailed experimental design is given Table 4.1.

Table 4.1: Experimental design for thermal degradation of MOR.

Run No.	**Amine Concentration (m)**	**CO_2 loading (mole CO_2/mole alkalinity)**	**Temperature (°C)**
1	5	0.00	135
2	5	0.10	135
3	5	0.20	135
4	5	0.30	135
5	5	0.48	135
6	5	0.00	150
7	5	0.10	150
8	5	0.20	150
9	5	0.30	150
10	5	0.48	150
11	5	0.00	175
12	5	0.20	175
13	5	0.30	175
14	5	0.48	175
15	5	0.00	190
16	5	0.20	190
17	5	0.30	190
18	5	0.48	190

Selection of experimental matrix is based on the literature survey. As earlier mentioned that five molal concentration (3.48 M) is based on MEA benchmark concentration (30 wt.%). Temperature and CO_2 concentration are two parameters, which keep changing throughout the process. As from absorber to heat exchanger, stripper and reboiler, their values are different. The values have been chosen from their minimum to maximum possible. The CO_2 loading generally goes from lean to rich, where we opted that method and CO_2 loading varied from 0.0 to 0.40 mol CO_2/mol alkalinity. The selection of thermal degradation temperature is based on the maximum estimated temperature. The reported MEST for morpholine is 170 °C (Freeman 2011), hence we selected minimum stripper to highest stripper temperature like from 135 to 190 °C.

4.2.3 Thermal degradation products of morpholine

Degradation products were identified by using GC-MS. Virgin as well as degraded samples were analyzed for degradation compounds. No products were found in virgin solutions. Whereas, degraded samples were cooled and poured into 20 ml glass bottles after removing them from oven. Samples were diluted in ethanol (Absolute ethyl alcohol for analysis). Spectra found from the MS for each peak was matched with the NIST database. Figure 4.1 and Figure 4.2 are two examples of chromatograms for the identification of degradation products of MOR with CO_2 loading of 0.4 mol CO_2/mol alkalinity at 175 and 190 °C respectively. Those compounds were selected degradation products, which had the highest similarity index as indicated in figures below. Table 4.2 shows list of degradation products from MOR at 135-190 °C.

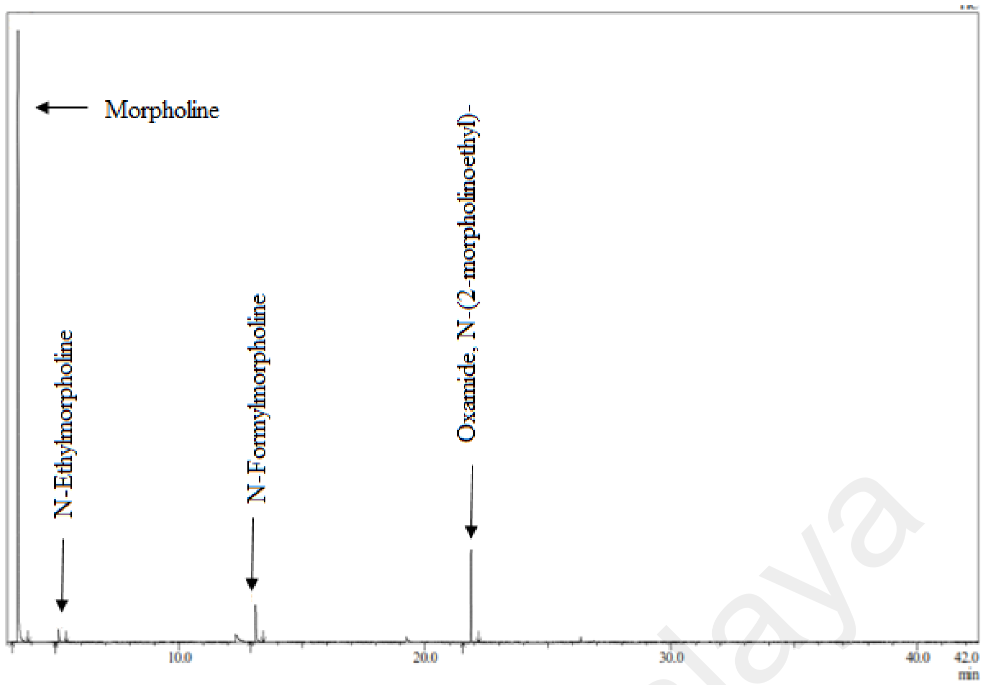


Figure 4.1: Chromatogram for thermal degradation of MOR at 175 **°C**

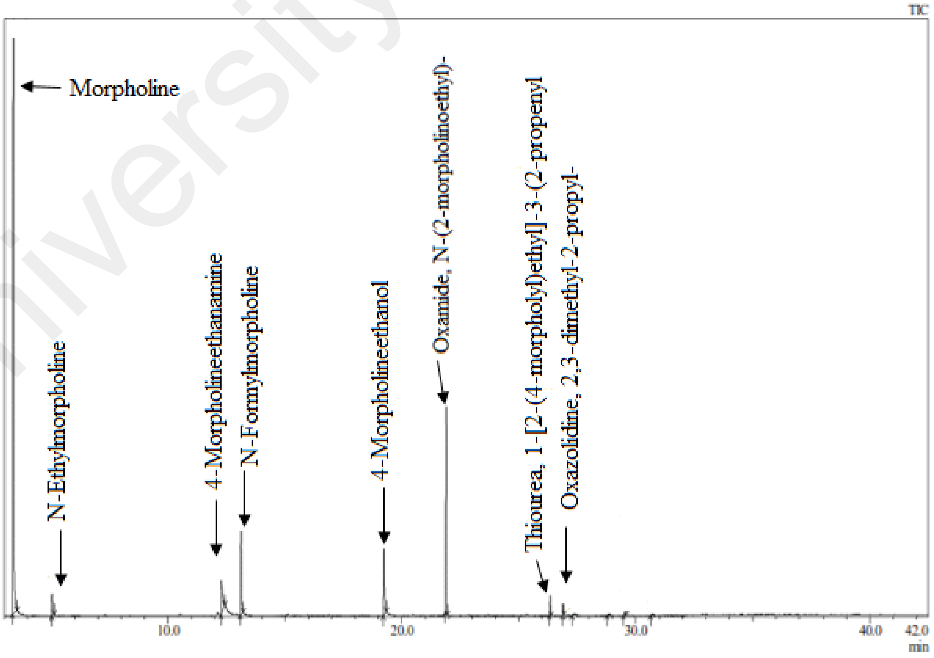


Figure 4.2: Chromatogram for thermal degradation of MOR at 190 **°C**

Table 4.2: Thermal degradation products of 5 m MOR with CO_2 loading of 0.0-0.48 mol CO_2/mol alkalinity at 135-190 °C

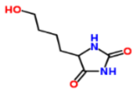
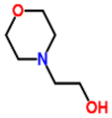
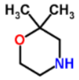
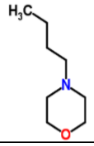
SNo.	Compound	Abbr.	Similarity Index	CAS Number	Structure
1	Oxamide	OA	95	471-46-5	
2	5-(4-Hydroxybutyl)-2,4-imidazolidinedione	HOBID	97	25860-42-8	
3	2-Morpholinoethanol	ME	92	622-40-2	
4	2,2-Dimethylmorpholine	DMM	90	147688-58-2	
5	4-Butylmorpholine	BM	81	1005-67-0	

Table 4.2 (Continued): Thermal degradation products of 5 m MOR with CO_2 loading of 0.0-0.48 mol CO_2/mol alkalinity at 135-190 °C

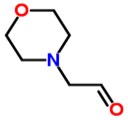
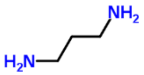
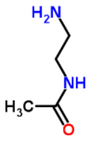
SNo.	Compound	Abbr.	Similarity Index	CAS Number	Structure
6	4-Morpholinylacetaldehyde	MAA	89	21977-09-3	
7	1,3 Propanediamine	PDA	80	109-76-2	
8	N-Formylmorpholine	FM	96	4394-85-8	
9	N-(2-Aminoethyl)acetamide	AEA	86	1001-53-2	

Table 4.2 (Continued): Thermal degradation products of 5 m MOR with CO_2 loading of 0.0-0.48 mol CO_2/mol alkalinity at 135-190 °C

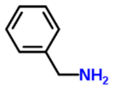
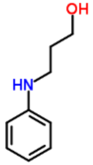
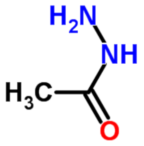
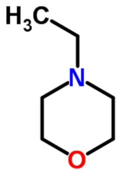
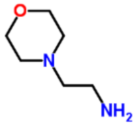
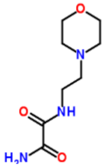
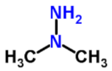
SNo.	Compound	Abbr.	Similarity Index	CAS-number	Structures
10	Benzenemethanamine	BEA	88	59-96-1	
11	Phenylpropanolamine	PPA	96	14838-15-4	
12	Acetohydrazide	AHZ	86	43183-98-8	
13	N-Ethylmorpholine	NEM	98	100-74-3	

Table 4.2 (Continued): Thermal degradation products of 5 m MOR with CO_2 loading of 0.0-0.48 mol CO_2/mol alkalinity at 135-190 °C

No.	**Compound**	**Abbr.**	**Similarity Index**	**CAS Number**	**Structures**
14	4-(2-Aminoethyl)morpholine	AEM	94	2038-03-1	
15	N-[2-(4-morpholinyl)ethyl]ethanediamide	MEDA	86	5625-80-9	
16	N,N-Dimethylhydrazine	DMH	92	57-14-7	

4.2.4 Morpholine loss

Quantification of MOR loss was conducted by using GC-FID. Effect of CO_2 concentration and temperature were examined on thermal degradation of MOR. At 135 °C, amine loss was small as followed until 10 weeks. Although, the loss of MOR was less, yet it increased by increasing the concentration of CO_2. CO_2 loading was in direct relation with the loss of MOR concentration. However, at 0.48 mol CO_2/mol alkalinity a small decline was noted in the loss of MOR. Further, temperature speeded up loss of MOR significantly. Figures 4.3 through 4.7 show the loss MOR with time under different temperatures and CO_2 loadings.

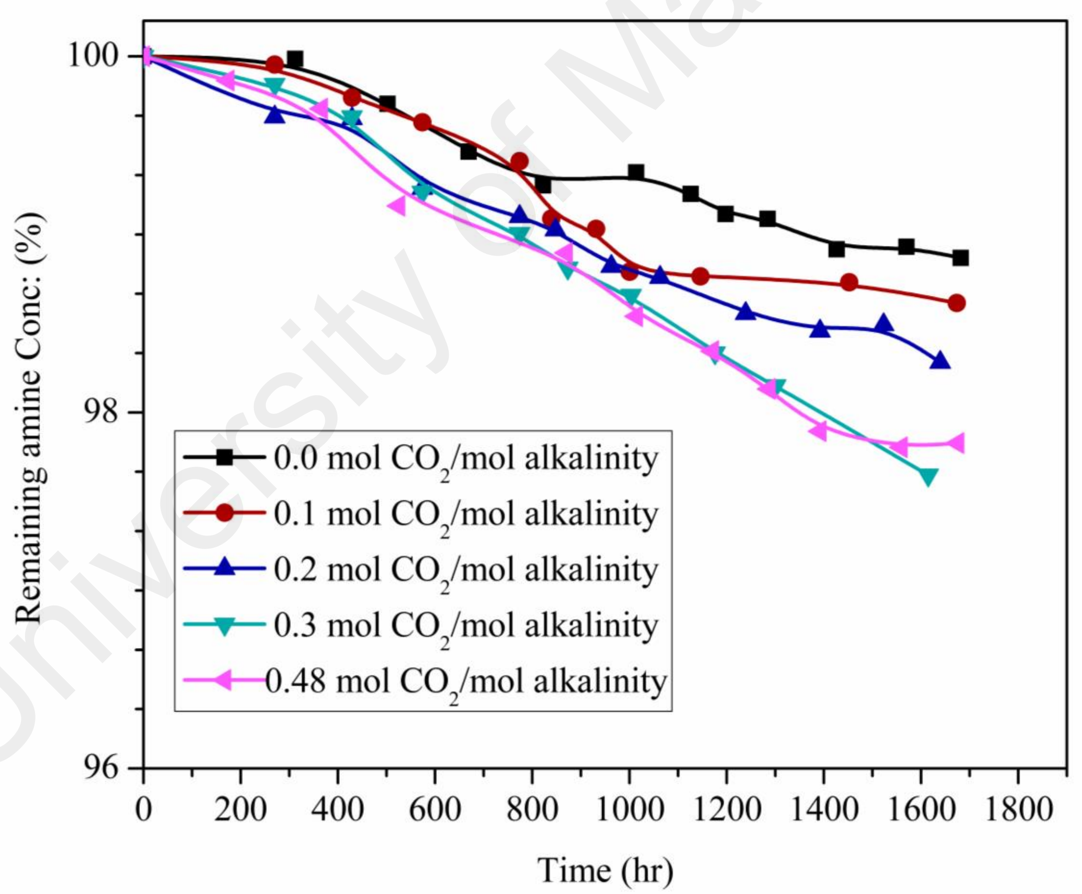


Figure 4.3: MOR loss under different CO_2 loadings at 135 °C

Figure 4.3 shows loss of MOR with respect to time with the CO_2 loading of 0.0-0.48 mol CO_2/mol alkalinity at 135 °C. For unloaded solution, degradation was almost none, however, 1.1% loss in concentration was observed for the span of 10 weeks. Furthermore, degradation increased as the CO_2 loading increased. Highest degradation was observed at 0.48 mol CO_2/mol alkalinity, which is 2.1%.

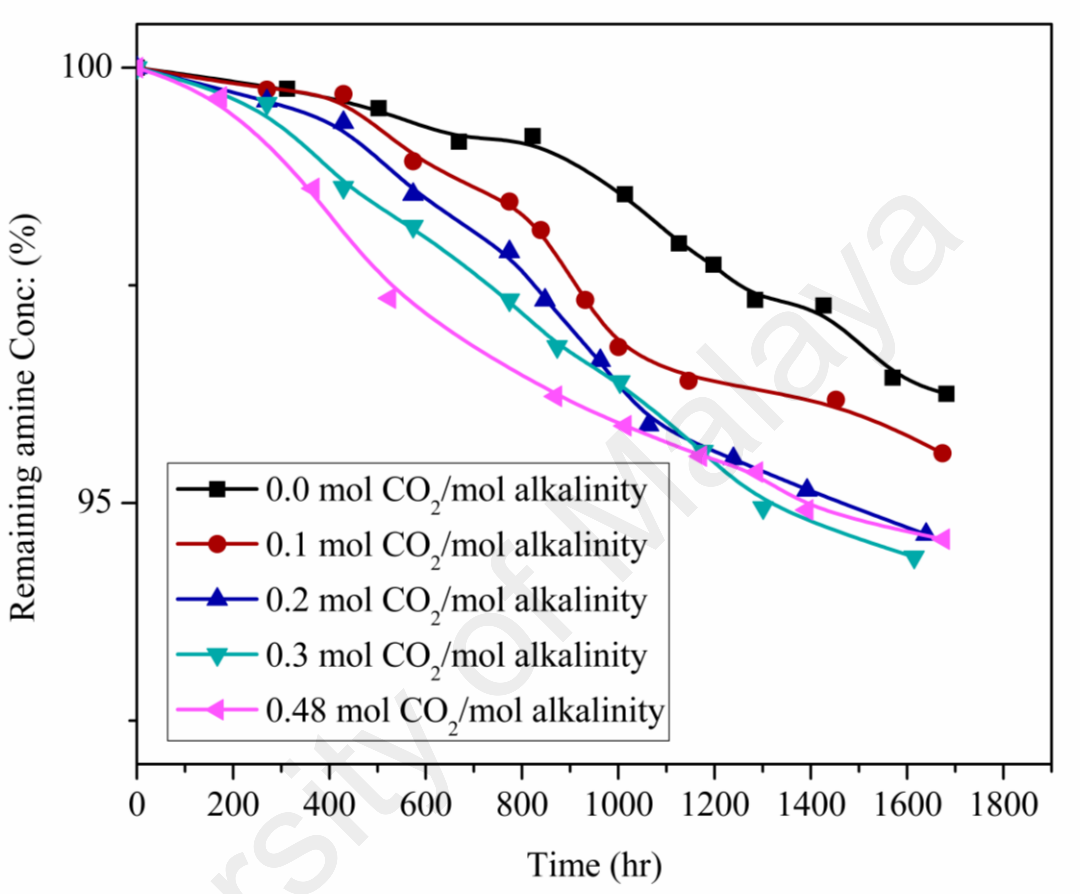


Figure 4.4: MOR loss under different CO_2 loadings at 150 °C

Figure 4.4 is pointing out the loss of MOR at 150 °C with CO_2 loading of 0.0 to 0.48 mol CO_2/mol alkalinity. With increase in temperature from 135 to 150 °C, loss of MOR increased almost up to three folds for the same span of experiment. As at 135 °C, the loss was 2.18%, which increased up to 6.42% at 0.48 mol CO_2/mol alkalinity. In addition, a similar trend has been viewed at all the CO_2 loadings.

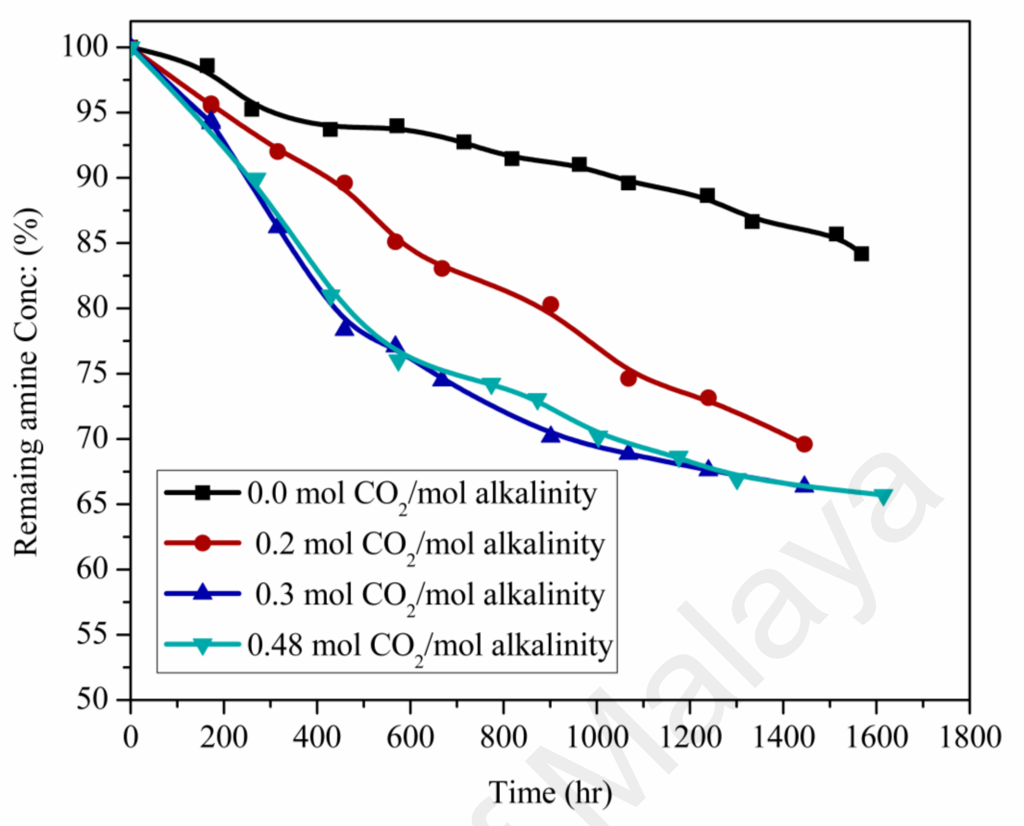


Figure 4.5: MOR loss under different CO_2 loadings at 175 °C

A tremendous increment in loss of MOR was observed at 175 °C in comparison with the loss at 135 and 150 °C as depicted in Figure 4.5. Even for unloaded solution, the MOR loss was 15.8% in 9 weeks. Furthermore, loss of MOR increased as the CO_2 loading increased. The maximum loss was observed at 0.48 mol CO_2/mol alkalinity. However, this is contradictory to the loss of MOR at other temperatures. Loss of MOR until 6 weeks was less than that at 0.3 mol CO_2/mol alkalinity but increased after 6th week of reaction.

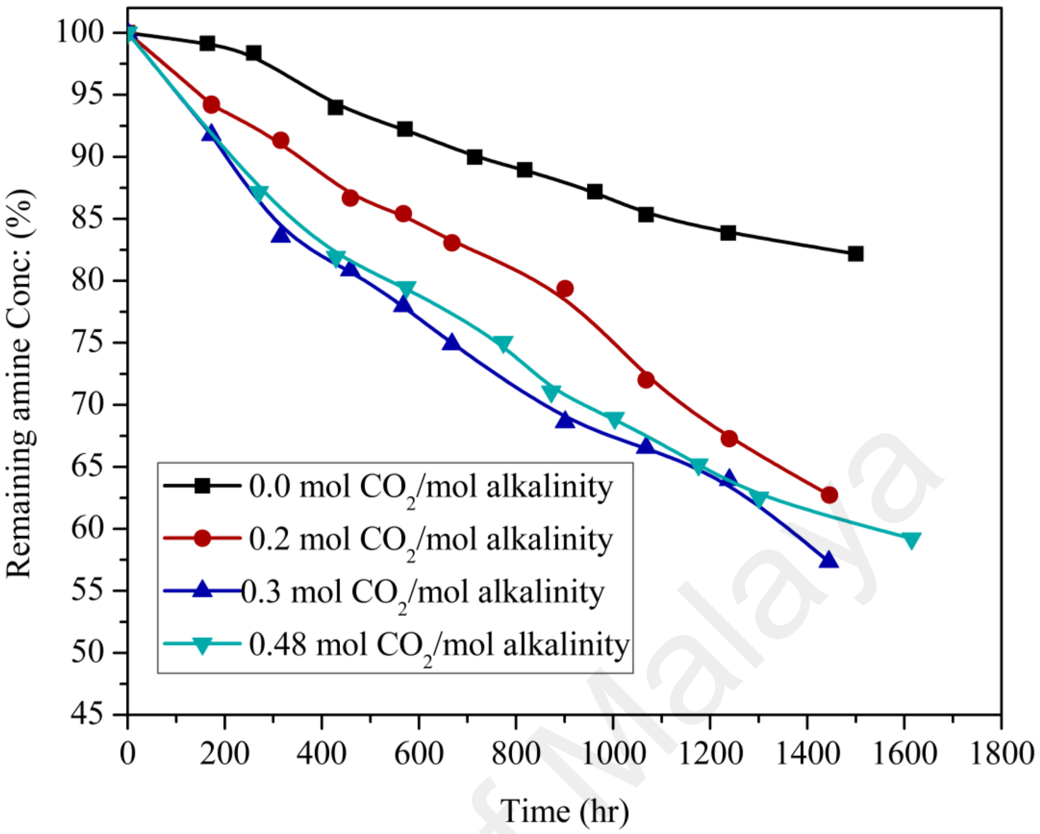


Figure 4.6: MOR loss under different CO_2 loadings at 190 °C

The maximum loss of MOR was observed at 190 °C. A 42% loss in initial concentration of MOR has been observed for almost 10 weeks at CO_2 loading of 0.30 mol CO_2/mol alkalinity.

4.2.5 First order rate determination of degradation of MOR

Thermal degradation of MOR is conducted under different temperatures and different CO_2 loadings. Raw concentration-time data was fitted against different rate laws like zero, first and second order rate law. An example of such comparison is given in in Figures 4.7-4.9. These Figures are showing the data of loss of MOR at 175 °C with a CO_2 loading of 0.48 mol CO_2/mol alkalinity. Where concentration data is in mmol/kg and time is seconds.

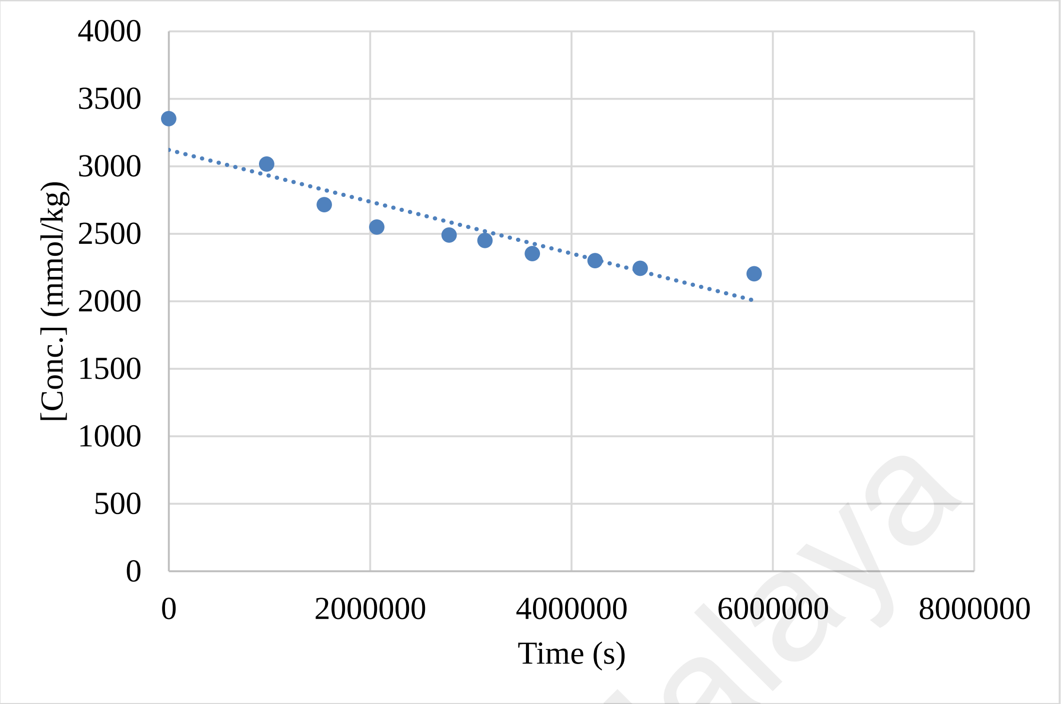


Figure 4.7: Zeroth order rate law determination for MOR with CO_2 loading of 0.48 mol CO_2/mol alkalinity at 175 °C

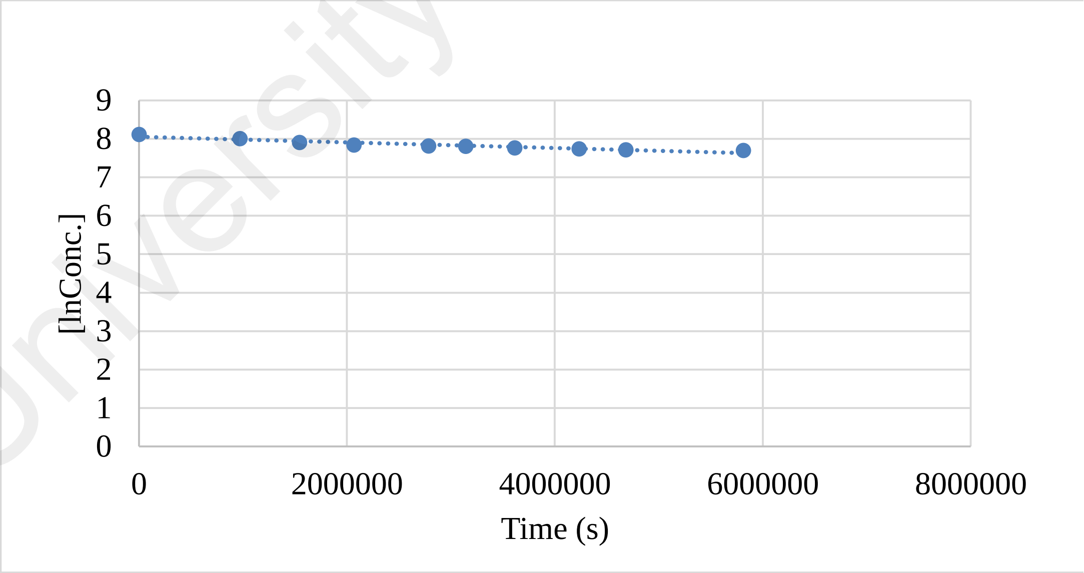


Figure 4.8: First order rate law determination for MOR with CO_2 loading of 0.48 mol CO_2/mol alkalinity at 175 °C

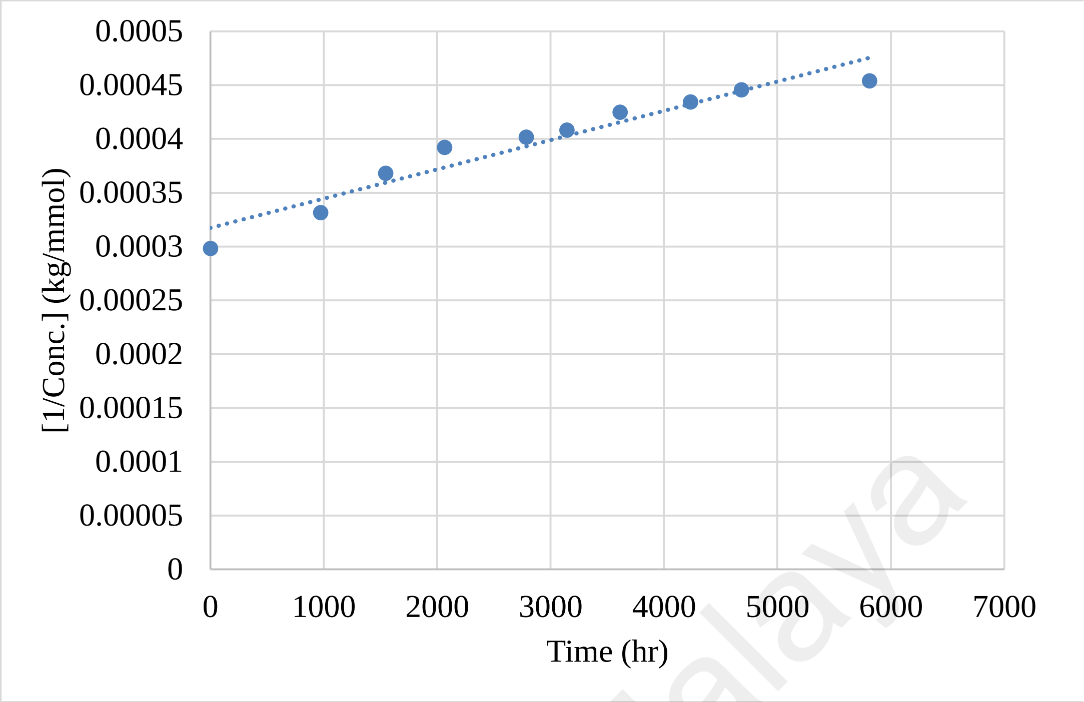


Figure 4.9: Second order rate law determination for MOR with CO_2 loading of 0.48 mol CO_2/mol alkalinity at 175 °C

First order rate law fitted the degradation data most appropriately depicted in Figure 4.8. Hence, the following equation was derived for the loss of MOR to find out the apparent rate constants.

$$-\frac{dC_{MOR}}{dt} = k_{1CMOR} \tag{4.1}$$

Integrating equation (4.1) gives:

$$C_{MOR} = C_{MOR,0} . e^{-k_1 t} \tag{4.2}$$

Taking natural log (ln) from both sides of equation gives,

$$\ln C_{MOR} = \ln C_{MOR,0} - k_1 t \tag{4.3}$$

Where, C_{MOR} is the concentration of MOR at time t, $C_{MOR,0}$ is the initial concentration of MOR, k_1 is the first order rate constant and t is the time in seconds.

Equation (4.3) is a linearized form of first order integrated rate law. The values of $\ln C_{MOR}$ were plotted against t, to determine the k_1 values of each reaction. A typical plot for the determination of first order rate constant k_1 is shown in Figure 4.10.

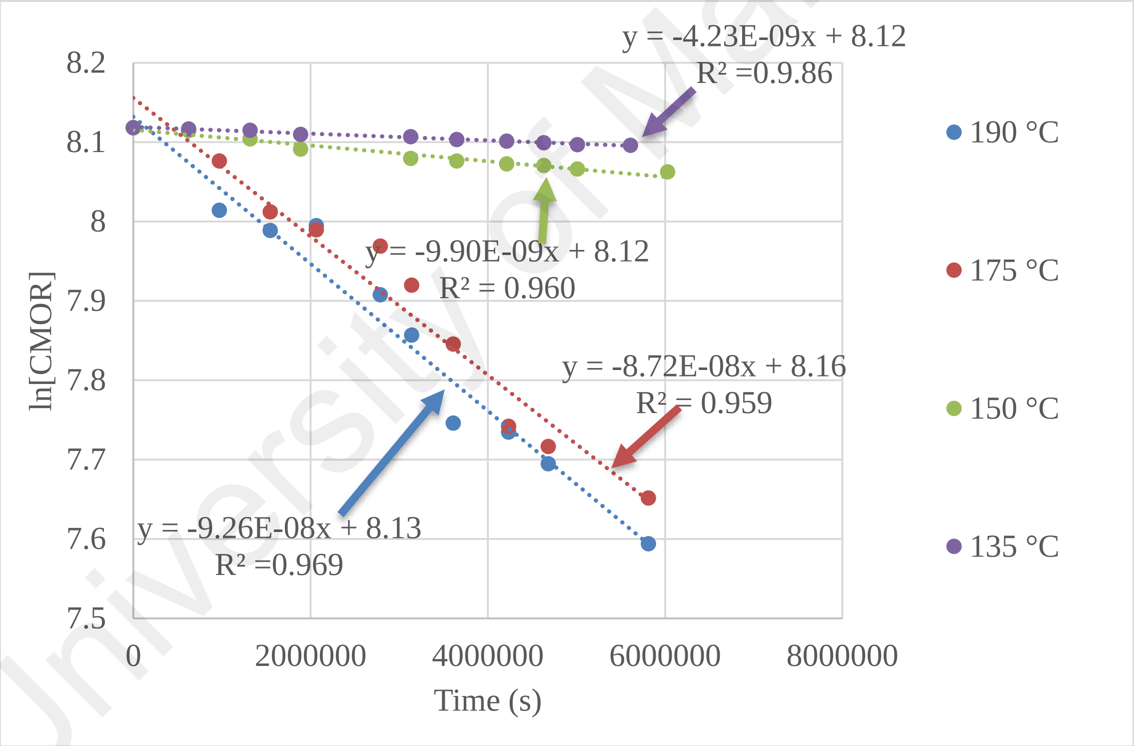


Figure 4.10: A typical fit for determination of first order rate constants (k_1) of degradation of MOR at the CO_2 loading of 0.48 mol CO_2/mol alkalinity at 175 and 190 °C

Figure 4.10 indicates that data is well fitted using the first order rate law under different conditions. In most of the cases regression coefficient (R^2) is higher than 0.90. A detailed list of k_1 values with their corresponding R^2 values is tabulated in Table 4.3.

Table 4.3: First order rate constants (k_1) for thermal degradation of MOR at 0.0 to 0.48 mol CO_2/mol alkalinity from 135-190 °C

Temperature (°C)	**CO_2 loading (mol CO_2/mol alkalinity)**	**k_1, (10^{-8}) (s^{-1})**	**R^2**
135	0.00	0.21	0.950
	0.10	0.28	0.900
	0.20	0.30	0.970
	0.30	0.43	0.987
	0.48	0.41	0.981
150	0.00	0. 68	0.932
	0.10	0. 87	0.961
	0.20	1.08	0.965
	0.30	1.10	0.986
	0.48	0.99	0.960
175	0.00	2.75	0.971
	0.20	7.05	0.993
	0.30	8.23	0.908
	0.48	7.17	0.901
190	0.00	4.02	0.982
	0.20	8.67	0.984
	0.30	10.0	0.985
	0.48	8.95	0.982

4.2.6 Temperature dependence and Arrhenius equation

Temperature plays a critical role in the rate of chemical reactions. Arrhenius relation is used in this study to investigate the effect of temperature on the reaction rate constants equation (4.4) was at first linearized into equation (4.5), and then lnk was plotted against inverse of temperature (1000/T) to know the effect of temperature on the rate constants of the MOR loss.

$$k = Ae^{(-\frac{Ea}{RT})} \tag{4.4}$$

Taking natural log of equation (4.4), it becomes:

$$\ln k = \ln A - \frac{Ea}{RT} \tag{4.5}$$

Where *k* is the rate constant (s^{-1}), A is the pre-exponential factor (s^{-1}), *Ea* is the activation energy (J/mol), *R* is universal gas constant (J/mol-K) and *T* is the operating temperature (K).

Figure 4.11 shows the temperature dependence of rate constants obtained from the degradation of MOR at CO_2 loadings of 0.2-0.48 mol/mol alkalinity at 135-190 °C.

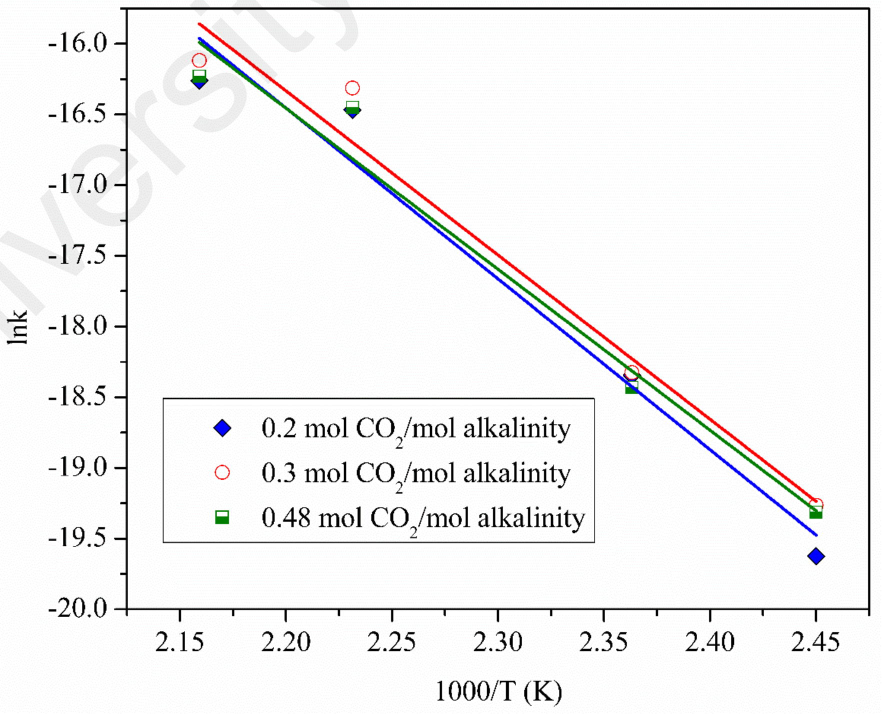


Figure 4.11: Temperature dependence of rate constants of degradation of MOR at CO_2 loading of 0.0-48 mol CO_2/mol alkalinity at temperatures ranging from 135 to 190 °C

Arrhenius equation suggests the rate constant rises with temperature. Initially, value increases exponentially, later it levels off once it approaches a limit. Arrhenius equation has well fitted at all temperatures for most of the CO_2 loadings. Figure 4.11 shows that loss of MOR is minimal until 150 °C. However, it sharply increases from 175 to 190 °C.

4.2.7 Overall rate constants for thermal degradation of MOR

Rate constants are supposed to be independent of concentration and time. In this study at each temperature, thermal degradation of MOR was investigated under different CO_2 loadings. Using Arrhenius equation (4.5) at each temperature for all CO_2 loadings, say 0.2 to 0.48 mol CO_2/mol alkalinity an overall rate constant was developed. The determined overall rate constants are plotted against the experimental rate constants for each CO_2 loading and temperature as shown Figure 4.12.

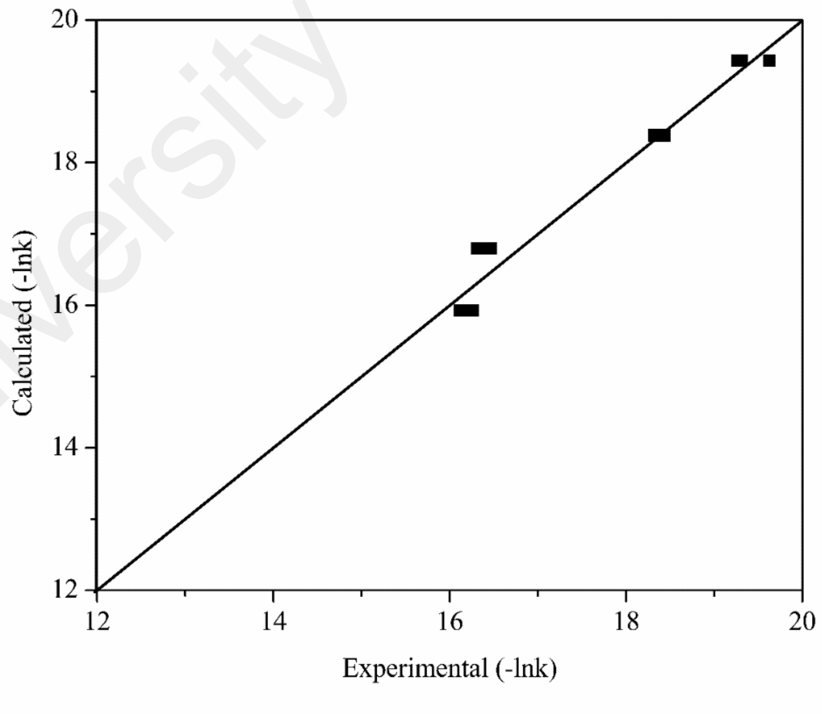


Figure 4.12: Plot of calculated -lnk values against experimental -lnk values for each temperature at CO_2 loading of 0.2, 0.3 and 0.48 mol CO_2/mol alkalinity

4.2.8 MOR thermal degradation kinetic model

4.2.8.1 Model development

Thermal degradation of aqueous MOR in the presence of CO_2 under stripper temperature and above like 135-190 °C is an example of gas-liquid contact reaction as the boiling point of MOR is 129 °C. Experimental data extracted is based on 10 weeks duration for the thermal degradation reaction. An empirical rate law, using power law model is postulated as shown in equation (4.6).

$$-r_{MOR} - k[C_{MOR}]^a[C_{CO_2}]^b \tag{4.6}$$

Where $-r_{MOR}$ is the rate of loss of MOR (mmol/kg.s), C_{MOR} is the concentration of MOR (in mmol/kg), C_{CO_2} is the initial concentration (in mmol CO_2/mol alkalinity) and k is the reaction rate constant (s^{-1}), a and b are the reaction orders with respect MOR and CO_2 respectively.

As thermal degradation is conducted under different temperatures, therefore effect of temperature is accounted for in this empirical model using Arrhenius equation (4.7).

$$k = Ae^{(-\frac{Ea}{RT})} \tag{4.7}$$

Where, *A* is the pre-exponential factor (units depends on the units of k), *Ea* is the activation energy (in J/mol), *R* is universal gas constant (8.314 J/K mol) and *T* is temperature (in K).

Adding equation (4.7) to 4.6 and linearizing it gives equation (4.8).

$$\ln(-r_{MOR}) = \ln A - \frac{Ea}{RT} + a[C_{MOR}] + b[C_{CO_2}] \tag{4.8}$$

As mentioned earlier, five batches of experiments ranging in CO_2 concentration like 0.0, 0.10, 0.20, 0.30 and 0.48 mol CO_2/mol alkalinity were run. For linearized rate law, none of the species concentration should be zero, so data gained from degradation batch with no CO_2 loading was not added in the model. Data with 0.1 mol CO_2/mol alkalinity was also eliminated, as at this CO_2 loading, experiments were not conducted at 175 and 190 °C. Data obtained with CO_2 loadings of 0.20, 0.30 and 0.48 mol CO_2/mol alkalinity were used to build up the model.

4.2.8.2 Parameter optimization

Parameters involving equation (4.8) were A, a, b and Ea. Using the multiple linear least-squares regression, the experimental data obtained was regressed with a confidence interval of 95%. Parameters were obtained as coefficients for each operating parameter. Overall data set well fitted the model, as the regression coefficient (R^2) was found as 0.964 and the values of F and significance F are 35.49 and 0.0005 respectively. The value of a maybe confusing as it is positive, where loss of concentration on increase in rate should have given a negative order. The model obtained the positive value because there is some variation in the rate of MOR loss due the variation in CO_2. One of examples is the lower thermal loss of MOR at 0.48 mol CO_2/mol alkalinity. Estimated parameters are enlisted in Table 4.4.

Table 4.4: Parameters of kinetic model

Parameter	Value
lnA	9.31±0.76
a	1.821±0.002
b	0.275±0.001
Ea (Joules/mole)	97215.60±2884.95

Furthermore, to diagnose the validity of the model, Absolute Average Deviation (AAD) between experimental and predicted values is determined, which is 3.70 %. Values of predicted $-\ln(-r_{MOR})$ to those of obtained through experiments are compared in Figure 4.13. Graph shows that predicted values are in good agreement with the experimental results.

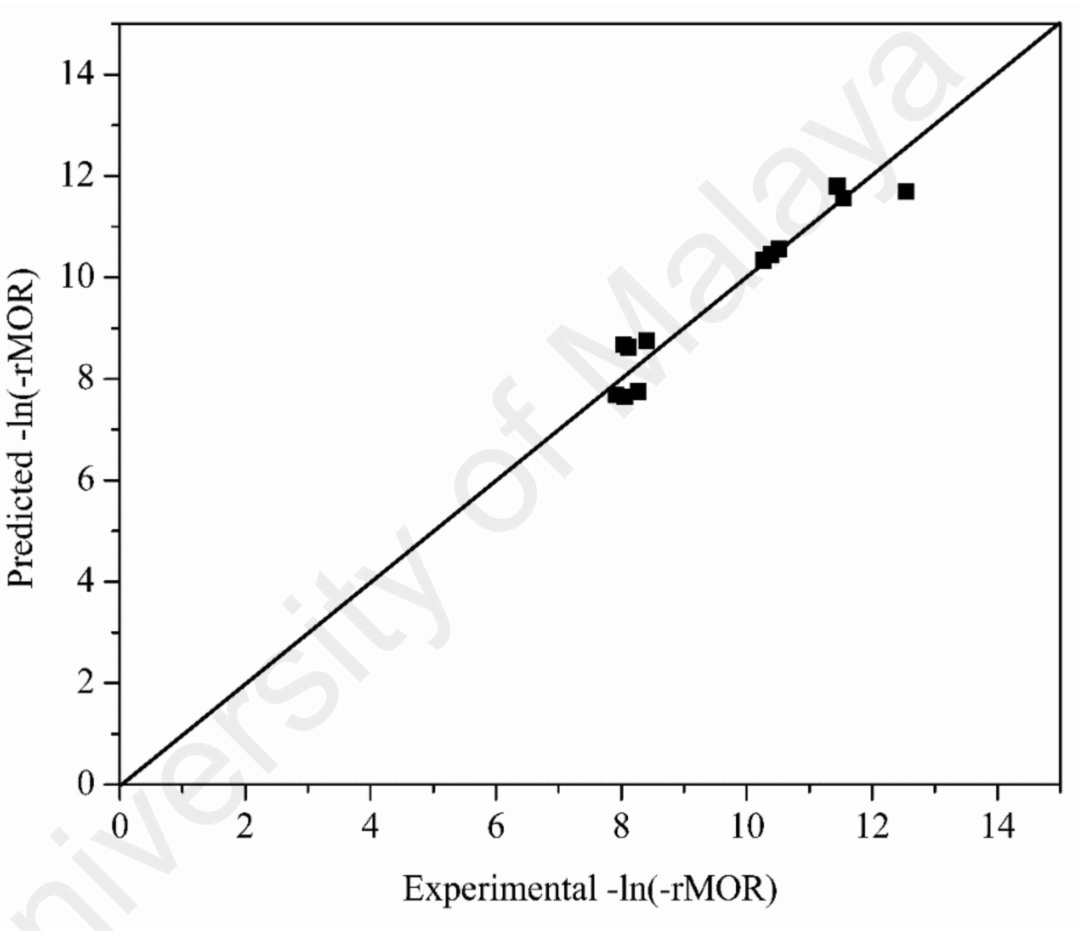


Figure 4.13: Parity chart of calculated against experimental values of $-\ln(-r_{MOR})$

4.2.9 Thermal degradation comparison of MOR with literature

Thermal degradation of MOR has not been investigated yet in details except few screening experiments. Current study shows a comparison MOR loss with other amines because of thermal degradation. Figure 4.14 shows the first order rate constants of each amine with respect to CO_2 loading. It may not be wrong to say that under similar lab scale operating conditions, MOR is the most stable solvent. The most vulnerable solvents to thermal loss are MEA, DEA and MDEA. However, PZ is significantly stable under similar conditions. The current study showed that at lower temperatures like 135 and 150 °C, PZ is slightly stable than MOR, however, MOR is more stable than PZ at high temperatures like 175 and 190 °C.

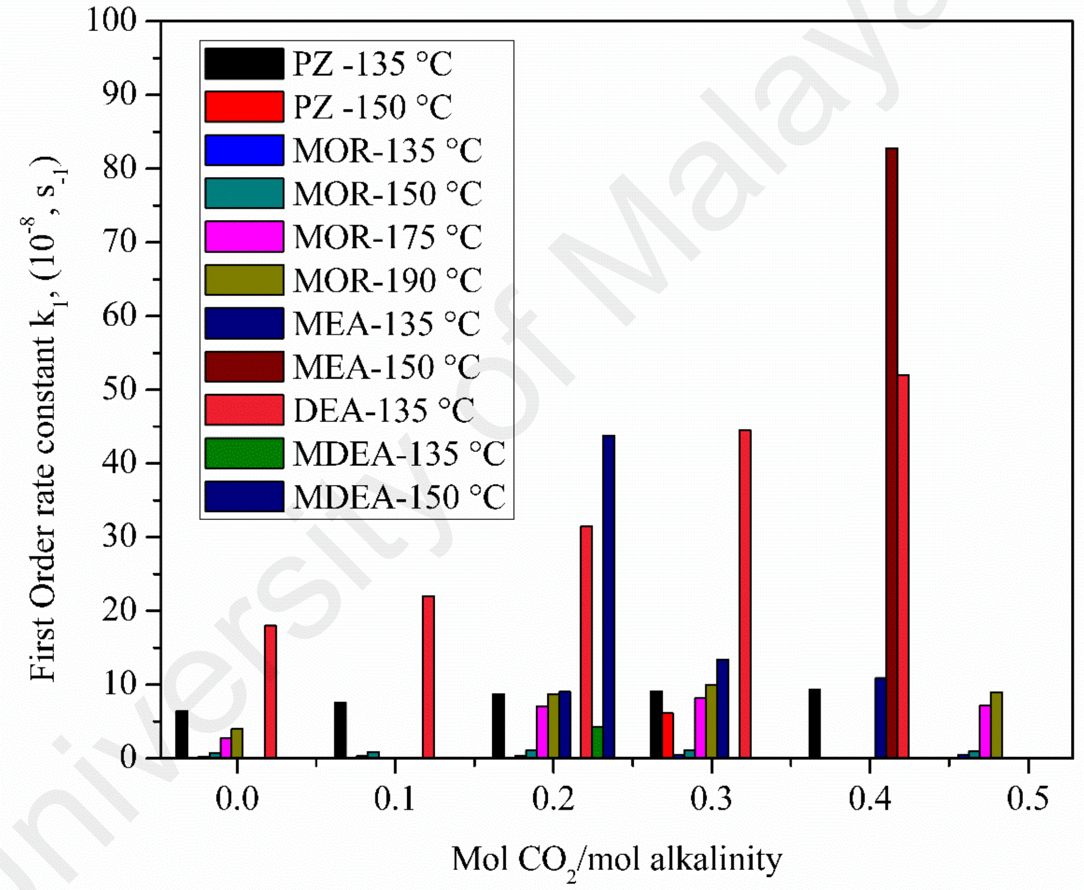


Figure 4.14: A comparison of thermal degradation of various amines (literature results are from (Mazari, Ali, et al., 2015)

4.3 Oxidative degradation of morpholine

4.3.1 Background

Morpholine is thermally a stable solvent as we discussed in the section 4.2. Literature reveals that amines are more prone to degradation in the presence of oxygen than temperature. The flue gas contains a significant amount of oxygen. Hence, it was necessary to investigate the oxidation of MOR under absorber conditions. In this thesis, two main parameters are investigated for the oxidative degradation of MOR, namely oxygen concentration (partial pressure) and temperature. The concentration of oxygen is however, not representative of coal-fired power plant flue gas but this concentration was chosen to enhance the oxidative degradation of MOR. A detailed experimental matrix is provided in Table 4.5.

Table 4.5: Experimental design of oxidative degradation of MOR

Run No.	O_2 (kPa)	CO_2 (kPa)	N_2 (kPa)	Temperature (°C)
1	50	10	40	40
2	90	10	0.0	40
3	50	10	40	50
4	90	10	0.0	50
5	50	10	40	60
6	90	10	0.0	60

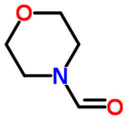
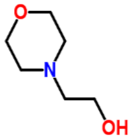
4.3.2 Materials and Methods

Detailed methodology on experimental setup and procedure is given in section 3. MOR (99%) for synthesis was purchased from Merck. Mix gases in 47 L cylinders (with 2000-psi pressure) were purchased from Alpha Gas Solution Sdn. Bhd (AGS). Concentration of amine solution was verified using titration and certificate of gas composition was checked before initiating the experiment. NaOH (0.1 N) and HCl (0.1 N) were purchased from J.T.Baker® Chemicals, whereas (99%) $BaCl_2$ was obtained from Merck Millipore.

4.3.3 Oxidation products

In the current work for identification of degradation products, only GC-MS is used. It is understood that there are some limitations of GC-MS, which disables to identify all degradation products. Degradation products such as $HCOO^-$, CH_3COO^-, $HOCH_2COO^-$, $(C_2O_4)_2^-$ NO_2^-, NH_4^+ etc. were not detectable using the current method. In the oxidation of MOR only two degradation products were continually identified, which are enlisted in Table 4.6.

Table 4.6: Oxidative degradation products of MOR

SNo.	Compound	Abb.	Similarity Index	CAS Number	Structure
1	4-Formylmorpholine	FM	91	4394-85-8	
2	2-Morpholinoethanol	ME	83	622-40-2	

4.3.4 Morpholine Concentration loss due to oxidation

Oxidation of MOR is observed for maximum of 6 days. Two parameters; temperature and oxygen concentration were evaluated for the oxidative degradation of MOR. Results of MOR loss show that its oxidation is dependent on both temperature as well as O_2 concentration. As the concentration of oxygen and temperature increase, it causes increase in degradation of MOR. The maximum degradation of 8.6% at 60 °C using 90 kPa O_2 in 134.65 hours and lowest degradation of 3% is observed at 40 °C and 50 kPa in 103.20 hours. Figure 4.15 shows the loss MOR with respect to time under different temperatures and oxygen partial pressures.

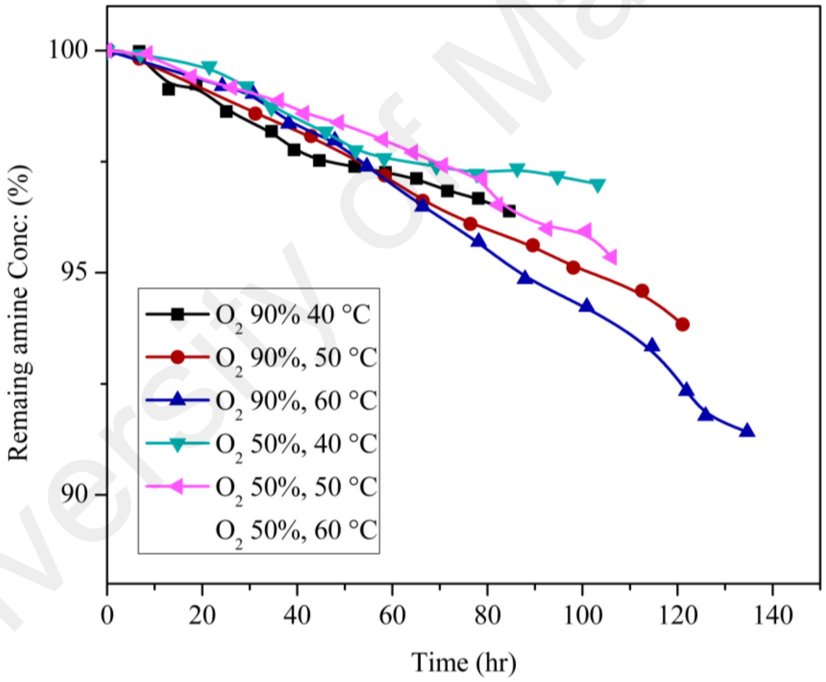


Figure 4.15: MOR loss with respect to time at temperatures 40 to 60 °C and 50 and 90 kPa O_2

4.3.5 Calculation and CO_2 loading verification

As input, CO_2 concentration was kept constant throughout the oxidation, which was 10%. Concentration of CO_2 being charged to the reactor was monitored continually. Samples taken from the reactor were analyzed for pH. At the start of the reaction pH of solutions was 11.4±0.1, and then later, changed to 8.90±0.1 at the end of experiments. At the end of experiments, three replicates of samples were analyzed for CO_2 loading. CO_2 loading was verified through titration, which shows that CO_2 concentration achieved by the solution in 80-120 hours is 0.38-0.46 mol CO_2/mole alkalinity. In terms of rate, the CO_2 absorption would be 0.00007145±0.00000765 mole CO_2/mol alkalinity per min. An example of CO_2 concentration with time and loss of MOR is given in Figure 4.16.

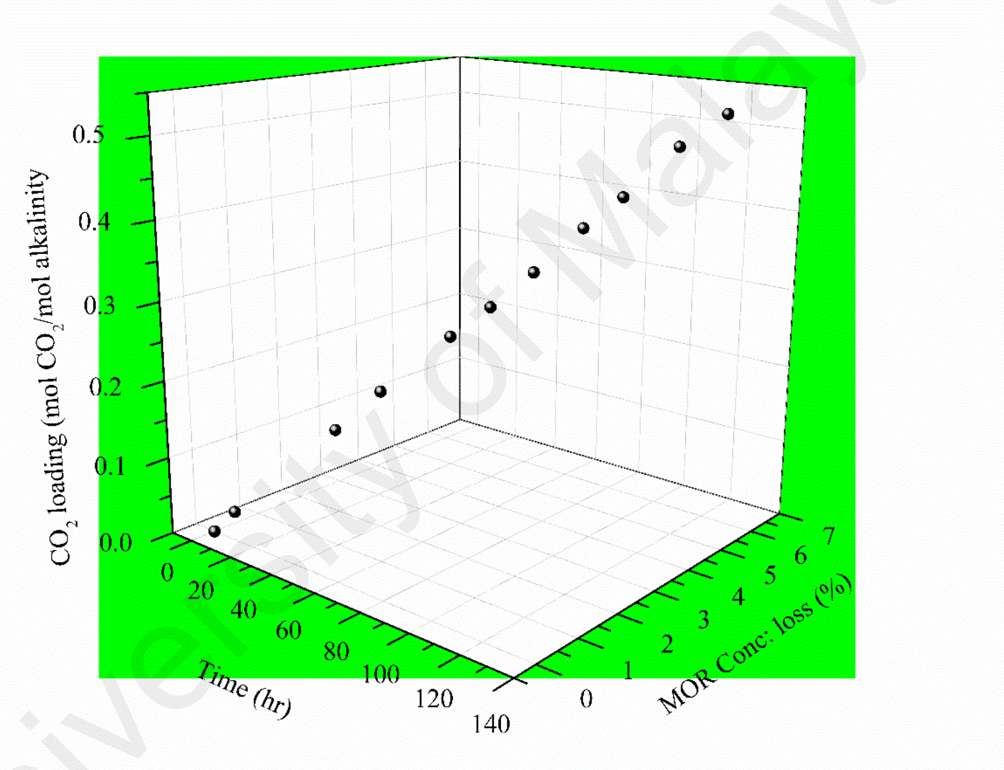


Figure 4.16: A three dimensional plot showing the loss of MOR with increase in time and CO_2 concentration (O_2 90 kPa and 50 °C)

4.3.6 First order MOR oxidation rate constants

Oxidation time-concentration data of MOR was fitted against, zero, first and second order integral rate laws. Data was found to follow first order rate law more appropriately. Equation (4.3) was used for determination of first order rate constants of the oxidative degradation of MOR. First order rate constants (k_1) for each reaction are provided in Table 4.7.

Table 4.7: First order rate constants of oxidation of MOR at different temperature and O_2 partial pressures

Temperature (°C)	**O_2 (kPa)**	**k_1, (10^{-7})**	**R^2**
40	90	1.23	0.962
50	90	1.45	0.997
60	90	1.98	0.983
40	50	0.91	0.910
50	50	1.24	0.979
60	50	1.66	0.983

Tabulated results of Table 4.7 show that rate constant is a function of temperature and O_2 partial pressure. The highest rate constant for oxidation of MOR was found at 60 °C and 90 kPa O_2 and the lowest was found at 40 °C and 50 kPa O_2. In comparison to the results of thermal degradation of MOR, the oxidation rate constants are numerously larger. This is a sign that the rate of oxidative degradation is higher than that of thermal. Furthermore, R^2 values are an indication that data well fitted the first order rate law as most of the values are above 0.90.

4.3.7 Temperature dependence of oxidation of morpholine

Temperature is an aspect for the rate of reactions as it lowers the activation energy enabling reactants and intermediates to proceed to the final product. Similarly, temperature is vital in post-combustion CO_2 capture process. Absorber temperature normally varies from 40 to 70 °C. In the presence of oxygen, these temperatures are more than sufficient to enable amines to produce irreversible products losing their initial concentration. In the current work, temperature is varied from 40 to 60 °C. Results of the experiments brought to light that increasing reaction temperature increased the rate of reaction. Arrhenius equation (4.5) is used to investigate the effect of temperature on the rate of reactions.

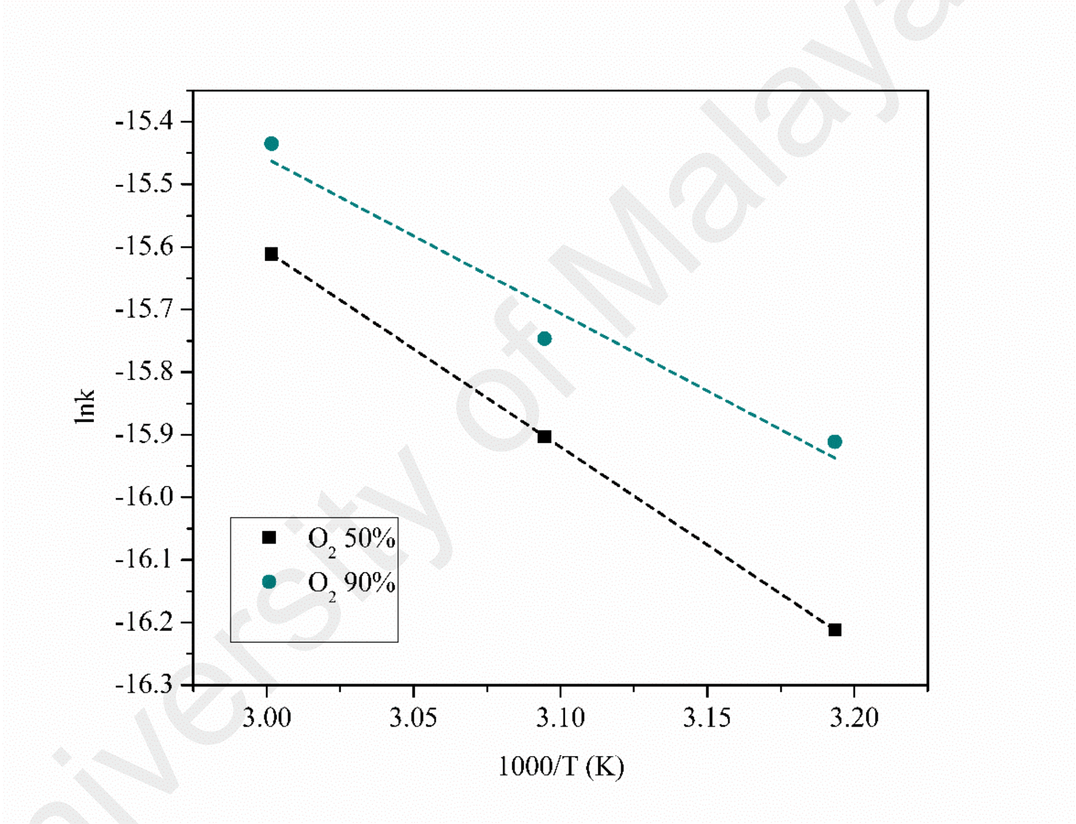


Figure 4.17: Temperature dependence of oxidation of MOR at 50 and 90 kPa O_2

Figure 4.17 shows the effect of temperature on the rate of oxidative degradation of MOR. Plot suggests that as temperature increases the value k increases and vice versa. Two different data plots has been drawn in Figure 4.17 one for 50 kPa O_2 and other for 90 kPa O_2. The values of rate constants at same temperature are higher at 90 kPa O_2 than that of 50 kPa. This shows that higher the O_2 partial pressure, higher will be the rate of degradation of MOR. Increase in rate of reaction virtually was linear at low O_2 partial, say 50 kPa. Whereas, at 90 kPa O_2 the rate seemed to increase drastically at 60 °C, which is a signpost for MOR that may be more stable up to 50 °C in presence of high O_2 partial pressure but at higher temperatures it would might degrade rapidly.

4.3.8 Morpholine oxidative degradation kinetic model

4.3.8.1 Development of the model

Oxidative degradation reaction was conducted using two parameters; varying O_2 concentration and temperature and keeping CO_2 concentration constant. Hence, effect of CO_2 concentration was neglected on the oxidation of MOR. The reaction for model may be written as;

$$MOR + O_2 \longrightarrow Products \tag{4.9}$$

The rate of oxidative degradation would be as;

$$-r_{MOR-0} = k[C_{MOR}]^c[C_{O_2}]^d \tag{4.10}$$

As experiments were conducted at different temperatures, hence effect of temperature on the oxidative degradation is investigated. Replacing k with Arrhenius equation in equation (4.10), it becomes

$$-r_{MOR-O} = Ae^{(-\frac{Ea}{RT})}[C_{MOR}]^c[C_{O_2}]^d \tag{4.11}$$

Where $-r_{MOR-O}$ is the rate of oxidative degradation of MOR (mmol/kg.s), A is pre-exponential factor (s^{-1}), Ea is the activation energy (J/mol), R is universal gas constant (8.314 J/K mol) and T is temperature (K), [C_{MOR}] is the concentration of MOR, C_{O_2} is the concentration of oxygen, c and d are order of reactions with respect MOR and O_2 concentrations respectively.

The linearized form (4.12) of equation (4.11) is regressed with a confidence interval of 95% to get the coefficients *lnA*, *c* and *d*.

$$\ln(-r_{MOR}) = \ln A - \frac{Ea}{RT} + c[C_{MOR}] + d[C_{O_2}] \tag{4.12}$$

As oxidative degradation is conducted under atmospheric pressure, hence oxygen partial pressure is based on the assumption that if flow rate of gas is 100 ml/min throughout the reaction thus individual concentration of each gas is equal to its partial pressure like 50 and 90% of O_2 should correspond to 50 and 90 kPa respectively. Partial pressure of O_2 is converted in terms of concentration using relation of solubility of O_2 in amines developed by Rooney and Daniels (P. C. Rooney & Daniels, 1998) also used by others (Supap et al., 2001).

$$\begin{aligned}[O_2](\frac{mmol}{l}) &= -2.545 + 0.807\times10^{-2}T - 84.14p + 2.096\times10^{-4}pT^2 \\ &+ 2.322\times10^{4}\frac{p}{T} + 1.027p^2 - 3.911\times10^{2}\frac{p^2}{T}\end{aligned} \tag{4.13}$$

Where $[O_2]$ is in mmol/l, p is pressure in MPa and T is temperature in K.

The calculated O_2 concentration values are given in Table 4.8 with respect to conditions described.

Table 4.8: Calculated dissolved O_2 concentration in amine system under different experimental conditions

O_2 (kPa)	[O_2] (mmol/l)	T (K)
50	0.502	313.15
50	0.542	323.15
50	0.584	333.15
90	0.931	313.15
90	0.926	323.15
90	0.936	333.15

4.3.8.2 Optimization of the parameters

Data analysis package of excel 2013 was used to perform multiple linear regression. Experimental data of [C_{MOR}], $[C_{O_2}]$ and average Ea values obtained from Arrhenius equation were used as independent parameters and $\ln(-r_{MOR})$ was kept as dependent parameter for the regression. Model was found to provide reasonable values for the coefficients with good model statistics. The F value of the model was 14.68 and significance F value was 0.064, which show that model is well representative of the optimized parameters. The optimized parameters are tabulated in Table 4.9.

Table 4.9: Optimized parameters of MOR oxidation kinetic model

Parameter	Value
lnA	7.1258±0.91
d	1.937±0.001
d	0.602±0.001
Ea (Joules/mole)	23297.90±2724.49

4.3.8.3 Comparison of experimental and predicted results

The model predicted results were compared with those of obtained from the experiments. Predicted results were found to well match with the experimental results. The AAD% of fit is 0.017, which is indicating the model predicted results are very close with experimental results. Hence, the equation formulated for the degradation rate of oxidation of MOR is well representative of the rate of MOR loss, at least under the lab scale experimental setup. Figure 4.18 shows a comparison of oxidative degradation model predicted rate results against experimental values.

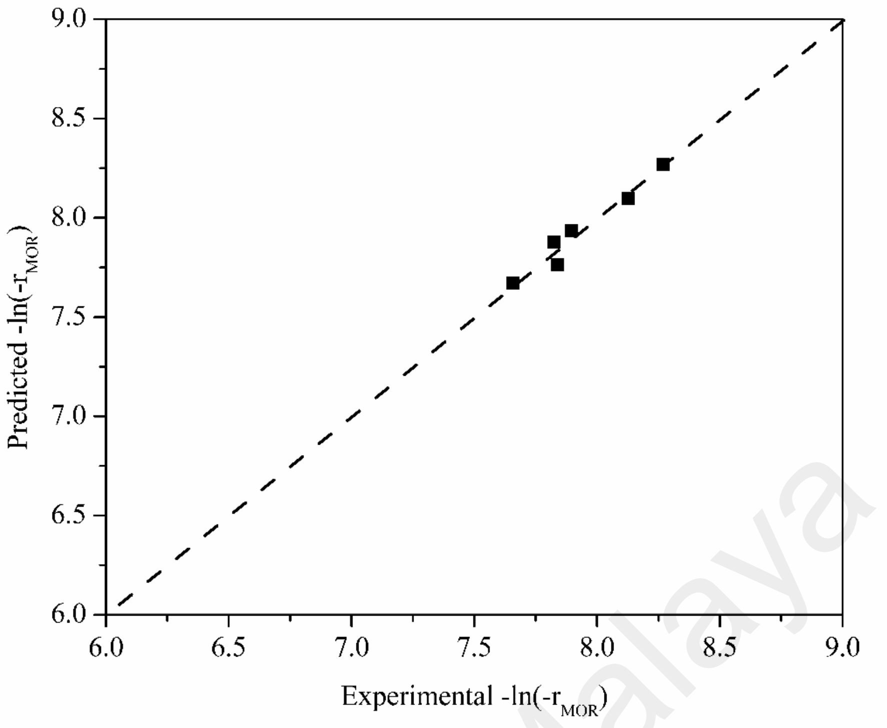


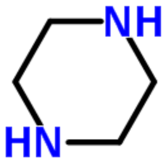
Figure 4.18: Comparison of model predicted rate of oxidative degradation of MOR to those of experimental

4.4 Thermal degradation of piperazine and diethanolamine blend

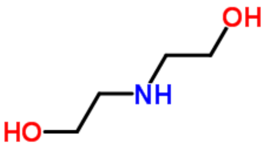
4.4.1 Background

PZ is a stable solvent with higher capacity of CO_2 capture, high CO_2 absorption rate and lower thermal and oxidative degradation (J. D. Davis, 2009; S A Freeman, 2011; Freeman et al., 2010; Stephanie Anne Freeman & Rochelle, 2012b; S. A. D. Freeman, Jason, Rochelle, Gary T., 2010; Andrew Ja Sexton, 2008). However, PZ has limited CO_2 solubility at both higher and lower CO_2 loadings (Mazari et al, 2014; 2015). PZ also produces higher amounts of nitrosamines as being a secondary amine (Dai et al., 2012; Mazari, et al., 2015; Voice, Hill, Fine, & Rochelle, 2015), which are highly carcinogenic (Bartsch & Montesano, 1984; Lijinsky & Epstein, 1970). To mitigate these problems, PZ blends with other alkanolamines may be investigated.

DEA is a less corrosive amine, which make it suitable candidate for CO_2 capture (Gunasekaran, 2012; Monoj K. Mondal, 2009; Monoj K Mondal, 2010). PZ in combination with DEA has shown competitive CO_2 capture properties like CO_2 solubility and CO_2 absorption rate as reported by M. K. Mondal (2009; 2010). Author stated that DEA/PZ blend has higher CO_2 loading capacity than other blends like DEA/AMP, DEA/MDEA, TIPA/PZ and has competitive CO_2 solubility at lower temperature and higher CO_2 partial pressure. Furthermore, Adeosun A., (2013) found that 10 wt.% DEA/20 wt.% PZ blend has the highest CO_2 absorption rate than 10 wt.% MEA/20 wt.% PZ, 10 wt.% AMP/20 wt.% PZ and 10 wt.% MDEA/20 wt.% PZ. However, stability of the PZ/DEA blend is not studied yet. This study emphasizes on the thermal degradation of 3.2 m DEA and 0.8 m PZ blend. The chemical structures of PZ and DEA are given in Scheme 2 and 3 respectively.



Scheme 2: Chemical Structure of piperazine



Scheme 3: Chemical Structure of diethanolamine

4.4.2 Materials and method

Fixed amounts PZ (0.8 m) and DEA (3.2 m) were poured into a two-liter volumetric flask. One kilogram (kg) of deionized and degassed water was then added into the flask to get the required molality. Using a heating plate with magnet, solution was stirred at 50 °C for 5 min in order to dissolve the amines properly. Concentration of prepared solution was then verified through titration using 0.1 M H_2SO_4. CO_2 was also loaded gravimetrically, using a pure saturated CO_2 stream. CO_2 loading was also verified by titration (Stephanie Anne Freeman, 2011; Hilliard, 2008; T. Wang, 2013).

Thermal degradation experiments were conducted in 316 stainless steel cylinders, the method introduced by J. D. Davis, (2009). The filled cylinders were kept in convection ovens at 135 °C. Each experiment was conducted for a maximum of 7 weeks. After every 4th or 5th day, a cylinder was removed, cooled to room temperature, weighed and poured into amber glass vials. Most of the samples were analyzed within 48 hours after removal from the oven.

4.4.3 Experimental Matrix

Experimental matrix was designed based on the literature reports and our study (Ghalib et al., 2016). Results of M K. Mondal, (2009; 2010) on CO_2 solubility and absorption rate in DEA and PZ blend show that 5% PZ and 25% DEA may be a better choice. In this thesis, we have investigated 3.2 m DEA and 0.8 m PZ in the blend. The same concentrations of each DEA (3.2 m) and PZ (0.8 m) were also investigated separately for the comparison purposes. CO_2 loading concentration was designed to be lean to high loading like 0.00 to 0.40 mole CO_2/mol alkalinity. Initially two temperatures were designed for the experiment like 135 and 150 °C. However, later 150 °C was removed from the design as very fast degradation rate of PZ was observed at 135 °C. A detailed experimental matrix is provided in Table 4.10.

Table 4.10: Experimental matrix for thermal degradation of PZ/DEA in blend and individually

Run No.	Amine Conc: (m)	DEA/PZ molar ratio	CO_2 loading (mole CO_2/mole alkalinity)	Temperature (°C)
1	4	3.2/0.8	0.00	135
2	4	3.2/0.8	0.10	135
3	4	3.2/0.8	0.20	135
4	4	3.2/0.8	0.30	135
5	4	3.2/0.8	0.40	135
6	3.2	3.2/0.0	0.00	135
7	3.2	3.2/0.0	0.10	135
8	3.2	3.2/0.0	0.20	135
9	3.2	3.2/0.0	0.30	135
10	3.2	3.2/0.0	0.40	135
11	0.8	0.0/0.8	0.00	135
12	0.8	0.0/0.8	0.10	135
13	0.8	0.0/0.8	0.20	135
14	0.8	0.0/0.8	0.30	135
15	0.8	0.0/0.8	0.40	135

4.4.4 Degradation products

In this study, effect of CO_2 loading, over the formation of degradation products and amine loss is investigated, whereas amine concentration and temperature were kept constant. Various degradation products were found from the degraded aqueous blend solution of PZ and DEA when exposed to elevated temperature with different CO_2 loadings. However, for both DEA and PZ, their degradation products are reported in literature on their separate investigations (C. Gouedard et al., 2012; C. J. Kim & G. Sartori, 1984). Thermal degradation products recognized from this study are provided in Table 4.11.

Table 4.11: Thermal degradation products of blended 3.2 m DEA/0.8 m PZ with CO_2 loading of 0.0-0.40 mol CO_2 per mol alkalinity, for 5 weeks at 135 °C

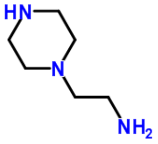
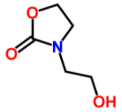
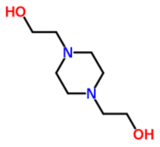
SNo.	Degradation product	Abbr.	Similarity Index	CAS Number	Structure
1	N-(2-Aminoethyl)piperazine	AEP	92	140-31-8	
2	3-(2-Hydroxyethyl)-2-oxazolidinone	HEOD	96	3356-88-5	
3	1,4-Bis(2-hydroxyethyl)piperazine	BHEP	95	122-96-3	

Table 4.11 (Continued): Thermal degradation products of blended 3.2 m DEA/0.8 m PZ with CO_2 loading of 0.0-0.40 mol CO_2 per mol alkalinity, for 5 weeks at 135 °C

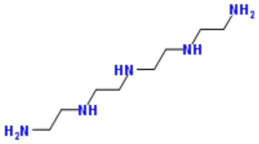
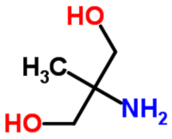
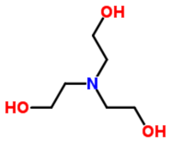
SNo.	Degradation product	Abbr.	Similarity Index	CAS Number	Structure
4	Tetraethylenepentamine	TEPA	76	112-57-2	
5	2-Amino-2-methyl-1,3-propanediol	AMPD	89	115-69-5	
6	Triethanolamine	TEA	86	102-71-6	

Table 4.11 (Continued): Thermal degradation products of blended 3.2 m DEA/0.8 m PZ with CO_2 loading of 0.0-0.40 mol CO_2 per mol alkalinity, for 5 weeks at 135 °C

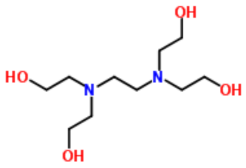
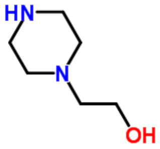
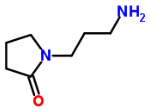
SNo.	Degradation product	Abbr.	Similarity Index	CAS Number	Structure
7	N,N,N',N'-Tetrakis(2-hydroxyethyl)ethylenediamine	THEED	80	140-07-8	
8	2-Piperazin-1-ylethanol	PZE	83	103-76-4	
9	1-(3-Aminopropyl)-2-pyrrolidone	APP	86	7663-77-6	

Table 4.11 (Continued): Thermal degradation products of blended 3.2 m DEA/0.8 m PZ with CO_2 loading of 0.0-0.40 mol CO_2 per mol alkalinity, for 5 weeks at 135 °C

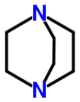
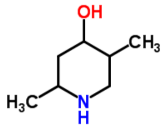
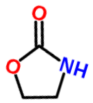
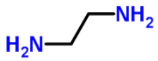
SNo.	Degradation product	Abbr.	Similarity Index	CAS Number	Structure
10	Triethylenediamine	TEDA	91	280-57-9	
11	2,5-Dimethyl-4-piperidinol	DMPD	88	2403-88-5	
12	Oxazolidone	OZD	94	497-25-6	

Table 4.11 (Continued): Thermal degradation products of blended 3.2 m DEA/0.8 m PZ with CO_2 loading of 0.0-0.40 mol CO_2 per mol alkalinity, for 5 weeks at 135 °C

SNo.	Degradation product	Abbr.	Similarity Index	CAS Number	Structure
13	Ethylene Oxide*	EO	Suspected	75-21-8	
14	Ethylenediamine*	EDA	Suspected	107-15-3	

*Reported in literature but not found in this study (Stephanie Anne Freeman, 2011; M. L. Kennard, 1983).

Thermal degradation and mechanism of loss of DEA and PZ is conveyed in literature on their individual basis (Amitabha Chakma, 1987; Stephanie Anne Freeman & Rochelle, 2012b; M. L. Kennard & Meisen, 1985). In the current study, many of the key degradation products are found in common for both DEA and PZ. PZ is acknowledged as one of the most reactive amine species in presence of alkanolamines for irreversible products. The most abundant degradation product formed are BHEP and TEA.

4.4.5 PZ and DEA loss

Amine loss was observed for three systems, PZ, DEA, and their blend investigated in this study. Loss of PZ and DEA is virtually comparable to the literature (Stephanie A. Freeman, Dugas, et al., 2010) when treated separately. However, degradation was very high when they were blended together. CO_2 loading also imparted a direct effect on the degradation of both amines. Rise in degradation rate is less for DEA as compared to PZ with increase in CO_2 loading, which is 11 times of its unloaded to 0.40 mol CO_2/mol alkalinity. Degradation rate of PZ increased up to 70 times from unloaded solution to 0.40 mol CO_2/mol alkalinity. However, in individual cases, rate of degradation of PZ and DEA increased up to 0.45 times for PZ and 1.8 times for DEA, which is minimal compared to their rates in blend. At higher CO_2 loading, said 0.40 mol CO_2/mol alkalinity, the degradation rate of PZ in blend is up to 70 times and is twice for DEA as shown in Figure 4.21, which indicates that PZ is highly vulnerable to degradation in blend than DEA. PZ was found to lose its concentration completely within two weeks. Results shown in the Figure 4.19 and Figure 4.20 are showing loss of PZ and DEA with time under different CO_2 loadings at same temperature respectively. Results were interpreted until the complete loss of PZ. Hence, results are depicted in Figure 4.19 and Figure 4.20 are representative until the complete loss of PZ but not the complete experimental span.

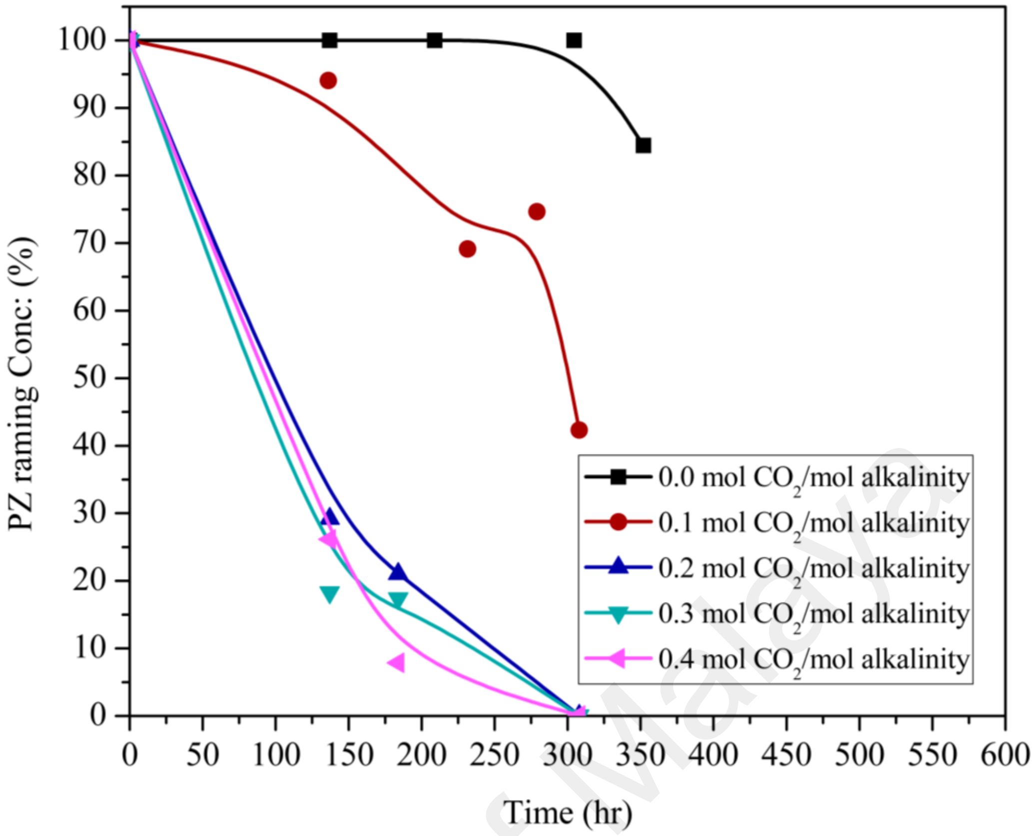


Figure 4.19: PZ concentration loss in blended PZ/DEA with CO_2 loading of 0.0-0.40 mole CO_2/mol alkalinity at 135 °C

Figure 4.19 indicates that PZ in carbonated blend started degrading at the start of the experiment. However, for the unloaded solution PZ shown stability for at least 250 hours, whereas, it started degrading drastically after 300 hours. This may be because of the formation of ethylene oxide from DEA in blend. Presence of ethylene oxide may play a role of a strong catalyzing agent for the degradation of PZ.

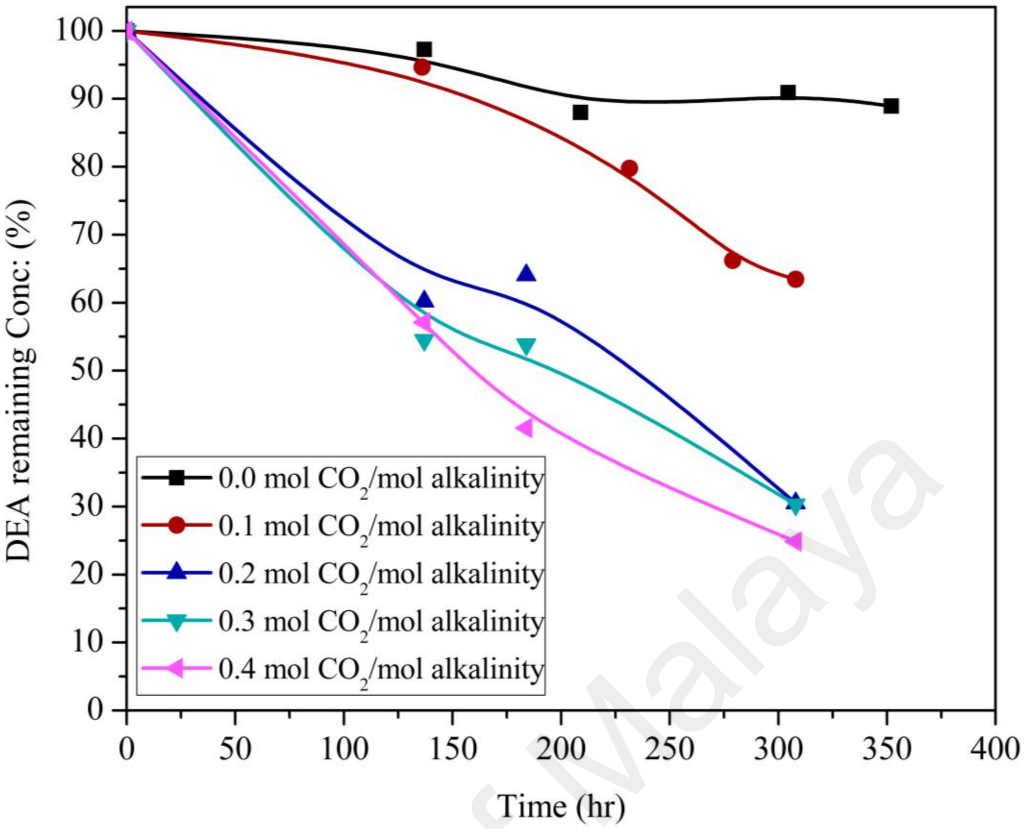


Figure 4.20: DEA concentration loss in blended PZ/DEA with CO_2 loading of 0.0-0.40 mole CO_2/mol alkalinity at 135 °C

Figure 4.20 shows the loss of DEA with time at each CO_2 loading in PZ/DEA blend. Results interpreted for DEA loss are based on loss of PZ. In the Figure 4.20, DEA loss is shown until the complete loss of PZ. Results suggest that as the CO_2 loading increases, the loss of DEA also increases.

Effect of blending on the degradation of PZ and DEA is also presented in Figure 4.21. Comparison is based on first order rate constants.

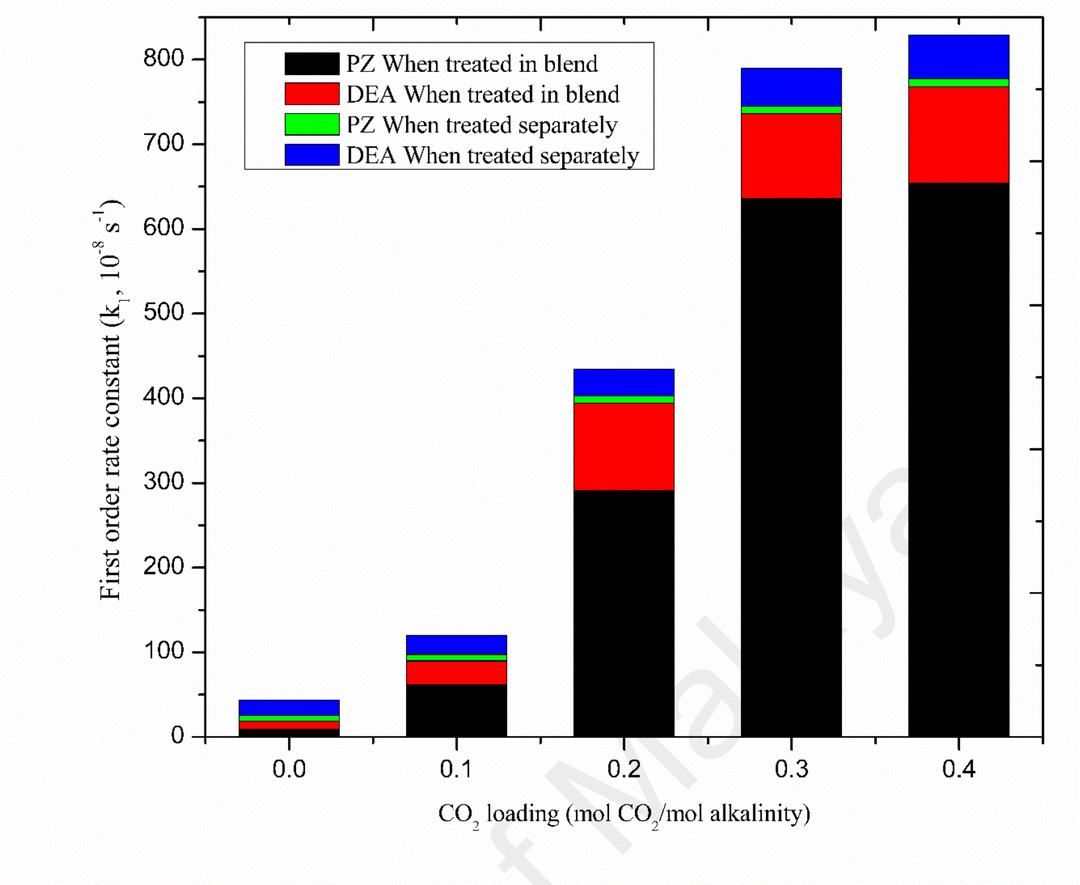


Figure 4.21: Thermal degradation of PZ and DEA with respect to CO_2 loading in blend and individually under identical experimental conditions.

4.4.6 First order rate constant determination

Time-concentration data of thermal degradation of blended PZ and DEA was analyzed against zeroth, first and second order rate laws. Data was found to fit first order rate of degradation fair enough than other two rate laws. First order rate constants of DEA and PZ in blend as well individually with their respective R^2 values are given in Table 4.12.

Table 4.12: First order rate constants of PZ and DEA in the blend

	k_1, 10^{-8}			
CO₂ loading	**PZ**	$\mathbf{R^2}$	**DEA**	$\mathbf{R^2}$
0.00	9.23	0.29	9.61	0.72
0.10	61.3	0.66	28.6	0.48
0.20	291	0.68	103	0.93
0.30	636	0.84	100	0.97
0.40	654	0.88	114	0.98

Table 4.13: Frist order rate constants of PZ and DEA when treated individually

	k_1, 10^{-8}			
CO₂ loading	**PZ**	$\mathbf{R^2}$	**DEA**	$\mathbf{R^2}$
0.00	6.42	0.53	18.0	0.78
0.10	7.58	0.26	22.0	0.80
0.20	8.67	0.622	31.5	0.42
0.30	9.12	0.45	44.5	0.54
0.40	9.36	0.78	52.0	0.47

4.4.7 Thermal degradation comparison of PZ/DEA blend with literature

Generally, PZ is well known for its stability (Stephanie A. Freeman, Davis, et al., 2010; Shaukat A. Mazari et al., 2014). Nevertheless, when it is blended with any amine (MEA, AMP or DEA) it degraded at a very high rate except MDEA (F. B. Closmann, 2011). Figure 4.22 shows the degradation rate of PZ in different blends. Experimental conditions are identical except PZ/AMP blend, for which reactions were conducted in a high-pressure reactor. Figure indicates that PZ loss is higher for PZ/DEA mixture than other mixtures. This may be due to the formation of ethylene oxide, which reacts with AMPD and ammonia to form TEA as one of the major degradation products of PZ/DEA system unlike PZ/AMP, PZ/MEA and PZ/MDEA. Figure 4.22 shows the loss of PZ in different blends.

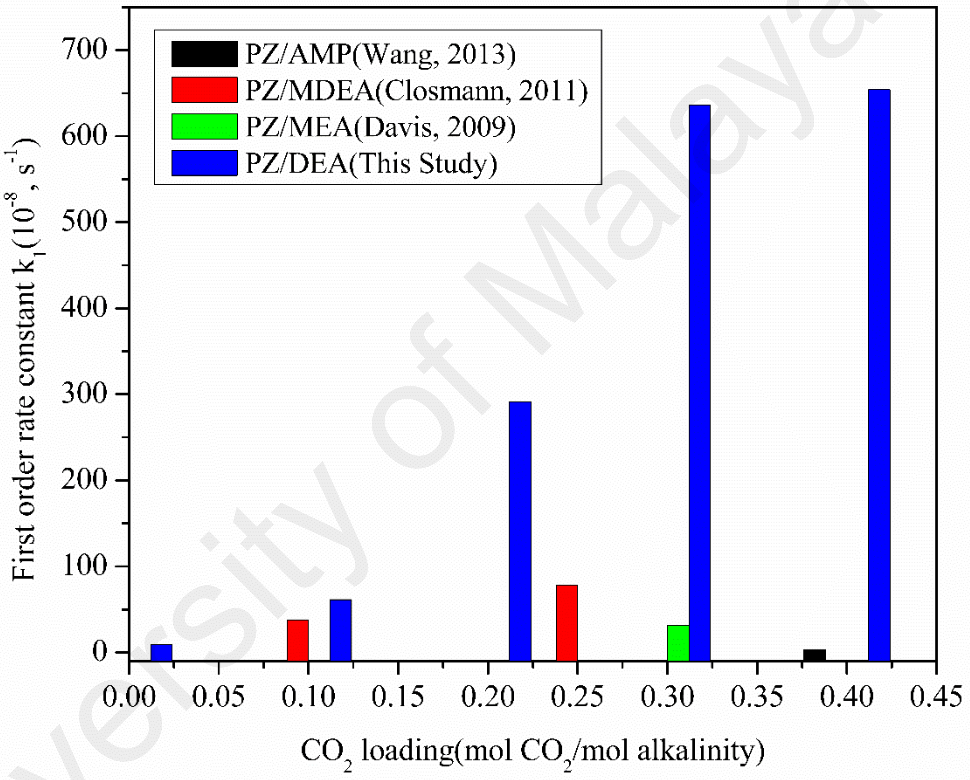


Figure 4.22: Thermal degradation of PZ in different blends under various CO_2 loadings at 135 °C

4.4.8 Kinetic models for blended system

4.4.8.1 PZ degradation rate model development

Focused component for thermal degradation kinetic model is PZ as the rate of its thermal degradation in blend is up to multiple times than its rate when treated individually. Reactions have been assumed to take place in liquid phase as a closed system is used for the degradation. Hence, the mass transfer is supposed to take place in liquid phase only as the DEA and PZ are nonvolatile. Degradation of amines is a complex phenomenon. Stripping out CO_2 at elevated temperatures involves some irreversible reactions, resulting formation of degradation products; consequently, causing a loss in the amine concentration. Empirical rate laws are generally based on the change in concentration of reactants, however, in the actual processes, a number of reversible and irreversible reactions take place simultaneously in the bulk solution. We have formulated an empirical rate model for the loss of PZ because of its high loss in blend than its individual, assuming the reaction to take place in forward direction only. Concentration of DEA, PZ and CO_2 were taken into account for the loss of PZ. The empirical rate model shows loss of PZ in general, in the presence of DEA and CO_2. Model is based on the time-concentration data obtained at lab scale under isothermal conditions. However, the temperature conditions may not meet the actual process temperature, where a temperature gradient is observed in the stripping column. This model may serve as a basic guideline for the loss of PZ in the presence of DEA and CO_2. Arrhenius equation has not been accounted in this model as the thermal degradation is conducted at a single temperature. The rate law equation is given as below.

$$-r_{PZ-T} = k[PZ]^e[DEA]^f[CO_2]^g \tag{4.14}$$

Where, $-r_{PZ-T}$ is the rate of thermal degradation of PZ (mmol/kg.s), k is the rate constant for the reaction (s^{-1}), $[PZ]$, $[DEA]$ and $[CO_2]$ are respective concentrations (mmole/kg) and e, f and g are reaction orders with respect to PZ, DEA and CO_2. Taking natural log from both sides, equation was linearized as under:

$$\ln(-r_{PZ-T}) = \ln k + e\ln[PZ] + f\ln[DEA] + g\ln[CO_{2]} \tag{4.15}$$

4.4.8.2 PZ rate model parameter optimization

Using experimental data of this study, data analysis package of MS Excel 2013 was used for the data regression to determine the coefficients of the model. Model provided coefficients with high coefficient of determination (R^2=0.998). The values of coefficients are as, 0.931, 1.711, and 0.303 with respect to e, f, and g. Model is verified using experimental results of this study. In each case, initial and final concentration of each component with respect to time at every CO_2 loading is used. Unloaded reaction is not considered in this model due to its limitations. The Absolute Average Deviation (AAD) of the model is 0.21%. Figure 4.23 shows the comparison of experimental thermal degradation rate and calculated rate.

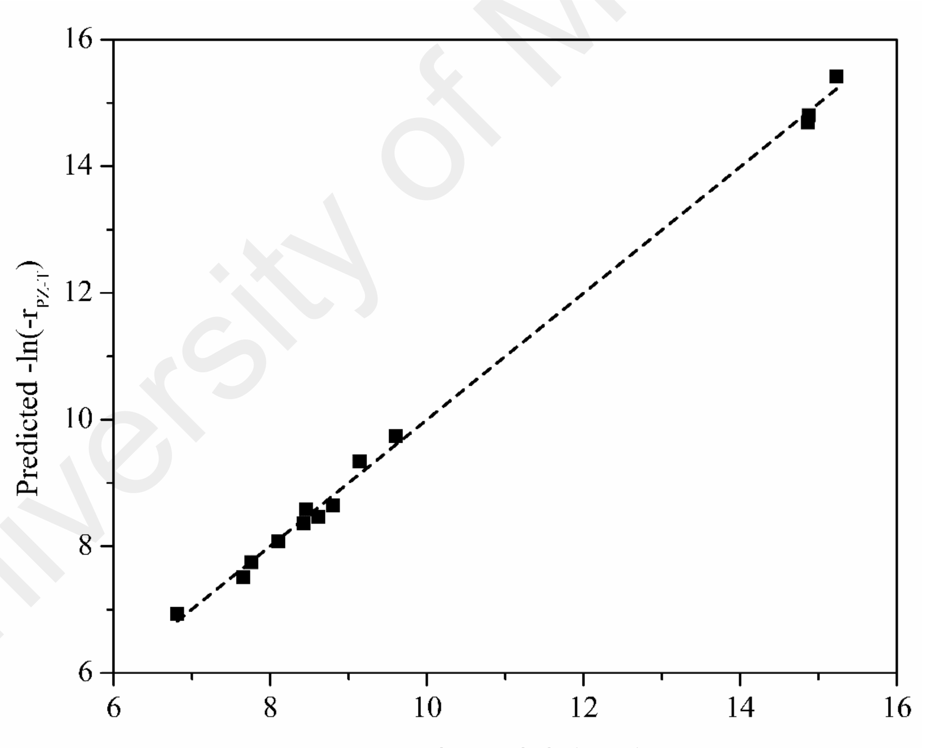


Figure 4.23: Comparison of experimental and calculated values of - $\ln(-r_{PZ-T})$ at each CO_2 loading

4.4.8.3 DEA thermal degradation rate model development

For the degradation rate of DEA, the following equation was formulated pertaining that the rate of degradation of DEA is a function of PZ, DEA and CO_2 concentrations.

$$-r_{DEA-T} = k[DEA]^i[PZ]^j[CO_2]^k \tag{4.16}$$

Where; $-r_{DEA-T}$ is the rate of thermal degradation of DEA (mmol/kg.s) $[DEA]$ is the concentration DEA (mmol/kg), $[PZ]$is the concentration of PZ and i, j, k are the orders of reaction with respect to concentrations of DEA, PZ and CO_2 respectively.

Linearized form of equation (4.16) as (4.17) was regressed for the findings of coefficients of the equation.

$$\ln(-r_{DEA-T}) = \ln k + i\ln[PZ] + j\ln[DEA] + k\ln[CO_2] \tag{4.17}$$

4.4.8.4 Parameter optimization for thermal degradation rate model of DEA

Parameter optimization method was same as defined earlier for other models. The optimized values of coefficients of the parameters were found as 0.47, -0.12 and 1.67 for *i, j,* and *k* respectively. Model was found to have lower fit and data may not properly represent the equation. The coefficient of determination of the model was 0.626, which is not significant enough to represent the experimental data. Hence, coefficients obtained through this model may not be representative of the actual effect. Furthermore, the values of F and significance F were found to be 1.295 and 0.349 respectively, which suggest that the model is not well representative for the data obtained through the experiments.

4.4.8.5 Comparison of predicted thermal degradation rate of DEA against experimental results

Values obtained from the model rate equations are compared with those of obtained through experiments. As mentioned before that this model for loss of DEA lacked the fitting of data as noticed from the statistics of the rate model. Figure 4.24 shows the results of model prediction against experimental results. Results from the plot indicate that there is a significant deviation in predicted values to those of obtained from the experiment. Although, AAD obtained from the model is 6.34%, which is not too high but rate of reaction is very sensitive parameter, hence this model (at least for current data) may not be suitable for thermal degradation of DEA in presence of PZ. Furthermore, other models like zeroth and second law were used but no adequate fit was find except first order rate law model.

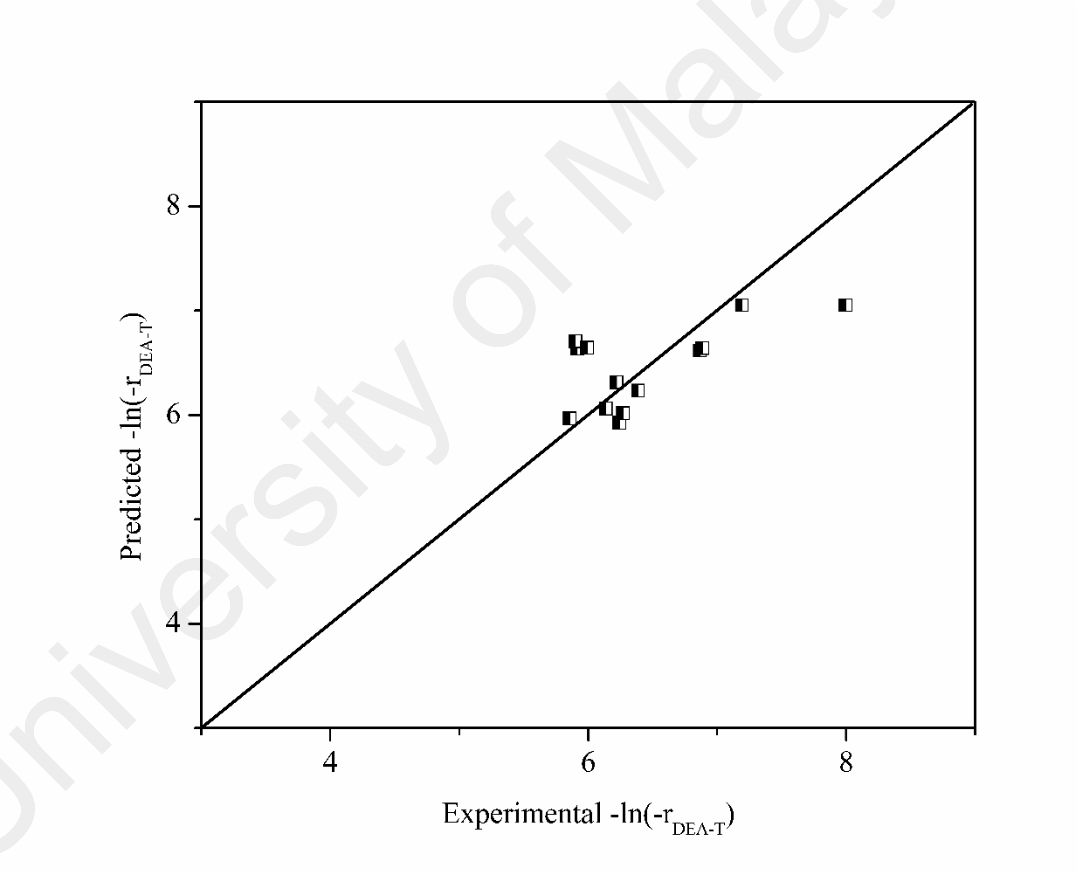


Figure 4.24: Comparison of predicted rate of DEA loss versus experimental results

4.5 Oxidative degradation of piperazine and diethanolamine blend

4.5.1 Research background

DEA is a less corrosive and less volatile amine, which makes it suitable for CO_2 capture (Gunasekaran, 2012; Monoj K. Mondal, 2009; Monoj K Mondal, 2010). PZ in combination with DEA has shown competitive CO_2 capture properties like CO_2 solubility and CO_2 absorption rate (Monoj K. Mondal, 2009; Monoj K Mondal, 2010). DEA/PZ blend has higher CO_2 loading capacity than other blends like DEA/AMP, DEA/MDEA, TIPA/PZ and has competitive CO_2 solubility at lower temperature and higher CO_2 partial pressure. Furthermore, Adeosun A., (2013) discovered that 10 wt.% DEA/20 wt.% PZ blend has the highest CO_2 absorption rate than 10 wt.% MEA/20 wt.% PZ 10 wt.% AMP/20 wt.% PZ and 10 wt.% MDEA/20 wt.% PZ. However, stability of the PZ/DEA blend is not studied yet. In this investigation, oxidation of 3.2 m DEA and 0.8 m PZ blend was carried out. Aim is to define the effect of O_2 concentration and temperature on the loss of PZ and DEA and predict rate of degradation of amine using rate equation models. Following matrix of experiments was used to conduct the experiments, in order to know the effect of O_2 partial pressure and temperature on degradation rate of PZ and DEA blend.

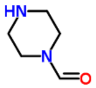
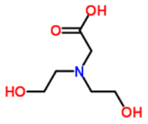
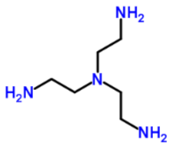
Table 4.14: Experimental design of oxidative degradation of PZ and DEA blend

Run No.	O_2 Concentration	CO_2 Concentration	N_2 Concentration	Temperature (°C)
1	50	10	40	40
2	90	10	0.0	40
3	50	10	40	50
4	90	10	0.0	50
5	50	10	40	60
6	90	10	0.0	60

4.5.2 Degradation products

Oxidation of amines produces a number of degradation products. However, equipment like GC-MS, and GC-FID may not able to detect all of the compounds as there is a number of ionic degradation products, which could only be identified through using Ion Chromatography (IC). Degradation products identified by GC-MS are tabulated in Table 4.15. However, it is suspected that species like $HCOO^-$, CH_3COO^-, $HOCH_2COO^-$, $(C_2O_4)_2^-$ NO_2^-, NO_3 CH_3NO, ethylene-diamine could be part of this system as have reported for PZ oxidation (Mazari et al., 2014).

Table 4.15: Oxidation products identified from the oxidation of 0.8 m PZ/ 3.2 m DEA

Degradation Product	Abbr.	Similarity Index	CAS Number	Structure
N-(1H-Imidazol-2-yl)acetamide	IAA	84	52737-49-2	
Formylpiperazine	FPZ	95	7755-92-2	
(Bis(2-hydroxyethyl)amino)acetic acid	Bicine	89	150-25-4	
Tris(2-aminoethyl)amine	TAEA	96	4097-89-6	

4.5.3 Amine loss

Amine loss for oxidative degradation of PZ/DEA blend was investigated for three to five days. Even though, the experimental duration is short but focusing on the kinetics of oxidative degradation of the PZ/DEA blend this duration should be sufficient. Equation (4.18) is used to determine the remaining percentage of amine concentration with respect to time.

$$Reaming\ Amine\ Conc : (\%) = 100 - \frac{C_0 - C_t}{C_0} \times 100 \tag{4.18}$$

Where, C_0 is the concentration of amine at time 0, and C_t is the concentration of amine at time t.

In this investigation two parameters were considered, temperature and O_2 concentration. Results of amine loss indicated that both temperature as well as O_2 partial pressure has a direct effect on the loss of amine.

4.5.3.1 Piperazine concentration loss in PZ/DEA blend oxidation

Generally, PZ is known as a stable solvent under oxidation conditions (Stephanie A. Freeman, Davis, et al., 2010). However, a contradiction has been observed in this study when under similar conditions it was oxidized in presence of 25 wt.% DEA. Freeman et al., (2010) using a low gas flow reactor, with a saturated gas stream of 98% O_2 and 2% CO_2 the solution also contained 1.0 mM Fe^{2+} at a temperature of 55 °C found that 8 m PZ loses 8% of its initial concentration in 450 hours keeping the agitator speed 1400 rpm. On the other hand, 0.8 m PZ investigated in the current study lost 29% of its initial concentration when oxidized in presence of 3.2 m DEA with a saturated gas stream of 90 % O_2 and 10% CO_2 at 60 °C in 85 hours keeping agitator speed at 1400 rpm. This increase in loss of PZ may be a synergy of DEA presence as shown the rate equation of PZ loss. Similarly, addition of AMP is also reported to synergize the degradation of PZ (T. Wang, 2013). Figure 4.25 shows loss of PZ with time under different operating conditions. It is obvious from the figure that loss of concentration of PZ is a function of O_2 concentration and reaction temperature.

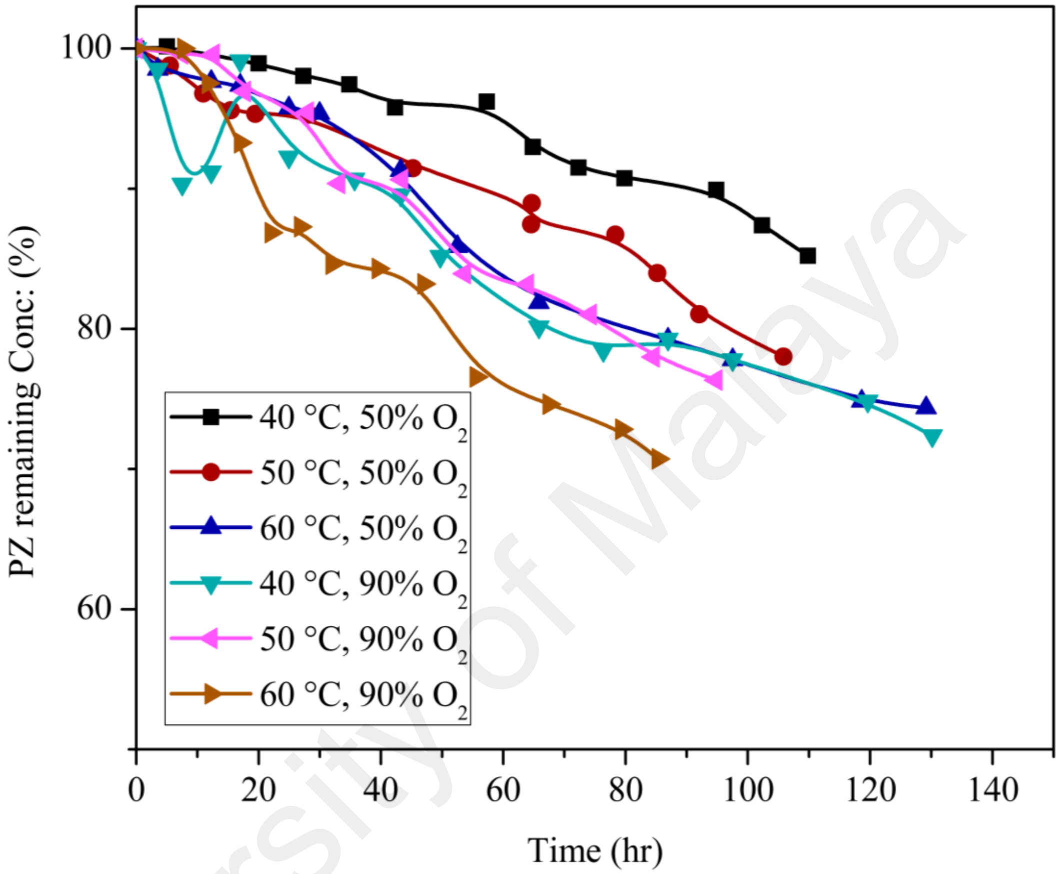


Figure 4.25: Loss of PZ at temperatures 40-60 °C with 50-90 kPa O_2 and 10 kPa CO_2

4.5.3.2 Diethanolamine concentration loss in PZ/DEA oxidation

Oxidation of DEA is relatively an understudied subject. Lepaumier et al., (2009b) studied Oxidation of 12 ethanolamines and ethylenediamines. Experiments were conducted in a stainless steel reactor at 140 °C under an air pressure of 2 MPa for 15 days. Study found that among twelve amines N,N-dimethylaminoethanol (DMAE), N,N'-dimethylpiperazine (DMP), N-(2-hydroxyethyl)ethylenediamine (HEEDA), N-methylaminoethanol (MAE) N,N,N',N',N''-pentamethyldiethylenetriamine (PMDETA), AMP, MEA, DEA etc., where DEA was the least stable among all.

Similarly, Wang & Jens, (2012; 2013; 2014); investigated the oxidation of PZ, MEA, DEA, AMP and MDEA. Authors found that under 350 kPa O_2 and 120 °C the DEA loss was the second highest among AMP, MDEA and MEA in 384 hours, which was 57.3 % after MEA (66.4%).

In this study, DEA loss was monitored for a maximum of six days under different operating conditions. Degradation rate was less for DEA until five days using 50 kPa O_2 at 40-60 °C compared to PZ. However, it increased on rise in O_2 concentration. A loss of 5% in initial concentration of DEA was observed until 70 hours at 50 kPa and 40 °C. On the other hand, DEA initial concentration loss increased up to 20% at 90 kPa and 60 °C for 85 hours. Figure 4.26 shows percentage loss of DEA with respect to time under various operating conditions.

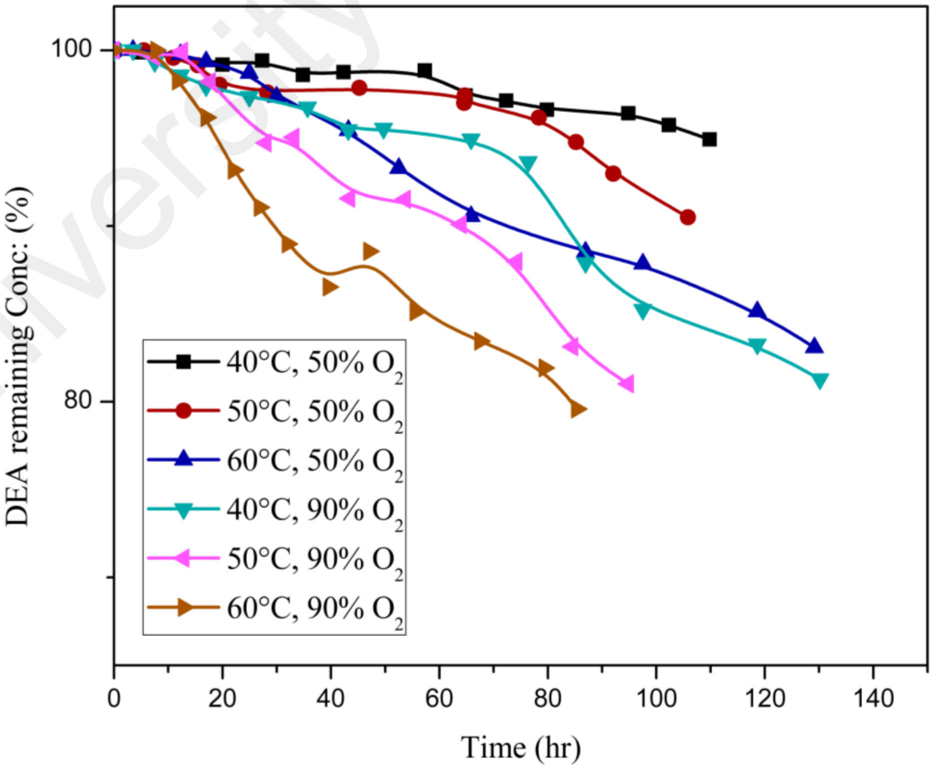


Figure 4.26: Loss of DEA at temperatures 40-60 °C with 50 and 90 kPa O_2 and 10 kPa CO_2

4.5.3.3 CO_2 loading and its effect on loss of DEA and PZ

The CO_2 concentration during the oxidation experiments was kept constant, which is 10%. Flowrate of the reaction gas was kept constant at 100 ml/min, which means the partial pressure of CO_2 was constant during the span of experiment. On the removal of every sample, pH was checked before putting them into refrigerator. The initial pH of PZ/DEA solution was 12.2±0.1, which changed with the time and at the end of experiments, it was 9.0±01. CO_2 loading verification was made at the end of the experiments, through titration, which was 0.50-0.60 mol CO_2/mol alkalinity. Based on the experimental span of 80-120 hours for each reaction, the CO_2 concentration intake would be 0.000102±0.000002 mole CO_2/mol alkalinity per min. Examples of CO_2 concentration increase with time and loss of MOR are given in Figure 4.27 and Figure 4.28.

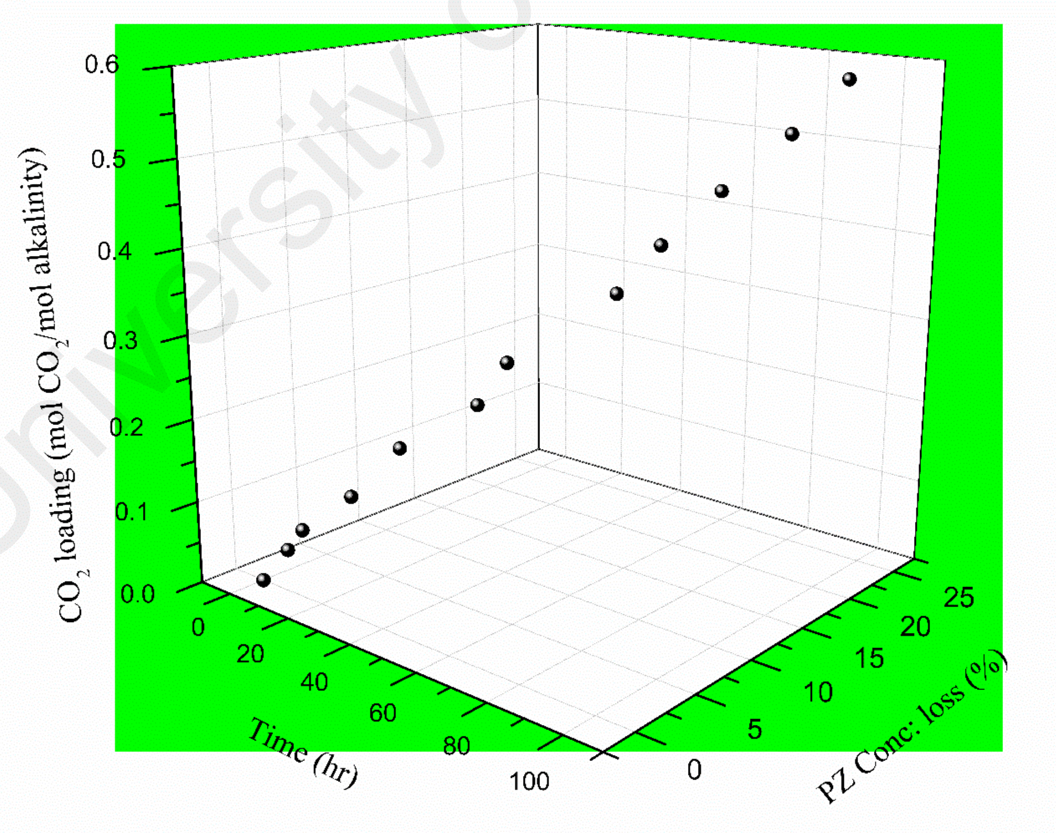


Figure 4.27: A three dimensional plot showing the loss of PZ with increase in time and CO_2 concentration (O_2 90 kPa and 50 °C)

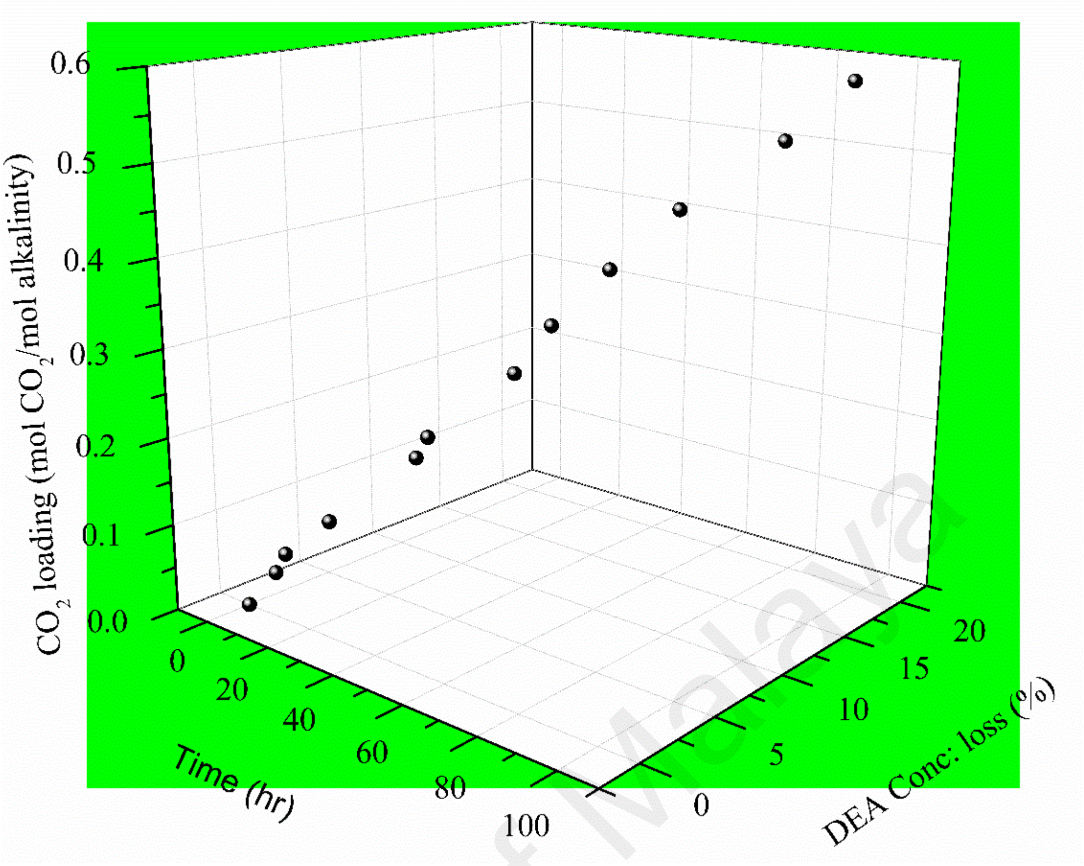


Figure 4.28: A three dimensional plot showing the loss of DEA with increase in time and CO_2 concentration (O_2 90 kPa and 50 °C)

4.5.4 Degradation kinetics of PZ and DEA

For the process design and in development of solvent, the degradation kinetics of solvent plays a crucial role. In the current work, orders of reactions were first determined by using integral method, which almost gave straight lines for the plots of lnC (natural log of concentration) vs time with decent R^2 values for most of the reactions. Hence, this employed the first order rate of reaction to be utilized. A detailed list of first order rate constants (k_1) is given in Table 4.16. Results indicate that the values of k_1 increased with increase in temperature as well as partial O_2 pressure.

Table 4.16: First order rate constants (k_1) of PZ and DEA at 40-60 °C and 50 and 90 kPa O_2

Temperature (°C)	**CO_2 (kPa)**	**O_2 (kPa)**	**k_1, (10^{-7})**		**R^2**	
			DEA	**PZ**	**DEA**	**PZ**
40	10	50	1.25	3.92	0.938	0.949
50	10	50	2.06	5.89	0.838	0.969
60	10	50	4.17	7.15	0.986	0.983
40	10	90	4.34	6.47	0.927	0.976
50	10	90	6.10	8.68	0.962	0.977
60	10	90	7.50	11.7	0.933	0.957

4.5.5 Temperature dependence of first order rate constant

Linear form of Arrhenius equation (4.19) is used in this study to investigate the effect of temperature on the reaction rate constants.

$$\ln k = \ln A - \frac{Ea}{RT} \tag{4.19}$$

Figure 4.29 shows the temperature dependence of first order rate constants under different O_2 partial pressures. It can be observed from the plot that temperature dependence of reaction is consistent at O_2 partial pressure of 90 kPa, however, there is some inconsistency at lower partial pressure of O_2 at 50 kPa.

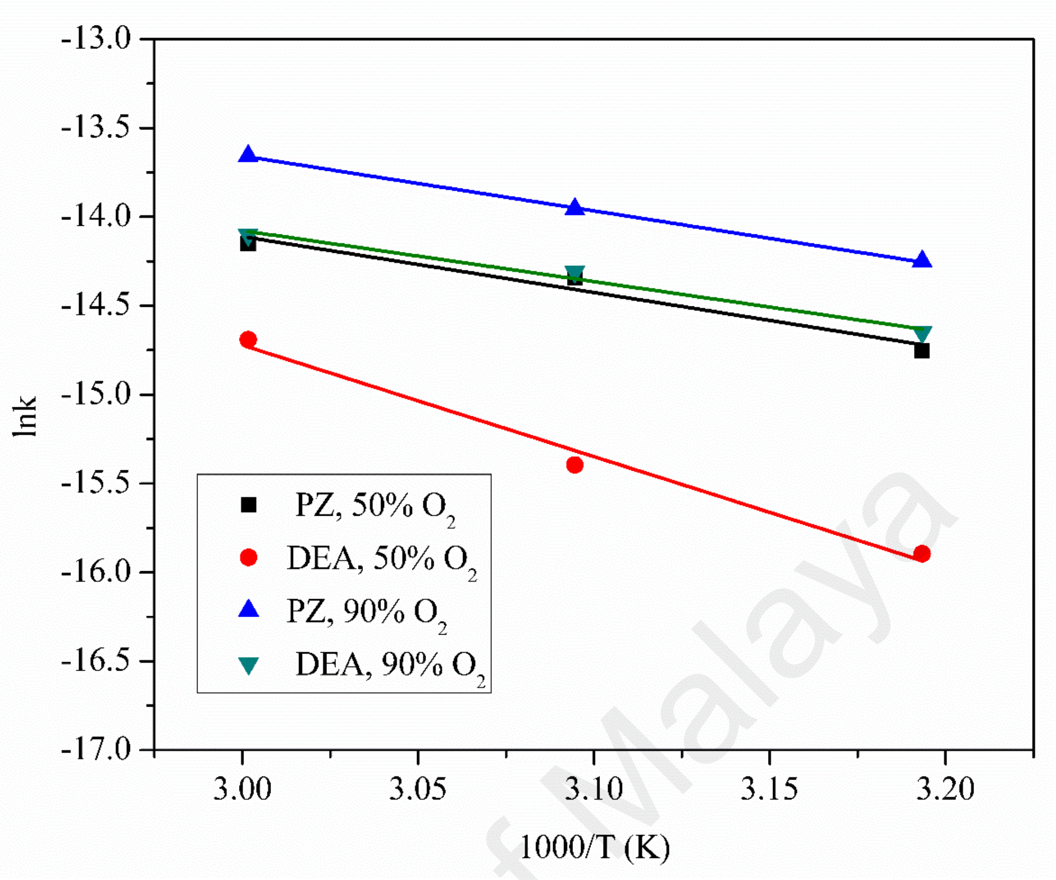


Figure 4.29: Temperature dependence of PZ and DEA reactions at 50 and 90 kPa O_2

4.5.6 Kinetic model for oxidation rate of PZ and DEA

4.5.6.1 PZ and DEA model development

Oxidation of aqueous PZ and DEA blend was investigated under absorber conditions simulating its temperature and CO_2 partial while extrapolating the oxygen partial pressure. Likewise, absorber temperature, the temperature of experiments is varied from 40 to 60 °C and O_2 partial 50 and 90 kPa but CO_2 partial pressure (10 kPa) was kept constant throughout the experimental matrix. In the current models rate of loss of amines (PZ and DEA) is predicted. Models are developed based on experimental results obtained from this study. As most of the experiments are conducted at a single initial concentration of each component at 3.2 m DEA and 0.8 m PZ, thus in the current models rate is based on the loss of amine after time interval (Δt); where a significantly quantifiable amine loss is observed. Therefore, the amine concentrations for model input are also taken with respect to that Δt. As oxidative degradation is conducted under atmospheric pressure, hence oxygen partial pressure is based on the assumption that if flow rate of gas is 100 ml/min throughout the reaction thus individual concentration of each gas is equal to its partial pressure like 50 and 90% of O_2 should correspond to 50 and 90 kPa respectively. Partial pressure of O_2 is converted in terms of concentration using relation (4.13) of solubility of O_2 in amines developed by P. C. Rooney & Daniels, (1998) also used by others (Supap et al., 2001). Oxygen concentrations used in this model are provided in Table 4.8.

4.5.6.2 Formulation of PZ degradation rate equation

As described in the experimental results that the PZ loss is very high in the blend than its loss when treated separately. This may be because of the presence of DEA in the system, hence in the rate equation developed considering all constraint as the concentration of PZ, DEA, O_2 and temperature. An empirical rate law, using power law model is postulated as presented in equation (4.20).

$$-r_{PZ-0} = k[C_{PZ}]^m[C_{DEA}]^n[C_{O_2}]^o \tag{4.20}$$

Where $-r_{PZ-0}$ is the rate oxidative degradation of PZ (mmol/l.s), C_{PZ} is the concentration of PZ (in mmol/l), [C_{DEA}] is the concentration of DEA (in mmol/l) C_{O_2} is the concentration of O_2 (mmol/l) and k is the reaction rate constant (s^{-1}).

As Oxidation is conducted under different temperatures, therefore effect of temperature is accounted for in this empirical model using Arrhenius equation based equation (4.21).

$$k = Ae^{(-\frac{Ea}{RT})} \tag{4.21}$$

Where, *A* is the pre-exponential factor (in s^{-1}), *Ea* is the activation energy (in J/mol), *R* is universal gas constant (8.314 J/K. mol) and *T* is temperature (in K).

Substituting equation (4.21) to (4.20) and linearizing it gives equation (4.22).

$$\ln(-r_{PZ-O}) = \ln A - \frac{Ea}{RT} + m[C_{PZ}] + n[C_{DEA}] + o[CO_2] \tag{4.22}$$

4.5.6.3 Parameter optimization for PZ oxidation rate model

Parameters involving equation (4.22) are*: A, m, n, o* and *Ea*. Using the multiple linear least-squares regression, the experimental data obtained were regressed with a confidence interval of 95%. Parameters were obtained as coefficients of each operating parameter. Overall data set well fitted the model, as the regression coefficient (R^2) was found as 0.992. Optimized parameters are listed in Table 4.17.

Table 4.17: Optimized parameters of PZ and DEA for oxidative degradation rate models

Parameter	**Value**	
	PZ Model	**DEA Model**
lnA	4.53135±0.140	4.785±0.692
Ea (Joules/mole)	25919.31±237.36	37986.66±14153.75
m	1.712±0.001	
n	4.413±0.001	
o	2.337±0.002	
p		2.910±0.001
q		-0.991±0.002
r		2.0179±0.001
AAD(%)	0.762	0.207

4.5.6.4 Formulation of DEA degradation rate equation

A number of variables like concentration of DEA itself, concentration PZ and O_2 and temperature effected degradation rate of DEA. An empirical rate law, using power law model is postulated as presented in equation (4.23).

$$-r_{DEA-O} = k[C_{DEA}]^{p}[C_{PZ}]^{q}[CO_2]^{r} \tag{4.23}$$

Considering the Arrhenius equation for temperature dependence, equation (4.23) is converted into equation (4.24).

$$\ln(-r_{DEA-O}) = \ln A - \frac{Ea}{RT} + p[C_{DEA}] + q[C_{PZ}] + r[C_{O_2}] \tag{4.24}$$

Where $-r_{DEA-O}$ is the rate of oxidative degradation of DEA, coefficients *p, q* and *r*; are orders of the reaction with respect to DEA, PZ and O_2 respectively.

4.5.6.5 Parameter optimization for PZ oxidation rate model

Parameters involving equation (4.24) were: *A, u, v, w* and *Ea*. Using the multiple linear least-squares regression, the experimental data obtained was regressed with a confidence interval of 95%. Model is found to fit data quite well as the R^2 obtained for parameter optimization is 0.999. Optimized parameters of the DEA rate model are presented in Table 4.17.

4.5.6.6 Discussion on predicted and experimental results

Table 4.17 shows parametric evaluation of both models. Coefficients determined through the model show the intent of concentration of each reactant in the reaction. A positive value is responsible for synergistic effect and vice versa. In the model of PZ degradation rate, highest positive order is found for DEA, which indicates that rate of PZ loss is highly influenced by the concentration of DEA. The second most order is of O_2 concentration, which makes it responsible for the loss of PZ. Similarly, DEA rate model indicates that loss of DEA is mainly a function of O_2 concentration. However, the presence of PZ may antagonize the rate of reaction, as its value is negative. Both rate models were found to fit experimental data quite well. Predicted results are compared to those of experimental ones and are provided in Figure 4.30 and Figure 4.31.

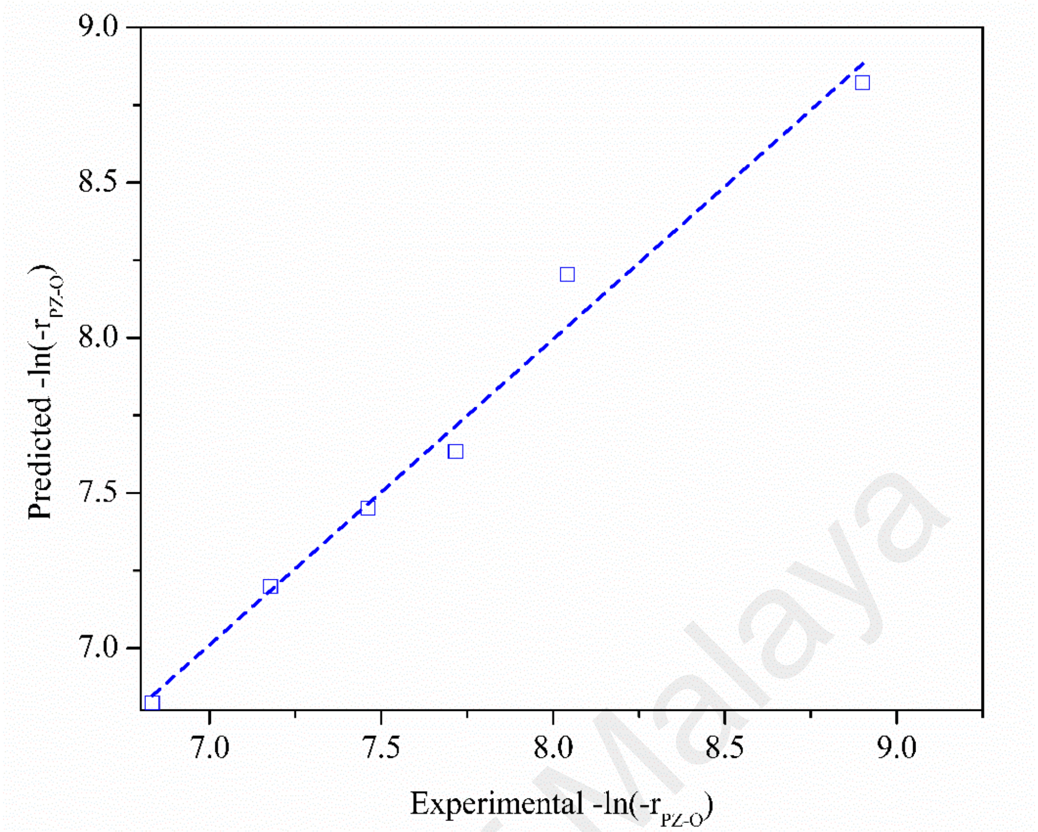


Figure 4.30: Parity chart of experimental and calculated values of $-\ln(-r_{PZ-O})$

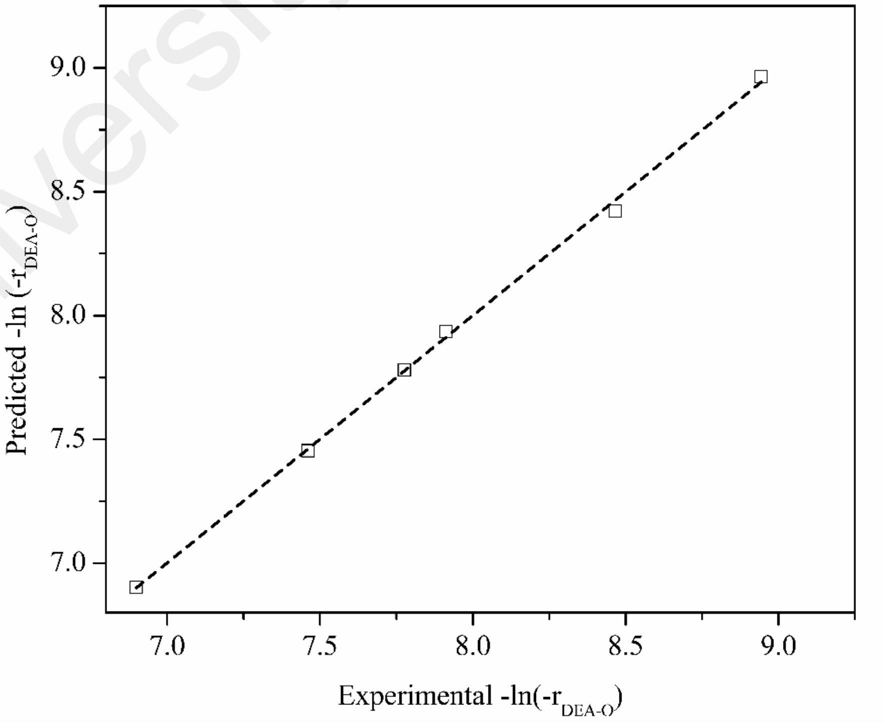


Figure 4.31: Comparison of calculated and experimental results of $-\ln(-r_{DEA-O})$

As shown in Figure 4.30 and Figure 4.31, the fit of predicted values against experimental looks in a good agreement. Furthermore, Absolute Average deviation percentage (AAD%) is less than one for both models as shown in Table 4.17, which signifies the authenticity of the models.

4.6 Contribution of the work

Current investigation shows a detailed stability evaluation of morpholine and blend of piperazine and diethanolamine under absorber and stripper conditions. The results of the blend, both under absorber and stripper conditions show that the system is vulnerable and may degrade quite significantly under process operating conditions. Hence, we do not suggest any further studies on the blended system. Whereas, results of morpholine are noteworthy and the amine is stable under absorber as well stripper conditions. Data obtained from this investigation can be used in designing the post-combustion CO_2 capture process and can be helpful for policymakers and engineers.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

5.1.1 Thermal degradation of morpholine

Five molal MOR was investigated for thermal degradation at 135-190 °C with a CO_2 loading of 0.0-48 mol CO_2/mol alkalinity. Several degradation products were identified using GC-MS. Carbonated solutions of MOR produced significant degradation products. At lower temperatures like 135 and 150 °C thermal degradation of MOR was minimal. However, loss of MOR sharply increased at 175 and 190 °C. Even though, loss of MOR is significant at higher temperatures, however, it is lower than most of the amines. Furthermore, CO_2 also imparted a positive effect on the loss of MOR, as CO_2 loading increased, loss of MOR increased. However, a higher CO_2 loading may inhibit the higher loss of MOR as observed at 0.48 mol CO_2/mol alkalinity. Loss of MOR was considered as first order, as natural log of amine concentration versus time provided almost a straight line. First order rate constants indicate that MOR is highly stable than other common amines like MEA, DEA, MDEA and PZ at elevated temperatures like 175 and 190 °C. Degradation kinetic model shows good results when matched with experimental results, and model's lower ADD % shows its validity.

5.1.2 Oxidative degradation of morpholine

Oxidation of five molal MOR was conducted at temperatures 40 to 60 °C and O_2 partial pressures of 50 and 90 kPa. In liquid phase solution, only two degradation products were identified. However, there are suspected ionic and gas phase products, which we could not identify due to limitations of the analytical apparatus. Degradation of MOR followed first order rate of reaction. The highest degradation was observed at 60 °C and 90 kPa, whereas the lowest was observed at 40 °C and 50 kPa. Results indicate that degradation of MOR is mainly a function of O_2 partial pressure; however, increase in temperature raises the rate of degradation. A rate equation is proposed for the degradation of MOR. Rate predicted by the model is in good agreement with the experimental results.

5.1.3 Thermal degradation piperazine and diethanolamine blend

Thermal degradation of PZ/DEA blend is investigated at 135 °C with a CO_2 loading range of 0 to 0.40 mol CO_2/mol alkalinity. A less number of degradation products in smaller quantities formed in unloaded blend. However, the formation of degradation products of DEA and PZ blend are higher and in bigger quantities at high CO_2 loading. BHEP, TEA, AEP, and OZD were the major degradation products of the blend. Formation of AEP and OZD was very less and inconsistent unlike BHEP and TEA. Increase in CO_2 loading increased the formation of BHEP and TEA. PZ was highly unstable in the blend and its degradation rate is up to 70 times of it individual at 0.40 mol CO_2/mol alkalinity at 135 °C. Meanwhile CO_2 loading also affected the loss of PZ in the blend to a similar margin as that of blend and individual. In comparison to other blends like PZ/MDEA, PZ/MEA and PZ/AMP, the loss of PZ was very high in PZ/DEA system. We anticipated the higher loss of PZ in PZ/DEA system to the formation of TEA, which was the most abundant degradation product of the system. EO formed from DEA is suspected to react with ammonia and AMPD to form TEA. We proposed an empirical rate law for the loss of PZ and DEA for the blended system in presence of CO_2. Calculated values of model are in good agreement with the experimental results for PZ. However, predicted results through DEA model are not in good agreement with the experimental results.

5.1.4 Oxidative degradation of piperazine and diethanolamine blend

Oxidation of PZ and DEA is a function of O_2 partial pressure and reaction temperature. Degradation rate of PZ was very high in the blend as compared to that of its individual degradation as reported in literature. On the other hand, DEA shown decent rate of degradation, which was relatively similar to literature. Proposed rate equations for degradation of DEA and PZ fitted experimental data with a good degree of agreement. The AAD (%) for DEA and PZ rate models are 0.207 and 0.762 respectively. Optimized parameters indicated that presence of DEA catalyze the degradation of PZ, however, PZ itself imparts an antagonistic effect on the degradation rate of DEA.

5.2 Recommendations

5.2.1 Reaction mechanism and its validation

Reaction mechanism helps in many ways, mainly in kinetics. We do not believe that based on basic chemistry any reaction mechanism can help in properly understanding and minimizing the kinetics of amine loss unless it is validated through different means, like kinetics and quantum mechanics. At present, a number of quantum thermochemical packages are available in market, which may be helpful in determining thermodynamics of the reaction. Once Gibbs free energy of reaction of the reaction is gained, this may help to determine that either reaction is spontaneous or non- spontaneous under conditions, reactions were conducted.

5.2.2 Further degradation experiments and analyses

In the current study, effect of metal concentration is not taken into the account. A good way to investigate furthermore the thermal and oxidative degradation of MOR may be to investigate the effect of metals on the rate of their degradation. Thermal degradation in a glass-lined reactor can provide the option of addition of metals. Furthermore, high-pressure reactor can also facilitate higher concentration of oxygen (partial pressure). We had limitations in our analytical and experimental setup. Online analyses of gaseous components would be very helpful in understanding the amine loss due to oxidation. Furthermore, to detect the concentrations of ionic species, ion chromatography can also be helpful for oxidation reactions.

5.2.3 Environmental aspect

Our findings on literature review show that amines degrade to form nitrosamines and nitramines, which are carcinogenic in nature. MOR should be investigated for the formation of nitrosamines and nitramines.

REFERENCES

Adeosun A., N., E Hadri, E., Goetheer, M. R.M., AbuZahra. (2013). Absorption of CO_2 by Amine Blends Solution: An Experimental Evaluation. *International Journal Of Engineering And Science, 3*(9), 12-23.

Al-Juaied, M., & Rochelle, G. T. (2006). Absorption of in aqueous blends of diglycolamine and morpholine. *Chemical Engineering Science, 61*(12), 3830-3837.

Ali, S. H., Al-Rashed, O., & Merchant, S. Q. (2010). Opportunities for faster carbon dioxide removal: A kinetic study on the blending of methyl monoethanolamine and morpholine with 2-amino-2-methyl-1-propanol. *Separation and Purification Technology, 74*(1), 64-72.

Alper, E. (1990). Kinetics of reactions of carbon dioxide with diglycolamine and morpholine. *The Chemical Engineering Journal, 44*(2), 107-111.

Aronu, U. E., Svendsen, H. F., Hoff, K. A., & Juliussen, O. (2009). Solvent selection for carbon dioxide absorption. *Energy Procedia, 1*(1), 1051-1057.

Bartsch, H., & Montesano, R. (1984). Relevance of nitrosamines to human cancer. *Carcinogenesis, 5*(11), 1381-1393.

Bello, A., & Idem, R. O. (2005a). Comprehensive Study of the Kinetics of the Oxidative Degradation of CO_2 Loaded and Concentrated Aqueous Monoethanolamine (MEA) with and without Sodium Metavanadate during CO_2 Absorption from Flue Gases. *Industrial & Engineering Chemistry Research, 45*(8), 2569-2579.

Bello, A., & Idem, R. O. (2005b). Pathways for the Formation of Products of the Oxidative Degradation of CO_2-Loaded Concentrated Aqueous Monoethanolamine Solutions during CO_2 Absorption from Flue Gases. *Industrial & Engineering Chemistry Research, 44*(4), 945-969.

Bindwal, A. B., Vaidya, P. D., & Kenig, E. Y. (2011). Kinetics of carbon dioxide removal by aqueous diamines. *Chemical Engineering Journal, 169*(1–3), 144-150.

Bishnoi, S., & Rochelle, G. T. (2000). Absorption of carbon dioxide into aqueous piperazine: reaction kinetics, mass transfer and solubility. *Chemical Engineering Science, 55*(22), 5531-5543.

Bishnoi, S., & Rochelle, G. T. (2002). Absorption of carbon dioxide in aqueous piperazine/methyldiethanolamine. *AIChE Journal, 48*(12), 2788-2799.

Bougie, F., & Iliuta, M. C. (2014). Stability of aqueous amine solutions to thermal and oxidative degradation in the absence and the presence of CO_2. *International Journal of Greenhouse Gas Control, 29*(0), 16-21.

BP. (2014). BP Energy Outlook 2035. *bp.com/energyoutlook*, 96.

Brúder, P., Grimstvedt, A., Mejdell, T., & Svendsen, H. F. (2011). CO_2 capture into aqueous solutions of piperazine activated 2-amino-2-methyl-1-propanol. *Chemical Engineering Science, 66*(23), 6193-6198.

Chakma, A. (1987). *Studies on DEA and MDEA Degradation.* University of British Columbia.

Chakma, A., & Meisen, A. (1986). Corrosivity of Diethanolamine Solutions and their Degradation Products. *Industrial & Engineering Chemistry Product Research and Development, 25*(4), 627-630.

Chakma, A., & Meisen, A. (1988). Identification of methyl diethanolamine degradation products by gas chromatography and gas chromatography-mass spectrometry. *Journal of Chromatography A, 457*, 287-297.

Chakma, A., & Meisen, A. (1997). Methyl-diethanolamine degradation—Mechanism and kinetics. *The Canadian Journal of Chemical Engineering, 75*(5), 861-871.

Chen, X., & Rochelle, G. T. (2011). Aqueous piperazine derivatives for CO_2 capture: Accurate screening by a wetted wall column. *Chemical Engineering Research and Design, 89*(9), 1693-1710.

Chi, S., & Rochelle, G. T. (2002). Oxidative Degradation of Monoethanolamine. *Industrial & Engineering Chemistry Research, 41*(17), 4178-4186.

Closmann, F., Nguyen, T., & Rochelle, G. T. (2009). MDEA/Piperazine as a solvent for CO_2 capture. *Energy Procedia, 1*(1), 1351-1357.

Closmann, F., & Rochelle, G. T. (2011). Degradation of aqueous methyldiethanolamine by temperature and oxygen cycling. *Energy Procedia, 4*, 23-28.

Closmann, F. B. (2011). *Oxidation and thermal degradation of methyldithanolamine/piperazine in CO_2 capture* pp. xxxi, 458

da Silva, E. F., Lepaumier, H., Grimstvedt, A., Vevelstad, S. J., Einbu, A., Vernstad, K., . . . Zahlsen, K. (2012). Understanding 2-Ethanolamine Degradation in Postcombustion CO_2 Capture. *Industrial & Engineering Chemistry Research, 51*(41), 13329-13338.

Dai, N., Shah, A. D., Hu, L., Plewa, M. J., McKague, B., & Mitch, W. A. (2012). Measurement of nitrosamine and nitramine formation from NO x reactions with amines during amine-based carbon dioxide capture for postcombustion carbon sequestration. *Environmental Science & Technology, 46*(17), 9793-9801.

Daniel Hatchell , G. R. (2014). Thermal Degradation of CO_2 Loaded Linear Diamines. *McKetta Department of Chemical Engineering, 4th Quarterly*.

Davis, J., & Rochelle, G. (2009). Thermal degradation of monoethanolamine at stripper conditions. *Energy Procedia, 1*(1), 327-333.

Davis, J. D. (2009). *Thermal degradation of aqueous amines used for carbon dioxide capture.* pp. xxix, 278.

Dawodu, O. F., & Meisen, A. (1996). Degradation of alkanolamine blends by carbon dioxide. *The canadian journal of chemical engineering, 74*(6), 960-966.

De Brito, M., Henriques, von Stockar, U. Bangerter, A. Menendez, Bomio, P. Laso, M. (1994). Effective Mass-Transfer Area in a Pilot Plant Column Equipped with Structured Packings and with Ceramic Rings. *Industrial & engineering chemistry research, 33*(3), 647-656.

Dennis Jr, W. H., Hull, L. A., & Rosenblatt, D. H. (1967). Oxidations of amines. IV. Oxidative fragmentation. *The Journal of Organic Chemistry, 32*(12), 3783-3787.

Derks, P., Hogendoorn, J., & Versteeg, G. (2010). Experimental and theoretical study of the solubility of carbon dioxide in aqueous blends of piperazine and N-methyldiethanolamine. *The Journal of Chemical Thermodynamics, 42*(1), 151-163.

Didas, S. A., Zhu, R., Brunelli, N. A., Sholl, D. S., & Jones, C. W. (2014). Thermal, Oxidative and CO_2 Induced Degradation of Primary Amines Used for CO_2 Capture: Effect of Alkyl Linker on Stability. *The Journal of Physical Chemistry C, 118*(23), 12302-12311.

Du, Y., Li, L., Namjoshi, O., Voice, A. K., Fine, N. A., & Rochelle, G. T. (2013). Aqueous Piperazine/N-(2-Aminoethyl) Piperazine for CO_2 Capture. *Energy Procedia, 37*(0), 1621-1638.

Dubois, L., & Thomas, D. (2009). CO_2 Absorption into Aqueous Solutions of Monoethanolamine, Methyldiethanolamine, Piperazine and their Blends. *Chemical Engineering & Technology, 32*(5), 710-718.

Dugas, R., & Rochelle, G. (2009). Absorption and desorption rates of carbon dioxide with monoethanolamine and piperazine. *Energy Procedia, 1*(1), 1163-1169.

Dumée, L., Scholes, C., Stevens, G., & Kentish, S. (2012). Purification of aqueous amine solvents used in post combustion CO_2 capture: A review. *International Journal of Greenhouse Gas Control, 10*, 443-455.

Eide-Haugmo, I., Lepaumier, H., Einbu, A., Vernstad, K., da Silva, E. F., & Svendsen, H. F. (2011). Chemical stability and biodegradability of new solvents for CO_2 capture. *Energy Procedia, 4*, 1631-1636.

Elnan, J. (2012). Screening of inhibitors for amine degradation. Norwegian University of Science and Technology. pp 110

Fredriksen, S. B., & Jens, K.-J. (2013). Oxidative Degradation of Aqueous Amine Solutions of MEA, AMP, MDEA, Pz: A Review. *Energy Procedia, 37*(0), 1770-1777.

Freeman, S. A. (2011). *Thermal degradation and oxidation of aqueous piperazine for carbon dioxide capture* pp.lvi, 734. Retrieved from https://repositories.lib.utexas.edu/bitstream/handle/2152/etd-ut-2011-05-3290/freeman-dissertation.pdf

Freeman, S. A., Chen, X., Nguyen, T., Rafique, H., Xu, Q., & Rochelle, G. T. (2013). Piperazine/N-methylpiperazine/N, N'-dimethylpiperazine as an Aqueous Solvent for Carbon Dioxide Capture. *Oil & Gas Science and Technology–Revue d'IFP Energies nouvelles*. 69 (5), 903-914

Freeman, S. A., Davis, J., & Rochelle, G. T. (2010). Degradation of aqueous piperazine in carbon dioxide capture. *International Journal of Greenhouse Gas Control, 4*(5), 756-761.

Freeman, S. A., Dugas, R., Van Wagener, D., Nguyen, T., & Rochelle, G. T. (2009). Carbon dioxide capture with concentrated, aqueous piperazine. *Energy Procedia, 1*(1), 1489-1496.

Freeman, S. A., Dugas, R., Van Wagener, D. H., Nguyen, T., & Rochelle, G. T. (2010). Carbon dioxide capture with concentrated, aqueous piperazine. *International Journal of Greenhouse Gas Control, 4*(2), 119-124.

Freeman, S. A., & Rochelle, G. T. (2011). Thermal degradation of piperazine and its structural analogs. *Energy Procedia, 4*(0), 43-50.

Freeman, S. A., & Rochelle, G. T. (2012a). Thermal Degradation of Aqueous Piperazine for CO_2 Capture. 1. Effect of Process Conditions and Comparison of Thermal Stability of CO_2 Capture Amines. *Industrial & engineering chemistry research, 51*(22), 7719-7725.

Freeman, S. A., & Rochelle, G. T. (2012b). Thermal Degradation of Aqueous Piperazine for CO_2 Capture: 2. Product Types and Generation Rates. *Industrial & engineering chemistry research, 51*(22), 7726-7735.

Freeman, S. A. D., Jason, Rochelle, Gary T. (2010). Degradation of aqueous piperazine in carbon dioxide capture. *International Journal of Greenhouse Gas Control, 4*(5), 1750-5836.

Ghalib, L., Ali, B. S., Ashri, W. M., & Mazari, S. (2016). Effect of piperazine on solubility of carbon dioxide using aqueous diethanolamnie. *Fluid Phase Equilibria, 414*, 1-13.

Goff, G. S., & Rochelle, G. T. (2004). Monoethanolamine degradation: O2 mass transfer effects under CO_2 capture conditions. *Industrial & engineering chemistry research, 43*(20), 6400-6408.

Goff, G. S., & Rochelle, G. T. (2004). Monoethanolamine Degradation: O_2 Mass Transfer Effects under CO_2 Capture Conditions. *Industrial & engineering chemistry research, 43*(20), 6400-6408.

Goff, G. S., & Rochelle, G. T. (2006). Oxidation inhibitors for copper and iron catalyzed degradation of monoethanolamine in CO_2 capture processes. *Industrial & engineering chemistry research, 45*(8), 2513-2521.

Gouedard, C., Picq, D., Launay, F., & Carrette, P.-L. (2012). Amine degradation in CO_2 capture. I. A review. *International Journal of Greenhouse Gas Control, 10*, 244-270.

Gouedard, C., Picq, D., Launay, F., & Carrette, P. L. (2012). Amine degradation in CO_2 capture. I. A review. *International Journal of Greenhouse Gas Control, 10*, 244-270.

Gunasekaran, P. (2012). *Corrosion Evaluation for Absorption-Based CO_2 Capture Process Using Single and Blended Amines.* Faculty of Graduate Studies and Research, University of Regina.

Hatchell, D., Namjoshi, O., Fischer, K., & Rochelle, G. T. (2014). Thermal Degradation of Linear Amines for CO_2 Capture. *Energy Procedia, 63*, 1558-1568.

Hilliard, M. D. (2008). *A predictive thermodynamic model for an aqueous blend of potassium carbonate, piperazine, and monoethanolamine for carbon dioxide capture from flue gas* pp. lvii, 1004. Retrieved from https://repositories.lib.utexas.edu/bitstream/handle/2152/3900/hilliardm66970.pdf

Holub, P., Critchfield, J., & Su, W.-Y. (1998). *Amine Degradation Chemistry in CO_2 Service.* Paper presented at the Proceedings of the Laurance Reid Gas Conditioning Conference.

Hsu, C. S., & Kim, C. J. (1985). Diethanolamine (DEA) degradation under gas-treating conditions. *Industrial & Engineering Chemistry Product Research and Development, 24*(4), 630-635.

Huang, Q., Thompson, J., Bhatnagar, S., Chandan, P., Remias, J. E., Selegue, J. P., & Liu, K. (2013). Impact of Flue Gas Contaminants on Monoethanolamine Thermal Degradation. *Industrial & Engineering Chemistry Research, 53*(2), 553-563.

Hull, L., Davis, G., Rosenblatt, D., Williams, H., & Weglein, R. (1967). Oxidations of amines. III. Duality of mechanism in the reaction of amines with chlorine dioxide. *Journal of the American Chemical Society, 89*(5), 1163-1170.

Idem, R., Wilson, M., Tontiwachwuthikul, P., Chakma, A., Veawab, A., Aroonwilas, A., & Gelowitz, D. (2005). Pilot Plant Studies of the CO_2 Capture Performance of Aqueous MEA and Mixed MEA/MDEA Solvents at the University of Regina CO_2 Capture Technology Development Plant and the Boundary Dam CO_2 Capture Demonstration Plant. *Industrial & engineering chemistry research, 45*(8), 2414-2420.

IEA. (2012). CO_2 emissions from fuel combustion highlights. *International Energy Agency, (2012) Edition*, 124.

IPCC. (2013). Climate Change 2013, the Physical Science Basis. *Intergovernmental panel on climate change, Fifth assessment report of the intergovernmental panel on climate change.*

Jamal, A., & Meisen, A. (2001). Kinetics of CO induced degradation of aqueous diethanolamine. *Chemical Engineering Science, 56*(23), 6743-6760.

Kenarsari, S. D., Yang, D., Jiang, G., Zhang, S., Wang, J., Russell, A. G., Fan, M. (2013). Review of recent advances in carbon dioxide separation and capture. *Rsc Advances, 3*(45), 22739-22773.

Kennard, M., & Meisen, A. (1980). Control DEA degradation. *Hydrocarbon processing, 60*(4), 103-106.

Kennard, M. L. (1983). *Degradation of diethanolamine solutions.* University of British Columbia.

Kennard, M. L., & Meisen, A. (1985). Mechanisms and kinetics of diethanolamine degradation. *Industrial & engineering chemistry fundamentals, 24*(2), 129-140.

Khosravi, B., Feyzi, F., Dehghani, M. R., & Kaviani, S. (2015). Experimental measurement and thermodynamic modeling of CO_2 solubility in aqueous solutions of morpholine. *Journal of Molecular Liquids*.

Kim, C., & Sartori, G. (1984). Kinetics and mechanism of diethanolamine degradation in aqueous solutions containing carbon dioxide. *International journal of chemical kinetics, 16*(10), 1257-1266.

Kim, C. J., & Sartori, G. (1984). Kinetics and mechanism of diethanolamine degradation in aqueous solutions containing carbon dioxide. *International Journal of Chemical Kinetics, 16*(10), 1257-1266.

Kindrick, R., Atwood, K., & Arnold, M. (1950). The relative resistance to oxidation of commercially available amines. *Girdler Corp. Report*(T2), 15-11.

Lawal, A. O., & Idem, R. O. (2006). Kinetics of the oxidative degradation of CO_2 loaded and concentrated aqueous MEA-MDEA blends during CO_2 absorption from flue gas streams. *Industrial & engineering chemistry research, 45*(8), 2601-2607.

Lawal, O., Bello, A., & Idem, R. (2005). The Role of Methyl Diethanolamine (MDEA) in Preventing the Oxidative Degradation of CO_2 Loaded and Concentrated Aqueous Monoethanolamine (MEA)−MDEA Blends during CO_2 Absorption from Flue Gases. *Industrial & Engineering Chemistry Research, 44*(6), 1874-1896. doi:10.1021/ie049261y

Lepaumier, H., da Silva, E. F., Einbu, A., Grimstvedt, A., Knudsen, J. N., Zahlsen, K., & Svendsen, H. F. (2011). Comparison of MEA degradation in pilot-scale with lab-scale experiments. *Energy Procedia, 4*, 1652-1659.

Lepaumier, H., Martin, S., Picq, D., Delfort, B., & Carrette, P.-L. (2010). New amines for CO_2 capture. III. Effect of alkyl chain length between amine functions on polyamines degradation. *Industrial & Engineering Chemistry Research, 49*(10), 4553-4560.

Lepaumier, H., Picq, D., & Carrette, P.-L. (2009a). New Amines for CO_2 Capture. I. Mechanisms of Amine Degradation in the Presence of CO_2. *Industrial & engineering chemistry research, 48*(20), 9061-9067.

Lepaumier, H., Picq, D., & Carrette, P.-L. (2009b). New amines for CO_2 capture. II. Oxidative degradation mechanisms. *Industrial & engineering chemistry research, 48*(20), 9068-9075.

Lepaumier, H., Picq, D., & Carrette, P. L. (2009). Degradation study of new solvents for CO_2 capture in post-combustion. *Energy Procedia, 1*(1), 893-900.

Li, H., Li, L., Nguyen, T., Rochelle, G. T., & Chen, J. (2013a). Characterization of Piperazine/2-Aminomethylpropanol for Carbon Dioxide Capture. *Energy Procedia, 37*, 340-352.

Li, L., Voice, A. K., Li, H., Namjoshi, O., Nguyen, T., Du, Y., & Rochelle, G. T. (2013). Amine blends using concentrated piperazine. *Energy Procedia, 37*(0), 353-369.

Lijinsky, W., & Epstein, S. S. (1970). Nitrosamines as environmental carcinogens. *Nature, 225*, 21-23.

Liu, K., Jinka, K. M., Remias, J. E., & Liu, K. (2013). Absorption of carbon dioxide in aqueous morpholine solutions. *Industrial & engineering chemistry research, 52*(45), 15932-15938.

Lowe, A., Beasley, B., & Berly, T. (2009). Chapter 3 Carbon Capture and Storage (CCS) in Australia *Carbon Capture: Sequestration and Storage* (Vol. 29, pp. 65-101): The Royal Society of Chemistry.

Luis, P. (2016). Use of monoethanolamine (MEA) for CO_2 capture in a global scenario: Consequences and alternatives. *Desalination, 380*, 93-99.

Ma'mun, S., Svendsen, H. F., Hoff, K. A., & Juliussen, O. (2007). Selection of new absorbents for carbon dioxide capture. *Energy Conversion and Management, 48*(1), 251-258.

MacDowell, N., Florin, N., Buchard, A., Hallett, J., Galindo, A., Jackson, G., Fennell, P. (2010a). An overview of CO_2 capture technologies. *Energy & Environmental Science, 3*(11), 1645-1669.

MacDowell, N., Florin, N., Buchard, A., Hallett, J., Galindo, A., Jackson, G., . . . Fennell, P. (2010b). An overview of CO_2 capture technologies. *Energy & Environmental Science, 3*(11), 1645-1669.

Mangalapally, H. P., Notz, R., Hoch, S., Asprion, N., Sieder, G., Garcia, H., & Hasse, H. (2009). Pilot plant experimental studies of post combustion CO_2 capture by reactive absorption with MEA and new solvents. *Energy Procedia, 1*(1), 963-970.

Matin, N. S., Remias, J. E., Neathery, J. K., & Liu, K. (2013). The equilibrium solubility of carbon dioxide in aqueous solutions of morpholine: Experimental data and thermodynamic modeling. *Industrial & engineering chemistry research, 52*(14), 5221-5229.

Mazari, S. A., Ali, B. S., Jan, B. M., & Saeed, I. M. (2014). Degradation study of piperazine, its blends and structural analogs for CO_2 capture: A review. *International Journal of Greenhouse Gas Control, 31*, 214-228.

Mazari, S. A., Ali, B. S., Jan, B. M., Saeed, I. M., & Nizamuddin, S. (2015). An overview of solvent management and emissions of amine-based CO_2 capture technology. *International Journal of Greenhouse Gas Control, 34*, 129--140.

McDonald, J. D., Kracko, D., Doyle-Eisele, M., Garner, C. E., Wegerski, C., Senft, A., . Rohr, A. (2014). Carbon Capture and Sequestration: An Exploratory Inhalation Toxicity Assessment of Amine-Trapping Solvents and Their Degradation Products. *Environmental Science & Technology*.

Mondal, M. K. (2009). Solubility of Carbon Dioxide in an Aqueous Blend of Diethanolamine and Piperazine†. *Journal of Chemical & Engineering Data, 54*(9), 2381-2385.

Mondal, M. K. (2010). Absorption of carbon dioxide into a mixed aqueous solution of diethanolamine and piperazine. *Indian J. Chem. Technol, 17*, 431-435.

Namjoshi, O., Li, L., Du, Y., & Rochelle, G. (2013). Thermal Degradation of Piperazine Blends with Diamines. *Energy Procedia, 37*(0), 1904-1911.

Nielsen, P. T., Li, L., & Rochelle, G. T. (2013). Piperazine Degradation in Pilot Plants. *Energy Procedia, 37*(0), 1912-1923.

Notz, R., Asprion, N., Clausen, I., & Hasse, H. (2007). Selection and Pilot Plant Tests of New Absorbents for Post-Combustion Carbon Dioxide Capture. *Chemical Engineering Research and Design, 85*(4), 510-515.

Paitoon, T., & Raphael, I. (2013). *Recent Progress and New Developments in Post-Combustion Carbon-Capture Technology with Reactive Solvents*: Future Science Ltd. pp 239

Pietsch, J., Sacher, F., Schmidt, W., & Brauch, H.-J. (2001). Polar nitrogen compounds and their behaviour in the drinking water treatment process. *Water research, 35*(15), 3537-3544.

Polderman, L., Dillon, C., & Steele, A. (1955). Why monoethanolamine solution breaks down in gas-treating service. *Oil Gas J, 54*(2), 180-183.

Puxty, G., Rowland, R., Allport, A., Yang, Q., Bown, M., Burns, R., . . . Attalla, M. (2009). Carbon Dioxide Postcombustion Capture: A Novel Screening Study of the Carbon Dioxide Absorption Performance of 76 Amines. *Environmental Science & Technology, 43*(16), 6427-6433.

Rao, A. B., & Rubin, E. S. (2002). A Technical, Economic, and Environmental Assessment of Amine-Based CO_2 Capture Technology for Power Plant Greenhouse Gas Control. *Environmental Science & Technology, 36*(20), 4467-4475.

Robert, R. B. (1930). Process for separating acidic gases: Google Patents.

Rochelle, G., Chen, E., Freeman, S., Van Wagener, D., Xu, Q., & Voice, A. (2011). Aqueous piperazine as the new standard for CO_2 capture technology. *Chemical Engineering Journal, 171*(3), 725-733.

Rochelle, G. T. (2009). Amine scrubbing for CO_2 capture. *Science, 325*(5948), 1652-1654.

Rochelle, G. T. (2012). Thermal degradation of amines for CO_2 capture. *Current Opinion in Chemical Engineering, 1*(2), 183-190.

Rooney, P., Dupart, M., & Bacon, T. (1998). *The Role of Oxygen in the Degradation of MEA, DGA, DEA and MDEA.* Paper presented at the proceedings of the laurance reid gas conditioning conference.

Rooney, P. C., & Daniels, D. D. (1998). Oxygen solubility in various alkanolamine/water mixtures. *Petroleum Technology Quarterly*, 97-102.

Rosenblatt, D., Hull, L., De Luca, D., Davis, G., Weglein, R., & Williams, H. (1967). Oxidations of amines. II. Substituent effects in chlorine dioxide oxidations. *Journal of the American Chemical Society, 89*(5), 1158-1163.

Rosenblatt, D. H., Hayes Jr, A. J., Harrison, B. L., Streaty, R. A., & Moore, K. A. (1963). The reaction of chlorine dioxide with triethylamine in aqueous solution1. *The Journal of Organic Chemistry, 28*(10), 2790-2794.

Samanta, A., & Bandyopadhyay, S. S. (2009). Absorption of carbon dioxide into aqueous solutions of piperazine activated 2-amino-2-methyl-1-propanol. *Chemical Engineering Science, 64*(6), 1185-1194.

Sexton, A. J. (2008). *Amine oxidation in CO_2 capture processes* pp. xxiv, 262. Retrieved from https://repositories.lib.utexas.edu/bitstream/handle/2152/18121/sextona75138.pdf

Sexton, A. J., & Rochelle, G. T. (2010). Reaction Products from the Oxidative Degradation of Monoethanolamine. *Industrial & Engineering Chemistry Research, 50*(2), 667-673.

Shao, R., & Stangeland, A. (2009). Amines used in CO_2 capture-Health and environmental impacts. *Bellona report, 49*.

Sherman, B., Chen, X., Nguyen, T., Xu, Q., Rafique, H., Freeman, S. A., Rochelle, G. T. (2013). Carbon Capture with 4 m Piperazine/4 m 2-Methylpiperazine. *Energy Procedia, 37*(0), 436-447.

Sieminski, A. (2013). International Energy Outlook 2013. *U.S. Energy Information Administration*, pp 33.

Strazisar, B. R., Anderson, R. R., & White, C. M. (2003). Degradation pathways for monoethanolamine in a CO_2 capture facility. *Energy & Fuels, 17*(4), 1034-1039.

Supap, T., Idem, R., Veawab, A., Aroonwilas, A., Tontiwachwuthikul, P., Chakma, A., & Kybett, B. D. (2001). Kinetics of the oxidative degradation of aqueous monoethanolamine in a flue gas treating unit. *Industrial & engineering chemistry research, 40*(16), 3445-3450.

Tontiwachwuthikul, P., Idem, R., Gelowitz, D., Liang, Z. H., Supap, T., Chan, C. W., . . . Smithson, H. (2011). Recent progress and new development of post-combustion carbon-capture technology using reactive solvents. *Carbon Management, 2*(3), 261-263.

Uyanga, I. J., & Idem, R. O. (2007). Studies of SO2- and O2-Induced Degradation of Aqueous MEA during CO_2 Capture from Power Plant Flue Gas Streams. *Industrial & Engineering Chemistry Research, 46*(8), 2558-2566.

Vevelstad, S. J., Grimstvedt, A., Elnan, J., da Silva, E. F., & Svendsen, H. F. (2013). Oxidative degradation of 2-ethanolamine: The effect of oxygen concentration and temperature on product formation. *International Journal of Greenhouse Gas Control, 18*, 88-100.

Vevelstad, S. J., Grimstvedt, A., Elnan, J., da Silva, E. F., & Svendsen, H. F. (2013). Oxidative degradation of 2-ethanolamine: The effect of oxygen concentration and temperature on product formation. *International Journal of Greenhouse Gas Control, 18*(0), 88-100.

Vevelstad, S. J., Grimstvedt, A., Knuutila, H., & Svendsen, H. F. (2013). Thermal Degradation on Already Oxidatively Degraded Solutions. *Energy Procedia, 37*(0), 2109-2117.

Voice, A. K., Closmann, F., & Rochelle, G. T. (2013). Oxidative Degradation of Amines With High-Temperature Cycling. *Energy Procedia, 37*(0), 2118-2132.

Voice, A. K., Hill, A., Fine, N. A., & Rochelle, G. T. (2015). Nitrosamine formation and mitigation in blended amines for CO_2 capture. *International Journal of Greenhouse Gas Control, 39*(0), 329-334.

Voice, A. K., & Rochelle, G. T. (2011). Oxidation of amines at absorber conditions for CO_2 capture from flue gas. *Energy Procedia, 4*(0), 171-178.

Wang, M., Lawal, A., Stephenson, P., Sidders, J., & Ramshaw, C. (2011). Post-combustion CO_2 capture with chemical absorption: A state-of-the-art review. *Chemical Engineering Research and Design, 89*(9), 1609-1624.

Wang, T. (2013). Degradation of Aqueous 2-Amino-2-methyl-1-propanol for Carbon Dioxide Capture. Doctoral dissertation, Telemark University College.

Wang, T., Hovland, J., & Jens, K. J. (2015). Amine reclaiming technologies in post-combustion carbon dioxide capture. *Journal of Environmental Sciences, 27*, 276-289.

Wang, T., & Jens, K.-J. (2012). Oxidative Degradation of Aqueous 2-Amino-2-methyl-1-propanol Solvent for Postcombustion CO_2 Capture. *Industrial & engineering chemistry research, 51*(18), 6529-6536.

Wang, T., & Jens, K.-J. (2012). A study of Oxidative Degradation of AMP for Post-combustion CO_2 Capture. *Energy Procedia, 23*, 102-110.

Wang, T., & Jens, K.-J. (2013). Oxidative Degradation of AMP/MEA Blends for Post-combustion CO_2 Capture. *Energy Procedia, 37*(0), 306-313.

Wang, T., & Jens, K.-J. (2014). Oxidative degradation of aqueous PZ solution and AMP/PZ blends for post-combustion carbon dioxide capture. *International Journal of Greenhouse Gas Control, 24*, 98-105.

Yang, H., Xu, Z., Fan, M., Gupta, R., Slimane, R. B., Bland, A. E., & Wright, I. (2008). Progress in carbon dioxide separation and capture: A review. *Journal of Environmental Sciences, 20*(1), 14-27.

Yu, C.-H., Huang, C.-H., & Tan, C.-S. (2012). A review of CO_2 capture by absorption and adsorption. *Aerosol Air Qual. Res, 12*(5), 745-769.

Zhang, X., Wang, J., Zhang, C.-f., Yang, Y.-h., & Xu, J.-j. (2003). Absorption rate into a MDEA aqueous solution blended with piperazine under a high CO_2 partial pressure. *Industrial & Engineering Chemistry Research, 42*(1), 118-122.

Zhou, S., Chen, X., Nguyen, T., Voice, A. K., & Rochelle, G. T. (2010). Aqueous Ethylenediamine for CO_2 Capture. *ChemSusChem, 3*(8), 913-918.

Zhou, S., Wang, S., & Chen, C. (2011). Thermal Degradation of Monoethanolamine in CO_2 Capture with Acidic Impurities in Flue Gas. *Industrial & Engineering Chemistry Research, 51*(6), 2539-2547.

Zhou, S., Wang, S., & Chen, C. (2012). Thermal degradation of monoethanolamine in CO_2 capture with acidic impurities in flue gas. *Industrial & Engineering Chemistry Research, 51*(6), 2539-2547.

Zoannou, K.-S., Sapsford, D. J., & Griffiths, A. J. (2013a). Thermal degradation of monoethanolamine and its effect on CO_2 capture capacity. *International Journal of Greenhouse Gas Control, 17*(0), 423-430.

Zoannou, K.-S., Sapsford, D. J., & Griffiths, A. J. (2013b). Thermal degradation of monoethanolamine and its effect on CO_2 capture capacity. *International Journal of Greenhouse Gas Control, 17*, 423-430.

LIST OF PUBLICATIONS AND PAPERS PRESENTED

ISI cited (Web of Science cited) publications from thesis

1. **Shaukat, A. Mazari,** Brahim Si Ali, Badrul M. Jan, and Idris Mohamed Saeed. "Degradation study of Piperazine, its blends and structural analogs for CO_2 capture: A review." International Journal of Greenhouse Gas Control 31 (2014): 214-228.
2. **Shaukat, A. Mazari,** Brahim Si Ali, Badrul M. Jan, Idris Mohamed Saeed, and S. Nizamuddin. "An overview of solvent management and emissions of amine-based CO_2 capture technology." International Journal of Greenhouse Gas Control 34 (2015): 129-140.
3. **Shaukat, A. Mazari,** Brahim Si Ali and Badrul M. Jan. "Thermal degradation of Piperazine and Diethanolamine blend for CO_2 capture." International Journal of Greenhouse Gas Control. 47C (2016): 1-7.
4. **Shaukat, A. Mazari**, Brahim Si Ali, Badrul M. Jan. (2016) "Thermal degradation of aqueous morpholine for CO_2 capture." International Journal of Greenhouse Gas Control (Under Review, JGGC-D-16-00266).
5. **Shaukat, A. Mazari,** Brahim Si Ali, Badrul M. Jan. (2016) "Degradation kinetics of oxidation of blended piperazine and diethanolamine for CO_2 capture." Journal of the Taiwan Institute of Chemical Engineers. (Under Review, JTICE-D-16-00616)
6. **Shaukat, A. Mazari,** Brahim Si Ali, Badrul M. Jan. "Degradation kinetics of oxidation of morpholine for CO_2 capture." (**Draft**).

Paper presentations

1. **Shaukat A. Mazari** and B.S. Ali (2014). “Regression Modeling of Thermal Degradation Kinetics, of Concentrated, Aqueous Piperazine in Carbon Dioxide Capture.” Seventh AUN/SEED-Net Regional Conference on Chemical Engineering (AUN/SEED-Net RCChE 2014).