

Experimental Studies for Development of a Purification Process for Single and Mixed Amine Solvents

A Thesis

Submitted to the Faculty of Graduate Studies and Research

In Partial Fulfillment of the Requirements

for the Degree of

Doctor of Philosophy

In Industrial Systems Engineering

University of Regina

By

Walid ElMoudir

Regina, Saskatchewan

October, 2012

Copyright 2012: W. ElMoudir

UNIVERSITY OF REGINA
FACULTY OF GRADUATE STUDIES AND RESEARCH
SUPERVISORY AND EXAMINING COMMITTEE

Walid Elmoudir, candidate for the degree of Doctor of Philosophy, has presented a thesis titled, ***Experimental Studies for Development of a Purification Process for Single and Mixed Amine Solvents***, in an oral examination held on October 4, 2012. The following committee members have found the thesis acceptable in form and content, and that the candidate demonstrated satisfactory knowledge of the subject material.

External Examiner: *Dr. Adesoji Adesina, University of New South Wales

Supervisor: Dr. Raphael Idem, Industrial Systems Engineering

Committee Member: Dr. Paitoon Tontiwachwuthikul,
Faculty of Engineering & Applied Science

Committee Member: Dr. R. Scott Murphy, Department of Chemistry & Biochemistry

Committee Member: Dr. David deMontigny, Industrial Systems Engineering

Chair of Defense: Dr. Dongyan Blachford, Faculty of Graduate Studies &
Research

*Not present at defense

Abstract

Amine solvents used for the removal of CO₂ from flue gas are subject to solvent degradation, which results from the reaction of impurities in the gas stream. This leads to the formation of degradation products, which could lead to many operational problems such as changes in the solvent absorption capacity and physical properties. Amine thermal (distillation) or non-thermal (ion-exchange or electrodialysis) reclamation are usually used to purify the solvents. In post-combustion CO₂ capture, thermal purification seems to be the only feasible method due to its ability to remove all types of degradation products. However, thermal reclamation has suffered from some challenges as follows:

- 1- The reclamation process might not effectively handle single or blended amine solvents. The solvent recovery could be low while its content in the waste stream could be high. The high consumption for water and energy cannot be justified.
- 2- Blended solvent could be difficult to purify due to the complicated nature of amine mixture with the degradation products.
- 3- The recovered solvent could be contaminated with light degradation products that have a closer boiling point to amine or are even lighter than amine.

To develop an efficient reclamation process, laboratory investigation was carried out for monoethanolamine (MEA) and monoethanolamine/methyldiethanolamine (MEA/MDEA). MEA is considered a reference solvent while MEA/MDEA is a potential candidate solvent for CO₂ capture. A number of degradation products were selected to create artificially-degraded solvents. The laboratory work was intended to address three

issues: understanding the impact of degradation, testing batch thermal reclamation and activated carbon treatment of contamination in recovered solvent.

The impact of degradation studies revealed that the degradation products have a noticeable impact on the solvent physical properties and absorption capacity. The measurement of density and refractive index showed proportional increases with degradation level. Moreover, the solvent absorption capacity diminished with increase of their concentrations. Process simulation of a CO₂ capture plant with ProTreat shows that the plant suffers from the presence of heat stable salts (HSSs).

In the thermal reclamation study, recovery of single and blended solvents was maximized to greater than 90-95% under deep vacuum. MEA was recovered in one step while MEA/MDEA was recovered in one or two steps. Optimum solvent recovery varied based on the degradation level and test conditions (temperature and pressure).

Recovered single or blended solvents exhibited at least some level of contamination; however, MEA solvent had less contamination than MEA/MDEA which depended on the types of degradation products selected for each system and the reclamation conditions. Adsorption treatment with three activated carbon types to remove the contamination was successful in the case of MEA/MDEA (50-60% removal), while the contamination removal for the MEA solvent was unsatisfactory (<10%).

Three industrial samples of degraded lean amine solvents were thermally purified and treated with adsorption. Almost all degradation products were eliminated in the two treatment steps, showing the new hybrid reclamation process (thermal at increased vacuum plus activated carbon) is a feasible method in treating industrial solvents.

Acknowledgment

I would like to express my grateful appreciation to Dr. Raphael Idem for his support and guidance to conduct this research. I would like to thank ITC staff for their assistance on utilizing GC-MC and HPLC. Special thanks go to Dr. Teera Supap and Robyn Fahlman. I would like to extend my appreciation to the Faculty of Engineering and Applied Science staff, especially in the Industrial System Engineering program. I specifically mention; Dr. Paitoon Tontiwachwuthikul, Dr. Pronnapa (Alex) Sanongboon, Dr. David deMontigny, Dr Christine Chan, Dr. Amr Henni, and Mr. William Misskey. Special thanks to Ms. Heidi Smithson for her time in proof reading of this thesis,

I would like to express my gratitude to HTC Pureenergy Inc. for providing the financial support necessary for this research and their assistance in getting industrial samples of amine solvent was really helpful in understanding the amine solvent degradation and purification. I want to thank the Libyan Petroleum Institute for the partial financial support. I would like also to express my acknowledgment to the financial support provided in the last year of studying by the Libyan Scholarship Program and Canadian Bureau for International Education. Activated carbon donation provided by Niort Americas Inc and Calgon Carbon Corporation is much appreciated.

Walid ElMoudir,

Regina, SK, Canada (June 2012)

Dedication

To my parents; **Mr Hosni ElMoudir** and **Ms. Rabia Alkhodar**

To my wife **Rabab** and my daughter **Ruqaya**

Table of Content

| | |
|---|------|
| Abstract | I |
| Acknowledgment | III |
| Dedication | IV |
| Table of Content | V |
| List of Tables | XV |
| List of Figures | XX |
| List of Photos | XXIX |
| Nomenclature/Abbreviation..... | XXX |
| Chapter 1: Introduction | 1 |
| 1.1 Chapter introduction | 1 |
| 1.2 Greenhouse gas effect and carbon dioxide contribution | 1 |
| 1.3 Available options for carbon dioxide emission control | 3 |
| 1.4 Post-combustion CO ₂ capture with amine solvents | 5 |
| 1.5 Solvent degradation and plant operation problems | 8 |
| 1.6 Solvent purification methods: the success and limitations..... | 11 |
| 1.7 Research objective | 12 |
| 1.8 Research Scope and Work Plan | 13 |
| Chapter 2: Amine Solvent Degradation (Literature Review) | 15 |

| | | |
|---------|---|----|
| 2.1 | Chapter introduction | 15 |
| 2.2 | Industrial samples of industrial lean amine and reclaimer waste..... | 15 |
| 2.3 | Amine solvent degradation | 16 |
| 2.3.1 | Solvent thermal degradation | 18 |
| 2.3.2 | Oxidative degradation..... | 18 |
| 2.3.2.1 | Heat Stable Salts (Organic Acids)..... | 19 |
| 2.3.2.2 | Amides | 20 |
| 2.3.2.3 | Amino Acids | 21 |
| 2.3.3 | CO ₂ or Carbamate Degradation..... | 23 |
| 2.3.3.1 | Primary Amine-CO ₂ -Degradations..... | 23 |
| 2.3.3.2 | Tertiary Amine-CO ₂ -Degradation | 24 |
| | Chapter 3: Problems Associated with Degradation Products (Literature Review)..... | 27 |
| 3.1 | Chapter introduction | 27 |
| 3.2 | Concentration and absorption capacity | 27 |
| 3.3 | Solvent physical properties | 27 |
| 3.4 | Solvent corrosivity | 29 |
| 3.5 | Solvent foaming tendency..... | 30 |
| 3.6 | Plugging, fouling, and deposition | 31 |
| 3.7 | Emission and effluent..... | 31 |
| 3.8 | Energy consumption | 32 |
| 3.9 | Solvent analysis..... | 32 |

| | | |
|---|---|----|
| 3.10 | Concluding remarks | 33 |
| Chapter 4: Amine Solvent Purification Methods (Literature Review) | | 34 |
| 4.1 | Chapter introduction | 34 |
| 4.2 | Solvent cleaning and degradation prevention methods..... | 34 |
| 4.2.1 | Change-over solvent inventory | 34 |
| 4.2.2 | Solvent purging/feeding..... | 35 |
| 4.2.3 | Mechanical filtration..... | 35 |
| 4.2.4 | Activated carbon filtration | 37 |
| 4.2.5 | On-line neutralization of heat stable salts | 38 |
| 4.2.6 | Solvent degradation inhibition | 40 |
| 4.3 | Recycling and Reclaiming Methods | 42 |
| 4.3.1 | Ion exchange reclaimer | 42 |
| 4.3.1.1 | Ion exchange reclaimer and CO ₂ capture applications | 44 |
| 4.3.2 | Electrodialysis reclamation | 49 |
| 4.3.3 | Thermal reclamation | 53 |
| 4.3.3.1 | Classical thermal reclaimer (atmospheric pressure or above)..... | 54 |
| 4.3.3.2 | Modern thermal reclaimers (atmospheric or below)..... | 61 |
| 4.3.3.3 | Molecular distillation reclaimer (deep vacuum) | 65 |
| 4.3.4 | Other reclamation methods | 66 |
| 4.3.4.1 | Combined reclamation processes..... | 66 |
| 4.3.4.2 | Removal of undesired primary and secondary amines in tertiary amines..... | 68 |

| | | |
|---|--|-----|
| 4.4 | Future trends for the reclamation industry | 69 |
| 4.4.1 | Need for hybrid processes..... | 69 |
| 4.5 | Concluding Remarks..... | 70 |
| Chapter 5: Experimental Work and Procedures..... | | 73 |
| 5.1 | Chapter introduction | 73 |
| 5.2 | Chemical, reagents, and adsorbents | 73 |
| 5.4 | Determination of amine solvent concentration and CO ₂ loading | 75 |
| 5.5 | Determination of total heat stable salt content..... | 76 |
| 5.7 | High pressure liquid chromatography with refractive index detector..... | 85 |
| 5.8 | Experimental set-ups for thermal purification and adsorption tests..... | 88 |
| 5.8.1 | Atmospheric and vacuum distillation set-ups | 89 |
| 5.8.2 | Adsorption Tests | 94 |
| Chapter 6: Amine Degradation Impact on Solvent Density and Refractive Index | | 99 |
| 6.1 | Chapter introduction | 99 |
| 6.2 | Solvent density measurements..... | 99 |
| 6.2.1 | Density measurement of pure amine solvent | 101 |
| 6.2.2 | Density measurement of degraded 5M MEA solvent..... | 103 |
| 6.2.3 | Density measurement of degraded 5M MEA/MDEA solvent | 108 |
| 6.3 | Refractive index measurements | 112 |
| 6.3.1 | Refractive index of MEA and MEA/MDEA concentrations | 113 |
| 6.3.2 | Refractive index of degraded 5M MEA and 5M MEA/MDEA solvents..... | 115 |

| | | |
|--|--|-----|
| 6.4 | Concluding remarks | 119 |
| Chapter 7: Heat Stable Salts and Their Neutralization in Amine Solvents..... | | 120 |
| 7.1 | Chapter introduction | 120 |
| 7.2 | Heat stable salts formation and their neutralization..... | 124 |
| 7.2.1 | Formic acid addition and neutralization..... | 124 |
| 7.2.2 | Acetic acid addition and neutralization..... | 129 |
| 7.2.3 | Impact of neutralization on degradation products (None-HSS)..... | 131 |
| 7.2.4 | Impact of neutralization of HSS in the presence of degradation products..... | 134 |
| 7.3 | Degraded 5M MEA with heat stable salts..... | 134 |
| 7.3.1 | MEA solvent available and unavailable with HSS | 134 |
| 7.3.2 | Neutralization of heat stable salts in 5M MEA solvent | 137 |
| 7.4 | Degraded 5M MEA/MDEA with heat stable salts..... | 138 |
| 7.4.1 | MEA/MDEA solvent available and unavailable with HSS | 138 |
| 7.4.2 | Neutralization of heat stable salts in MEA/MDEA solvent..... | 143 |
| 7.5 | Concluding remarks | 145 |
| Chapter 8 MEA Solvent Purification by Thermal Distillation..... | | 146 |
| 8.1 | Chapter introduction | 146 |
| 8.2 | Thermal degradation studies | 146 |
| 8.2.1 | Pure solvent thermal degradation..... | 149 |
| 8.2.2 | 5M MEA solvent thermal degradation..... | 150 |
| 8.3 | Recovery of 5M MEA solvent experiments..... | 153 |

| | | |
|----------|--|-----|
| 8.3.1 | First series of experiments for MEA solvent purification..... | 153 |
| 8.3.1.1 | MEA Recovery at 760 mmHg (MEA-1-760mmHg) | 154 |
| 8.3.1.2 | MEA Recovery at 660 mmHg (MEA-2-660mmHg) | 159 |
| 8.3.1.3 | MEA Recovery at 550 mmHg (MEA-3-550mmHg) | 159 |
| 8.3.1.4 | MEA Recovery at 460 mmHg (MEA-4-460mmHg) | 162 |
| 8.3.1.5 | MEA Recovery at 360 mmHg (MEA-5-360mmHg) | 162 |
| 8.3.1.6 | MEA Recovery at 260 mmHg (MEA-6-260mmHg) | 166 |
| 8.3.1.7 | Degraded solvent recovery at 260 mmHg (MEA-7-260mmHg) | 168 |
| 8.3.2 | Summary of first series of MEA purification tests | 168 |
| 8.3.3 | Second series of experiments for MEA solvent purification | 173 |
| 8.3.3.1 | Introduction..... | 173 |
| 8.3.3.2 | Thermal reclamation of MEA-1-0.00%-190mmHg..... | 173 |
| 8.3.3.3 | Thermal reclamation of MEA-2-0.00%-90mmHg..... | 178 |
| 8.3.3.4 | Thermal Reclamation of MEA-3-0.50%-210mmHg | 178 |
| 8.3.3.5 | Thermal Reclamation of MEA-4-1.50%-180mmHg | 181 |
| 8.3.3.6 | Thermal Reclamation of MEA-5-2.50%-180mmHg | 181 |
| 8.3.3.7 | Thermal reclamation of MEA-6-3.50%-180mmHg..... | 181 |
| 8.3.3.8 | Thermal Reclamation of MEA-7-4.0%-190mmHg | 185 |
| 8.3.3.9 | Thermal reclamation of MEA-8-5.0%-180mmHg..... | 188 |
| 8.3.3.10 | Identification of major chemicals contaminating the MEA distillate | 194 |
| 8.3.4 | Summary of Second Series of MEA Solvent Purification | 199 |

| | | |
|--|--|-----|
| 8.4 | Concluding Remarks..... | 201 |
| Chapter 9 MEA/MDEA Solvent Purification by Thermal Distillation..... | | 203 |
| 9.1 | Chapter introduction | 203 |
| 9.2 | Thermal degradation studies | 203 |
| 9.2.1 | Pure solvent thermal degradation..... | 204 |
| 9.2.2 | 5M MEA/MDEA solvent thermal degradation..... | 205 |
| 9.3 | Recovery of 5M MEA/MDEA solvent experiments..... | 209 |
| 9.3.1 | First series of experiments for MEA/MDEA solvent purification..... | 209 |
| 9.3.1.1 | MEA/MDEA recovery at 160 mmHg (MEA/MDEA-1-160mmHg)..... | 210 |
| 9.3.1.2 | MEA/MDEA recovery at 110-160 mmHg (MEA/MDEA-2-110/160mmHg)..... | 210 |
| 9.3.1.3 | MEA/MDEA recovery at 100-160 mmHg (MEA/MDEA-3-100/160mmHg)..... | 213 |
| 9.3.1.4 | MEA/MDEA recovery at 70-130 mmHg (MEA/MDEA-4-70/130mmHg)..... | 215 |
| 9.3.1.5 | MEA/MDEA recovery at 60-260 mmHg (MEA/MDEA-5-60/260mmHg)..... | 217 |
| 9.3.1.6 | MEA/MDEA recovery at 65 mmHg(MEA/MDEA-6-65mmHg)..... | 219 |
| 9.3.1.7 | MEA/MDEA recovery at 70-205 mmHg (MEA/MDEA-7-70/205mmHg)..... | 223 |
| 9.3.2 | Summary of first series of MEA/MDEA purification..... | 227 |
| 9.3.3 | Second Series of Experiments for MEA/MDEA Solvent Purification | 229 |
| 9.3.3.1 | Thermal reclamation of MEA/MDEA-1-0.0%-70mmHg..... | 232 |
| 9.3.3.2 | Thermal reclamation of MEA/MDEA-2-0.0%-75mmHg..... | 232 |
| 9.3.3.3 | Thermal reclamation of MEA/MDEA-3-0.5%-75mmHg..... | 234 |
| 9.3.3.4 | Thermal reclamation of MEA/MDEA-4-1.0%-70mmHg..... | 237 |

| | | |
|--|--|-----|
| 9.3.3.5 | Thermal reclamation of MEA/MDEA-5-2.0%-75mmHg..... | 237 |
| 9.3.3.6 | Thermal reclamation of MEA/MDEA-6-3.0%-75mmHg..... | 243 |
| 9.3.3.7 | Thermal reclamation of MEA/MDEA-7-4.0%-75mmHg..... | 243 |
| 9.3.3.8 | Thermal reclamation of MEA/MDEA-8-5.0%-70mmHg..... | 249 |
| 9.3.4 | Summary of Second Series of MEA/MDEA Solvent Purification..... | 256 |
| 9.4 | Concluding Remarks..... | 258 |
| Chapter 10 Purifying Solvent Distillates by Activated Carbon Adsorption..... | | 261 |
| 10.1 | Chapter introduction..... | 261 |
| 10.2 | Purifying of MEA distillates..... | 264 |
| 10.2.1 | Wettability of Activated Carbon..... | 264 |
| 10.2.2 | Isothermal tests to treat MEA distillates..... | 266 |
| 10.2.2.1 | SGL activated carbon treatment..... | 266 |
| 10.2.2.2 | M-1657 activated carbon treatment..... | 270 |
| 10.2.2.3 | M-1731 activated carbon treatment..... | 270 |
| 10.2.3 | Dynamic adsorption of 5M MEA distillates..... | 274 |
| 10.2.3.1 | Closed-loop dynamic adsorption..... | 274 |
| 10.2.3.2 | Open-loop dynamic adsorption..... | 276 |
| 10.3 | Purifying of MEA/MDEA Distillates..... | 280 |
| 10.3.1 | Wettability of Activated Carbon..... | 280 |
| 10.3.2 | Isothermal adsorption to treat MEA/MDEA distillates..... | 282 |
| 10.3.2.1 | SGL activated carbon treatment..... | 282 |

| | | |
|--|---|-----|
| 10.3.2.2 | M-1657 activated carbon treatment | 287 |
| 10.3.2.3 | M-1731 activated carbon treatment | 287 |
| 10.3.3 | Isothermal adsorption to treat distillate of MEA/MDEA-4-1.0%-70mmHg | 290 |
| 10.3.4 | Dynamic adsorption for MEA/MDEA solvent | 295 |
| 10.4 | Concluding Remarks..... | 303 |
| Chapter 11: Evaluation of Purification and Treating Industrial Samples | | 305 |
| 11.1 | Chapter introduction | 305 |
| 11.2 | Evaluation of industrial samples from Plant A | 305 |
| 11.2.1 | Thermal reclamation of plant A lean amine..... | 306 |
| 11.2.2 | Activated carbon treatment of recovered distillate of Plant A..... | 309 |
| 11.3 | Evaluation of industrial samples from Plant B | 311 |
| 11.3.1 | Thermal reclamation of Plant B lean amine..... | 313 |
| 11.3.2 | Activated carbon treatment of recovered distillate of Plant B | 315 |
| 11.4 | Evaluation of industrial samples from Plant C | 317 |
| 11.4.1 | Thermal reclamation of Plant C lean amine..... | 317 |
| 11.4.2 | Activated carbon treatment of recovered distillate of Plant C | 320 |
| 11.5 | Concluding Remarks..... | 320 |
| Chapter 12: Simulation of CO ₂ Capture Plant with/without HSS | | 322 |
| 12.1 | Chapter introduction | 322 |
| 12.2 | CO ₂ capture plant with MEA solvent..... | 322 |
| 12.3 | CO ₂ capture plant with MEA/MDEA solvent | 329 |

| | | |
|------|--|-----|
| 12.4 | Concluding Remarks..... | 333 |
| | Chapter 13: Conclusions and Recommendation for Future Work..... | 334 |
| 13.1 | Conclusions..... | 334 |
| 13.2 | Recommendations for future work..... | 336 |
| | Reference | 338 |
| | Appendices..... | 350 |
| | Appendix A: The Impact of Slip Ratio of Lean Amine on the Solvent Reclamation..... | 350 |
| | Appendix B: Analysis Sample of acid gas loading, HSS and Solvent Concentration | 352 |
| | Appendix C: ProMax process simulator prediction for MEA-water VLE..... | 355 |
| | Appendix D: Tables of laboratory equipments, tools and consumables | 356 |
| | Appendix E: Material ad Energy Balance for MEA solvent with 0% HSS Case | 365 |

List of Tables

| | |
|--|-----|
| Table 1 MPR service recommendation for HSS limitation | 22 |
| Table 2 MEA and MEA/MDEA Degradation with presence of CO ₂ and/or O ₂ | 22 |
| Table 3 Impact of degradation products on solvent physical properties..... | 28 |
| Table 4 Difference between natural gas and CO ₂ capture processes | 47 |
| Table 5 Development of ion-exchange reclaimer | 48 |
| Table 6 Development of classical thermal reclaimer..... | 58 |
| Table 7 Advantages and disadvantages of solvent thermal reclamation | 60 |
| Table 8 Ability comparison of different contamination mitigation methods | 72 |
| Table 9 Chemicals utilized in this research | 74 |
| Table 10 Degradation products selected for MEA and MEA/MDEA solvents..... | 77 |
| Table 11 Titration method to determine the solvent concentration and CO ₂ loading | 78 |
| Table 12 GC-MS conditions for determination of amine solvents and degradation products..... | 82 |
| Table 13 Purification of primary, secondary, and tertiary amines (Armarego and Chai 2009) | 91 |
| Table 14 Predict the degradation content in random prepared amine solvents | 117 |
| Table 15 Comparison of heat unstable and stable salts (Cummings et al 2007) | 122 |
| Table 16 Heat stable salt matrix in amine system..... | 122 |
| Table 17 Organic acids selected for formation of HSSs in amine solvents..... | 123 |
| Table 18 Impact of heat stable salts on MEA solvent concentration..... | 136 |
| Table 19 Determination of heat stable salts on 5M MEA solvent | 136 |

| | |
|---|-----|
| Table 20 Comparing four bases in neutralization of organic acids (or HSS) in 5M MEA | 139 |
| Table 21 Impact of heat stable salt on MEA/MDEA solvent concentration | 141 |
| Table 22 Determination of heat stable salts in 5M MEA/MDEA solvent | 141 |
| Table 23 MEA and MDEA content with HSS and their concentration change..... | 142 |
| Table 24 Comparing four bases in neutralization of organic acids (or HSS) in 5M MEA/MDEA..... | 144 |
| Table 25 Analysis of degraded pure solvents by GC-MS..... | 151 |
| Table 26 Thermal degradation of 5M MEA at different temperature..... | 151 |
| Table 27 Summary for recovery of degraded MEA (MEA-7-260mmHg) | 169 |
| Table 28 Series I summary of MEA reclamation | 171 |
| Table 29 Analysis summary of MEA-1-0.00%-190mmHg samples | 176 |
| Table 30 Analysis summary of MEA-2-0.00%-90mmHg samples | 179 |
| Table 31 Analysis summary of MEA-3-0.50%-210mmHg samples | 179 |
| Table 32 Analysis Summary of MEA-4-1.50%-180mmHg Samples..... | 182 |
| Table 33 Analysis summary of MEA-5-2.50%-180mmHg samples | 182 |
| Table 34 Analysis summary of MEA-6-3.50%-180mmHg samples | 183 |
| Table 35 Analysis Summary of MEA-7-4.0%-190mmHg Samples..... | 183 |
| Table 36 GC-MS inditification for chemicals found in distillate of MEA-7-4.0%- 190mmHg | 186 |
| Table 37 Analysis Summary of MEA-8-5.0%-180mmHg Samples..... | 189 |
| Table 38 GC-MS inditification for degradation prodcuts found in distillate (MEA-7- 4.0%-190mmHg) | 193 |

| | |
|---|-----|
| Table 58 GC-MS identification for degradation products added/found in distillate MEA/MDEA-5-2.0%-75mmHg | 245 |
| Table 59 GC-MS identification for degradation products added/found in distillate MEA/MDEA-7-4.0%-75mmHg | 247 |
| Table 60 Analysis Summary of MEA/MDEA-8-5.0%-70mmHg Samples | 250 |
| Table 61 GC-MS Identification for Degradation Products Added/Found in Blended Solvent MEA/MDEA-7-4.0%-75mmHg | 253 |
| Table 62 GC-MS Identification for Degradation Products Added/Found in Distillate MEA/MDEA-7-4.0%-75mmHg | 254 |
| Table 63 Estimated molecular size based on chemicalize.org..... | 263 |
| Table 64 Activated carbon characteristics selected for this study | 263 |
| Table 65 Wettability of activated carbons with water and MEA solvent | 265 |
| Table 66 Wettability of activated carbons with water and MEA/MDEA solvent | 281 |
| Table 67 Degradation products distribution in distillate MEA/MDEA-4-1.0%-70mmHg | 291 |
| Table 68 Amines and degradation products used for dynamic adsorption test | 297 |
| Table 69 Summary of Reclamation of Plant A Lean Amine | 307 |
| Table 70 Summary of reclamation of Plant B lean amine | 307 |
| Table 71 Predicted degradation products in lean amine of Plant B | 312 |
| Table 72 Summary of reclamation of Plant C lean amine | 318 |
| Table 73 Degradation products found in distillate of Plant C | 318 |
| Table 74 Flue gas conditions used for simulation (Hendriks 1994) | 324 |
| Table 75 ProTreat simulation model parameters for MEA solvent cases..... | 325 |

| | |
|---|-----|
| Table 76 Predicted impact of HSS in MEA solvent on CO ₂ capture plant | 327 |
| Table 77 ProTreat simulation model parameters for MEA solvent cases..... | 330 |
| Table 78 Predicted impact of HSS in MEA/MDEA solvent on CO ₂ capture plant | 331 |
| Table 79 Supporting equipments and devices..... | 356 |
| Table 80 GC and HPLC consumables | 360 |
| Table 81 Adsorption set-up components | 361 |
| Table 82 Distillation set-up components | 361 |
| Table 83 Summary of M&EB for MEA solvent with 0% HSS (Part 1)..... | 365 |
| Table 84 Summary of M&EB for MEA solvent with 0% HSS (Part 2)..... | 366 |

List of Figures

| | |
|---|-----|
| Figure 1 World energy supply by fuel type (A) and CO ₂ emissions (B), OPEC (2010).... | 2 |
| Figure 2 Options for CO ₂ capture from flue gas streams (StatoilHydro 2009)..... | 4 |
| Figure 3 CO ₂ capture process with illustration of Amine-CO ₂ chemical reactions..... | 7 |
| Figure 4 GC chromatograph of lean amine (A) and reclaimer waste (B)..... | 17 |
| Figure 5 Dow Electrodialysis Process: UCARSEP (Burns and Gregory 1995a; Parisi and Bosen 2006b) | 51 |
| Figure 6 ElectroSep electrodialysis process (Parisi and Bosen 2006b)..... | 51 |
| Figure 7 Liquid-gas equilibrium curve of a MEA-water system (Dow 1962)..... | 59 |
| Figure 8 Results of obtaining calibration curves of MEA solvent..... | 83 |
| Figure 9 GC-MS chromatograph for degraded MEA (A) and summary of chemical identification for each peak (B) | 84 |
| Figure 10 HPLC system for determination of amine concentration..... | 86 |
| Figure 11 Simple (A) and fractionation (B) distillation set-ups (Lehman 2008)..... | 92 |
| Figure 12 Distillation of liquid mixture and impact of boiling point of contents on separation (Krell 1981) | 93 |
| Figure 13 Porosity and its role in adsorption in activated carbon (Norit Activated Carbon 2001) | 97 |
| Figure 14 Carbon loading for activated carbon (Norit Activated Carbon 2001)..... | 97 |
| Figure 15 Dynamic breakthrough curve of activated carbon (Clark and Jr 1989) | 98 |
| Figure 16 Observed density of pure MEA vs. ProMax and ProTreat predictions | 102 |

| | |
|---|-----|
| Figure 17 Parity chart of observed density of pure MEA vs. ProMax and ProTreat predictions..... | 102 |
| Figure 18 Observed density of pure MDEA vs. ProMax and ProTreat predictions | 104 |
| Figure 19 Parity chart of observed density of pure MDEA vs. ProMax and ProTreat predictions..... | 104 |
| Figure 20 Observed density of 5M MEA vs. ProMax and ProTreat predictions | 106 |
| Figure 21 Parity chart of observed density of 5M MEA vs. ProMax and ProTreat predictions..... | 106 |
| Figure 22 Observed density of 5M MEA solvents vs. temperature and total degradation product concentration..... | 107 |
| Figure 23 Observed density of 5M MDEA vs. ProMax and ProTreat predictions..... | 110 |
| Figure 24 Parity chart of observed density of 5M MDEA vs. ProMax and ProTreat predictions..... | 110 |
| Figure 25 Observed density of 5M MDEA vs. temperature and total degradation product concentration..... | 111 |
| Figure 26 Refractive Index vs. MEA Concentration | 114 |
| Figure 27 Refractive Index vs. MEA/MDEA Concentration | 114 |
| Figure 28 Refractive Index of MEA solvent vs. degradation product concentration | 118 |
| Figure 29 Refractive Index of MEA/MDEA vs. degradation product concentration..... | 118 |
| Figure 30 MEA GC Chromatographs of clean solvent (A), solvent with formic acid (B), and neutralized solvent (C) | 127 |
| Figure 31 GC Chromatograph for MEA/MDEA with formic acid..... | 128 |

| | |
|---|-----|
| Figure 32 MEA GC Chromatographs with acetic acid before (A) and after neutralization (B) | 130 |
| Figure 33 GC Chromatographs for MEA/MDEA with acetic acid | 130 |
| Figure 34 GC chromatograph of degraded MEA/MDEA and impact of the neutralization on degradation products | 132 |
| Figure 35 GC chromatograph of neutralization of heat stable salts in a degraded MEA/MDEA solvent | 133 |
| Figure 36 Dow thermal stability tests for MEA and DEA (Dow 1962) | 148 |
| Figure 37 Refractive index for thermally degraded 5M MEA..... | 152 |
| Figure 38 Series I for MEA recovery tests | 155 |
| Figure 39 Vapour-liquid relationship for MEA-Water system (MEA-1-760 mmHg) ... | 157 |
| Figure 40 Enhanced recovery of MEA with water dilution vs. dilution and reclamation cycles (MEA-1-760 mmHg) | 158 |
| Figure 41 Vapour-liquid relationship for MEA-Water system (MEA-2-660 mmHg) ... | 160 |
| Figure 42 Enhanced recovery of MEA with water dilution vs. dilution and reclamation cycle (MEA-2-660 mmHg)..... | 161 |
| Figure 43 Enhanced recovery of MEA with water dilution vs. dilution and reclamation cycle (MEA-3-550 mmHg)..... | 163 |
| Figure 44 Enhanced recovery of MEA with water dilution vs. dilution and reclamation cycle (MEA-4-460 mmHg)..... | 164 |
| Figure 45 Vapour-liquid relationship for MEA-Water system (MEA-5-360 mmHg) ... | 165 |
| Figure 46 Vapour-liquid relationship for MEA-Water system (MEA-6-260 mmHg) ... | 165 |

| | |
|---|-----|
| Figure 47 Enhanced recovery of MEA with water dilution vs. dilution and reclamation cycle (MEA-6-260 mmHg)..... | 167 |
| Figure 48 GC chromatograph of MEA, distillate, and residue (MEA-7-260mmHg)..... | 170 |
| Figure 49 Summary of total solvent and pure MEA recoveries for Series I..... | 172 |
| Figure 50 Procedure for test solvent preparation..... | 175 |
| Figure 51 Series II for MEA recovery tests | 175 |
| Figure 52 Distillation evaluation sheet of MEA-1-0.00%-190mmHg..... | 177 |
| Figure 53 GC chromatograph of residue MEA-2-0.00%-90mmHg | 180 |
| Figure 54 GC chromatograph of distillate of MEA-3-0.50%-210mmHg..... | 180 |
| Figure 55 GC chromatograph of distillate of MEA-6-3.50%-180mmHg..... | 184 |
| Figure 56 GC chromatograph of distillate of MEA-7-4.0%-190mmHg..... | 187 |
| Figure 57 GC-MS chemical identification of peak 11.088 min in distillate MEA-7-4.0%-190mmHg | 187 |
| Figure 58 Top and bottom temperature profiles for MEA-8-5.0%-180mmHg | 190 |
| Figure 59 Distillation evaluation sheet of MEA-8-5.0%-180mmHg..... | 191 |
| Figure 60 GC chromatograph of distillate of MEA-8-5.0%-180mmHg..... | 192 |
| Figure 61 GC-MS chemical identification of peak 17.581 min of distillate (MEA-8-5.0%-180mmHg) | 192 |
| Figure 62 GC chromatograph of MEA-Ammonium hydroxide system | 195 |
| Figure 63 GC-MS evaluation of first unknown peak (Ammonia) MEA-NH ₄ OH system | 195 |
| Figure 64 Spectrum of ammonia of MEA-Ammonium hydroxide system | 196 |

| | |
|--|-----|
| Figure 65 GC-MS evaluation of second unknown peak (ammonium carbamate) MEA-NH ₄ OH System..... | 197 |
| Figure 66 GC chromatograph of MEA-Ethylamine system | 197 |
| Figure 67 GC-MS evaluation of unknown peak MEA-Ethylamine system | 198 |
| Figure 68 Spectrum of Ethylamine of MEA-Ethylamine system..... | 198 |
| Figure 69 MEA solvent recovery for 8 tests excluding solvent recovered by washing.. | 200 |
| Figure 70 MEA solvent recovery for 8 tests including solvent recovered by washing .. | 200 |
| Figure 71 Refractive index for thermally degraded 5M MEA/MDEA..... | 207 |
| Figure 72 GC chromatograph for distillate (A) and residue (B) of MEA/MDEA-1-160mmH | 208 |
| Figure 73 Series I for MEA/MDEA recovery tests..... | 211 |
| Figure 74 GC chromatograph of degraded solvent (A), distillate (B), and residue (C) (MEA/MDEA-3-100/160mmHg) | 214 |
| Figure 75 GC chromatograph for solvent (A), distillates (B &C), and residue (D) (MEA/MDEA-5-60/260mmHg) | 218 |
| Figure 76 Temperature profiles of top and bottom (MEA/MDEA-6-65mmHg)..... | 220 |
| Figure 77 GC chromatograph for solvent (A), distillates (B,C,D,E), and residue (F) (MEA/MDEA-6-65mmHg) | 221 |
| Figure 78 Temperature profiles of top and bottom (MEA/MDEA-7-70/205mmHg)..... | 225 |
| Figure 79 GC chromatograph for solvent (A), distillates (B,C,D), and residue (E)(MEA/MDEA-7-70/205mmHg) | 226 |
| Figure 80 MEA/MDEA solvent recovery vs. degradation level..... | 228 |
| Figure 81 Test Solvent Preparation Procedure for MEA/MDEA Solvent..... | 230 |

| | |
|--|-----|
| Figure 82 Series II Tests and Degradation Products/HSS Used for MEA/MDEA..... | 230 |
| Figure 83 Chromatograph of loaded and degraded mixed solvent and distillate of MEA/MDEA-3-0.5%-75mmHg | 236 |
| Figure 84 Chromatograph of loaded and degraded mixed solvent and distillate of MEA/MDEA-4-1.0%-70mmHg | 239 |
| Figure 85 Chromatograph of unloaded and degraded mixed solvent and distillate of MEA/MDEA-5-2.0%-75mmHg | 242 |
| Figure 86 Chromatograph of unloaded and degraded mixed solvent and distillate of MEA/MDEA-6-3.0%-75mmHg | 246 |
| Figure 87 Chromatograph of unloaded and degraded mixed solvent and distillate of MEA/MDEA-7-4.0%-75mmHg | 248 |
| Figure 88 Top and Bottom Temperature Profiles for MEA/MDEA-8-5.0%-70mmHg . | 251 |
| Figure 89 Distillation experiment calculation sheet of MEA/MDEA-8-5.0%-70mmHg | 252 |
| Figure 90 Chromatograph of Unloaded and Degraded Mixed Solvent and Distillate of MEA/MDEA-8-5.0%-70mmHg | 255 |
| Figure 91 MEA/MDEA recovery tests excluding the solvent recovered by washing. | 257 |
| Figure 92 MEA/MDEA recovery tests including the washing solvent recovered..... | 257 |
| Figure 93 Isotherm of dry SGL for contaminants and others species in MEA..... | 267 |
| Figure 94 Isotherm of water wetted SGL for contaminants and others species in MEA | 267 |
| Figure 95 Isotherm of water wetted SGL for contaminants and others species in MEA | 268 |
| Figure 96 Isotherm SGL for removing ammonia (A) and ethylamine (B) in MEA | 269 |
| Figure 97 Isotherm of dry M-1657 for contaminants and others species in MEA | 271 |

| | |
|--|-----|
| Figure 98 Isotherm of water wetted M-1657 for contaminants and others species in MEA | 271 |
| Figure 99 Isotherm of MEA wetted M-1657 for species in MEA solvent | 272 |
| Figure 100 Isotherm of dry M-1731 for species in MEA solvent..... | 272 |
| Figure 101 Isotherm of water wetted M-1731 for species in MEA solvent | 273 |
| Figure 102 Isotherm of MEA wetted M-1731 for species in MEA solvent | 273 |
| Figure 103 Schematic diagram of closed-loop activated carbon dynamic adsorption test – MEA solvent | 277 |
| Figure 104 Closed-loop dynamic adsorption curves of water wetted SGL with water .. | 278 |
| Figure 105 Closed-loop dynamic adsorption curves of MEA wetted SGL with MEA .. | 278 |
| Figure 106 Open-loop dynamic adsorption curves of MEA wetted SGL with MEA | 279 |
| Figure 107 Open-loop dynamic adsorption curves of MEA wetted M-1731 with MEA | 279 |
| Figure 108 Isotherm of dry SGL for contaminants in MEA/MDEA..... | 284 |
| Figure 109 Isotherm of water wetted SGL for contaminants in MEA/MDEA..... | 284 |
| Figure 110 Isotherm of amines wetted SGL for contaminants in MEA/MDEA | 285 |
| Figure 111 Isotherm SGL loading for 3-Picoline vs. 3-Picoline remaining in MEA/MDEA..... | 286 |
| Figure 112 Isotherm SGL loading for N-(2-hydroxyethyl) ethanol vs. N-(2-hydroxyethyl) ethanol remaining in MEA/MDEA..... | 286 |
| Figure 113 Isotherm M-1657 loading for 3-Picoline vs. 3-Picoline remaining in MEA/MDEA..... | 288 |
| Figure 114 Isotherm M-1657 loading for N-(2-hydroxyethyl) ethanol vs. N-(2- hydroxyethyl) ethanol remaining in MEA/MDEA | 288 |

| | |
|---|-----|
| Figure 115 Isotherm M-1731 loading for 3-Picoline vs. 3-Picoline remaining in MEA/MDEA..... | 289 |
| Figure 116 Isotherm M-1731 loading for N-(2-hydroxyethyl) ethanol vs. N-(2-hydroxyethyl) ethanol remaining in MEA/MDEA..... | 289 |
| Figure 117 GC chromatograph of degraded solvent (A) and contaminated distillate (B) of MEA/MDEA-4-1.0%-70mmHg | 292 |
| Figure 118 Treated distillate at low SGL carbon dosage 0.04 gm Solvent / gm Carbon (MEA/MDEA-4-1.0%-70mmHg)..... | 293 |
| Figure 119 Isotherm of amine wetted SGL for contaminants for contaminated distillate of MEA/MDEA-4-1.0%-70mmHg | 294 |
| Figure 120 Isotherm of amine wetted M-1731 for contaminants for contaminated distillate of MEA/MDEA-4-1.0%-70mmHg | 294 |
| Figure 121 Schematic diagram of open-loop activated carbon dynamic adsorption test – MEA/MDEA solvent | 298 |
| Figure 122 Dynamic adsorption curves of amine wetted SGL with MEA/MDEA | 300 |
| Figure 123 Dynamic adsorption curves of amine wetted M-1731 with MEA/MDEA... | 300 |
| Figure 124 SGL dynamic adsorption curves: degradation product concentrations vs. time in MEA/MDEA..... | 301 |
| Figure 125 M-1731 dynamic adsorption curves: degradation product concentrations vs. time in MEA/MDEA..... | 301 |
| Figure 126 Refractive index measurement of treated MEA/MDEA solvent for SGL ... | 302 |
| Figure 127 Refractive index measurement of treated MEA/MDEA solvent for M-1731 | 302 |

| | |
|---|-----|
| Figure 128 Presence of light degradation products in Plant A lean amine and distillate | 308 |
| Figure 129 Isotherm treatment for Plant A distillate with SGL and M-1731 activated carbon..... | 310 |
| Figure 130 GC chromatograph of Plant B lean amine..... | 310 |
| Figure 131 Presence of light degradation products in the Plant B lean amine and distillate | 314 |
| Figure 132 Isotherm treatment for Plant B distillate with SGL and M-1731 activated carbon..... | 316 |
| Figure 133 GC chromatograph of Plant C lean amine (A) and distillate (B) | 319 |
| Figure 134 Isotherm treating for Plant C distillate with SGL activated carbon | 321 |
| Figure 135 ProTreat process flow diagram for CO ₂ capture plant with MEA solvent .. | 326 |
| Figure 136 HSS impact on CO ₂ production and solvent capacity (A) and utilities consumption and wastewater produced (B) in MEA case | 328 |
| Figure 137 HSS impact on CO ₂ production and solvent capacity (A) and utilities consumption and wastewater produced (B) in MEA/MDEA case | 332 |
| Figure 138 Hybrid Reclaimer proposed in this research..... | 337 |
| Figure 139 Reclaimer cycle vs. slip ratio lean feed to the reclaimer | 351 |
| Figure 140 VLE of MEA-Water with best model proposed for amine system | 355 |

List of Photos

| | |
|---|-----|
| Photo 1 Thermal degradation study set-up, full reflux distillation | 147 |
| Photo 2 Distillation set-up used for Series I of MEA/MDEA purification..... | 156 |
| Photo 3 Distillation set-up used for Series II of MEA/MDEA purification | 231 |

Nomenclature/Abbreviation

AmiPur = ion-exchange reclaimer developed by Eco-Tec

Bicine = N-N-Bis(2hydroxyethyl)glycine, $(\text{OHCH}_2\text{CH}_2)_2\text{NCH}_2\text{CHOO}$

C = the correction for air buoyancy, in kg/m^3

CHOOH = Formic acid

$\text{C}_2\text{H}_4\text{O}$ = acetaldehyde

$\text{C}_2\text{H}_4\text{O}_2$ = Acetic acid

CCAR = Carbon Capture Amine Reclamation developed by MPR service inc.

CCR = Canadian Chemical Reclaiming

CO_2 = Carbon dioxide

CO_3^{-2} = Carbonate ion

CS = carbon steel

DCC = Direct contact cooler

DEA = Diethanolamine

DEAH^+ = Protonated Diethanolamine

DEHA = N,N-diethylhydroxyamine

DGA = Diglycolamine

DIPA = Diisopropanolamine

$[\text{DP}_{\text{MEA}}]$ = Degradation product concentration in wt. % in MEA solvent,

$[\text{DP}_{\text{MEA}/\text{MDEA}}]$ = Degradation product concentration in wt. % in MEA/MDEA solvent

E = efficiency factor for electro dialysis system

ED = Electrodialysis reclamation

EDTA = ethylenediaminetetraacetate

F = Faradays constant (96,480 Coulombs/g-eq)

Fe = iron (element)

Fe²⁺ = the bivalent iron (II) or ferrous

GC-MS = Gas chromatography–mass spectrometry

H. = High

H⁺ = Hydrogen ion

H₂O = Water

H₂S = Hydrogen sulfide

HCO₃⁻ = Bicarbonate ion

HCX = Process developed by MPR service for removing hydrocarbons

He = Helium

HPLC-RID = High Pressure Liquid Chromatography with Refractive Index Detector

HS⁻ = bisulfate

HSSs = Heat stable salts

HSSX = ion-exchange reclaimer developed by MPR service Inc.

I = current (Amps) applied for electro dialysis system

Iodine number = is a measure of the micropore content of the activated carbon (0 to 20

Å) that means high adsorption of small molecules.

K₂CO₃ =Potassium carbonate

KOH = Potassium hydroxide

KVO₃ = Potassium metavanadate

L. = Low

M. = Medium

M = Molarity, mole/liter

M-1657 = activated carbon produced by Norit America Inc.

M-1731 = activated carbon produced by Norit America Inc.

MEA = Monoethanolamine

[MEA] = MEA solvent concentration in mole/liter

[MEA/MDEA] = Total MEA/MDEA concentration in mole/liter at 1:1 molar ratio

MEA⁺H⁺ = Protonated Monoethanolamine

MDEA = Methyldiethanolamine

Molasses number = is a measure of the mesopore content of the activated carbon (greater than 20 Å) that means high adsorption of big molecules.

m_o = the apparent mass in air, in g, of the empty pycnometer

m_c = the apparent mass in air, in g, of the pycnometer filled with water at t_c

m_t = the apparent mass in air, in g, of the pycnometer filled with amine at t_t

N = number of membrane cell pairs for electro dialysis system

NO = Nitric oxide

NO₂ = Nitrogen dioxide

NO_x = term use for combination of NO₂ and NO

NaOH = sodium hydroxide

Na₂CO₃ = sodium carbonate

NH₃ = Ammonia

NH₄HCO₃ = ammonium bicarbonate

(NH₄)₂CO₃ = ammonium carbonate

NIST = National Institute of Standards and Technology

O₂ = Oxygen

OH⁻ = Hydroxide ion

OPEC = Organization of the Petroleum Exporting Countries

OXEX = Treatment process for Oxazolidone developed by MPR service Inc.

pKa = the acid dissociation constant at logarithmic scale

ProTreat = non-equilibrium process simulator developed by Optimized Gas Treating

r = Removal rate (g-eq/sec) for electro dialysis system

RR'NH = amine

RR'NH₂⁺ = Protonated amine ion

RR'NCOO⁻ = Carbamate ion

R₃N = Tertiary amine

R₃NH⁺ = Protonated tertiary amine

RI_{MEA}^{20°C} = Refractive Index at 20°C for MEA solvent

RI_{MEA/MDEA}^{20°C} = Refractive Index at 20°C for MEA/MDEA solvent

RI_{Deg-MEA}^{20°C} = Refractive Index at 20°C for degraded 5M MEA solvent

RI_{Deg-MEA/MDEA}^{20°C} = Refractive Index at 20°C for degraded 5M MEA/MDEA solvent

Saybolt = is a measurement unit of kinematic viscosity

SGL = activated carbon produced by Calgon Carbon corporation

SO₂ = Sulfur dioxide

SO₃ = Sulfur trioxide

SO_x = term use for combination of SO₂ and SO₃

SSX = Process developed by MPR service for removing fine solid particles

T = Temperature of 5M MEA or 5M MEA/MDEA solvents in °C,

t_c = the temperature at which the pycnometer is calibrated with water

TEA = Triethanolamine

t_r = the reference temperature, e. i. 15°C

t_t = the temperature at which the pycnometer is filled with amine

Ucarsep = Electrodialysis Dow process

VFS = N, N-diethanolglycine

Greek letters:

ρ_t^1 = apparent density at specific temperature

ρ_c = the density of water, in kg/m³ at t_c

ρ_{5M-MEA} = Predicted observed density of degraded 5M MEA solvent,

$\rho_{5M-MEA/MDEA}$ = Predicted observed density of degraded 5M MEA/MDEA solvent

Subscripts:

5M-MEA = for 5M MEA clean solvent

5M-MEA/MDEA = for 5M MEA/MDEA clean solvent

c = measurement at calibration condition

Deg – MEA = for degraded MEA solvent

Deg – MEA/MDEA = for degraded MEA/MDEA solvent

MEA = for MEA solvent

MEA/MDEA = for MEA/MDEA solvent

r = measurement at reference condition

t = measurement at temperature, t

o = measurement for empty pycnometer

Chapter 1: Introduction

1.1 Chapter introduction

This chapter introduces this research work. It begins with an explanation of the link between energy demand, CO₂ emissions, and CO₂ capture with amine systems. It also briefly introduces amine systems, amine degradation, problems due to degradation, and possible solutions available to clean the degraded solvent. Research objectives and the scope of work are outlined.

1.2 Greenhouse gas effect and carbon dioxide contribution

CO₂ emissions from power and industrial emitters are identified as one of the main contributors to global warming, which has gained increasing attention since the Kyoto Protocol. The Organization of the Petroleum Exporting Countries (OPEC 2010) has reported that the world demand for energy will continue to increase, as shown in Figure 1 (A). The primary leading consumed fuels are gas, oil, and coal. Other sources of fuel are not significant, but their projected consumption and utilization will increased relatively. This obviously means that more CO₂ will be produced due to the burning of these fuels. The projections for CO₂ emissions from developed and undeveloped countries are given in Figure 1 (B) as reported by OPEC (2010). Without doubt, the emission of CO₂ is directly linked to fossil fuel consumption.

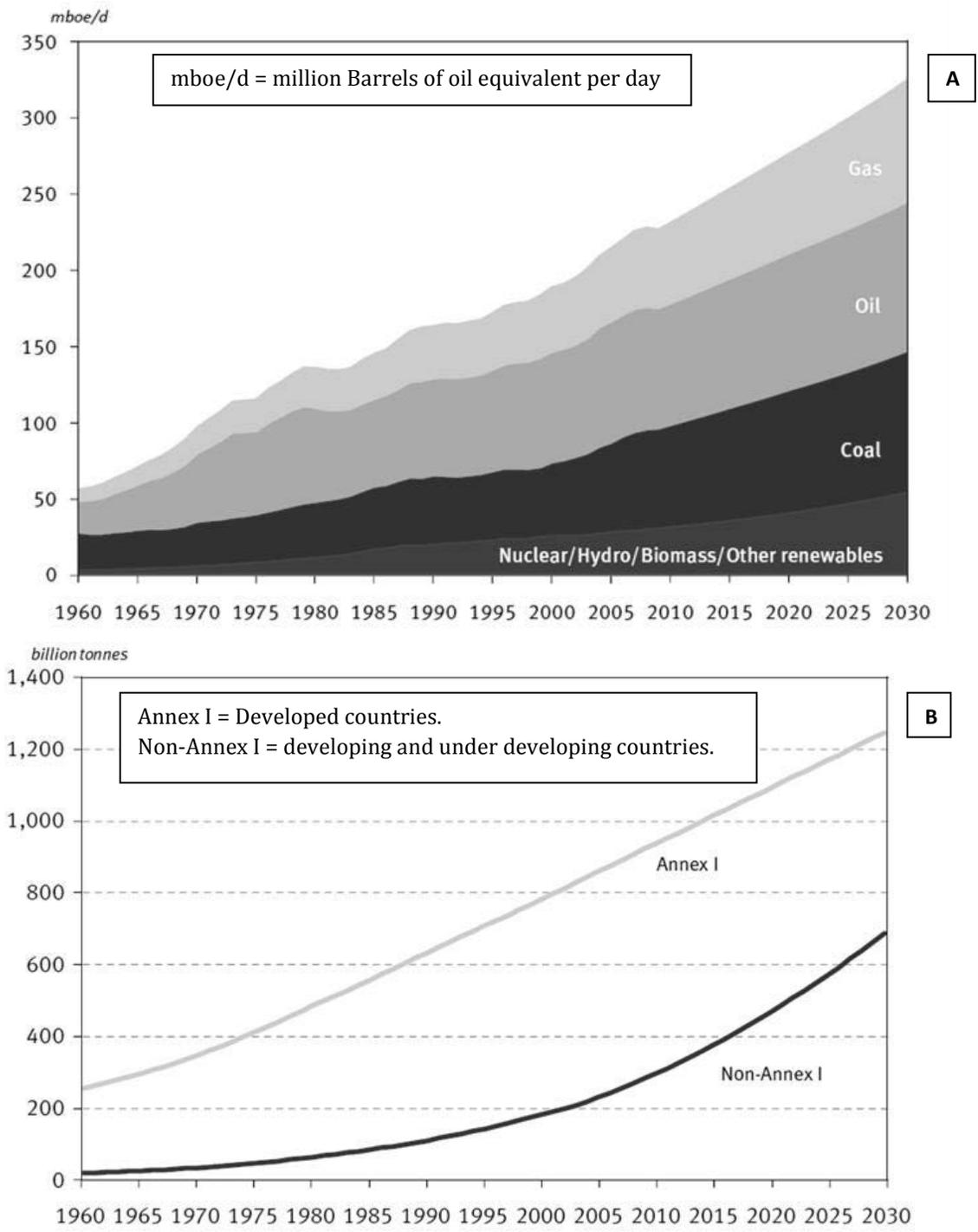


Figure 1 World energy supply by fuel type (A) and CO₂ emissions (B), OPEC (2010)

1.3 Available options for carbon dioxide emission control

The CO₂ emissions vary from one source to another. For example, Ciferno et al. (2009) report that coal-fired power plants produce CO₂ at high concentrations (10-15 Volume %) compared to natural-gas power plants (5-3 Volume %). The best option in reducing CO₂ emissions from existing and future new power plants is to capture the CO₂ which can be used in many ways that are not harmful to the environment. For instance, the captured CO₂ could be stored in geological structures, used to enhance oil recovery, or utilized in food or fertilizer industries. The selection of CO₂ emission redemption method is based on two main criteria: technical process and economic feasibilities (Astarita 1983a). There is a variety of options to remove the acid gases from a gas stream, such as physical solvent, hybrid solvent, absorption, and cryogenic distillation (Astarita 1983a). However, the most attractive option is a chemical solvent system utilizing amine solvents (Astarita 1983a). This is due to many features, as can be summarised as follows:

- It has high loading capacity.
- It reduces the acid gas concentration to very low levels.
- It has selectivity for removal of acid gas.
- Process performance optimization is feasible.

Figure 2 shows the options that would be feasible for power plants. Post-combustion technology is based on amine and chilled ammonia absorption processes. Amine solvents have been used for years in natural gas and food-grade CO₂ production. Chilled ammonia still suffers from a shortage of complete fundamental research, and pilot plant data needs to be done to confirm the process performance.

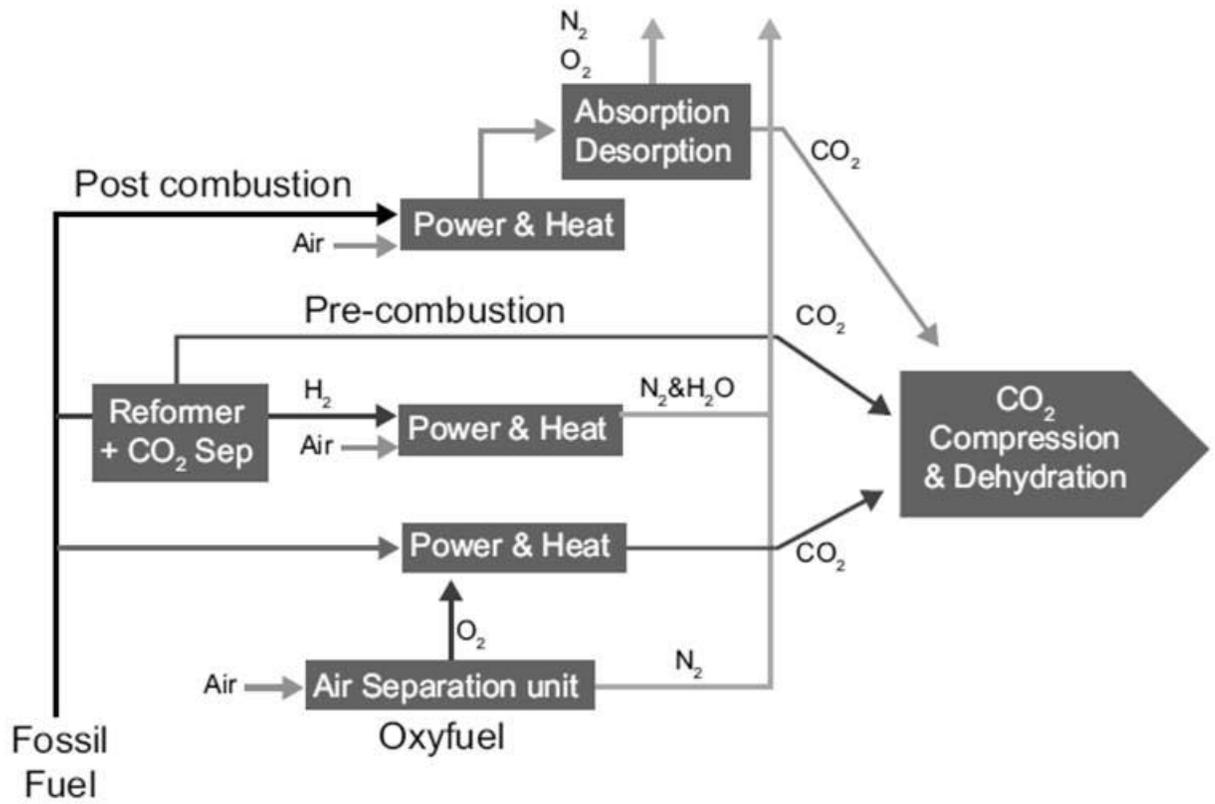


Figure 2 Options for CO₂ capture from flue gas streams (StatoilHydro 2009)

1.4 Post-combustion CO₂ capture with amine solvents

Amine solvents are weak bases that are able to absorb and react with CO₂; they capture CO₂ through a chemical reaction where amine forms a chemical complex salt with the acid gas. This salt can be easily broken at an elevated temperature, making the solvent reusable, and this is the merit of this process technically and economically.

The amine process used for CO₂ capture has been adopted in natural gas sweetening with minor process configuration differences. MEA was first utilized for removing CO₂ due to its fast reaction and good absorption capacity. The largest MEA plant is still in operation in the USA with the production of 800 TPD of CO₂ (Duke et al. 2009). Nowadays, more formulated amines are being investigated as possible CO₂ absorbents. Blended amine such as MEA/MDEA can reduce energy, increase absorption capacity, and reduce the circulation rate (the plant size) as reported by Chakravarty et al (1985). Solvent circulation has been found to be responsible for 50-70% of capital cost, as it directly affects the equipment and pipe sizes. Energy consumption from steam production is considered 70-80% of operating costs, followed by chemical make-up due to degradation and solvent loss of up to 20% (Astarita 1983a).

The main commercial amine technology providers are Fluor Corporation (30wt% MEA solvent, Econamine Process) and Mitsubishi Heavy Industries (KS solvents, KM-CDR Process). The University of Regina is developing more energy effective processes compared to its competitors (Idem et al. 2010).

As shown in Figure 3, the amine process consists of two main sections: absorption and stripping. In the absorber section, lean amine solvent containing a small amount of CO₂

is brought into contact with flue gas containing CO₂. The contact and reaction between amine and CO₂ usually occurs on the mass transfer equipment's packed bed or trays. The lean amine loaded with CO₂ now is called rich amine. It is sent to the stripping section where first it exchanges energy with hot lean amine from the reboiler of the stripper to maximize energy integration and help the stripping of CO₂. Then, the warmed rich amine is introduced to the stripper column, which might contain a packed bed or trays, and is brought in contact with the stripping steam, which helps to break the reaction bond between amine and CO₂. Then, CO₂ is released from the amine and travels up to the overhead condenser with the stripping steam, which should condense in order to maintain the water balance. The CO₂ stream can then be sent as a product for further treatment and conditioning to be used in one of the utilization options mentioned previously (e.g., EOR). The amine leaving the stripper is sent to the stripper reboiler where steam is evaporated and used for stripping and the rest of the amine, which now can be called lean amine, is sent to the absorption section, and the cycle repeats.

The reactions between amine and CO₂ are shown in Figure 3 for both the absorption and stripper sections. In the absorption process, low temperature is favoured for CO₂ absorption. Meanwhile the reaction products of absorption can be broken down by the heat applied to the amine solvent, so the reaction is reversed, releasing the CO₂ and freeing the amine, which can be recycled for further absorption of CO₂.

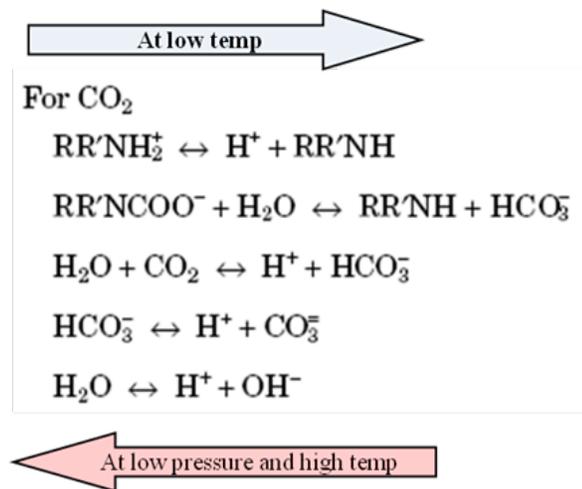
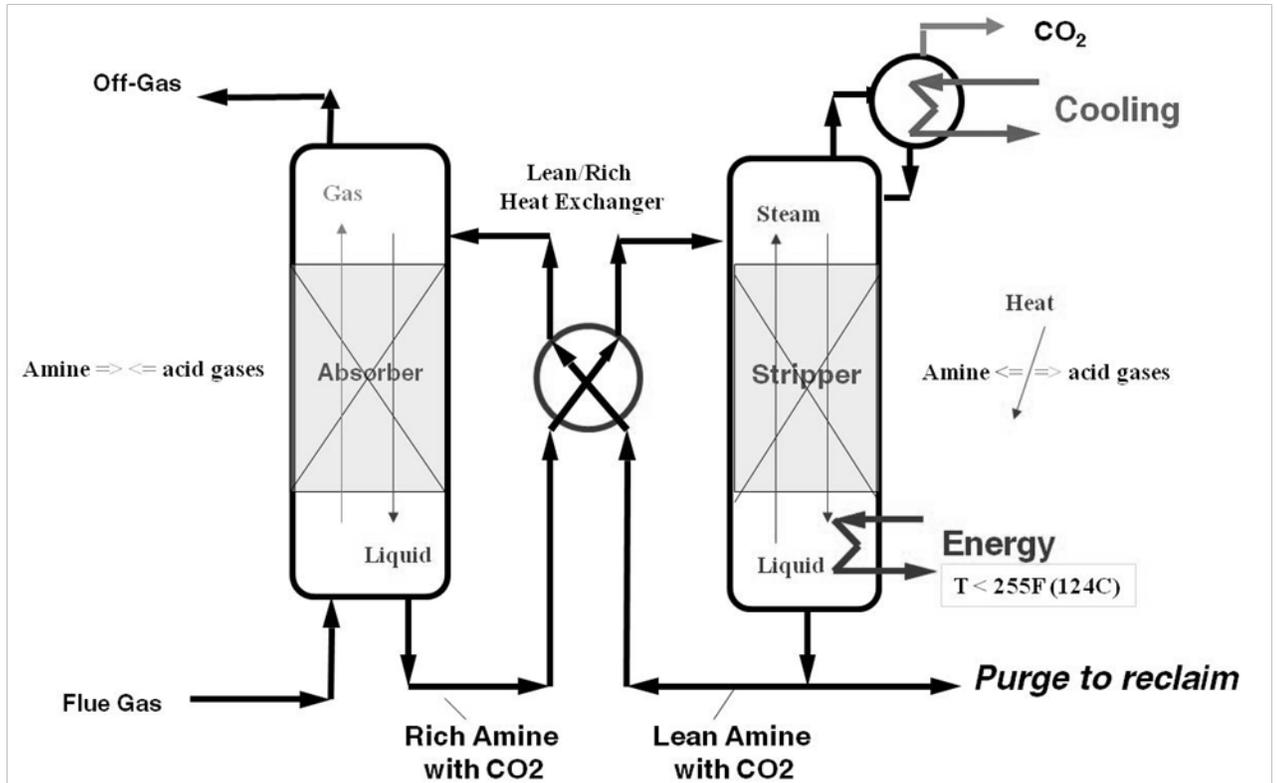


Figure 3 CO₂ capture process with illustration of Amine-CO₂ chemical reactions

1.5 Solvent degradation and plant operation problems

The main problems of post-combustion CO₂ capture with amine solvents are high energy, foaming, fouling, corrosion, and solvent loss (Ciferno et al. 2009). Surprisingly, these problems can be directly linked to each other, as will be shown in Chapter 2, and possibly due to one main contributor, solvent degradation. To make the amine process more affordable and attractive, these challenges should be addressed and controlled.

Amine solvents, whether they are single or mixed, are subject to degradation. Solvent loss can occur in three ways: solvent carry over and entrainments, evaporation due to solvent volatility, and solvent degradation. Tertiary amines are less volatile than secondary ones, and secondary amines are less volatility than primary ones (Kohl and Nielsen 1997). Carry over and evaporation can be controlled by having a good design for the absorber column, good operating conditions, and installation of a water washing section above the absorption section. A typical target for amine solvent emission with off-gas is 1 to 4 ppm. However, solvent degradation can be minimized to a certain extent but not eliminated. Solvent reclamation helps reduce the impact of build-up of degradation products on amine plant performance.

Degradation in the solvent can occur in either one of two forms, thermal degradation or chemical reaction, with some impurity components that might be introduced to the solvent (Kohl and Nielsen 1997). Thermal degradation is usually avoided by proper design of the reboiler and hot sections in the plant to avoid exposure of the solvent to temperatures that will lead to the decomposing of the solvent. Also, during the operation, the plant operator will monitor the pressure inside the stripper to avoid excessive pressure

that might lead to considerable increase of the solvent temperature. The second type of degradation is an operational concern of amine plant operators. Astarita (1983a) mentioned that one important key of selection of appropriate amine solvent is solvent degradation and whether that solvent can be reclaimed easily or not. Some impurities in the flue gas steam can react with amine solvent and cause solvent degradation and heat stable salts (Wilson et al. 2004).

Astarita (1983a) mentioned that amines degrade when exposed to O_2 and SO_x (SO_2 and SO_3), and small portions of CO_2 will deactivate some amine as well. It has been reported that for each mol of SO_2 , 2 mol of MEA solvent is lost. The recommended level of SO_2 in flue gas for amine systems is 10 ppmv or less (Hendriks 1994). They form degradation products and heat stable salts in which their formation pathways might not be well understood, especially for blended amines (Astarita 1983b). Some advanced studies to understand amine degradation for single and blended amine have been carried out (Supap et al. 2001), (Lawal et al 2005), (Lawal and Idem 2005), (Lawal and Idem 2006), (Supap et al. 2006), (Idem et al. 2007), and (Uyanga and Idem 2007).

Wilson et al. (2004) published test results for Fluor amine solvent of 30 wt% MEA at Boundary Dam plant with coal flue gas. Fly ash was found to catalyze solvent degradation and its made of a mixture of inorganic oxides such as SiO_3 , Al_2O_3 , Fe_2O_3 , CaO , MgO , Na_2O , K_2O , and P_2O_5 . The presence of SO_2 and NO_2 cause HSS formation. The main HSSs found are sulphate, oxalate, and thiocynate due to the oxidation of MEA. The level of HSS reached 0.5 wt% in only 10 days. Soluble iron increased during this time from 50 to 300 ppm after 7 days.

Degradation product accumulation in amine solvent will lead to tremendous operation problems and failures within the amine plant. The potential problems from accumulation of degradation products can be listed as follows:

- 1- Reduction in the scrubbing efficiency of the solvent due to loss of solvent as degradation products,
- 2- Foaming and increased solvent foaming tendency due to change of surface tension,
- 3- Solvent corrosivity can significantly increase, which will lead to equipment failure and increased particle concentration in the solvent, which will act as a degradation promoter,
- 4- Fouling of heat exchangers and column internals from corrosion and degradation products,
- 5- High concentration of degradation products and salts in the solvent stream will lead to the replacement/change-out increase of mechanicals and activated carbon filters and this, by itself, increases the operating and maintenance costs,
- 6- Loss of solvent will be partially overcome by adding some fresh solvent as make-up to temporarily restore the solvent strength, and this will increase operating costs including costs of fresh solvent,
- 7- The accumulation of degradation products and salts will lead to change of the physical properties of the solvent, such as density and viscosity, and this will lead to consumption of more power for pumping of solvent and change of the mass transfer characteristics of the solvent in the absorption tower.

These degradation products and any foreign materials accumulated in the solvent should be removed to maintain the integrity of the solvent and reduce the plant problems. Amine reclaiming technologies are used to achieve the required solvent quality and maintain smooth operation.

1.6 Solvent purification methods: the success and limitations

The contaminated solvent will lose its effectiveness in capturing CO₂ with time due to the build-up of degradation products and heat stable salts. They should be removed from the amine to ensure stable and high plant operations. A number of solvent reclamation technologies are used in industry: ion exchange, electrodialysis, and thermal treatment. Further explanation of each technology is given in Chapter 4. The first two technologies are mainly developed to remove heat stable salts, which are the primary troublemakers in gas treating units in the oil refineries and natural gas sweetening. They are used in constant operation (24 hours/day, 7 days/week) to assure maintenance of low levels of HSS. The removal of HSS will have direct impacts on reducing formation of other degradation products, which would not be removed by these technologies. However, the ion exchange technology seems more predominant than electrodialysis due to the many operating problems with the membranes used in the electrodialysis design.

Thermal reclamation was used, as it could remove all impurities in the contaminated solvent, but it suffers from lower solvent recovery compared to other technologies, and its operation is quite complex. It takes time and demands energy and water make-up. For instance, during the reclamation of MEA, water and steam is repeatedly used to recovery

the solvent by the effect of dilution, but this causes an interruption in the water balance and consumes more energy (as steam) to evaporate that amount of water.

In CO₂ capture applications, the main degradation products are not heat stable salts, similar to the case in the natural gas sweetening or oil refinery tail gas. Actually, both heat stable salts and other degradation products are very important and should be treated equally. Therefore, the first two reclamation technologies are unlikely to be appropriate candidates for solvent reclamation in CO₂ applications, and thermal reclamation would be the only feasible option. The other fact supporting this is that the lean amine in CO₂ applications has higher CO₂ loading than natural gas sweetening or oil refining. The CO₂ absorbed in amine would be removed from amine by ion-exchange or electro dialysis, and this will lead to the reduction of the efficiency and capacity of these reclaimers. Despite the fact that thermal reclamation appears to be the only feasible option for reclamation of amines in CO₂ capture, it needs further improvement to:

- Enhance solvent recovery (currently 90-95%),
- Reduce solvent loss in reclaimer waste (i.e., +60 wt%),
- Reduce consumption of water make-up and steam (energy),
- Address the problem of some degradation products going back into the system,
- Eliminate or reduce the disturbance of plant operations.

1.7 Research objective

It has been found that amine solvent reclaiming is not well addressed in the open literature, especially in CO₂ capture applications, due to lack of information or confidentiality of results and data obtained by companies dealing with solvent reclaiming.

Moreover, no information is available for reclaiming of mixed or formulated amine solvent in the open literature.

Therefore, this research is aimed at exploring and obtaining useful data on the most feasible technology for solvent reclaiming, thermal distillation, for MEA and MEA/MDEA solvents used in the CO₂ capture applications. It is feasible that the drawbacks of the thermal reclaimer mentioned previously could be overcome by altered operation philosophy. Therefore, the research objective is *to study the thermal solvent purification of MEA and MEA/MDEA solvents at laboratory scale to investigate the opportunities to enhance the reclaimer operation and how its product purity could be improved.*

1.8 Research Scope and Work Plan

The research involved studying thermal purification of MEA and MEA/MDEA solvents. Laboratory investigation with a thermal distillation set-up is the primary method used to assess the reclamation performance, and this has been practiced in the field of reclamation by many researchers (Sokolik et al 1983; Yan 1992b; Van Grinsven and Van Heeringen 1999). Two major experiments carried out were thermal distillation to purify the solvent from its degradation products and adsorption tests to examine the removal of contamination, that is, some degradation products, in the recovered amine from the thermal distillation step. The partial degraded solvents used in these tests were prepared in the laboratory based on the information available in the open literature on the relevant degradation products of the CO₂ capture system (Strazisar et al 2003; Lawal et al 2005; Supap et al. 2006). Selected heat stable salts, degradation products, and strong bases for neutralization of heat stable salts were mixed for each sample used for each experiment

as required. For instance, sometimes only degradation products were considered while in other tests, only heat stable salts were present in the tested samples, without other degradation products, to investigate their influence. Industrial samples were obtained from three operating amine plants to test their purification in this research, as well. The studies were conducted as follows:

1. A comprehensive literature survey was conducted in order to collect all the relevant information, especially amine solvent degradation and reclamation.
2. Partial degraded solvents were prepared by mixing pre-prepared amine solvent at different concentrations with degradation products and heat stable salts at desired concentrations. Then, those samples with heat stable salts were neutralized with strong base, usually NaOH.
3. Optimum conditions for thermal purification were determined for MEA and MEA/MDEA solvent with and without degradation products and/or heat stable salts. Also, determination of solvent purity of distillate and whether any degradation products could be present in the distillate were investigated.
4. Collected distillates or artificial distillates prepared with light degradation products, which could cause contamination, were treated with activated carbon to examine the capability of activated carbon in removing the contamination in distillates.
5. Process simulation was lastly used to check and predict the impact of HSSs on the amine plant and to simulate the amine purification unit.

Chapter 2: Amine Solvent Degradation (Literature Review)

2.1 Chapter introduction

In this chapter, amine solvent degradation has been assessed for possible reaction routes and pathways as well as resulting degradation products. Examples of industrial samples for lean amine and reclaimer waste were analysed and the GC-MS results obtained will be discussed.

2.2 Industrial samples of industrial lean amine and reclaimer waste

Amine solvent used in the CO₂ capture processes are vulnerable when exposed to some impurities in the flue gas stream, such as SO_x, NO_x, O₂, and even CO₂, which act as catalysts to some of the degradation reactions. To demonstrate the solvent degradation, two industrial samples have been obtained from a CO₂ capture plant using the MEA solvent. Figure 4 (A) illustrates a GC chromatograph for lean amine samples and eight degradation products found. The heat stable salt measured by titration was 0.15 wt% as MEA. This means the MEA solvent is kept clean by a using 24/7 thermal reclaimer. From the GC-MS result, it can be concluded that the total degradation products level is < 0.5 wt% in the lean amine solvent.

Figure 4 (B) gives the GC-MS chromatograph for reclaimer waste from this amine plant. Obviously, the reclaimer accumulates all possible degradation products that might exist in the solvent, even in small concentrations that cannot be seen in Figure 4 (A). More than thirty degradation products were found, including MDEA solvent and acetic acid, which is one of the heat stable salts (HSS). Most of HSSs cannot be determined by GC-

MS, and it is not possible to measure the total heat stable content due to the presence of soda ash, which will interfere with the titration. From the chromatograph, it can be concluded that the MEA content in the reclaimer waste is roughly just more than 50 wt% (acid titration shows +60 wt% MEA), and this is high, in that the reclaimer waste. This is the main drawback of thermal reclamation currently in service for primary amines. Some degradation products used in this study have been found in the reclaimer waste shown in Figure 4 (B). The number of degradation products and their chemical classifications is evidence that the degradation reaction is quite complex and leads to whole series of reactions with multiple products, which might react among themselves (Lawal and Idem 2005).

2.3 Amine solvent degradation

Solvent degradation can occur in three ways: thermal degradation, oxidative degradation, and carbamate degradation. Thermal degradation is controlled or minimized by an appropriate design for the amine plant in order to prevent solvents from exposure to high temperature that might lead to solvent thermal degradation or decomposition. The majority of amines are degradable at high temperature before they can reach their boiling point. For instance, monoethanolamine (MEA) is considered to be thermally decomposed if it is exposed to temperatures higher than 147°C (Dow 1962). Oxidative degradation involves the reaction of O₂ or SO₂ with amines. Most of degradation products of O₂ and SO₂ are organic acids (heat stable salts) and amides. The third degradation type is a reaction that involves CO₂ or carbamate.

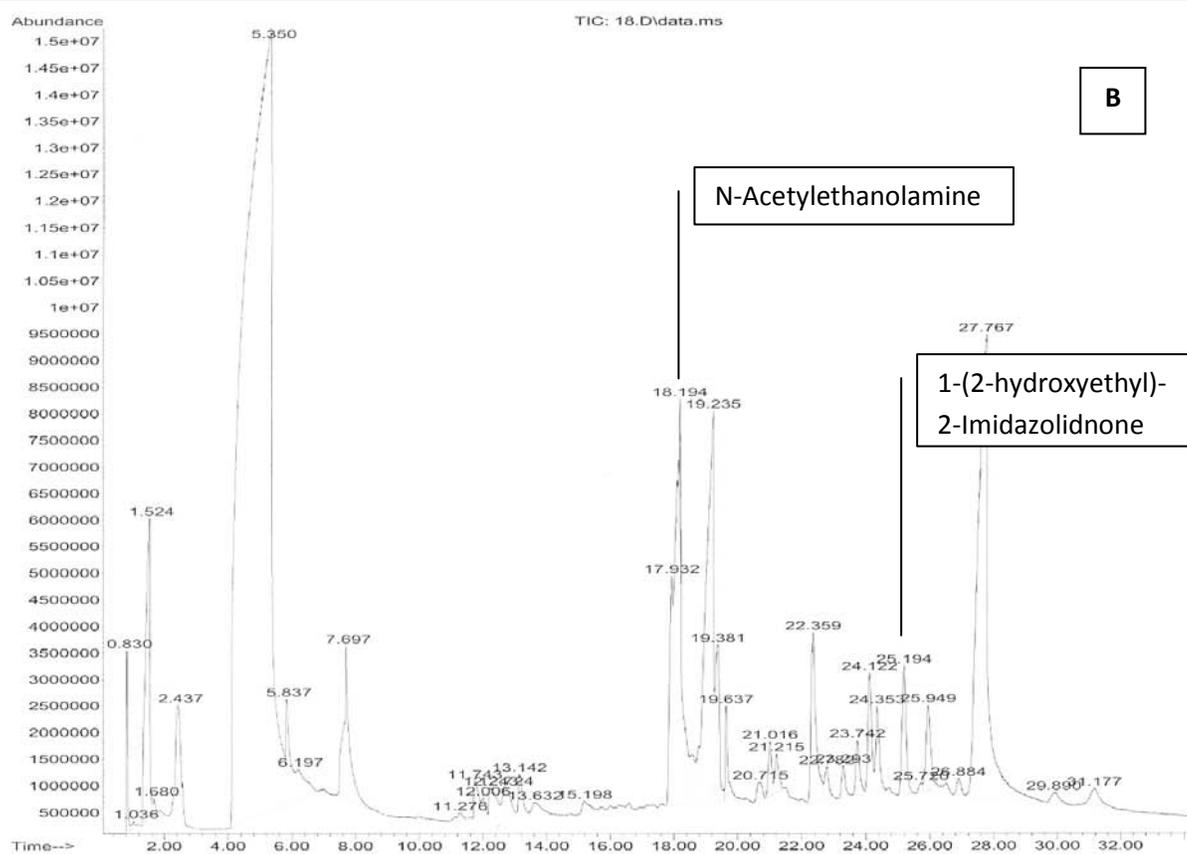
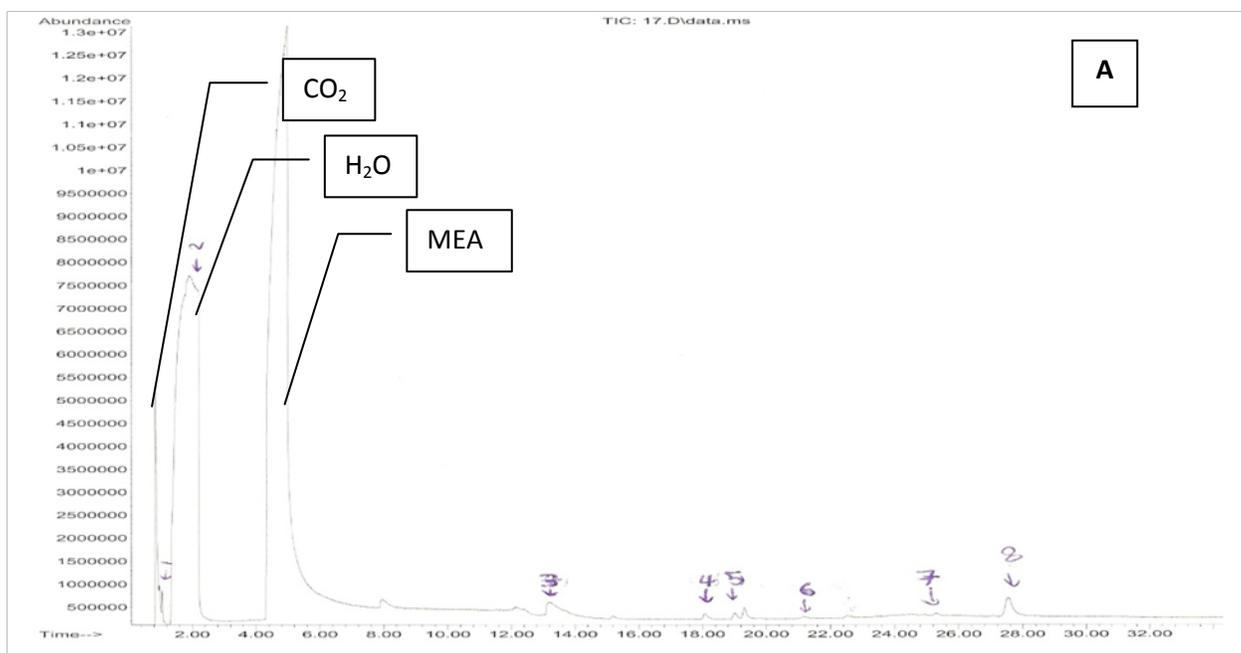


Figure 4 GC chromatograph of lean amine (A) and reclaimer waste (B)

2.3.1 Solvent thermal degradation

Most amine solvents thermally decompose before they reach their boiling point (Dow 1962) and (Maddox and Morgan 1998). Thermal degradation of solvent can be prevented by controlling the design temperature of the reboiler and the hot parts of the amine plant. If thermal degradation occurs, certain degradation products could be formed, such as ammonia, polymers, and cyclic compounds, as mentioned by (Bacon 1987). Ammonia could be formed in oxidative and carbamate degradation reaction (Kohl and Nielsen 1997). Davis and Rochelle (2009) studied MEA thermal degradation and found it to be 2.5-6% per week at 135°C for loaded solvent with CO₂ and a total concentration of 7M.

MEA is thermally stable up to 300°F (148°C) as reported in (Dow 1962). Meisen & Kennard (1982) described thermal degradation of DEA and MDEA as minimal up to 400°F (204°C) and this was also mentioned for DEA in (Dow 1962). Strazisar et al (2003) did study thermal stability of pure and diluted MDEA solutions. Based on their findings, pure MDEA starts its thermal decomposition at 167°C and becomes obvious at 231°C, while for diluted solution of (48 wt%) starts at 173°C and intensifies at 267.4°C. Dow (1962) reports that the dilution amine with water in order to prepared solution would reduce the thermal degradation.

2.3.2 Oxidative degradation

As mentioned previously, amine reactions with O₂ or SO₂ will lead to formation of carboxylic acids (or heat stable salts) and amides. Oxidative degradation was reported in many papers (Ballard 1966), (Bacon 1987), and (Kohl and Nielsen 1997). Hofmeyer et al (1956) have shown that MEA reaction with O₂ will lead to the formation of formic acid,

formamides, ammonia, and high molecular weight polymers. Ammonia would be readily dissolved in amines and could react with CO₂ to form ammonium carbonate (NH₄)₂CO₃ and bicarbonate NH₄HCO₃. Blanc et al (1981) did oxidative degradation studies involving MEA, DEA, and MDEA. They found a variety of formations of heat stable salts such as: formic acid, acetic acid, and oxalic acid. They also mentioned that the analysis of samples obtained from DEA and MDEA plants contain heat stable amine salts within the range of 0.24 to 3 wt%, and they are mainly acetic acid, formic acid, propionic acid, and oxalic acid. Bacon (1987) gave the general degradation reaction between amine and O₂ as given in equation (2.1):



Ammonia formation mechanisms have been proposed by Strazisar et al (2003) as shown in equation (2.2) and (2.3):



2.3.2.1 Heat Stable Salts (Organic Acids)

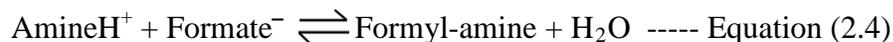
Heat stable salts, HSS, are formed from stronger acids than CO₂, and they cannot be regenerated thermally in the stripper. The presence of HSS reduces the solvent absorption capacity, lowers pH, increases conductivity, and dissolves protective films if they are formed. They were considered problematic only in the last 15 years according to (Cummings et al 2007).

Heat stable salts are formed from base-acid reactions between the organic acids formed from oxidation degradation and amine solvents. As a result, part of the amine solvent would be bonded with these salts and prevented from capture of any further CO₂. Heat stable amine salts are formed in amine systems and usually include: acetate, formate, thiosulfates, sulfates, thiocyanetes, oxalates, butyrates, and propionates. The other HSSs introduced to the system from, possibly, the water make-up are chloride, phosphate, and nitrates. To reduce contamination from make-up water, demineralized water or condensate should be used as per (Harston and Ropital 2007). Total concentration of HSS can vary from 0.1 to 3 wt% or higher (Harston and Ropital 2007). Cummings et al (2005) mentioned that the tolerated total HSS level is 5,000 – 8,000 ppm. Table 1 gives more information on tolerated HSS content as reported by MPR Service Inc.

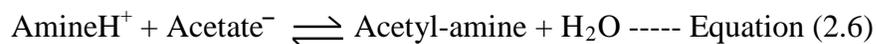
2.3.2.2 Amides

Cummings and Mecum (2000) report amides are formed when acid anions react with protonated amine, as illustrated in equations (2.4) to (2.8):

Formamides



Acetamides



Amides have been found in MEA, DEA, and DIPA systems. As can be seen from these reactions, each formation of 1 mol amide leads to loss of 1 mol of amine. Their formation depends on four operational factors: temperature, residence time, pH, and concentration. The first two factors are always fixed, based on the plant design, but the last two may vary. The reaction can be reversed if one of the reactants, such as formate, is removed from the system. This has been achieved in the ion-exchange reclaimer system, as will be explained later. Amides can be removed by ion-exchange, electrodialysis and distillation.

2.3.2.3 Amino Acids

According to (Cummings and Mecum 2000), (Lawson et al 2003), and (Cummings et al 2005), the main degradation product found in the amine system as amino acid is bicine or N-N-Bis(2hydroxyethyl)glycine “(OHCH₂CH₂)₂NCH₂CHOO”. Bicine can be formed from degradation of DEA, TEA, and MDEA through many expected mechanisms. Bicine is blamed as being a contributor to the corrosion by channeling action ((Lawson et al 2003) and (Cummings et al 2003)). Bicine cannot be removed by thermal reclamation according to (Cummings and Mecum 2000) and (Lawson et al 2003). They report it can be removed by the ion-exchange process of HSSX developed by MPR Service. However, more recent publications claim bicine can be removed only by ion-exchange and distillation reclamation processes (Cummings et al 2005). Cummings et al (2007) report electrodialysis can partially remove bicine. In the current experimental work, our results for thermal reclamation show that bicine can be removed from the solvent. Cummings et al (2003) recommend the level of bicine to be 250 ppm or less.

Table 1 MPR service¹ recommendation for HSS limitation

| Limitation of HSAS anion content | ppm |
|--|------------|
| Oxalate | 250 |
| Formate, glycolate, malonate, sulfite or sulfate | 500 |
| Acetate, succinate | 1,000 |
| Thiosulfate | 10,000 ppm |

Table 2 MEA and MEA/MDEA Degradation with presence of CO₂ and/or O₂

| | Systems | Temp | Degradation % | |
|---|-------------------------------------|-------|---------------|------|
| | | | MEA | MDEA |
| MEA-H ₂ O-O ₂ | 5M | 55 | 0.8 | - |
| | | 120 | 49.2 | - |
| MEA-H ₂ O-CO ₂ | 7M | 120 | 1.7 | - |
| MEA-H ₂ O-O ₂ -CO ₂ | 7M, 0.27 mol/mol | 120 | 15.7 | - |
| MEA-MDEA-H ₂ O-O ₂ | MEA/MDEA (5/2)7 M | 55°C | 3.4 | 2.0 |
| | | 120°C | 22.2 | 27.9 |
| MEA-MDEA-H ₂ O-CO ₂ | MEA/MDEA (7/2), 9 M | 120°C | 0.0 | 2.5 |
| MEA-MDEA-H ₂ O-CO ₂ -O ₂ | MEA/MDEA (7/2), 9 M, 0.4 mol/mol | 120°C | 5.8 | 6.0 |

¹ www.mprserver.com

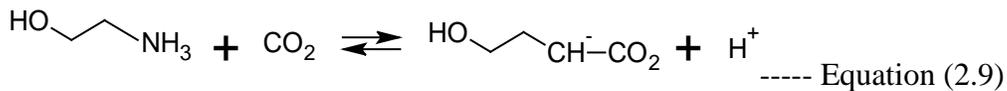
2.3.3 CO₂ or Carbamate Degradation

Despite the fact that the main reaction between amine and CO₂ is the formation of carbamate, which can be reversed easily in the stripper, small portions of CO₂ are involved in catalysis degradation reactions, which leads to the formation of degradation products, depending on the type of amine used for CO₂ capture. Ballard (1966) reported that CO₂ causes degradation reactions that eventually lead to solvent loss. Bacon (1987) also reported that all amines are subject to solvent CO₂ degradation and one of the main degradation products is oxazolidinone.

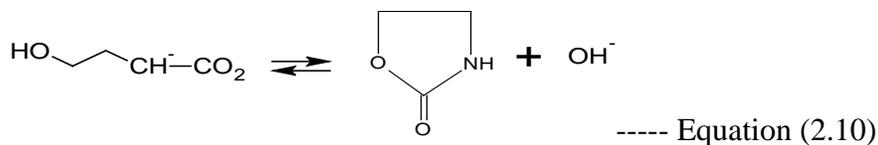
2.3.3.1 Primary Amine-CO₂-Degradations

Degradation of primary amines, such as MEA and DGA, with CO₂ leads to formation of imidazolidone, diamines, and urea. These degradation products could possibly be removed by thermal reclamation. In some cases, urea formed from DGA degradation could be reversed back to the amine under reclamation conditions. Polderman et al (1955b) and Polderman et al (1955a) proposed the CO₂-degradation reactions for monoethanolamine as given in equations (2.9) to (2.12):

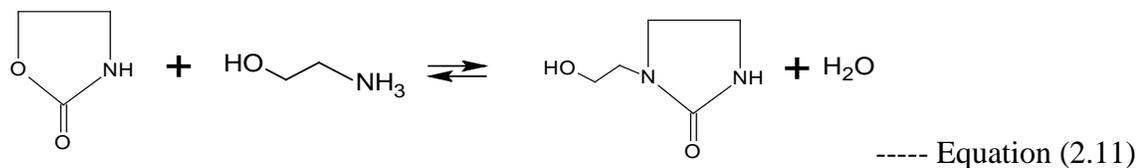
MEA reacts with MEA to form Monoethanolamine Carbamate:



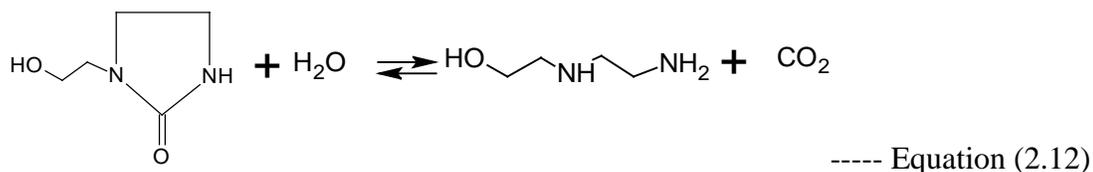
Carbamate will condense to form Oxazolidone-2:



Oxazolidone-2 reacts with another molecule of MEA to form *1-(2-hydroxyethyl)-imidazolidone-2*:



1-(2-hydroxyethyl)-imidazolidone-2 reacts with water to form N-(2-hydroxyethyl)-ethylenediamine (HEED)



HEED is a stronger base than MEA and contributes to the CO₂ capture. However, its carbonate salt is not easily regenerated, and this leads to un-real or false CO₂ loading in the amine solutions.

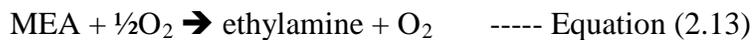
2.3.3.2 Tertiary Amine-CO₂-Degradation

It has been claimed that tertiary amines are not degradable in the presence of CO₂ (Kohl and Nielsen 1997); however, many recent studies confirm that they do degrade. The combined impact of CO₂ and O₂ on solvent degradation has been studied for single and mixed amine solvent of MEA and MDEA by (Lawal et al (2005) and (Lawal and Idem

2005). To show the extent of the influence of impurities on flue gas on the solvent degradation, Uyanga & Idem (2007) did an oxidation degradation study for unloaded and loaded MEA with CO₂ in the presence or absence of SO₂. They derived two empirical equations for rate of MEA degradation: one for coal flue gas streams of power plants and another for natural gas-fired power plants (where SO₂ might be zero). Uyanga & Idem (2007) predicted that the degradation rate would be increased when O₂, SO₂, temperature, and solvent concentration are increased. However, they found that the increase of CO₂ loading would have slightly the opposite effect on MEA degradation. They mentioned that this effect might be due to CO₂ acting as a kind of degradation inhibitor by preventing more SO₂ or O₂ from dissolving into the amine solvent and consequently reducing the oxidative degradation intensity; similar observations were reported by (Lawal and Idem 2006).

Lawal and Idem (2005) and Lawal et al (2005) published results of an oxidative degradation study of a blend of MEA/MDEA to understand the degradation pathways and the degradation products. However, Lawal et al (2005) studied MEA oxidation degradation and compared it with MEA/MDEA blends (Lawal and Idem 2006). A change in the MEA-MDEA ratio affected the rate of degradation of both MEA and MDEA in a complex manner. Although it was thought that MDEA does not directly degrade in the presence of CO₂, MDEA might degrade after it is protonated based on a suggestion given by (Critchfield and Rochelle 1987). In the blend of MEA and MDEA, protonated MEA can protonate some MDEA, freeing MEA to absorb more CO₂. This is called a shuttle mechanism, which has been described by (Astarita 1983b).

The degradation extent for the MEA/MDEA system has been studied by (Lawal and Idem 2005). They found the number of the degradation products would be higher in the following order: MEA-MDEA-H₂O-O₂ > MEA-MDEA-H₂O-O₂-CO₂> MEA-MDEA-H₂O-CO₂. However, the degradation severity is in the following order: MEA-MDEA-H₂O-O₂ > MEA-MDEA-H₂O-O₂-CO₂> MEA-MDEA-H₂O-CO₂. Lawal et al (2005) reported different system concentrations and conditions than (Lawal and Idem 2005), and the results are as shown in Table 2. Lawal et al (2005) showed that even in tests where O₂ is not used, O₂ has been formed by a decomposition reaction of MEA at high temperature (i.e., 100°C):



They have illustrated the degradation products for blended amines in the presence of O₂ and for unloaded and loaded amine with CO₂. The details of the proposed reaction mechanisms of their formation can be found elsewhere (Lawal and Idem 2005) and (Lawal et al 2005). Lawal and Idem (2005) have relied on standard solvent, whenever the stock solvent was available, and/or the mass spectrum to indentify the degradation products.

Chapter 3: Problems Associated with Degradation Products (Literature Review)

3.1 Chapter introduction

This chapter provides an explanation of the contributions of degradation products to CO₂ capture plant operation problems such as change of solvent absorption capacity and physical properties, corrosion, foaming, fouling, emission and effluent, energy consumption, and laboratory analysis. Many of these problems were already reported years ago by (Astarita 1983b).

3.2 Concentration and absorption capacity

Whenever 1 mol of degradation products or heat stable salts (HSSs) is formed from an amine solvent due to degradation reactions, 1 mol (at least) of the solvent is lost. As a direct consequence, solvent absorption capacity is reduced and solvent characteristics are changed due to the change of the solvent composition. In order to address this problem, Cummings and Mecum (2000) suggested that operators increase the solvent make-up, the solvent circulation rate, and steam consumption to compensate for this loss. This has immediate consequences for the plant's integrity, both technically and economically.

3.3 Solvent physical properties

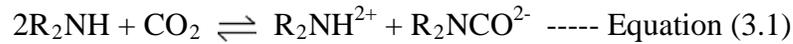
Once degradation products and HSSs build-up in the amine solvent, the solvent composition is changed, along with its physical properties, which can lead to many operational difficulties, as explained in Table 3.

Table 3 Impact of degradation products on solvent physical properties

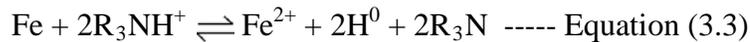
| Property | Description of the impact |
|------------------------|--|
| Density | The amine plant equipment and pipes have been designed to handle a specific range of solvent density. However, as the degradation product level is increased and water content reduced, a new density of contaminated solvent emerges. It is usually higher than the clean amine solvent and can lead to operational problems with the pumps and heat transfer equipment. The density also has an impact on the mass transfer due to change of the absorption characteristics. |
| Viscosity | Similar to the density, viscosity of contaminated solvent is usually increased compared to the clean solvent. The viscosity would have a direct impact on the solvent absorption properties, pumping, and heat transfer. |
| Conductivity | Increase of conductivity means more salts and ionic species have been introduced or formed within the solvent, and this will lead to increased corrosion or enhance it. |
| pH | pH could be reduced due to the presence of heat stable salts and this will lead to corrosion and could disturb plant operation. |
| Surface Tension | Surface tension could be changed due to build up of impurities, degradation products, and fine solid particles in the solvent. Change of surface tension has a direct impact by increasing the solvent foaming tendency. |

3.4 Solvent corrosivity

Corrosion problems in amine systems are very serious and can lead to consequences for the plant operation and plant equipment integrity. Corrosion types that occur in amine systems are liquid phase liquid acid gas corrosion and gas phase wet acid gas corrosion. Possible corrosion locations are reported in (Kohl and Nielsen 1997), and they include the bottom of the absorber due to wet CO₂ corrosion, rich/lean heat exchangers, stripper, stripper reflux section, reboiler, and reclaimer. Degradation products and heat stable amine salts cause or contribute to corrosion, as mentioned by (Ballard 1966), (Cummings and Mecum 2000), and (Cummings et al 2003). Amine solutions are not corrosive because they have low conductivity and high pH, but once they become CO₂ loaded and contaminated, they become corrosive, as seen in equations (3.1) and (3.2).



Alkanolammonium (R₂NH²⁺ or R₃NH⁺) ions can contribute to corrosion by providing protons for the corrosion reaction equation (3.3).



(Astarita 1983b) reported that amine solvents are very corrosive when their concentration and CO₂ loading are high unless corrosion inhibitors such as potassium metavanadate (KVO₃) and sodium nitrite (NaNO₂) are used. Primary amines (difficult stripping of CO₂) are more corrosive than secondary and tertiary amines (easy stripping of CO₂). Carbamate formation in primary and secondary amines might act like HSS in amine systems and cause corrosion. Factors that contribute to corrosion problems in amine

plants are as follows: high temperature (higher corrosion), amine degradation products and organic acids, amine type and CO₂ loading (corrosivity of primary > secondary > tertiary), amine concentration, and degradation products act like chelate for iron.

CO₂ and degradation products reduce the pH, making the solution more acidic and destroying any protective “passive” film that might form by the formation of a metal complex. Astarita (1983b) recommended the use of 304 SS for some parts of amine plants that are prone to corrosion. Harston and Ropital (2007) reported that in amine plants, a variety of materials of construction can be used, depending on the location and operating conditions in that particular part of the plant. In low temperature sections of the plant, CS is preferred, while in hot sections, 304L, 316L, and 2205 duplex SS are used.

3.5 Solvent foaming tendency

Amine solvents by themselves do not generate foaming until they become contaminated with certain contaminants such as hydrocarbon, amine degradation products, lubricating oil, surface active agents (such as inhibitors from well and pipe treatments), introduced materials in excessive amounts (i.e., antifoam, chemicals, etc.), and fine solid particles. Foaming can lead to the disruption of the absorption process by interfering with the gas liquid interface or creating higher pressure drop, which will lead to the consumption of more power in the flue gas blowers (Ballard 1966). The temporary solution for foaming is using antifoam agents in small quantities (Cummings et al 2007). Foaming source analysis should be carried out immediately to identify the source of foaming. Activated carbon is usually used to remove surface active agents. Thermal reclamation removes the solid particles and the surface active agents that cause or enhance the foaming. Harston

and Ropital (2007) have shown that foaming is more dominant in MEA and DEA than MDEA plants due to the fact that these two amines are more degradable than MDEA.

3.6 Plugging, fouling, and deposition

Kohl and Nielsen (1997) described the fouling and accumulation of solid particles in heat transfer and mass transfer equipment as problematic. One of the major problems of a degraded solvent is corrosion. Corrosion products accumulate and lead to plugging and precipitation of salts and fine solid particles in dead zone areas all over the plant. Fouling and deposits can be formed from the degradation products, as well as HSSs. Any formation of fouling on the heat transfer equipment reduces the heat transfer performance in the heat exchangers and reboiler and makes it difficult for the plant operation to meet design targets. They can also cause disturbance in mass transfer process.

3.7 Emission and effluent

High degradation products can have dramatic impacts on the environment and on the plant operation. Degradation products can find their way into the atmosphere through the off-gas stream, even if there is a washing section, which can be easily overloaded with chemicals not considered in its design. The washing section in an amine plant is usually designed to reduce the amine and ammonia level in off-gas and not prevent the degradation products from going to the atmosphere (Goff and Rochelle 2004). Increase of washing water to remove any excess impurities or ammonia can lead to an impact on the plant water balance and generate more effluent water. Effluent containing some amine can harm the microbes used in the waste water plant or reduce its treating capacity.

3.8 Energy consumption

Contaminated solvent will lead to increased energy demand due to high false CO₂ loading from the bonding of amine with HSSs or the presence of degradation products that are stronger than amine already loaded with CO₂ (Hatcher et al. 2006). Also, high circulation rate is implemented to maintain the same removal efficiency of CO₂ when degradation products have accumulated in the solvent. (Ballard 1966) showed that the typical temperature for the reboiler to strip H₂S and low CO₂ content would be 112.7-115.5°C while in the case of CO₂, it should only be about 123.8°C. This means that more energy is needed in the case of CO₂ compared to H₂S or H₂S/CO₂ systems, and in the case of degraded solvent and CO₂ absorption, the energy would be much higher.

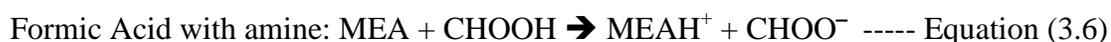
3.9 Solvent analysis

The presence of HSSs might interfere with the colour titration method applied to determine the solvent concentration and CO₂ loading in amine solvent, which are base-acid reactions according to (Cummings et al. 1990). For solvent concentration, a titration amine sample of unknown concentration is tested with a known concentration of a strong acid such as HCl or H₂SO₄. Based on how much acid is consumed, it is possible to determine the amine concentration precisely when the indicator colour changes at the end point, as in equation (3.4):

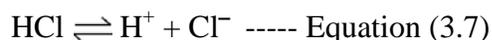


For CO₂ loading, titration with strong acid is continuous by adding double the amount of acid used to determine the end point. This will release all CO₂ absorbed by the amine

solvent, and this CO₂ can be collected and measured to determine the CO₂ loading. In the case of the presence of amine bonded with heat stable anions in amine solvent, the determination of amine concentration can be made inaccurate by shifting the end point pH, as illustrated by (Cummings et al. 1990). Therefore, part of the amine is not available for CO₂ absorption, as seen in equations (3.5) and (3.6).



During the titration, HCl dissociates hydrogen and chloride. The hydrogen is attacked by the carbonylate to form a weak acid. This means that HCl is consumed but does not neutralize the amine, and the calculation will show that the amine concentration is higher than what really exists in the solvent. The following equations (3.7) and (3.8) illustrate this:



3.10 Concluding remarks

- 1- Amine solvent could suffer from degradation that forms degradation products. These chemicals could lead to many operational problems within the amine plant.
- 2- Solvent degradation should be prevented by keeping the solvent clean using solvent purification techniques.

Chapter 4: Amine Solvent Purification Methods (Literature Review)

4.1 Chapter introduction

Purification of solvent is required to maintain its quality and absorption capacity for better performance and economics for CO₂ capture plants. An effective technique must be used to separate degradation products from their parent amines to prevent the operational problems. Operational problems often reported in post-combustion CO₂ capture processes with amine solvents are high energy consumption, foaming, fouling, corrosion, and solvent loss (Ciferno et al. 2009). In general, these problems and other reported in Chapter 3 have one thing in common in that they can all be induced by solvent degradation (Cummings et al 2007; Jouravleva and Davy 2000). To operate the amine process more effectively, these problems should be addressed and solvent degradation should be controlled. Many temporary and long-termed solutions could be used and can be divided into two categories. Each category has various methods, which will be explained in this chapter.

4.2 Solvent cleaning and degradation prevention methods

4.2.1 Change-over solvent inventory

Change-over solvent inventory is the oldest and the least effective method to overcome solvent degradation product build-up. Standard Oil Development Company used on-line neutralization with caustic soda to control HSSs. However, sodium salts produced during neutralization would accumulate in the amine solvent, which led to increase of the viscosity and reduction of the solvent capture capacity. If the viscosity exceeds 4 saybolt,

the whole solvent inventory should be changed with fresh solvent (Paulsen et al 1955). A complete replacement of solvent could still have up to 80% of usable solvent. Therefore, this option is no longer attractive due to concerns over the operating and disposal costs and environmental regulations (Abdi et al 2001).

4.2.2 Solvent purging/feeding

The purge/feed method was seemingly the first method used to overcome the build-up of contamination in the amine solvent (Cummings et al 2007; Kohl and Nielsen 1997; Jouravleva and Davy 2000; Shao, Lu, and Ye 2002). This approach consists of the removal of a portion of contaminated solvent and replacement with fresh and clean ones to reduce the contamination concentration. However, this approach is not practical and is undesirable due to the following reasons:

- It is only a short-term solution and does not address the degradation problem.
- The contaminated solvent, now a waste product, generates more problems in terms of disposal and costs.
- Loss of valuable solvent in waste.
- It involves high operating costs associated with solvent disposal and make-up.

4.2.3 Mechanical filtration

Mechanical filters are usually used to remove suspended fine solid particles and corrosion products from amine solutions (Kohl and Nielsen 1997; Bacon 1987). In the early stages of utilization of amine solvents in the gas processing treatment, it was thought that mechanical filtration could help maintain solvent quality (Cummings et al 2007).

However, mechanical filtration can remove neither HSSs nor degradation products. Therefore, it will not be discussed in detail in this thesis. There are various types of filter materials that could be used in amine systems, which are summarized as follows (Kohl and Nielsen 1997):

- String-wound cotton cartridge filters (low cost, depth filter and flexible type but requires frequent replacement)
- Proprietary cartridge filters (made from special microfabric depth filter but can be expensive)
- Pre-coated filter (requires significant attention and it is not widely used)
- Bag filters (consists of multilayer material and provides high filtration efficiency)
- Sintered metal fiber filters (high filtration capacity and can be back flushed)

The normal design for a filter is based on the amine slipstream varying from 5% to 10% of total lean amine circulation (Harston and Ropital 2007). Slipstream of up to 15% or 20% or sometimes a full filtration stream is also used (Kohl and Nielsen 1997; Ballard 1966). Typically, a filter is selected for capturing 10 micron-sized particles. In reality, there is no standard design that can be followed; thus, it still depends on a rule of thumb in many cases. Some successful filtration systems are reported in the literature. For instance, 3M can be considered one of the largest providers of mechanical filtration solutions, and their performance has also demonstrated within amine plants (Fabio et al 1992). MPR Services has introduced a new technology known as SSX, which has a high efficiency in removing fine solid particles (Cummings et al 2007). Some features of this process are low pressure drop and removal of as small as 1 micron particles. Also, the

system can be cleaned with water and reused for many cycles. MPR Services claims that SSX can remove solid particles better than other mechanical filters (Lawson et al 2003).

4.2.4 Activated carbon filtration

Activated carbon filtration was used as a method to purify and clean the amine solvent (Cummings et al 2007; Dow 1962). The activated carbon was traditionally considered for the removal of foaming formation sources such as surface active organic compounds, high molecular compounds (e.g., polymeric degradation products), dissolved hydrocarbons, lubricants, and very small fine solid particles (Kohl and Nielsen 1997; Scheirman 1973; Perry 1966). The carbon could also remove some degradation products at different rates. However, its adsorption capacity for those degradation products is very small and, therefore, not recommended for a continuous operation (Jouravleva and Davy 2000; Paulsen et al 1955). MPR Services has introduced a new technology, HCX, which has a better performance in removing hydrocarbons when compared with activated carbon (Cummings et al 2007).

Some operators and researchers have strongly recommended activated carbon for secondary and tertiary amine systems but not for primary amine systems (Kohl and Nielsen 1997). To achieve better results from carbon filtration, it is recommended that it be used to treat a cold lean amine stream having a temperature range of 118-142°F. The stream should also be pre- and post-filtered, respectively, with 5 and 10 micron filters before and after treating with the activated carbon. The slipstream of lean amine initially is passed through a pre-mechanical-filter where fine solid particles are removed. The size of slipstream fed through the activated carbon could vary, reported from 1% (Scheirman

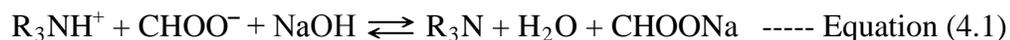
1973) to 2% (Ballard 1966), 3-10% (Harston and Ropital 2007), and 10-20% (Kohl and Nielsen 1997). Then, it is fed into the activated carbon bed after which the treated amine is passed through post-mechanical-filters to remove activated carbon particles possibly leaked out from the carbon bed.

Not all types of activated carbon can be used in the amine system. The recommended ones with a broad range of pore sizes should be hard, fine in mesh size, and steam pre-treated activated carbon. Commercial sizes of activated carbon filters are 5 x 7, 4 x 10, and 8 x 30 meshes. Despite the fact that a smaller size might have a lower pressure drop, 8 x 30 mesh is used the most (Kohl and Nielsen 1997). Activated carbons with iodine numbers between 900 - 1100 are not efficient in removing degradation products, whereas, carbons with molar numbers greater than 200 are more effective in removing liquid hydrocarbons (Pauley 1991).

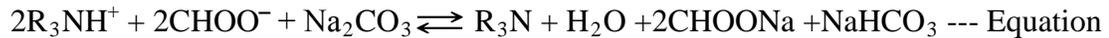
4.2.5 On-line neutralization of heat stable salts

Two examples are given in Equations (4.1) to (4.3) show the neutralization process of formic acid (organic acid forming HSS) in a tertiary amine solution using sodium hydroxide (NaOH) and sodium carbonate (Na₂CO₃) (Cummings et al 2007). As shown in Equation (4.1), 1 mole of NaOH could liberate one mole of amine. In comparison, 1 mole of Na₂CO₃ could liberate two moles of amine and generate one mol CO₂ as given in Equations (4.2) and (4.3). Although Na₂CO₃ may be preferred, its cost is higher than NaOH.

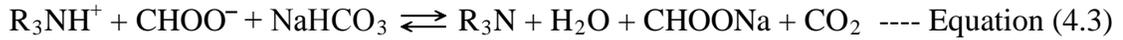
Sodium hydroxide:



Sodium carbonate:



(4.2)



On-line neutralization with Na_2CO_3 or $NaOH$ was reported in many DEA systems when HSS level reached 0.5 wt% or more (Scheirman 1973). The addition of the strong base was usually more than the required quantity by 50%, and DEA solution can tolerate up to 20 wt% sodium salts before any precipitation could occur. Potassium compounds are more soluble by 25% than sodium compounds and, thus, could be used. However, they are more expensive and also more corrosive than $NaOH$ (Berlie, Estep, and Ronicker 1965).

Dow suggested a method to reduce solid formation during the neutralization by mixing an alkali metal-based solution with the relevant amine prior to neutralization. However, the impact obtained was a dilution effect of the amine on the overall system rather than any other mechanisms (Rooney 1999). In one of Dow's publications, they claimed that the on-line neutralization could reduce corrosion. However, their investigation was only based on laboratory tests without confirmation from actual plant observations (Asperger et al 1995). Apparently, the expected reason for corrosion reduction is the increase of pH with addition of a strong base and the liberation of bound amines with HSSs that contributes to increase of the solvent pH (Liu et al 1995). More advantages of on-line neutralization are reported, including decrease of fouling, increase of efficiency of heat exchangers, and absence of foaming (Liu et al 1995).

In some plants without on-site reclaimers, on-line neutralization was utilized as a temporary solution to recovery the amine until the solvent could be reclaimed off-site or with a mobile reclaimer (Burns and Gregory 1995b). On-line neutralization could give a false sense of solvent purity even when HSSs are under control, which is usually indicated by more stable operation with reduction of corrosion and foaming tendency and restoration of solvent absorption capacity by freeing bound amines (Cummings et al 2007; Cummings and Mecum 1998). In fact, HSS organic/inorganic acid anions do not actually disappear from the solution. Rather, they form neutralized salts, which could subsequently lead to a number of problems such as increase of corrosion, salt precipitation, high viscosity and density, reduction in surface tension, increase of foaming formation tendency, formation of false high loading, and reduced solvent for scrubbing the acid gases (Cummings et al 2007; Verma and Verma 2009). To overcome such problems, it has been proposed to integrate on-line neutralization with electro dialysis reclaimers, which will remove both acid anions and sodium cations (Burns and Gregory 1995b).

4.2.6 Solvent degradation inhibition

Increase of solvent degradation resistance has been one of the most active research and development areas since the 1940s (Kindrick 1950; Kindrick et al 1950; Blachly and Ravner 1964). This is achieved by selecting amine solvents that have a high resistance for oxidative degradation. Also, chemical additives in small concentrations can be added either to inhibit the solvent degradation or eliminate/reduce the availability of degradation inducing impurities such as O₂ and SO₂. The US Navy reported a comprehensive study done by the Girdler Corporation to evaluate potential amine solvents for CO₂ removal

and their resistance to oxidative degradation (Kindrick 1950; Kindrick et al 1950). The evaluation was done for 39 single and 4 mixed amines. The outcome from the Girdler Corp. evaluation showed that 12 single and 3 mixed amines were promising, showing high resistance to oxidation degradation. They concluded that the tertiary amines had the highest oxidation resistance, followed by secondary and, finally, primary amines. However, only monoethanolamine (MEA) was selected and used. The rest of the amines proposed by the Girdler Corp. were not considered for real application at the time, possibly due to lack of fundamental information (Blachly and Ravner 1964).

The US Naval Research Laboratory (US NRL) also issued a report on inhibition of MEA degradation (Blachly and Ravner 1964). It mentioned that N, N-diethanolglycine (VFS) and ethylenediaminetetraacetic acid (EDTA) or their blends were found to stabilize MEA solvent by destroying the amine degradation products. However, these additives were not effective in the presence of metals (i.e., copper, iron, nickel and chromium), which acted as catalysts in the solvent degradation process (Blachly and Ravner 1964).

MEA could be made more stable by adding a 0.5 to 5 wt% tertiary amine (i.e., triethanolamine, triisopropanolamine, and triisobutanolamine) as shown in one of Union Carbide's patents (Singh 1970). Based on laboratory tests, these inhibitors reduced the MEA degradation by over 98% in the presence of acid gases (i.e., CO₂ and H₂S). However, no evidence was found to show that this method was also tested in a real plant. Ten years later, UOP found methyldiethanolamine (MDEA) in concentrations of 4-25 wt% more suitable to inhibit MEA degradation, and also for DEA, than other trialkanolamines (Faucher 1989). UOP claimed that trialkanolamines could not be

recovered during regeneration (reclamation) due to their high boiling points and molecular weights.

Another inhibition method for amine degradation is given by Cata Chem Inc. in which the formation of HSSs can be reduced by addition of N,N-diethylhydroxyamine (DEHA) catalyzed by hydroquinone at a ratio of 0.5-6 ppm for every ppm of hydroquinone added (Soria 1998). On the other hand, DEHA used alone has no impact on inhibition. Recently, researchers from the University of Regina have proposed a method to inhibit O₂ and SO₂ induced degradation of MEA solvent by the addition of sodium sulfite (Na₂SO₃), potassium sodium tartrate tetrahydrate (KNaC₄H₄.4H₂O), ethylenediaminetetraacetic acid (EDTA), hydroxylamine (NH₂OH), and their mixtures (Idem et al. 2009).

4.3 Recycling and Reclaiming Methods

4.3.1 Ion exchange reclaimer

The ion exchange action is similar to online neutralization with strong bases, but there is little difference in mechanisms of neutralization. Ion exchange occurs between liquid (i.e., amine solution) and solid (i.e., strong base resin containing hydroxide-resin), whereas online neutralization occurs between liquid (amine solution) and liquid (strong base solution) (Cummings et al 2007). The ion exchange technology has been adopted based on its success in other industrial applications such as treatment of boiler water and recoveries of acids and metals. The two major ion exchange commercial providers are Eco-Tec² and MPR Services³ based in Pickering, Ontario and Dickinson, Texas,

² www.eco-tec.com

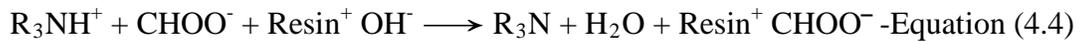
³ www.mprserve.com

respectively. The ion exchange-based reclaimer technologies commercialized respectively by Eco-Tec and MPR Services are AmiPur Plus and HSSX.

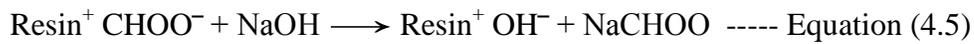
These technologies have been claimed to provide the optimum removal of major solvent contaminants (“heat stable salts”) with less chemical, energy, and water consumption. Also, waste (i.e., brine) is produced in small quantity and contains only traces of amine solvent or none at all. Previous ion exchange reclaimers suffered from many drawbacks, as mentioned by MPR services or Eco-Tec. For instance, MPR has pointed out the drawbacks in the previous ion exchange processes used in amine systems, as they were ineffective and produced huge quantities of waste, which sometime contained significant amounts of amine solvent, making it untreatable in waste water plants in some cases (Cummings et al 2007).

The resin’s hydroxide ions (OH^-) were exchanged with organic acid anions, thereby freeing the amine to acid gas absorption cycle. Based on this, it can be seen that the effect of ion-exchange is similar to acid-base neutralization, with the exception that the product of neutralization is held on the resin until the resin is regenerated (Cummings et al 2007; Verma and Verma 2009), while the cleaned solvent is released to the amine process. The typical ion exchange process involves two steps, as shown in equations (4.4) and (4.5): the loading step (to remove contaminants from solution) and the regeneration step (treating the resin with strong base solution to remove contaminants from the resin by replacing acid anions with hydroxide to restore adsorption capacity of the resin and forming base salts, which will be sent to waste treatment).

Loading step:



Regeneration step:



The ion-exchange usually operates in a continuous or “semi-continuous” mode to treat a small slipstream of cold and contaminated lean amine, but it could be a batch operation in some cases. Sizes of reclaimer and slipstream depend on the severity of the contamination. Continuous operation has proven to be more efficient than batch treatment, as contaminants of acid anions are treated as they are formed, thereby instantly preventing operational problems. The process operates with a number of cycles in a specific sequence: loading (removing contaminants), regeneration (removing neutralized salts), and washing (water). After water washing, the bed is ready to accept a new batch of contaminated slipstream. The cycle is then repeated to maintain the target level of contamination in the lean amine solution. The waste is sent to the wastewater plant, which it is biologically degradable (Cummings et al 2007). Table 5 summaries the ion exchange reclaimer developers and providers.

4.3.1.1 Ion exchange reclaimer and CO₂ capture applications

It can be understood that the ion-exchange process might be acceptable in natural gas treating services, as the acid gas loading is preferred to be as small as possible (or even zero) to achieve pipeline specifications (Kohl and Nielsen 1997). The acid gas in solvent, or the bisulfate (HS⁻), carbonate (CO₃²⁻), and bicarbonate (HCO₃⁻), would not interfere or compete with HSSs adsorption in the ion exchange reactions. In CO₂ capture, particularly from flue gases, the lean amine usually contains a higher acid gas loading (0.1-0.2 mol CO₂/mol amine or even higher) compared to natural gas sweetening (Kohl and Nielsen

1997; Hendriks 1994). The high loading is desired, as it helps reduce the energy demand of the reboiler, improve the plant economics, and reduce the solvent degradation by reducing the solvent ability to dissolve the impurities in the flue gas feed (Uyanga and Idem 2007). The high acid loading or high level of CO_3^{2-} and HCO_3^- in the amine solution could interfere and compete with HSSs anions in the resin, leading to reduced effectiveness of the ion exchange process in removing HSSs.

An informative website (IDSWater, the Information Resource for the Water Industry! 2011) dealing with water treatment for manufacture of industrial products mentioned that the Eco-Tec's AmiPur ion exchange technology was integrated to Fluor's amine process Econamine. Furthermore, Fluor Corporation has mentioned that the ion-exchange process was used and tested in its Econamine technology (Reddy et al 2008). However, very little information was available on its performance. Despite the fact that ion exchange technology can be applied for removal of organic acids from amine solution, the process alone cannot be considered an optimum solution for CO_2 capture application. Contamination of amine solvent used in treating flue gases is completely different from those in natural gas sweetening processes. Differences between both applications are summarized in Table 4. In addition to HSSs, major troublesome contaminants in CO_2 capture applications from flue gas are amine degradation products. However, their formation, such as amides, has been reported to decrease after organic acid anions are removed by ion exchange (Cummings and Mecum 2000).

MPR Services has proposed a new ion exchange process known as Carbon Capture Amine Reclamation (CCAR) to treat the contaminated amine solvents used in CO_2 capture systems (MPR Services 2011). However, no information on its performance or

testing in any CO₂ capture plant is reported. In a recent announcement on its website, Eco-Tec has developed a new technology to treat the contaminated solvent used in CO₂ capture processes given under the name of AmiPur-CCS. However, information is not given to verify if the process has ever been tested in a real CO₂ capture system.

Table 4 Difference between natural gas and CO₂ capture processes

| | Natural Gas Sweetening | CCS application |
|---------------|--|---|
| System Design | <ul style="list-style-type: none"> • High pressure • Carbon steel with some section with stainless steel • Smaller- to medium-size equipment and solvent inventory. | <ul style="list-style-type: none"> • Low pressure • Stainless steel or high resistance alloy for corrosion • Large-size plant (equipment and solvent inventory). |
| Chemistry | Absorption of H ₂ S &/or CO ₂ from natural or process gas stream or hydrocarbon liquids. | Absorption of CO ₂ from flue gas stream. |
| Impurities | Mercaptanes, cyanides and thiocyanides, organic acids, sulphate and thiosulfates, hydrocarbons, leaked oxygen (low concentration). | Oxygen (high concentration), SO _x , NO _x , fly ash. |
| Degradation | Heat stable salts are major degradation products to be addressed, while amine degradation products are minor to moderate in importance! | Heat stable salts and amine degradation products are almost in equivalent ratio in terms of importance to be addressed! |

Table 5 Development of ion-exchange reclaimer

| Company | Ion Exchange Reclaimer | Reference |
|------------------------------|---|---|
| MPR Services | <ul style="list-style-type: none"> • First generation of HSSX reclaimer to treat HSSs anions | (Keller et al. 1992), (Coberly et al. 1998), |
| | <ul style="list-style-type: none"> • Second generation of HSSX Reclaimer to treat all HSSs anions, • reduce the water chemical consumption • report on their successful story • amides could be removed | (Cummings et al. 2007; Cummings and Mecum 2000; Cummings et al. 2003; Cummings et al. 2005) |
| Eco-Tec | <ul style="list-style-type: none"> • First generation from AmiPur reclaimer • Recoflo technology was introduced, which is compact, efficient, and provides a uniform distribution of treated liquid within the resin | (C. J. Brown 1987), (Jouravleva and Davy 2000) |
| | <ul style="list-style-type: none"> • fine mesh resins, short and packed resin bed, • low resin loading and fast treatment cycle, • counter current regeneration, | (S. Reddy et al. 2003), (Dandekar and Shao 2011), (Pearson et al. 2005), (Verma and Verma 2009) |
| Lo-Vaca Gathering co. | <ul style="list-style-type: none"> • Developed process for treat HSS in DEA system | (Morgan and Klare 1977) |
| Conoco Inc. | <ul style="list-style-type: none"> • ion-exchange process specifically using a two bed system of anion and cation ion exchange resins to remove HSSs | (Keller 1991) |
| | <ul style="list-style-type: none"> • they improved the process by using two resins consisting of stronger and weaker base anion resins, as opposed to the original containing only one strong base anion exchange resin | (Cummings et al. 1992) |
| Mobile Oil Corporation | <ul style="list-style-type: none"> • ion exchange process consisting of a three-stage operation: mechanical and activated carbon filtration, type I strong base resin to remove strong anions such as thiocyanate and sulfate, and type II strong base resin to remove other weaker anions such as formate and acetate | (George 2001) |
| Cansolv Technologies | <ul style="list-style-type: none"> • an ion exchange reclaimer to treat three amine solvents used in their capture process | (Sarlis 2007) |
| National Iranian Gas Company | <ul style="list-style-type: none"> • The developed their own ion exchange system based on laboratory investigations to control HSS | (Jameh 2010) |

4.3.2 Electrodialysis reclamation

A typical electrodialysis process involves utilization of electrical current, potential voltage, and ion-selective membranes to separate ionic degradation products and HSSs. The separation is done with a process set-up consisting of a stack of alternating cation- and anion-selective membranes located between two electrodes. The filtered degraded amine feed can be treated with or without NaOH/Na₂CO₃ prior to being introduced to specific channels between stacks of the cells. It is recommended to use cold lean amine at 110°F or less to be treated in the electrodialysis reclaimer (Burns and Gregory 1995c). The separation is carried out between cations and anions towards their opposite electrodes and through the selective-ion membrane, which only allows cations or anions to pass and prevents the others from passing. Therefore, the ED process is only capable of removing HSSs while other degradation products or contaminants are left in the amine solvent. Due to the temperature sensitivity and limitations of the materials used in manufacturing the ion-exchange membrane, the recommended amine feed should not be very warm. Thus, downstream of the lean amine cooler is the best location to extract the slipstream, which is then fed through 10 micron filters before sending it to the ED unit to prevent membrane fouling (Kohl and Nielsen 1997; Burns and Gregory 1995b). A schematic diagram illustrating the concept of the electrodialysis process is shown in Figure 5.

During the design of the ED process, there are some important factors that affect the process performance (Burns and Gregory 1995c): ion-exchange membrane type, surface

area, type of solution to be treated, and the applied current, which is the main effluence factor that affects the removal efficiency.

$$r = \frac{E \times n \times I}{F} \quad \text{----- Equation (4.6)}$$

where: r = Removal rate (g-eq/sec),
I = current (Amps)
N = number of membrane cell pairs
F = Faradays contact (96,480 Coulombs/g-eq)
E = efficiency factor

Electrodialysis (ED) reclamation has been pioneered by the Union Carbide Corporation (which was later acquired by Dow) and the Dow Chemical Company (Kohl and Nielsen 1997). The process was patented for treating contaminated amine solvent in 1989 (Bedell and Tsai 1989b; Bedell and Tsai 1989a) which was successfully tested on a laboratory scale to remove formic acid from degraded MDEA solvent, and the waste mobile phase was 0.1N NaCl in water to facilitate the separation of formate from MDEA. The process was further tested and developed to be integrated with the amine process for capture of acid gases (Liu et al 1995; Roy et al 1994). The addition of a strong base such as caustic soda to amine prior to feeding to the ED process was found to help free the amine from HSSs, making removal from the amine stream easier (Gregory and Cohen 1999). The removal efficiency of HSSs was reported from 60 to 90%. Dow's Ucarsep ED process uses the recirculation of amine and brine to remove HSSs. The process has helped to reduce chemical consumption and improved of the reclamation performance as shown in Figure 5.

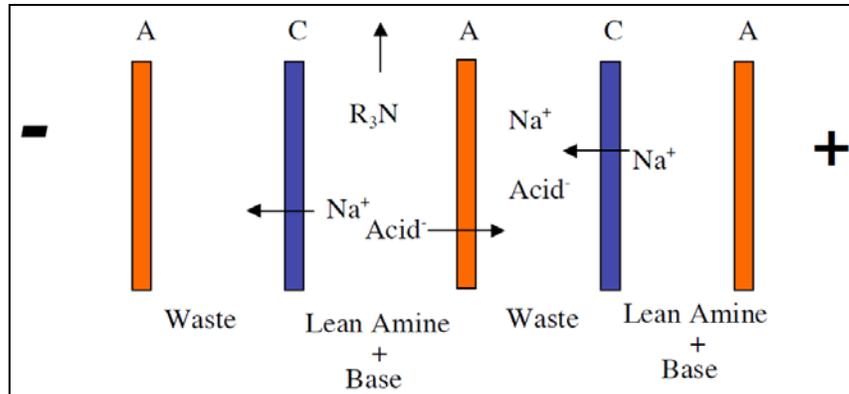


Figure 5 Dow Electrodialysis Process: UCARSEP (Burns and Gregory 1995a; Parisi and Bosen 2006b)

(Used with permission from ElectroSep and Gas Processors Association)

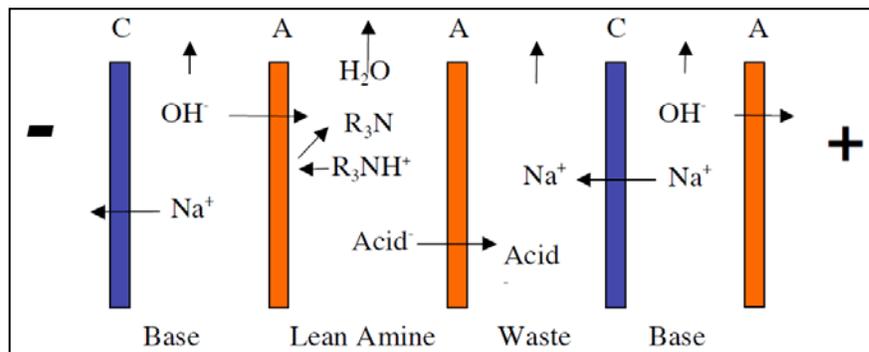


Figure 6 ElectroSep electrodilysis process (Parisi and Bosen 2006b)

(Used with permission from ElectroSep and Gas Processors Association)

The Ucarsep process has proven to be an effective on-line reclamation process that helps resolve operational problems caused by HSSs during amine plant operation, as well as to maintain low levels of HSSs (i.e., <1 wt%). The Ucarsep performance was satisfactory when tested in various amine plants operated in oil refineries (Burns and Gregory 1995c; Burns and Gregory 1995a).

ElectroSep is another ED provider that was also tested in some oil refineries (Parisi and Bosen 2006b; Parisi and Bosen 2006a). ElectroSep⁴ was likely adapted and modified from Dow's ED technology to reduce the utility consumption and enhance separation (Parisi and Bosen 2006b). As shown in one of ElectroSep patents, the improvements include recirculation of the salt mobile phase for enhanced removal of HSSs and reduction of water and chemical consumption (Byszewski 2002). As well, the technique proposed different arrangements for the membrane stack (Parisi and Bosen 2006b), as shown in Figure 6.

As reported by Dow, the Ucarsep process has some limitations and drawbacks. For instance, it is possible to lose 1-2% of amine inventory during the reclamation process, and membrane fouling could develop with time, resulting in reduction of permeability (Burns and Gregory 1995a). On the other hand, ElectroSep was claimed to recover more than 99% of amine (Parisi and Bosen 2006b). However, MPR Services, an ion-exchange reclaimer competitor, mentions some drawbacks of the ED process as follows (Cummings et al 2007):

- ED requires filtration pretreatment of amine feed down to 1 micron to avoid fouling

⁴ www.electrosep.com

- ED demands more energy than distillation and ion-exchange
- ED produces more waste than distillation
- The waste might be considered hazardous and cannot be treated in wastewater plants

Another limitation of the ED process is the loss of water from the amine stream due to osmosis, which could affect water balance in the amine system. Also, amine carbamate (CO₂-amine), carbonate, and bicarbonate could be separated and lost in the waste stream. This could occur especially if the acid gas loading is high. Furthermore, sodium cations used in the regeneration step could leak to the amine system from the ion exchange (Burns and Gregory 1995c). The ED is not the optimum choice for CO₂ capture process since it cannot remove neutral amine degradation products usually present with HSSs.

4.3.3 Thermal reclamation

Thermal reclaimers use evaporation to purify an amine solvent from its degradation products. Typically, the degraded amine slipstream is mixed with a strong base, such as caustic soda or soda ash, to release the amine trapped by HSSs. Then, the mixture is either allowed to settle for some time to remove the solids and precipitated matters or sent directly to the reclaimer where evaporation is carried out inside a special distillation equipment. Usually, the added amount of sodium carbonates/hydroxide is slightly greater or less than the stoichiometric amount of HSSs (Bedell and Tsai 1989b). One mole of sodium carbonate could release two moles of amine, while hydroxide could release one mole of amine, as explained earlier in Equations (4.1) to (4.3).

The companies that have developed/commercialized the thermal reclamation include Dow Chemicals, Mobil Oil Corp., Huntsman, Praxair, Shell, Canadian Chemical

Reclaiming Technologies, and other companies that do not exist anymore. All have developed fixed and mobile reclamation units, and few of them have sophisticated reclamation facilities that will reclaim the amine off-site. The drawbacks and merits of a typical thermal reclaimer are summarized (Cummings et al 2007). The operating conditions of a thermal reclaimer depend on the type of solvent.

Dow conducted a thermal stability study for MEA and concluded it is stable up to 300°F. Dow also mentioned that diluting the amine with water would enhance the thermal stability. MDEA has been thermally degraded at 360°F (Bedell et al. 2010); thus, this temperature should be avoided in its reclaiming. High boiling point amines such as DEA and MDEA should be reclaimed under vacuum (Bacon 1987).

Reclamation of secondary and tertiary amine solvents, used singly or in mixed formulations, has not been extensively reported in the literature. The secondary and tertiary amines or their mixtures are reported to be reclaimed by thermal distillation under vacuum with temperatures not exceeding 400°F (Kohl and Nielsen 1997). Limited information exists as a guideline in reclaiming these amines. DEA or DIPA reclamation is carried out under deep vacuum (using a tray distillation process with direct steam, pressure of 50-100 mmHg, and maximum temperature of 300°F) (Kohl and Nielsen 1997). The reason for this limitation is that the reclamation process may be quite complex and not ready to be utilized for many single, mixed or formulated amine solvents.

4.3.3.1 Classical thermal reclaimer (atmospheric pressure or above)

Dow published a book giving details of classical amine thermal reclaimers (atmospheric or above atmospheric pressure or vacuum) (Dow 1962). Operating pressure will control

the reclamation cycle. For example, high pressure operation would indicate a short cycle and large dumping, while atmospheric reclamation exhibits the opposite trend (Blake and Rothert 1962). As reported by Dow, an atmospheric reclaimer is suitable for easy-to-recover amines such as MEA, in which case the reclaimer could be designed to operate in either batch, semi-continuous, or continuous mode (Dow 1962). Easy reclamation means degradation products have very low vapour pressure compared to the amine solvent (Butwell 1968). Dow suggested that a 1 - 2% lean amine slipstream be fed into the reclaimer in continuous mode. The slip ratio can be varied based on the amount of contamination in the solvent and amount of solvent inventory (Wonder et al. 1959). An example is given in the appendix to show the impacts of slip ratio on the reclamation cycle (it cleans the whole inventory). Dow suggested heat flux be limited to 5000 Btu/hr/ft² in order to control thermal degradation due to excess heat. The water and amine vapour from the reclaimer could be injected to the stripper bottom or mixed with vapour stream from the stripper reboiler. Neutralization with sodium hydroxide or carbonate could be used to liberate trapped amine in HSSs. The size of the traditional atmospheric reclaimer is usually designed based on the volume slipstream sent to the it, as well as and targeted residence time, as shown in Equation (4.7) (Blake and Rothert 1962).

Reclaimer Size = Scale up factor × Slip Stream × residence time - Equation (4.7)

The scale-up factor can be varied depending on amine plant size, economics, and expected solvent degradation rate. For instance, this factor could be varied from 50 to 100 (Blake and Rothert 1962) in which small values are used for a large reclaimer and vice versa for small ones (Jefferson Chemicals 1963). For preliminary sizing calculation, a factor of 75 could be used.

The classical reclaimers are designed based on the lean amine solvent concentration, temperature, and pressure as reported by Dow (Dow 1962). Such a design is made to ensure an effective amine recovery operation using suitable temperature/pressure away from the thermal degradation temperature of the amine. In the reclaimer operation, the boiling liquid inside the reclaimer is brought into equilibrium with the amine vapour leaving the reclaimer. This ensures that the exiting vapour also contains the same concentration as the feed amine stream. This relationship can be explained by the vapour-liquid equilibrium graph for a MEA system as shown in Figure 7. As the boiling liquid becomes more concentrated with salts and degradation products, its boiling temperature steadily increases (Kohl and Nielsen 1997; Blake 1963). The reclaimer operation is held steady when the temperature reaches the maximum allowable point to avoid thermal degradation. The diluting water (usually from reflux water) or steam is added to recover as much amine as possible. Addition of water also helps reduce the amine partial pressure and control the temperature inside the reclaimer. The reclaimer feed to water dilution can vary from 3 to 5 per determination of the plant operators, which would be the optimum to enhance the solvent recovery (Corsi et al. 2002). Table 6 summaries some other thermal reclaimer developers and providers.

The reclaimer cycle is terminated when the temperature approaches the maximum temperature or the amount of amine in the vapour stream falls sharply below the amine concentration in the feed (i.e., 1wt%) (Dow 1962). This means the maximum technically amine recovery is achieved and can no longer be enhanced by addition of water. Once the reclamation cycle is terminated, the reclaimer is cleaned and prepared for the next cycle. The reclaimer waste is usually a thick, viscous, and sludge-like crude oil.

Due to high levels of many degradation products, reclaimer waste could be considered hazardous and should be handled via a professional waste management company. The waste could contain high amounts of useable solvent. In one case reported by Union Carbide Chemicals Company, the residue waste from a MEA reclaimer could contain at least 74.6% MEA (Wonder et al. 1959). MPR Services claimed that in the classical reclaimer with primary amines, the waste contains high levels of amine. To explain this, MPR Services has introduced a factor to evaluate this loss, which is the ratio of amine to HSS. It is advisable to have this ratio in waste be less than the ratio in the lean amine stream. However, based on MPR Services observations, this does not happen in many cases (Cummings et al 2007). The general advantages and disadvantages of this reclamation are given in Table 7.

Table 6 Development of classical thermal reclaimer

| Company | Thermal Reclaimer | Reference |
|--|---|-----------------------|
| Tidewater Oil Company | <ul style="list-style-type: none"> Neutralization HSSs with single strong base and thermal recovery of amine at 460⁰F in a distillation column. Vent if washed by water to capture amine | (Anderson 1959) |
| | <ul style="list-style-type: none"> Neutralization HSSs with mixed strong base and thermal recovery of amine in a distillation column. Vent if washed by water to capture amine | (Anderson et al 1959) |
| Union Carbide Corporation (Dow currently) | <ul style="list-style-type: none"> Neutralization HSSs with single strong base and thermal recovery of MEA or TEA solvent used to capture SO₂ | (Sokolik et al 1983) |
| Huntsman | <ul style="list-style-type: none"> Develop thermal reclaimer for DGA which operate at 1 bar or slightly higher | (Huntsman 2005) |
| Praxair Inc. | <ul style="list-style-type: none"> They did calculation work towards developing of thermal reclaimer for MEA and MEA/MDEA solvents. Operating envelop of this reclaimer is 0.5-65 psia and 250-300⁰F. | (Burgers et al 2007) |

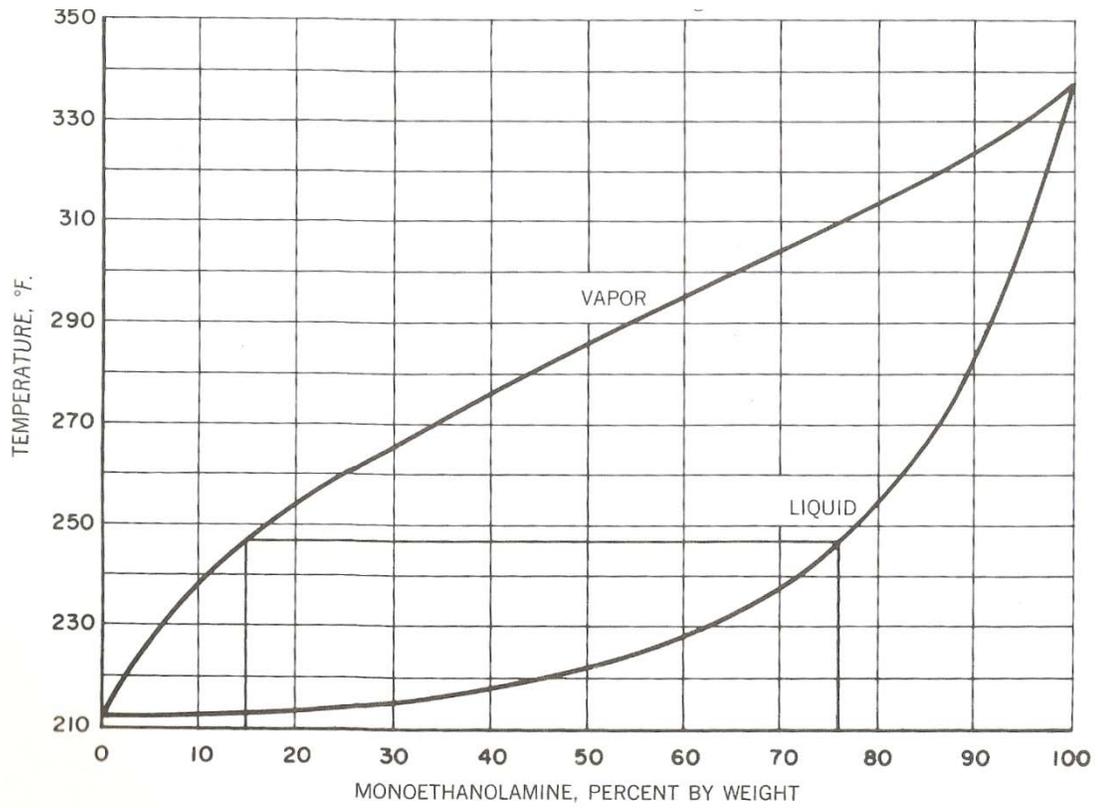


Figure 7 Liquid-gas equilibrium curve of a MEA-water system (Dow 1962)

(Used with permission from Dow Chemical Company)

Table 7 Advantages and disadvantages of solvent thermal reclamation

| | Advantages | Disadvantages |
|----------------------|--|--|
| Solvent | <ul style="list-style-type: none"> • Can be used for many single solvents. • Solvent recovery can be as high as 95%. | <ul style="list-style-type: none"> • Solvent loss in reclaimer waste can be as high as 60%, which is higher than other reclamation technologies. • High boiling point or blended solvent might need special designs. |
| Degradation products | High removal for most degradation products and all impurities. | Volatile degradation products might escape and contaminate the recovered solvent. |
| Heat Stable Salts | Neutralization is required to convert all HSS to salts that cannot be evaporated. | If neutralization or mixing of a neutralizer with solvent is not complete, it is possible to evaporate and contaminate the recovered solvent. |
| Energy | Energy can be supplied through steam or heating oil or fire heat. | <ul style="list-style-type: none"> • Energy demands could be very high and costly. • Type or condition of energy required might not be available. • Hot spots and high temperature could lead to thermal degradation and fouling. |
| Operation | Reclaimer operation is flexible and needs minimum attention. | <ul style="list-style-type: none"> • Could be required for 24/7 operation. • Special operation philosophy might be needed for blended solvents. |
| Chemicals | Chemical consumption is less than any other reclaimer technology. | High addition of chemicals might lead to increase in overall boiling point of solvent and to greater solvent loss. |
| Waste | It generates low quantities of waste and wastes a low amount of water. | Waste is hazardous. |

4.3.3.2 Modern thermal reclaimers (atmospheric or below)

Modern thermal reclaimers can be considered the second generation of thermal reclaimers. The process is designed to reclaim high boiling point secondary and tertiary amine solvents or their blends, which are sensitive to decomposition at high temperature. It is well known that many amine solvents start to thermally decompose (degrade) if the temperature exceeds 400°F.

The leading company in developing modern thermal reclamation is Canadian Chemical Reclaiming (CCR) Technologies⁵, Calgary, Alberta (Canada). According to CCR, their tests and evaluation of all the potential options to purify contaminated solvent only showed vacuum distillation as the most effective method for purification (Millard and Beasley 1993). CCR claimed that their processes could reclaim any single or blended amines.

The CCR reclaimer first appeared in detail in a patent by its founders in 1992 (Beasley and Merritt 1992a; Beasley and Merritt 1992b). Their first reclaimer, called version 1, was to be distinguished from the other versions proposed later. The CCR reclaimer objectives are the removal of contamination, enhancement of solvent recovery (90 to 95%), and reduction of the potential thermal degradation and corrosion within the reclaimer (Beasley and Merritt 1992a; Beasley and Merritt 1992b). The contaminations targeted by the CCR reclaimer are thermal degradation products, HSSs, hydrocarbons, and suspended solid matters with removal efficiency set to exceed 99% (Millard and Beasley 1993). DEA solvent was used to demonstrate the reclaimer performance in which a recovery rate of 90 to 95% was achieved. Amine content in waste could vary from 5 to

⁵ www.reclaim.com

15% to ensure fluidity within the process and the handling of the reclaimer waste. The reclaimer can operate in continuous or batch mode (Meisen et al. 1996).

The CCR reclaimer (version 1) has a unique design. The amine feed (at 40-75°F) is supplied to a feed tank, which helps maintain constant flow to the reclaimer. After mixing the amine with hot recycled amine bottom stream from the heater, it is preheated in a heat exchanger and then fed to an evaporator at vacuum pressure (16-25" Hg). Water and some amine evaporate and partial condensation occurs in the heat exchanger where the coming amine feed is also preheated. Then, the partially condensed stream is sent to a separator to separate liquid (condensate) from vapour. The condensate (i.e., recovered amine) is cooled and filtered before being sent back to the amine system. The separator top stream, consisting of water, non-condensable gases, light hydrocarbon, and traces of amine, is sent to the condenser for water and amine recovery. Non-condensable gases and light hydrocarbons are fed to the heater/burner to destroy them before they can be released to the atmosphere. In the evaporator, the bottom stream is split into two streams: part is recycled (at a ratio of 40 times to the feed (Millard and Beasley 1993)) and mixed with amine feed after heating it up in the heater, while portions of the bottom are taken as waste to control the salt and degradation product content in the recycled stream and avoid fouling. The heater is designed to have a limited heat transfer at 5,000 Btu/hr/ft², 30 - 60 seconds of amine solvent residence time with velocity varying from 6 to 10 ft/sec, and 400°F maximum temperature.

The version 1 reclaimer could be used to reclaim amine solvent (for the removal of acid gas), glycol solvent (for dehydration), and physical solvent. Successful reclamation by this reclaimer includes recovery of MDEA, ethylene glycol, Sulfinol M solution (Millard

and Beasley 1993), DEA, Sulfinol-D solution, and formulated solvent (MDEA-based solvent) (Meisen et al. 1996). In 1995, CCR generated a patent for a new application of their version 1 reclaimer to manage chemical waste and recover water to reduce the amount of waste produced for easy handling and disposal (Beasley and Merritt 1992b; Beasley and Merritt 1995).

CCR and the University of British Columbia modified the version 1 reclaimer to overcome co-evaporation of amine and its degradation products of similar boiling points. The modified process (version 2) used a new separator with two separation steps connected in series: 1) inert liquid extraction (i.e., normal paraffinic oil) to remove degradation products from the amine and 2) distillation to recover amine and water at the top while the inert liquid, richer in the light degradation products and non-volatile materials, is separated at the bottom (Meisen et al. 1996). The example use of the version 2 reclaimer demonstrated by CCR was to recover DEA from its light degradation product, Bis-Hydroxyethyl Piperazine (BHEP). This reclaimer, as claimed by CCR, has the following features: high solvent recovery, low solubility of inert liquid in amine, and significant reduction of thermal degradation of amine in the heater. Waste from the gravity separator that was also claimed mainly consisted of degradation products with very small amounts of inert liquid. However, this has not been tested and unlikely will be. One shortcoming of the proposed process is that contamination and accumulation of the extractive liquid in the amine system could occur and possibly induce foaming and plugging problems.

A third version reclaimer was invented by CCR at the end of the 1990s (Abry et al. 1999). The process proposed by CCR consists of two heating zones. The first zone is

used to evaporate water and amine solvent while purging of the evaporator bottom is done from time to time to control solids build up. In this zone, the amine feed is first mixed with hot recycled bottom liquid stream from the reclaimer evaporator using an appropriate type of mixing equipment. The hot mixture is introduced to the evaporator vessel operated under a deep vacuum pressure (i.e., 16" Hg) at which most of the amine and water are evaporated. The evaporator bottom, consisting of solid, degradation products, and some water and amine, is heated and recycled to enhance recovery of solvent, as well as to help heat up the coming feed. Some of the bottom liquid is recycled before heating and sprayed in the evaporator to control foaming formation. The second heating zone is composed of a distillation unit used to separate water and amine, as well as the non-condensable gases in the vapour leaving the first heating zone. Within the CCR patent (Abry et al. 1999), two other modifications of the first heating zone are proposed: one without the foaming control bottom stream and the second with the use of any filtration equipment to separate solids from the foaming control stream of bottom mixture going to the evaporator. However, the processes with both proposed configurations are similar to the third version.

CCR's version 4 reclaimer was modified from the version 3 reclaimer (Razzaghi et al. 2000; Razzaghi et al. 2000). The difference between the two versions is recycling of some of the recovered water and recovered amine and mixing them with incoming feed. This is believed to enhance solvent recovery and minimize the energy consumption. According to CCR, enhancement in the reclaimer performance will help to control foaming and temperature and maximize solvent quality. CCR also suggested another configuration change for the reclaimer of version 4 to its version five reclaimer. The

version 5 reclaimer has a second distillation zone to handle recovery of mixed amine (Razzaghi et al. 2000; Razzaghi et al. 2000). However, CCR has not provided any performance data on either of these two proposed reclaimers.

4.3.3.3 Molecular distillation reclaimer (deep vacuum)

Molecular distillation is specifically operated so that evaporation and condensation can occur in a short period of time. Evaporated molecules only travel a short distance from the evaporating surface to where they get condensed. Thus, resistance in vapour space experienced by the molecules is reduced. As a result, there is no condensation back to the boiling surface, which is usually found in normal distillation. Moreover, the molecular distillation equipment is usually run at a very deep vacuum (i.e., $\ll 10$ mmHg), and the system is degassed from non-condensable gases before proceeding in operation, which could interfere in the distillation process. A number of apparatuses in molecular distillation could be used, but each apparatus has a different approach and productivity load in achieving the concept of molecular distillation. These apparatuses are as follows:

- Pot (Batch) stills
- Rotary stills
- Falling film stills (high residence time and lower production)
- Centrifugal stills (short residence time and high production)
- Wiped-film stills

Molecular distillation is used to recover temperature sensitive chemicals (Lohwater 1967); thus, this type of distillation is used to purify vitamins, fish liver oil, vegetable oils, lubricants, and heavy petroleum residues (Beasley and Merritt 1992a). It was

reported that tertiary amine was separated from other amines by molecular distillation (Lohwater 1967; Hollo et al 1971). Shell has a patent proposing the use of a falling film or wiped-film evaporator to recover DIPA in two evaporation steps in which water is first recovered followed by the amine (Van Grinsven and Van Heeringen 2000). ChemGroup⁶ has reported that wiped-film distillation can be used to reclaim different types of amines (i.e., primary, secondary, and tertiary), glycols, heating oil, and lubricants. On their website, ChemGroup reported two case studies for the reclamation of DGA and DEA. However, molecular distillation is unlikely used in normal amine plants due to cost and complications of operation and maintenance.

4.3.4 Other reclamation methods

4.3.4.1 Combined reclamation processes

Combined reclamation uses a combination of more than one process to remove HSSs and degradation products. Early in 1955, Standard Oil Development Company proposed a DEA reclamation process that consisted of five stages to manage solvent degradation problems. The process replaced the ineffective on-line neutralization of HSSs, which was considered to induce additional problems. They reported that online neutralization increased viscosity and reduced CO₂ capture efficiency of the solvent. The heavily-degraded solvent, having viscosity of more than 4 Saybolt, should be eventually discarded and replaced with fresh solvent. The five steps proposed in their patent are given as follows (Paulsen et al 1955):

⁶ www.chem-group.com

1. Neutralization of HSS with 5-30 wt% caustic soda
2. Dehydration of amine solvent by thermal distillation
3. Extraction distillation of DEA with isopropyl alcohol
4. Filtration to remove sodium salts
5. Distillation to segregate alcohol (recycled) from amine (sent to amine system)

The DEA recovery rate was reported as high as 90%. However, it is highly suspected this will lead to solvent contamination with time, which has not been reported in the patent (Paulsen et al 1955).

Mobil Oil Corporation's first thermal reclaimer consisted of reactive and separation zones (Yan 1992b). Their reclaimer was designed to initially convert amine degradation products back to their parent amine (i.e., DEA). Then, a suitable separation method such as distillation or ion exchange was used to purify the reactor products from HSSs and unconverted degradation products. Conversion of the degradation products was carried out using metallic catalysts on alumina, silica, or zeolite supports in a reactor operated at 470°F and mild pressure. Though, the process provides high solvent recovery, as claimed by Mobil, thermal degradation can occur in the reactor due to the sensitivity of amine solvent to high temperatures (DEA is degraded once temperature exceeds 400°F).

Mobil Oil Corporation developed their second thermal reclaimer based on the reactive distillation for amine solvents (i.e., DEA) (Yan 1992a). The process works by supplying the degraded amine loaded with acid gas to a distillation zone operated at 320°F and atmospheric or vacuum pressure (i.e., 21-150 mmHg). Stripping steam is directly supplied to the distillation zone for heating, control of distillation temperature, and the

hydration process, which involves conversion of amine degradation products back to the amine in the presence of steam. The residence time is a crucial factor in the conversion process, which should be adjusted to get the optimum conditions recommended within a range of 0.5 to 2 hours. The recovered amine is taken from the top of the distillation zone while the waste, rich in degradation products and salts, is taken from the bottom. The experimental results show that few degradation products and HSSs could contaminate the distillate, but the overall conversion of amine is greater than the feed.

4.3.4.2 Removal of undesired primary and secondary amines in tertiary amines

It is very important to remove DEA, which could form from oxidative degradation of TEA. Build-up of DEA concentration can reduce TEA solvent quality. Societe Francaise Hoechst suggested a process to remove undesired DEA in TEA solvent. The process uses glyoxal (dialdehyde) to initially convert DEA to N,N-bis(2-hydroxyethyl) glycine, which could be easily separated later from TEA by distillation (Claud and Blanc 1994). BASF has also proposed a process to overcome contamination of tertiary amines with primary or secondary amines by adding carboxylate at a ratio of 1:1 to 5:1 to undesired primary or secondary amines (Fuchs et al 1996). The primary and secondary amines would form alkylamides, which could be separated from the tertiary amine by distillation.

According to Rooney (Rooney 2002), DEA can be formed from MDEA oxidation and thermal degradation, which degrades further to other degradation products. Although, DEA could be removed by vacuum distillation, solvent loss rate could be high due to close boiling points between degradation products and the amine. Activated carbon could be used, but it has a very limited adsorption capacity. Therefore, they proposed a method

to convert primary/secondary amines (i.e., DEA) to tertiary amine (i.e., MDEA) using monoaldehyde or dialdehyde. The addition of these chemicals to tertiary amine solvent is to initially turn primary/secondary amines chemically to other forms before converting them further to tertiary amines by hydrogenation (Rooney 2002).

4.4 Future trends for the reclamation industry

The future trends for amine reclamation will likely take three paths: 1) improving the current technologies, 2) process integration between the current technologies, and 3) introducing new methods for reclamation. Regardless of method types and operations, the techniques used must be able to handle newly developed and complicated formulated solvents. Also, the techniques should be readily available to help improve solvent quality and recovery and reduce solvent loss in waste, chemical consumption, process and heat integration, and expenses for capital cost and operation. Furthermore, overall wastewater quantity must be reduced as these could also contain traces of amine. High levels of amine in waste water could overload the waste water treatment plant by killing the microbes (Cummings and Mecum 2000).

4.4.1 Need for hybrid processes

The integration of two or more reclaiming techniques such as the use of ion exchange or electrodialysis with a thermal reclaimer to eliminate the HSS neutralization step can be investigated. This might involve treatment of amine solvent with ion exchange/electrodialysis to remove HSSs. The HSS-free amine would be treated further in a thermal reclaimer to remove other degradation products and recover amine. Also, the sequence applied can be vice versa. Process integration between the amine process and

thermal reclaimer could be used to utilize the energy exchange so that the external utility consumption and operating costs can be reduced. Combinations of different methods or hybrid process for controlling the degradation products would be feasible by using amine reclamation and solvent degradation inhibition. *This is what has been developed in this thesis research.*

4.5 Concluding Remarks

- 1 Solvent degradation was managed in the early stages by change-over and purge/feed of solvent, which are unattractive option from technical and economic points of view. For some time, mechanical filtration and activated carbon were thought to reduce the effect of degradation on amine plant operation; however, this is inaccurate.
- 2 On-line neutralization to avoid the presence of HSSs was used for some time, but it has introduced many operational problems and, therefore, has been discontinued.
- 3 Solvent degradation inhibition seems to be one method of protecting solvent and will see more application in the future with the development of new inhibitors.
- 4 Ion exchange and electro dialysis purification could be utilized to reduce HSSs and some degradation products. However, these technologies are not suitable for the removal of the other degradation products, and this would be a challenge for these processes to be integrated into a CO₂ capture plant.
- 5 At present, thermal reclamation is the only technology that can remove all degradation products, HSSs, and non-volatile impurities (i.e., fine solid particles, corrosion products, and salts). Therefore, thermal reclamation would likely be the most attractive purification option for a CO₂ capture plant.

- 6 Primary single amines can be thermally reclaimed at atmospheric pressure and preferably under vacuum. Vacuum reclamation must be used for secondary and tertiary amines to avoid thermal degradation. In cases of blended solvents (i.e., primary/secondary or tertiary amines), solvent reclamation becomes a difficult task.
- 7 Effective degradation inhibitors can protect up to 98% of amine from being degraded, thereby reducing reclaimer load in CO₂ capture operation.
- 8 Hybrid reclamation processes have seen steady growth; however, they might only be applicable in certain cases.
- 9 Many solvent reclamation technologies are under improvement/development with the aim to simplify the process and enhance the process performance parameters such as solvent recovery and utility consumption reduction.

Many methods of amine reclamation were used, and each one has different abilities in removing contaminants, as illustrated in Table 8. It is clear that no process could remove all degradation products. Some processes are not attractive due to their limited ability in the removal of contamination.

Table 8 Ability comparison of different contamination mitigation methods

| Purification Method | HSS | Amino Acids | Other Amines Formed | Amides | Oxazolidones | Diamines | Ureas | Solid | Hydrocarbon | Surfactants | Solvent Loss |
|------------------------------------|-----|-------------|---------------------|--------|--------------|----------|-------|-------|-------------|-------------|--------------|
| Change-over | H. | H. | H. | H. | H. | H. | H. | H. | H. | H. | H. |
| Bleed/FEED | L. | L. | L. | L. | L. | L. | L. | L. | L. | L. | H. |
| Mechanical Filter | | | | | | | | H. | | | L. |
| Activated Carbon | L. | | | M. | L. | M. | M. | M. | H. | H. | L. |
| On-line Neutralization | M. | M. | | | | | | | | | |
| Degradation Inhibition | M. | M. | M. | M. | M. | M. | M. | | | | |
| Conversion of degradation products | | | M. | | H. | | | | | | |
| Ion- Exchange | H. | H. | | H. | | | | | | | L. |
| Distillation | H. | H. | H. | H. | H. | H. | H. | H. | M. | M. | M. |
| Electrodialysis | H. | H. | | H. | | | | | | | M. |
| Extraction | H. | | | | | | | | | | |

* H. = High, M. = Medium, L. = Low.

Chapter 5: Experimental Work and Procedures

5.1 Chapter introduction

The key to understanding the success of amine solvent reclamation is through the experiential and analysis tools that are utilized. Chemicals representing the amine solvent, degradation products, and heat stable salts have been obtained. This will help to create different scenarios of their combination in the amine solvent. Analysis equipment, such as GC-MS and HPLC, are useful for analyzing the amine and degradation products quantitatively and qualitatively. Different titration systems were used and tested to help determine three things: amine solvent concentration, CO₂ loading, and total heat stable salts (HSSs). This chapter will give brief information about the distillation tests, activated carbon treatments and analysis techniques. All equipment, tools, and consumables used within this work have been listed in Appendix D.

5.2 Chemical, reagents, and adsorbents

The chemicals used in the research described are shown in Table 9. Most of chemicals have been obtained from Sigma-Aldrich Canada, while a few have been obtained from other providers. These chemicals can be divided into three main groups: amine solvent, degradation products, and organic acids to generate HSSs. Other chemicals used for acid-base titration tests or neutralization are also given in Table 9. The adsorption tests with activated carbon have been utilized for treatment. Three types of activated carbon used in industrial amine services have been obtained from two companies: Calgon Carbon Corporation (Pittsburgh, PA) and Norit Activated Carbon (Marshall, TX).

Table 9 Chemicals utilized in this research

| | Chemicals | Purity | Source |
|--|---|---------------|-------------------|
| Amine Solvents | Monoethanolamine | >99% | Sigma-Aldrich |
| | Methyldiethanolamine | >99% | Sigma-Aldrich |
| Degradation Products | Imidazole | >99% | Sigma-Aldrich |
| | Acetamide | >99.5% | Sigma-Aldrich |
| | N-Acetyethanolamine | >99% | Sigma-Aldrich |
| | 1-(2-Hydroxyethyl)-2-imidazolidinone | 75% | Sigma-Aldrich |
| | Amino-2-propanol | >93% | Sigma-Aldrich |
| | 2-(Methylamino)ethanol | >98% | Sigma-Aldrich |
| | 3-Picoline | >99% | Sigma-Aldrich |
| | Bicine (Amino-Acid) | >99% | Sigma-Aldrich |
| | 1-3 Diaminopropane | >99% | Sigma-Aldrich |
| Organic Acid (for formation of Heat Stable Salts) | Formic Acid | > 98% | Sigma-Aldrich |
| | Acetic Acid | >99.7% | Sigma-Aldrich |
| | Oxalic Acid | 99.99% | Sigma-Aldrich |
| | Malonic Acid | >99% | Sigma-Aldrich |
| | Glycolic Acid | >99% | Sigma-Aldrich |
| | Propionic Acid | >99% | Sigma-Aldrich |
| | Lactic Acid | >85% | Sigma-Aldrich |
| | Butyric Acid | >99% | Sigma-Aldrich |
| | Sodium thiosulfate | >99 | Aldrich |
| | Sodium thiocyanate solution | 8M | Fluka |
| Standards solutions and buffers | NaOH | 1N | Fisher scientific |
| | HCl | 1N | Fisher scientific |
| | pH 1.68, 4.01, 7.00, 10.01, 12.46 Buffers | 98% | Oakton |
| | Methyl Orange Indicator | 0.1% | Riedal - DeHaen |
| | NaOH | 50% | Sigma-Aldrich |
| | KOH | 50% | Fluka |
| | K ₂ CO ₃ | >99% | Sigma-Aldrich |
| | Na ₂ CO ₃ | >99.5% | Aldrich |

5.3 Solvent and degradation products selection

5M (30 wt%) MEA solvent is considered as a reference solvent in CO₂ capture applications (Aboudheir and ElMoudir 2009). MEA solvent can be thermally reclaimed at atmospheric or slightly higher pressure; however, solvent content in the reclaimer waste is quite high. Therefore, this solvent is selected to be reclaimed in this study in order to search for a better solvent purification strategy. MEA/MDEA blended solvent, specifically at a blend mole ratio of 1:1, has been found to be attractive for CO₂ capture applications due to a number of features discovered by many scholars (Kindrick et al 1950; Faucher 1989; Dawodu and Meisen 1996; Aroonwilas and Veawab 2004). These features are summarised as follows: high absorption capacity, lower solvent circulation rate, low regeneration energy, and lower degradation, as MDEA inhibits the oxidative degradation of MEA. Such a blend requires different purification conditions than MEA and, therefore, requires a different strategy for purification. Degradation products selected for this research have been based on those chemicals reported in the open literature from the above solvents (i.e., MEA or MEA/MDEA). Table 10 lists these degradation products.

5.4 Determination of amine solvent concentration and CO₂ loading

Solvent concentrations and CO₂ loading can be determined by three methods, and all of them are based on acid-base titration, in which strong acids such as HCl or H₂SO₄ can be used. Each method has a different definition for the end-point. These methods are summarized in Table 11. Also, similar methods have been obtained from Huntsman. They differ from each other in the method of conducting the determination, but determination of the end-point using a pH meter seems to be most accurate. For further

details of the procedure, chemicals, equipment, and glassware required, the reader is advised to refer to the original sources given in Table 11. Example of determination of solvent concentration and acid gas loading for single amine solvent are given in Appendix B.

5.5 Determination of total heat stable salt content

The HSS contents can be determined by the use of acid-base titration. Three such techniques have been developed in the literature. In one way or another, heat stable content equates to the bonded amine in the solvent (portion of solvent deactivated by reacting with organic or inorganic acids). The presence of CO₂ in the sample might prevent accurate determination of HSS content due to interference with the available titration. Therefore, it is emphasized that any CO₂ content in the sample should be stripped out by a full reflux distillation system. Table 3 further illustrates the techniques available to measure HSS content in degraded amine solvent. For further information on these techniques, it is recommended to refer to the original sources for a complete illustration of the methods and procedures of analysis. Example of determination of HSS for single amine solvent is given in Appendices B.

Table 10 Degradation products selected for MEA and MEA/MDEA solvents

| | Chemical | MEA Degradation Products | | MEA/MDEA Degradation Products | |
|--|--------------------------------------|--------------------------|---|-------------------------------|-----------------------|
| | | Expected | Confirmed | Expected | Confirmed |
| Degradation Products | Ammonium Hydroxide | | Strazisar et al (2003) | | |
| | 2-(Methylamino) Ethanol | | Supap et al (2006) | | Lawal and Idem (2005) |
| | Amino-2-propanol | | | | Lawal and Idem (2005) |
| | 3-Picoline | | | | Lawal and Idem (2005) |
| | Ethylamine | | Supap et al (2006) | | Lawal and Idem (2005) |
| | 1,3-Diaminopropane | | | | Lawal and Idem (2005) |
| | Imidazole | | Supap et al (2006) | | |
| | Bicine | Supap et al (2006) | | | Lawal and Idem (2005) |
| | Acetamide | | Supap et al (2006) | | |
| | N-Acetyethanolamine | | Strazisar et al (2003), Supap et al (2006) | | Lawal and Idem (2005) |
| | 1-(2-Hydroxyethyl)-2-Imidazolidinone | | Strazisar et al (2003), Supap et al (2006) | | Lawal and Idem (2005) |
| | Monomethylethanolamine | | | | Smit et al (2002) |
| Heat stable salts (HSS) Neutralized or Organic Acids Cause them | Formic Acid | | Supap et al (2006) | Smit et al (2002) | Lawal and Idem (2005) |
| | Acetic Acid | | Strazisar et al (2003), Supap et al (2006) | Smit et al (2002) | |
| | Propionic Acid | | Strazisar et al (2003) | | |
| | Butyric Acid | | Strazisar et al (2003) | | |
| | Lactic Acid | | | | Lawal and Idem (2005) |
| | Malonic Acid | | | | Kohl & Nielsen (1997) |
| | Glycolic Acid | Supap et al (2006) | | | Smit et al (2002) |
| | Oxalic Acid | Supap et al (2006) | | | |
| | Sodium Thiocyanate | | | | Liu et al (1995) |
| | Sodium Thiosulfate | | Strazisar et al (2003) | | Liu et al (1995) |

Table 11 Titration method to determine the solvent concentration and CO₂ loading

| | Titration Method | End-Point | Reference |
|-------------------------------|---------------------------------|--|--|
| Solvent Concentration | Colorimetric Titration | Methyl orange indicator is used. Colour change will give the end-point | (Wonder et al. 1959), (UOP LLC (A) 1981) (deMontigny 1998), (Setameteekul 2006) |
| | Conductometric Titration | the electrical conductance change with titrant | (Cummings et al. 1990) |
| CO₂ Loading | Colorimetric Titration | Methyl orange indicator is used. Colour change will give the end-point | (UOP LLC (B) 1981) (deMontigny 1998), (Setameteekul 2006) |
| | Conductometric Titration | the electrical conductance change with titrant | (Cummings et al. 1990) |
| HSS content | Colorimetric Titration | Methyl orange indicator is used. Colour change will give the end-point | (Blake 1963) |
| | Conductometric Titration | the electrical conductance change with titrant | (Cummings et al. 1990) |

5.6 Gas Chromatography – Mass Spectrometry (GC-MS)

This method has been developed to identify and determine the concentration of the amine solvent and degradation products by Supap et al. (2006), but it has been modified to optimize the degradation product detection, especially when their concentration is low <250 ppm. The liquid sample containing amines and degradation product chemical mixture is injected at the GC inlet, which is set at a specific temperature to vaporize the whole sample content. Then, the sample is eluted into the GC column using an inert carrier gas (i.e., He). The chemicals in the samples will be eluted to different degrees along the column, where the lighter compounds will appear first in the detector, followed by heavier and heavier compounds. This is roughly based on the boiling point for the current column used in this study with assistance of temperature programming and interaction between these chemicals and stationary phase on the GC-column surface. The eluted amines then enter into the detector (MS), and an electrical response linearly related to the solute concentration can be obtained. The following are descriptions of the equipment used:

- Equipment and apparatus

GC-MS (HP6890/5973) with HP-INNOWax Polyethylene Glycol (manufactured by Agilent and is designed for max. temp of 260°C) capillary column and NIST database, auto sample injector, GC vials, pipettor (0.2-1.0 ml), and pipettor tips.

- Reagent

1 mol/L standard HCl solution, ultra-high-purity-grade Helium, distilled water

- Procedure

The sample of concentrated amine can be diluted with DI water prior to injection in the GC-MS to improve the amine separation and detection. High amine solvent concentration (i.e., residue) can overload the GC-column. No dilution is required for normal amine samples or wash water and reflux water samples.

1. The sample should be filtered using a 0.20 μm nylon membrane filter prior to the analysis to avoid column fouling and blockage.
2. Introduce 0.5-1 ml of samples into the GC vials and close them tightly to avoid leakage.
3. GC-MS operating condition is set up per Table 12.
4. GC chromatographs are obtained for the chemicals under study. Examples of GC chromatographs obtained from GC-MS for MEA solvent and five degradation products are given in Figure 9 (A). GC-MS could also provide identification of the chemicals for each peak obtained, Figure 9 (B). Verification of this identification should be combined with standards for these chemicals and checked with the spectrum database of GC-MS.
5. Prepare amine or degradation product standard solutions at at least 3 desired concentrations in the range of interest. Inject 1 μL of standard solution with various concentrations at the GC inlet. Record the peak area accordingly, and prepare the calibration curve (peak area versus amine concentration). Calibration of MEA with GC was successfully obtained as illustrated in Figure 8.
6. The integration parameters should be fixed. Three integration methods can be used:

- ChemStation: Recommended for most GC/MS analysis; highly accurate
 - RTE: Recommended for Routine Analysis; less accurate
 - Manual integration
7. Step four should be repeated for each amine or degradation product used
 8. Inject 1 μL of sample solution at the GC inlet. Record the peak area accordingly.
Each sample is analyzed twice to check for reproducibility.
 9. Amine measurements are done based on concentration calibrated with amine standard solutions and peak area. Amine concentration can also be expressed based on area percent. The former gives the absolute concentration for each component while the latter gives the relative concentrations in terms of each component to the total chemicals detected by GC.

Table 12 GC-MS conditions for determination of amine solvents and degradation products

| Oven | | | | Front inlet | | |
|---------------------------|------------|------|--------|---------------------|-------|--------|
| Initial temp | | 70 | °C | Mode | split | |
| Initial time | | 0 | min | Initial temp | 250 | °C |
| Maximum temp | | 260* | °C | Pressure | 9.21 | psi |
| Equilibration time | | 0.5 | min | Split ratio | 10:1 | |
| Ramps | Rate | 10 | °C/min | Split flow | 10.3 | ml/min |
| | Final temp | 240 | °C | Total flow | 13.9 | ml/min |
| | Final time | 0 | min | Gas saver | on | |
| Post temp | | 0 | °C | Saver flow | 20 | ml/min |
| Post time | | 0 | min | Saver time | 2 | min |

* This should not be used so as to prolong column life.

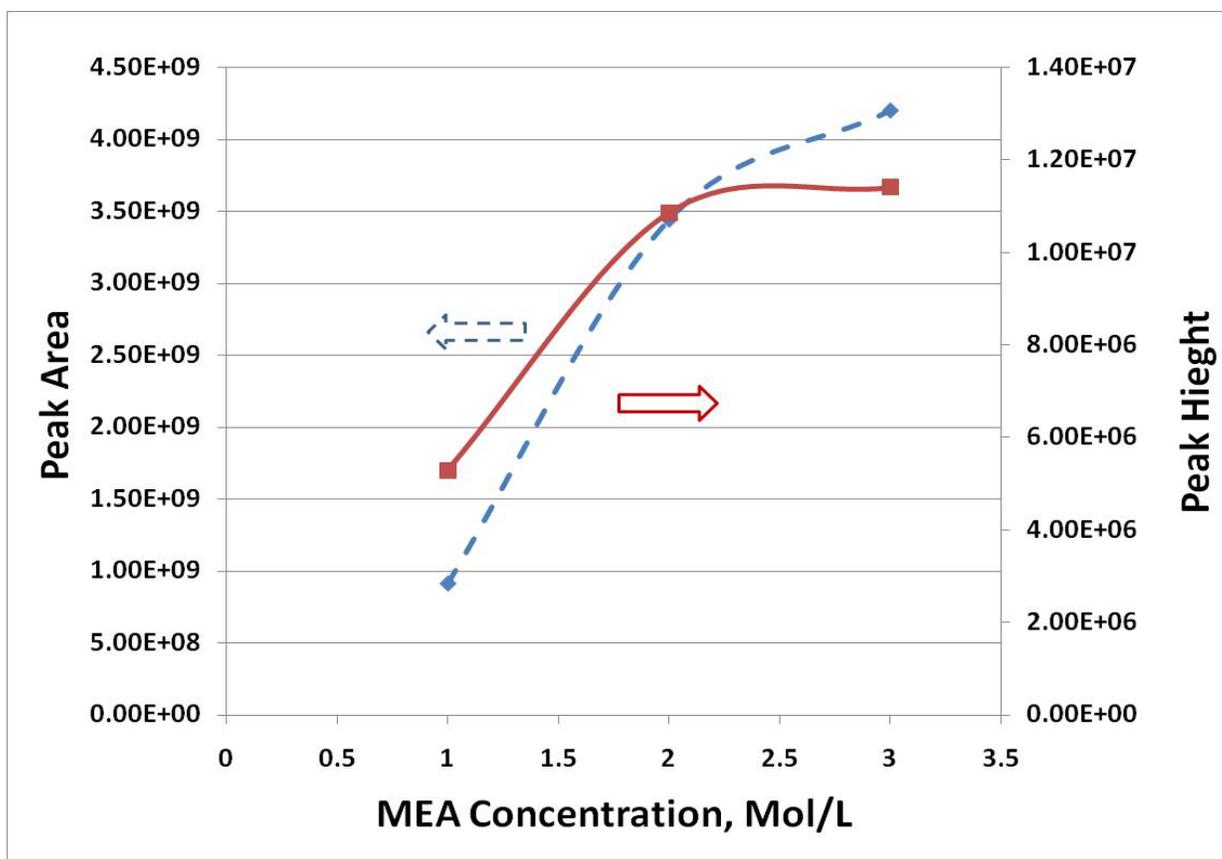
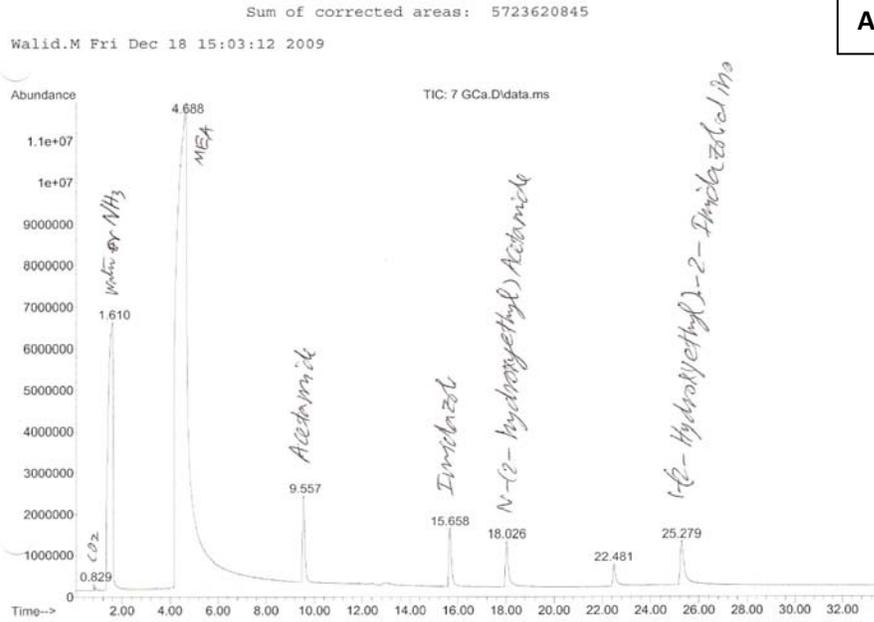


Figure 8 Results of obtaining calibration curves of MEA solvent



A

Library Search Report

Data Path : C:\msdchem\1\DATA\Walid\
 Data File : 7.GCa.D
 Acq On : 15 Dec 2009 15:25
 Operator : Walid
 Sample : MEA 5M + 1000 ppm
 Vial : 1-121109
 ALS Vial : 7 Sample Multiplier: 1

Search Libraries: C:\Database\NIST98.L Minimum Quality: 0

Unknown Spectrum: Apex
 Integration Events: ChemStation Integrator - autoint1.e

| PK# | RT | Area% | Library/ID | Ref# | CAS# | Qual |
|-----|--------|-------|---|---------------------------|--|----------------|
| 1 | 0.831 | 0.04 | C:\Database\NIST98.L 2-Pentanamine Carbon dioxide 2-Butanamine, (S)- | 110491 10466 10463 | 000625-30-9 000124-38-9 000513-49-5 | 5 5 4 |
| 2 | 1.612 | 15.80 | C:\Database\NIST98.L Ammonia Water | 19 22 | 007664-41-7 007732-18-5 | 2 1 |
| 3 | 4.686 | 75.17 | C:\Database\NIST98.L 2-Propanol, 1-amino- Monoethanolamine 4-Amino-1-butanol | 108169 108158 783 | 000078-96-6 000141-43-5 013325-10-5 | 59 47 42 |
| 4 | 9.556 | 2.46 | C:\Database\NIST98.L Acetamide Acetamide Acetamide | 110577 19497 113231 | 000060-35-5 000060-35-5 000060-35-5 | 90 90 86 |
| 5 | 15.656 | 1.86 | C:\Database\NIST98.L 1H-Imidazole 1H-Imidazole 1H-Pyrazole | 113957 21751 113959 | 000288-32-4 000288-32-4 000288-13-1 | 78 78 64 |
| 6 | 18.029 | 1.66 | C:\Database\NIST98.L Acetamide, N-(2-hydroxyethyl)- Acetamide, N-(2-hydroxyethyl)- N,N'-Diacetylenediamine | 5918 113403 108193 | 000142-26-7 000142-26-7 000871-78-3 | 74 56 38 |
| 7 | 22.481 | 0.77 | C:\Database\NIST98.L 3-Methyl-4-amino-4,5(1H)-dihydro-1, 2,4-triazole-5-one 3-Cyclobutene-1,2-dione, 3,4-dihyd roxy- 2,4-Imidazolidinedione, 1-methyl- | 51305 120303 51312 | 1000145-62-5 002892-51-5 000616-04-6 | 53 45 25 |
| 8 | 25.278 | 2.23 | C:\Database\NIST98.L 1-(2-Hydroxyethyl)-2-imidazolidino ne 1-Piperidinamine 3,5-Diamino-1,2,4-triazole | 43140 43332 118543 | 003699-54-5 002213-43-6 001455-77-2 | 47 9 9 |

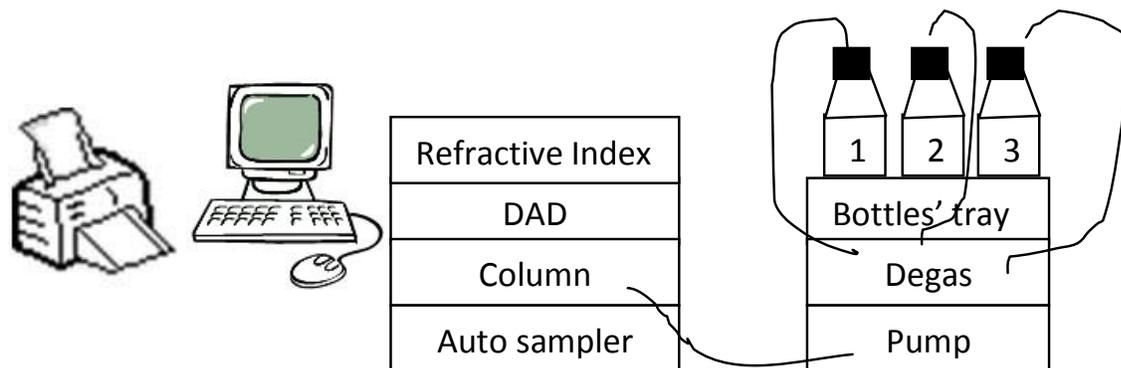
B

Figure 9 GC-MS chromatograph for degraded MEA (A) and summary of chemical identification for each peak (B)

5.7 High pressure liquid chromatography with refractive index detector

HPLC-RID method is used to determine the amine solvent concentration for single or mixed amine solvents (Supap et al. 2006). A liquid sample that contains a mixture of chemicals is injected at the HPLC inlet, Figure 10. Then, the sample is eluted with the liquid mobile phase and passes through the column. The compounds are separated based on the affinity with the column packing. Then, the eluted amines enter into the refractive index detector (RID). An electrical response linearly related to the amine concentration is obtained. HPLC provides an alternative method to determine the amine concentration to the calorimetric titration, especially for single solvents. However, in the case of mixed amines, the calorimetric titration will only give the total concentration of amines but will not tell how much of each amine is in the solution. HPLC is capable of determining the ratio between amines in mixed solvents.

- | | |
|------------------|--|
| Chemicals | <ul style="list-style-type: none">- Nano pure water- Potassium di-hydrogen phosphate (KH_2PO_4)- Phosphoric acids (H_3PO_4)- acetonitrile |
| Apparatus | <ul style="list-style-type: none">- HPLC -RID Agilent 1100 Series with Auto sample injector (Figure 19) obtained from Agilent Technologies Canada Inc., Mississauga, ON, Canada- Chromatography Column is CC 250/4.6 NUCLEOSIL 100-5 SA obtained from MACHEREY-NAGEL Inc., Bethlehem, PA, USA- HPLC vials,- 3 ml Syringe,- 0.2 um NY filter,- Ultra sound cleaner (for degassing) |



Bottles on the bottles tray are:

Bottle 1: 1 litre of nanopure water (for flushing the system and reference cell)

Bottle 2: 1 litre of acetonitrile (storing liquid in the system during stand-by mode)

Bottle 3: 1 litre of mobile phase

Figure 10 HPLC system for determination of amine concentration

- **Procedure**

In contrast to GC-MC samples, HPLC samples should be diluted by nanopure water 40 times to improve their detectability per the method developed at the ITC for detection of MEA and MDEA, single and blended, solvents. However, if the amine solvent concentration is less than 1 wt%, such as in the case of washing water or reflux sample water, there is no need for dilution. After dilution, filtration is followed by using a 0.20 μm nylon membrane filter prior to the injection.

- **Mobile Phase Preparation**

- 1- Take 6.82 gm of Potassium Phosphate Monobasic (Salt) and dissolve it in a 1 litre beaker with nanopure water and complete water up to the 1 litre line.
- 2- Adjust the pH of the solution by adding dew drops of phosphoric acid, and measure the pH until it measures pH 2.60.
- 3- An auto injector (series 1100 supplied by Agilent Technologies Canada Inc, Mississauga, ON) with a 100 ul syringe is used automatically for better reproducibility.
- 4- The 1 litre beaker content is transferred to a 1 litre flask.
- 5- The flask is placed in the sonic bath and left for 3 hours to remove all gas bubbles.
- 6- After that, the solution is filtered in 0.2 μm and then is transferred to a mobile phase bottle.
- 7- It is ready to be used as soon as it is effective, and should be used as soon as possible because the mobile phase will deteriorate if it is stored for more than a day.

- **Measurement**

- a. Introduce 2.5 ml of prepared samples into the HPLC vials.
- b. Set up HPLC operating conditions; the columns are kept at 30°C. All analyses are done using a simple isocratic approach in which 100% of a single mobile phase flowing at a rate of 1 ml/min is used throughout the analysis. The RID optical unit is set at a temperature of 30°C and operated under positive mode.
- c. Inject 8 μ L of various concentration standard samples of a specific amine prepared and injected to HPLC to establish a relationship between amine concentration and either the peak height or peak area. Read the data of the corresponding solute concentration and obtain the calibration curve.
- d. Inject 8 μ L of unknown concentration sample. Record the peak area accordingly.
- e. Each sample should be injected two times and the average considered.

5.8 Experimental set-ups for thermal purification and adsorption tests

The experimental works can be divided mainly into two sections: thermal distillation and adsorption. The distillation set-ups have been based on typical simple distillation and fractionation distillation with the ability to operate at atmospheric pressure or under vacuum down to 60 mmHg (close to the maximum ability of the vacuum pump available for this study). Regarding the adsorption tests, they have been based on isotherm (screening) and dynamic evaluations. More details are given in this section.

5.8.1 Atmospheric and vacuum distillation set-ups

Distillation is one of the well known methods for purification and separation of chemicals. The objective of using this technique is to simulate the effectiveness of solvent thermal reclamation for single and blended amines. In industrial reclamations, the primary amines that have been reported could be reclaimed at atmospheric or slightly higher pressure while secondary and tertiary could be reclaimed under vacuum with special thermal reclamation systems (Kohl and Nielsen, 1997). However, in laboratory utilization, amines have been thermally purified under deep vacuum distillation as reported by Armarego and Chai (2009) and shown in Table 13.

The concept of the distillation is that a desired liquid is brought to boiling at specific pressures, and at this point, the vapour pressure of liquid reaches the same pressure as the system, allowing the liquid to convert (evaporate) to vapour and transfer to the condensation section where it can be collected in as pure a form as possible (Krell, 1981). If there is more than one chemical in the liquid, one of the first chemicals has been recovered, and the distillation flask temperature will increase until it reaches the boiling point of the second chemical relevant to the applied pressure, and then the second distillate cut can be collected and so on. What is left behind after recovering the desired solvent is the residue, which usually contains all the impurities. In our study, the residue could be considered as the reclaimer waste.

Distillation of a mixture of liquid can be carried out in two different possible set-ups as shown in Figure 4. The simple distillation can be effectively used to purify one chemical from small traces of impurities. In this set-up, the separation can be translated into one

stage of “equilibrium” separation. In the case of the separation of two or more components in the liquid mixture, it is recommended to use a distillation column packed with mass transfer equipment to facilitate this separation. Figure 11 illustrates the differences between simple and fractionation distillation set-ups. All equipments and glassware were obtained from Scientific Glass and Plastic (SG & P), Freeport, Texas.

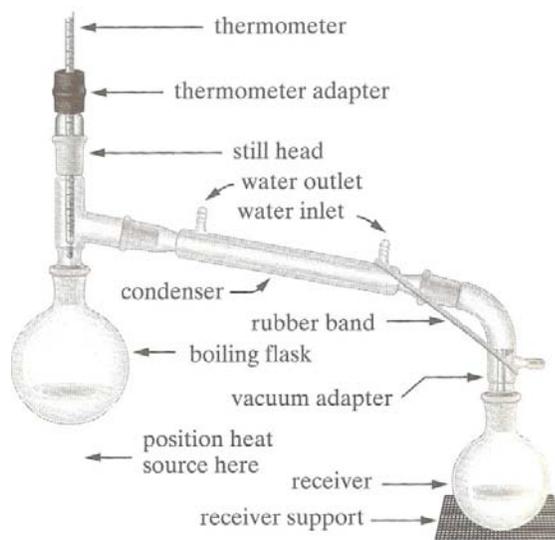
One important feature of successful separation between chemicals in a mixture is the difference of boiling points between these components of that mixture, as shown in Figure 12. However, this is not the case in all systems, as will be seen in degraded amine systems where some degradation products could potentially have boiling points either similar or close to the amine system. The steps taken for thermal purification of degraded amines can be summarized as follows:

- 1- Clean or degraded solvent is prepared with/without degradation products.
- 2- If the sample has any HSSs or amino-acids, neutralization with strong base (i.e., NaOH) would be required.
- 3- Amine concentration and heat stable content could be checked by titration.
- 4- Then the sample is ready to be introduced to the distillation set-up (either under atmospheric or vacuum pressure).
- 5- Distillate and residue are collected and analyzed with GC-MS and HPLC to determine the distribution of amine and degradation products.

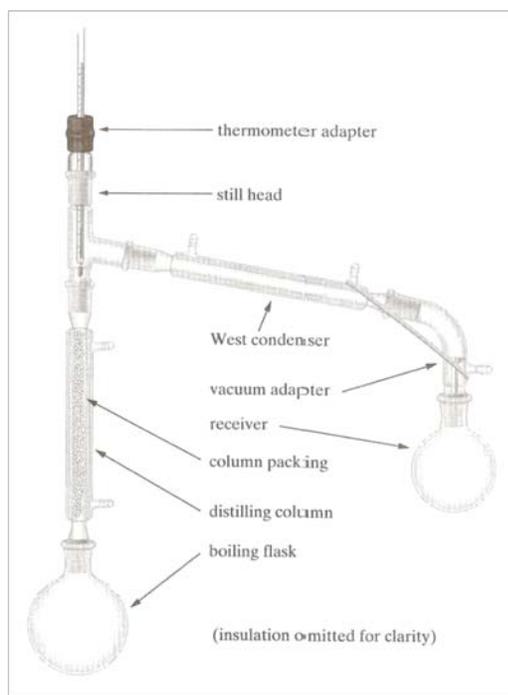
Evaluation of success of solvent recovery is made, and the experiment is repeated to confirm the results or to examine different operating conditions to maximize the solvent recovery in the case that low recovery is observed.

Table 13 Purification of primary, secondary, and tertiary amines (Armarego and Chai 2009)

| | Purification Method | | Distillation | Washing | Crystallized |
|-------------------------------------|--|-----------------|--------------|---------|--------------|
| <u>Monoethanolamine, MEA</u> | Distillation + Washing + Crystallisation | Approach | Vac. Dist. | Ether | EtOH (low T) |
| | | Steps | I | II | III |
| | Distillation + Crystallisation | Approach | Vac. Dist. | | Cooling |
| | | Steps | I & III | | II |
| | Distillation | Approach | Aze. Dist. | | |
| | | Steps | I | | |
| <u>Diethanolamine, DEA</u> | Distillation + Crystallisation | Approach | Vac. Dist. | | Cooling |
| | | Steps | I & II | | III |
| <u>Triethanolamine, TEA</u> | Distillation | Approach | Vac. Dist. | | |
| | | Steps | I & II | | |



A



B

Figure 11 Simple (A) and fractionation (B) distillation set-ups (Lehman 2008)

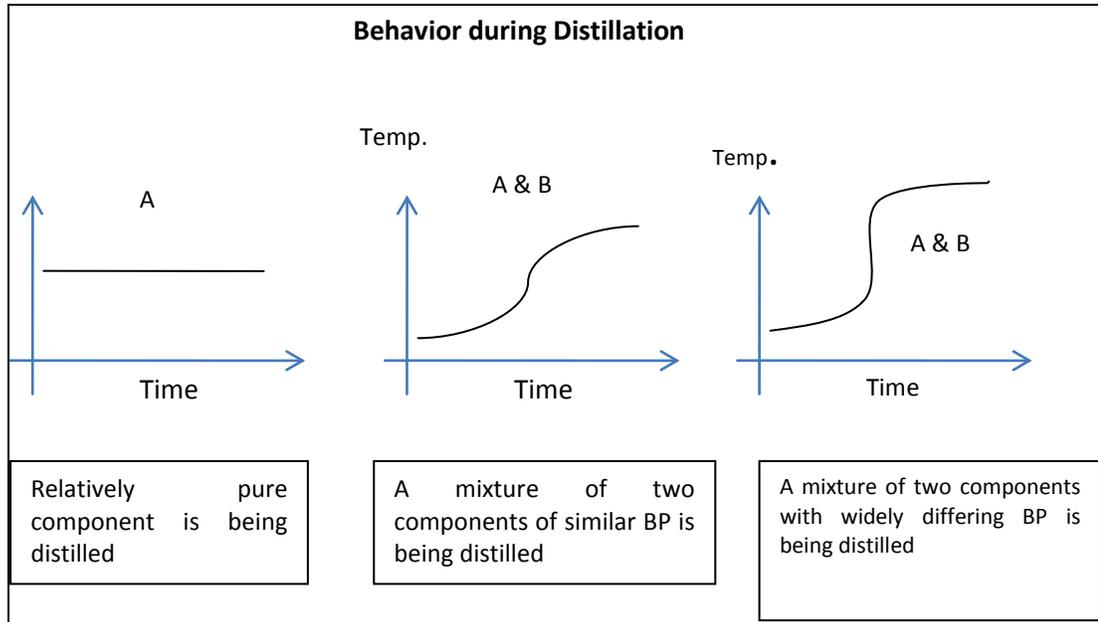


Figure 12 Distillation of liquid mixture and impact of boiling point of contents on separation (Krell 1981)

5.8.2 Adsorption Tests

Activated carbon is used in the natural gas sweetening process to remove dissolved heavy hydrocarbon and surface activate agents that can cause foaming in the process. Activated carbon performance in removing degradation products has been investigated by many researchers (Chakma & Meisen, 1989), (Islam & Chakma, 1990), and (Kohl & Nielsen, 1997). They concluded that the activated carbon has been found to have a low removal capacity for degradation products during continuous treatment within a few days. However, if the activated carbon were used only to remove degradation products left after the thermal purification for amine, this would be a new interesting area of application for activated carbon. Granular activated carbons obtained from two well known vendors have been tested to check whether the activated carbon can remove light or contaminant degradation products from recovered amine solvents. The carbons selected for the investigation are SGL from Calgon Carbon and M-1657 and M-1731 from Norit America Inc. More information on these carbons is given in Chapter 10.

The concept of activated carbon involves removing any impurities or chemicals by adsorption. Adsorption of impurities can occur in two ways: physical or chemical Adsorption (Norit Activated Carbon, 2001). Physical adsorption mechanisms are controlled by weak electrostatic forces of the pore walls, while in the case of chemisorption, a strong attraction force or chemical bonds are formed between the activated carbon and impurities, Figure 13. It is believed that the first adsorption phenomenon is controlled in the treatment of degradation products based on laboratory observation. The porosity in the activated carbon plays a role in the adsorption process, as the pore size could control which chemical could be pass and adsorbed and which might

not. As there are many pores, especially small ones, the surface area available for adsorption is much higher. Figure 7 shows the distribution of adsorption in the pores of activated carbon.

Two experiments should be carried out in order to evaluate the effectiveness of the removal of degradation products, isotherm adsorption tests and dynamic adsorption tests (Cheremisinoff and Ellerbusch, 1978), (Neely, 1982), (Clark and Jr, 1989) and (ASTM D3860-98, 2008). These will help with selection of the most suitable carbon for a specific task and its selectivity towards specific impurities. During the isotherm adsorption test, two key parameters of adsorption should be obtained, as shown in Figure 14: equilibrium carbon dosage required for treatment at equilibrium. If sufficient time is given for the system to approach equilibrium where the rate of adsorption is equal to the rate of desorption, there is no need to construct an equilibrium contact time curve, and this is what is followed in this study. Such curves are usually used to construct the relation between the adsorption of impurities versus concentration, and they might be called Langmuir or Freundlich models (Neely, 1982). However, this model is valid for ideal adsorption cases while in non-ideal adsorption, deviation from this model could be observed (Cheremisinoff and Ellerbusch, 1978).

One pretreatment requirement for carbon prior to the test is hydration of the carbon to enhance the adsorption process by removing the air trapped within the carbon pores. This process might take 2 to 3 days, as mentioned by Cheremisinoff and Ellerbusch (1978). In this study, three forms of activated carbon are tested: dry form, carbon wetted with water,

and carbon wetted with the amine solvent. The wettability of carbon with the solvent is proposed in this study to see if this has any advantages over the water wettability.

Prior to the test, activated carbon should be soaked in water or amine solvent for at least 48 hours to remove all air pockets; otherwise, the carbon could be used in its dry form. The first step is the isotherm evaluation (Norit Activated Carbon, 2001). Adsorption or carbon dosage should be obtained as follows:

- 1- Five to six bottles containing the liquid under evaluation are prepared
- 2- Different amounts of activated carbon are added to each bottle
- 3- Agitate these bottles based on the optimum contact time obtained earlier
- 4- Immediately, the bottles' contents are filtered and analyzed
- 5- Adsorption capacity or loading can be calculated for each sample using:
Carbon loading = weight of impurity removed / carbon weight used
- 6- The optimum dosage amount can be determined as shown in Figure 7.

Once the carbon loading is obtained, it becomes easy to compare the effectiveness of a number of different activated carbon types. This will allow proceeding to the second evaluation, the dynamic adsorption of activated carbon, which gives the breakthrough information and a large amount of accurate, comparative data between activated carbons under evaluation. This test involves the loading of activated carbon in a column(s) to act as a packed bed and allow the contaminated liquid to pass through it until the concentration of the impurity at the inlet is similar to the outlet, at which point, the whole carbon bed is spent, and this will determine the real amount of activated carbon needed to design the treatment unit, as shown in Figure 15.

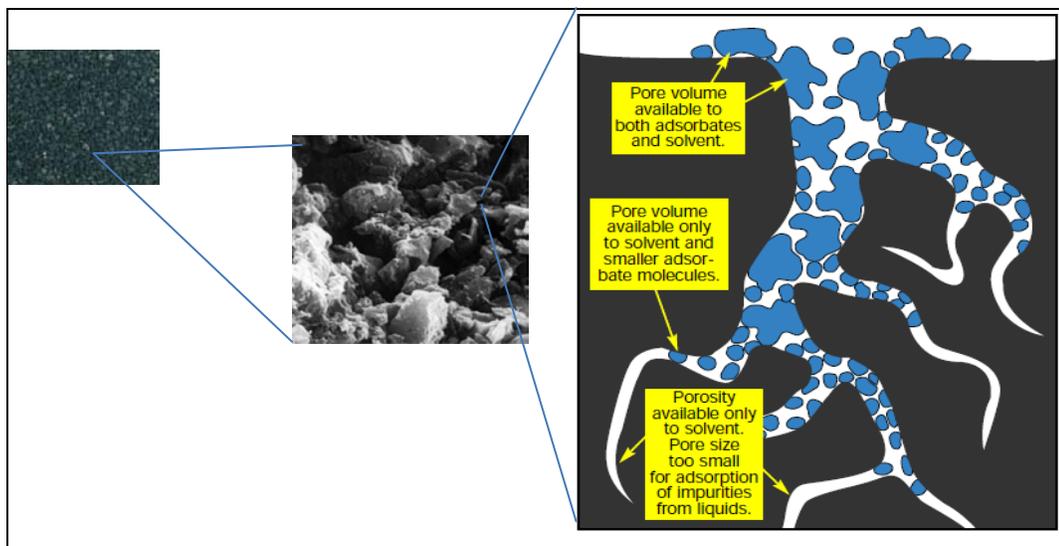


Figure 13 Porosity and its role in adsorption in activated carbon (Norit Activated Carbon 2001)

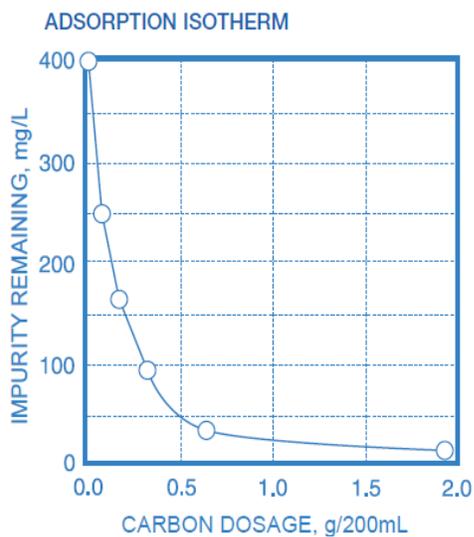


Figure 14 Carbon loading for activated carbon (Norit Activated Carbon 2001)

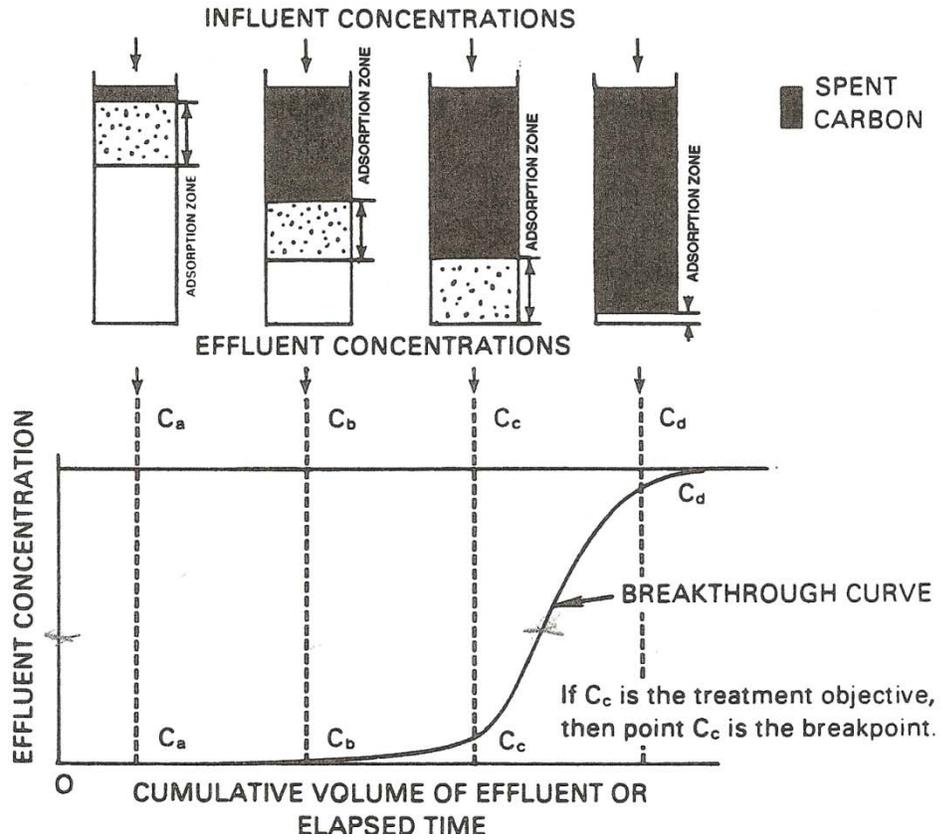


Figure 15 Dynamic breakthrough curve of activated carbon (Clark and Jr 1989)

Chapter 6: Amine Degradation Impact on Solvent Density and Refractive Index

6.1 Chapter introduction

Degradation products formed in MEA or MEA/MDEA could affect the solvent in different ways. For instance, the solvent physical properties, such as the density and viscosity, could be changed leading to changes in the solvent absorption characteristics. To help understand the impact of degradation products on the amine solvent, measurements of solvent density and refractive index were carried-out.

6.2 Solvent density measurements

Density is a very important physical property that influences the design of amine plant equipment and transport phenomena, such as the liquid pump (head required), piping, heat exchanger design (heat transfer process), mass transfer process and equipment (packed columns), and valves and instruments. Therefore, the impact of solvent degradation on the amine density is important to evaluate. Solvent density could deviate or change from the values used to design any of the equipment mentioned above. The consequences of this change are that the equipment could no longer function as intended or its performance could deteriorate. We have found little information and data on density of degraded amine solvents in the open literature.

Measurements of density have been carried out based on British Standard BS 2000-189/190 using the pycnometer or the Gay-Lussac Bottle (BS 2000-189/190 BRITISH STANDARD (BSi) 2004). The standard covers the use of these bottles for petroleum and its products. Other standards applicable for this approach of measuring the density are

ASTM D 369 and D 854. Four bottles (volumes: two 5mls and two 2mls) were obtained from Cole-Parmer Canada, Montreal, QC.

We have found that this method is also applicable for amine solvents, whether they are pure or in aqueous solution. All precautions and procedures reported in BS 2000-189/190 were followed in conducting the experiment. The method suggests a number of equations to calculate the density or observed density, which is uncorrected for glass expansion. In this study, the general form of the borosilicate glass bottle would be used, which is shown below (Equation 6.1). The reader is advised to read the standard method for more details. For accurate measurements, it is recommended to conduct the measurements more than one time with fresh samples to make sure the measurements are acceptable.

$$\rho_t^1 = \left[\frac{(m_t - m_o)\rho_c}{(m_c - m_o)} + C \right] [1 + (10 \times 10^{-6})t_r + (25 \times 10^{-6})t_t - (15 \times 10^{-6})t_c]$$

---Equation (6.1)

where:

ρ_t^1 = apparant density at specific temperature

t_r = the reference temepature, e. i. 15°C

t_c = the temepature at which the pyknometer is calibrated with water

t_t = the temepature at which the pyknometer is filled with amine

m_o = the apparent mass in air, in g, of the empty pyknometer

m_c = the apparent mass in air, in g, of the pyknometer filled with water at t_c

m_t = the apparant mass in air, in g, of the pyknometer filled withg amine at t_t

C = the correction for air buoyancy, in kg/m^3

ρ_c = the density of water, in kg/m^3 at t_c

6.2.1 Density measurement of pure amine solvent

Density of pure MEA has been measured by Pycnometer and compared with the prediction of density by ProMax and ProTreat process simulators. Figure 16 illustrates this comparison of pure MEA solvent density. We have elected to compare the results of measurements with two reference process simulators (ProMax and ProTreat) that are used extensively in amine plant design and can be considered as a reference for predicting the physical properties of amines and their aqueous solutions. ProMax uses the Hankinson-Brost-Thomson method correlations to predict the amine solvent density (Hankinson & Thomson, 1979). ProTreat calculation of density is based on their own-correlations and proprietary data. As can be seen from Figure 17, the density of pure MEA is a little bit higher than the prediction from both softwares, specifically at high temperature ranges (30 to 40°C) while the slope of the curve does not completely match the trend of slopes from both predicted curves. However, it should be noted that both software predictions are not the same and the differences get bigger at low temperature ranges compared to high temperature ranges. To translate the differences observed, Figure 17 is the parity chart between the observed density and those predicted by ProMax and ProTreat. The parity chart shows that all measurements of the density are under prediction for pure MEA.

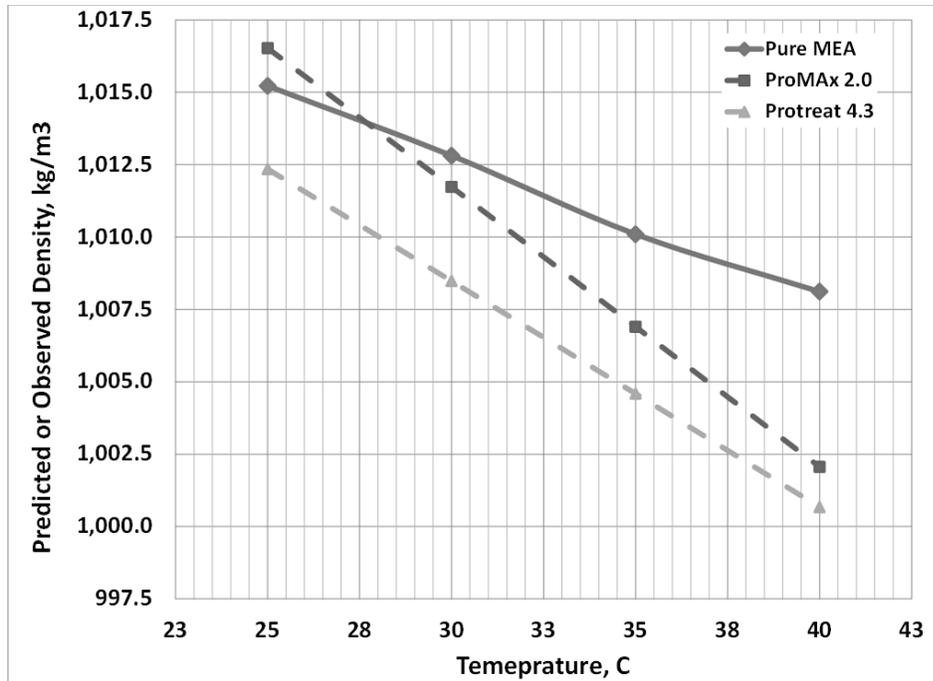


Figure 16 Observed density of pure MEA vs. ProMax and ProTreat predictions

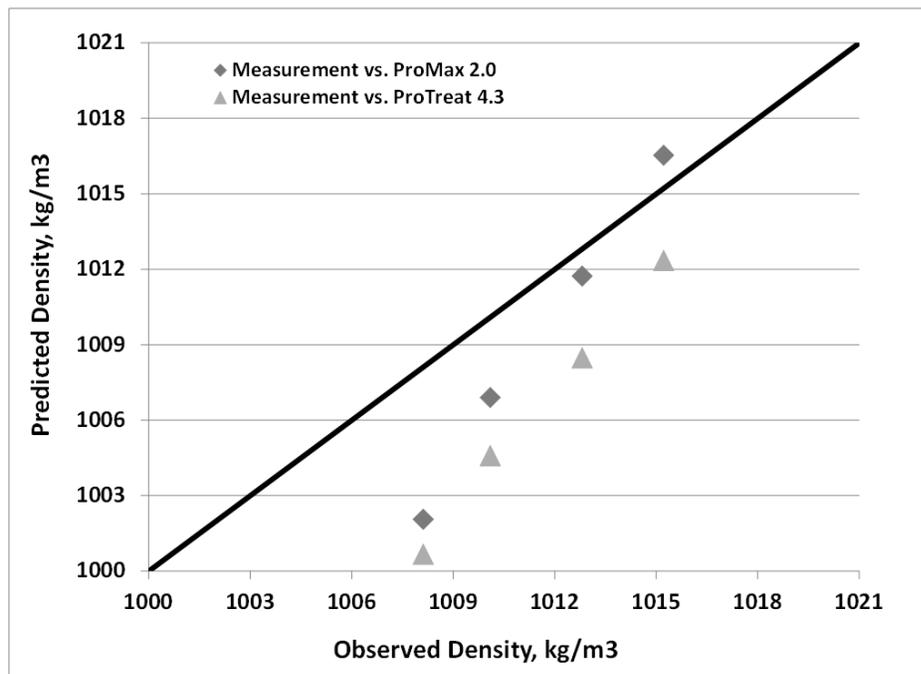


Figure 17 Parity chart of observed density of pure MEA vs. ProMax and ProTreat predictions

Density measurement of pure MDEA solvents was conducted according to the BS 200-185/190, the standard method. Figure 18 illustrates the comparison of density between the observed for measurements and predicted from ProMax and ProTreat. In contrast to pure MEA solvent, the pure MDEA observed density has been laid down between the predicted curves from the two softwares: higher than ProTreat but lower than ProMax. Also, the trend or slope of observed density curve from ProMax matches the one predicted by ProTreat. The differences are translated into the parity chart on Figure 19.

It can be seen from the measurements of density of pure MEA and pure MDEA that the Pycnometer method can be used satisfactory in measuring the density. MEA density would be likely lower than the real experimental value, which could be measured by different and much more accurate and sophisticated methods. The lower value could be due to solvent loss through the evaporation and loss of some sample mass. In case of pure MDEA, the prediction was fairly close to the real density measurements. The tertiary amine has lower vapour pressure, making it difficult to evaporate when compared to primary amine, MEA.

6.2.2 Density measurement of degraded 5M MEA solvent

Density measurements of 5M MEA aqueous solution were conducted. To study the accuracy of the measurement of density by Pycnometer over selected temperature ranges, comparisons between the measurement figures of 5M MEA solution with those predicted by ProMax and ProTreat were done as shown in Figure 20. The solvent is not degraded or loaded with CO₂.

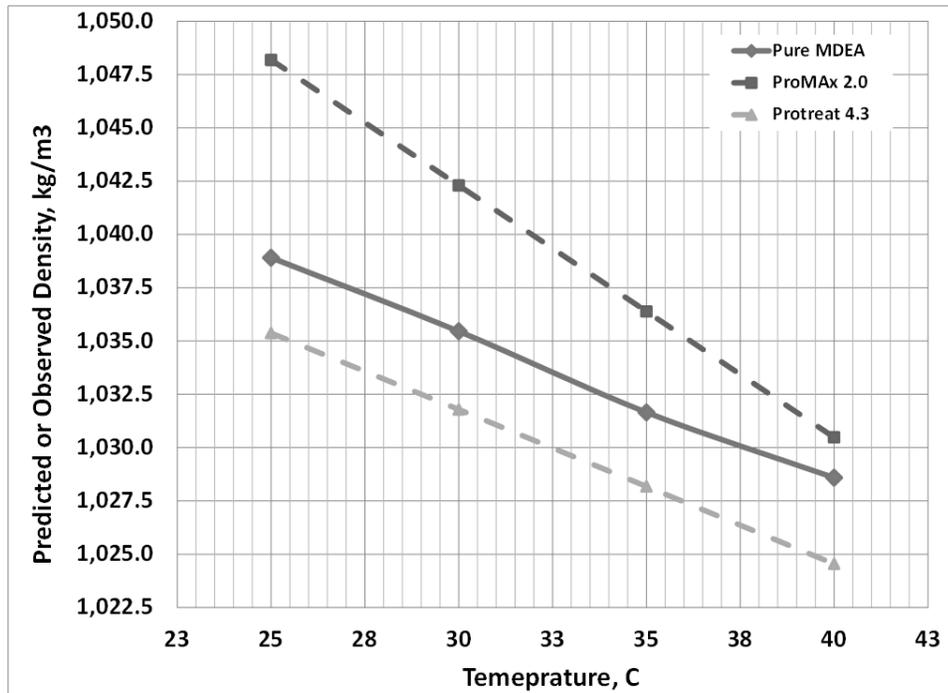


Figure 18 Observed density of pure MDEA vs. ProMax and ProTreat predictions

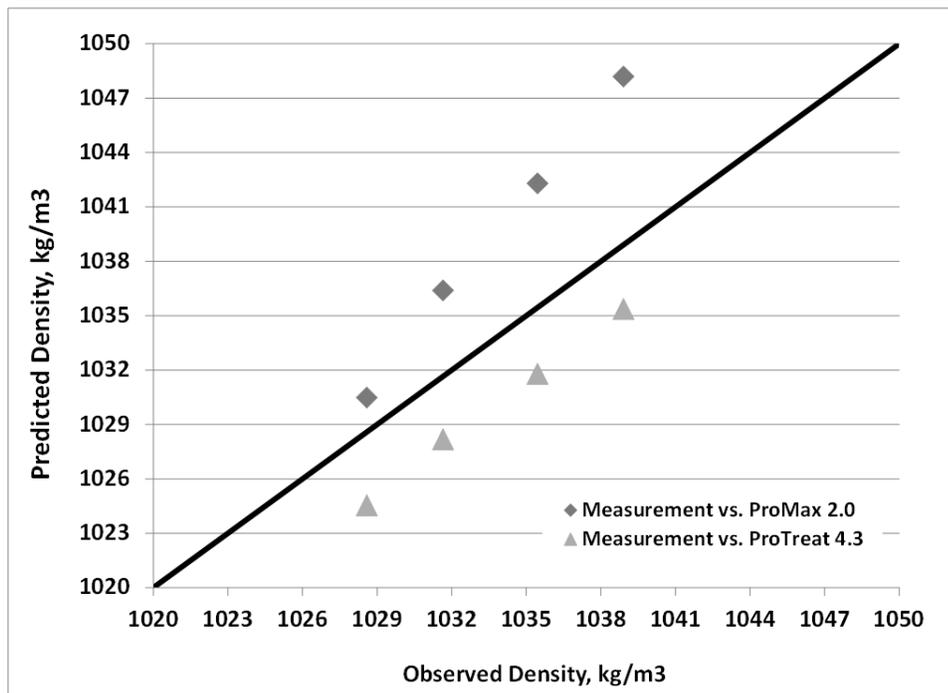


Figure 19 Parity chart of observed density of pure MDEA vs. ProMax and ProTreat predictions

The experimental value of density was found to be closely matched with the ProMax prediction, while it is lower than those obtained by ProTreat. Figure 21 gives the parity chart of the comparison between measurements and predictions from both softwares. From these results, it can be concluded that the measurement of density with a Pycnometer is quite satisfactory for 5M MEA solvents and can be used to determine the density of degraded solvent.

To compare the density measurements between clean and degraded 5M MEA solvents, six degraded MEA solvents have been prepared with different concentrations of total degradation products ranging from 0.5 to 5 wt%, Figure 22. It can be seen that the density of solvent increases with the increase of the degradation products. Observed density of degraded MEA solvents have been fitted to a two variable linear equation (6.2). The regression of data was completed by using the non-linear regression software, NGLEG. The coefficient of determination, R^2 , was 98.32%, and average absolute deviation of equation (6.2) was 0.0479%, which is very good. Equation (6.2) can be used to predict the solvent density of 5M MEA if the degradation content and temperature are known. It can also be used to predict the degradation content if density and temperature are measured.

$$\rho_{5M-MEA} = 2.3772 \times [DP_{MEA}] - 0.4304 \times T + 1022.5864 \text{ ----- Equation (6.2)}$$

where:

$[DP_{MEA}]$ = Degradation product concentration in wt. % in 5M MEA solvent,

T = Temperature of 5M MEA solvent in °C,

ρ_{5M-MEA} = Predicted observed density of degraded 5M MEA solvent,

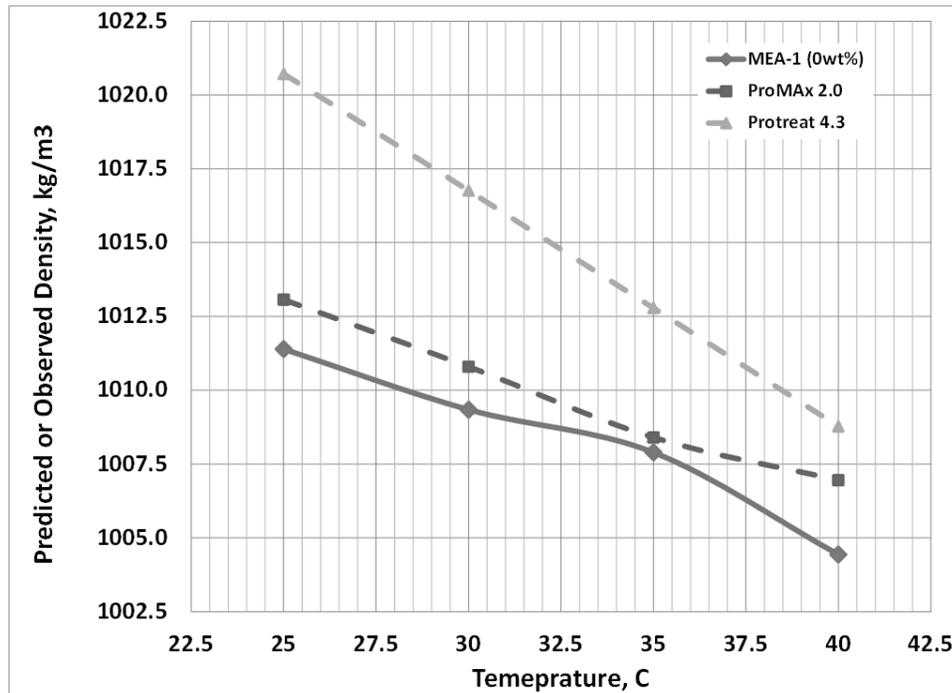


Figure 20 Observed density of 5M MEA vs. ProMax and ProTreat predictions

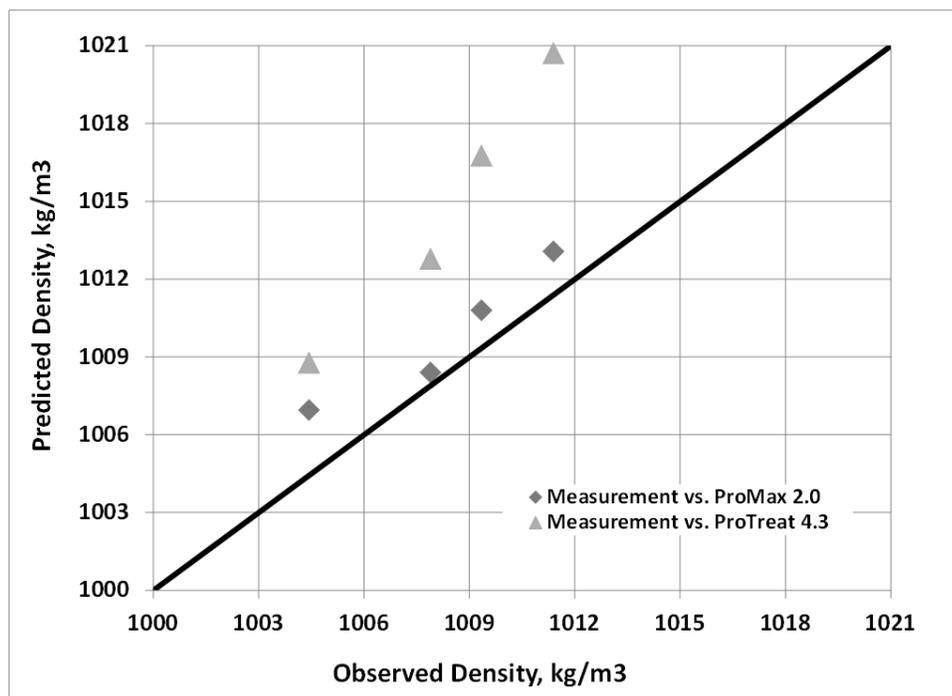


Figure 21 Parity chart of observed density of 5M MEA vs. ProMax and ProTreat predictions

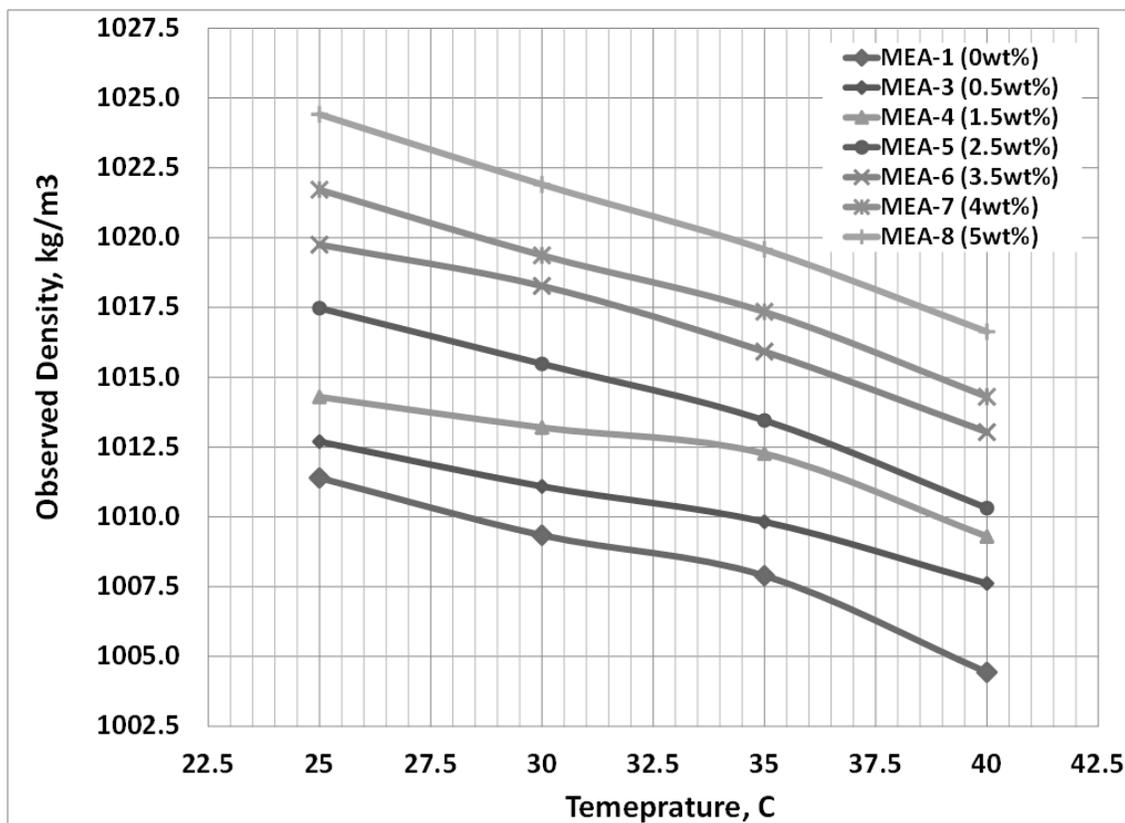


Figure 22 Observed density of 5M MEA solvents vs. temperature and total degradation product concentration

6.2.3 Density measurement of degraded 5M MEA/MDEA solvent

The density measurements of 5M MEA/MDEA aqueous solution were conducted with no CO₂ content. To study the accuracy of the measurement of density by the Pycnometer over selected temperature ranges, comparisons between the measured density of 5M MEA/MDEA solution with those predicted by ProMax and ProTreat were carried out as shown in Figure 23. The experimental value of density was found to be between the ProMax and ProTreat predictions. Figure 24 gives the parity chart of the comparison between measurement and prediction from both softwares. Therefore, we could conclude that the measurements of density with a Pycnometer are quite satisfactory and can be used to determine the degraded solvent density by the Pycnometer method.

To compare the density measurements between clean and degraded 5M MEA/MDEA solvents, six degraded MEA/MDEA solvents were prepared with different concentrations of total degradation products that varied from 0.5 to 5 wt%, Figure 25. The solvent density increased with the increase of the degradation product content. For instance, the 5M MEA/MDEA solvent with 4 wt% degradation products could deviate by 0.75% more than the clean solvent. The deviation of density of mixed amine of MEA/MDEA is lower than single MEA solvent, but this could be due to some evaporation loss during the test.

Observed density of degraded 5M MEA/MDEA solvents were fitted with two variable linear equations (6.3). The regression of the data was completed using the non-linear regression software, NGLEG. The coefficient of determination, R^2 , was 97.14%, and the average absolute deviation of equation (6.2) was 0.0554%, which is very good. Equation (6.3) can be used to predict the solvent density of 5M MEA/MDEA if the degradation

content and temperature are known. It can be also used to predict the degradation content if the density and temperature are measured.

$$\rho_{5M-MEA/MDEA} = 1.9439 \times [DP_{MEA/MDEA}] - 0.4061 \times T + 1042.2363 \quad \text{-----}$$

Equation (6.3)

where:

$[DP_{MEA/MDEA}]$ = Degradation product concentration in wt. % in 5M MEA/MDEA

T = Temperature of 5M MEA/MDEA solvent in °C

$\rho_{5M-MEA/MDEA}$ = Predicted observed density of degraded 5M MEA/MDEA solvent

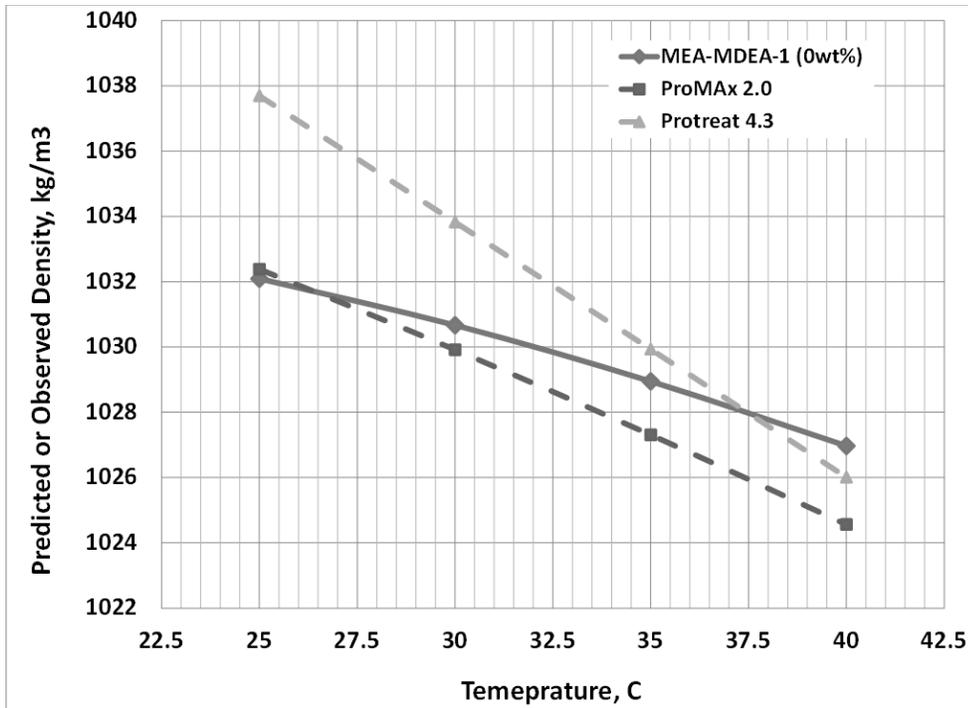


Figure 23 Observed density of 5M MDEA vs. ProMax and ProTreat predictions

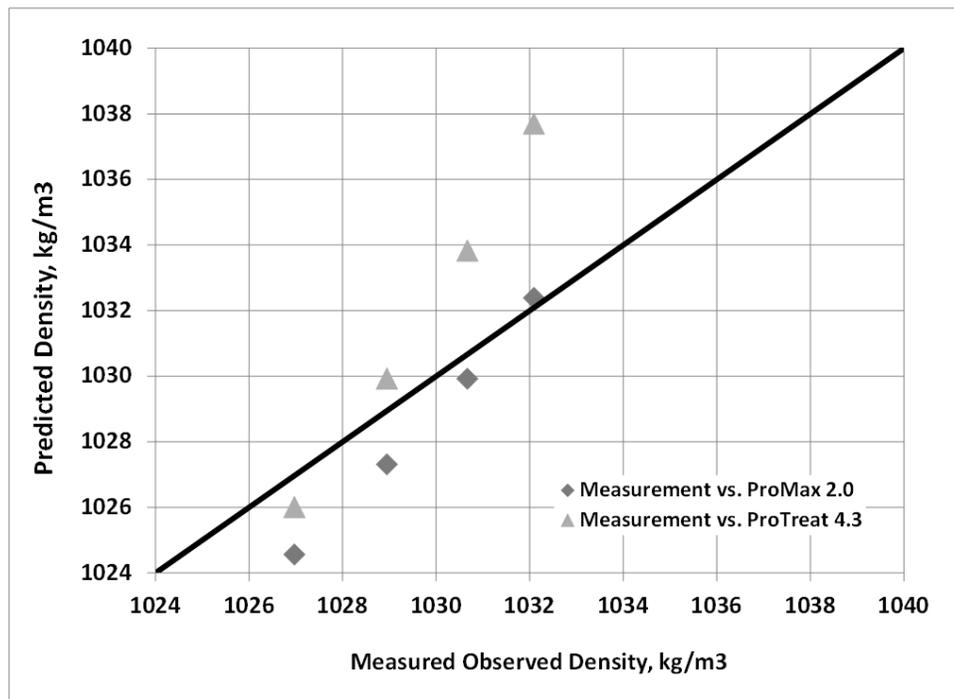


Figure 24 Parity chart of observed density of 5M MDEA vs. ProMax and ProTreat predictions

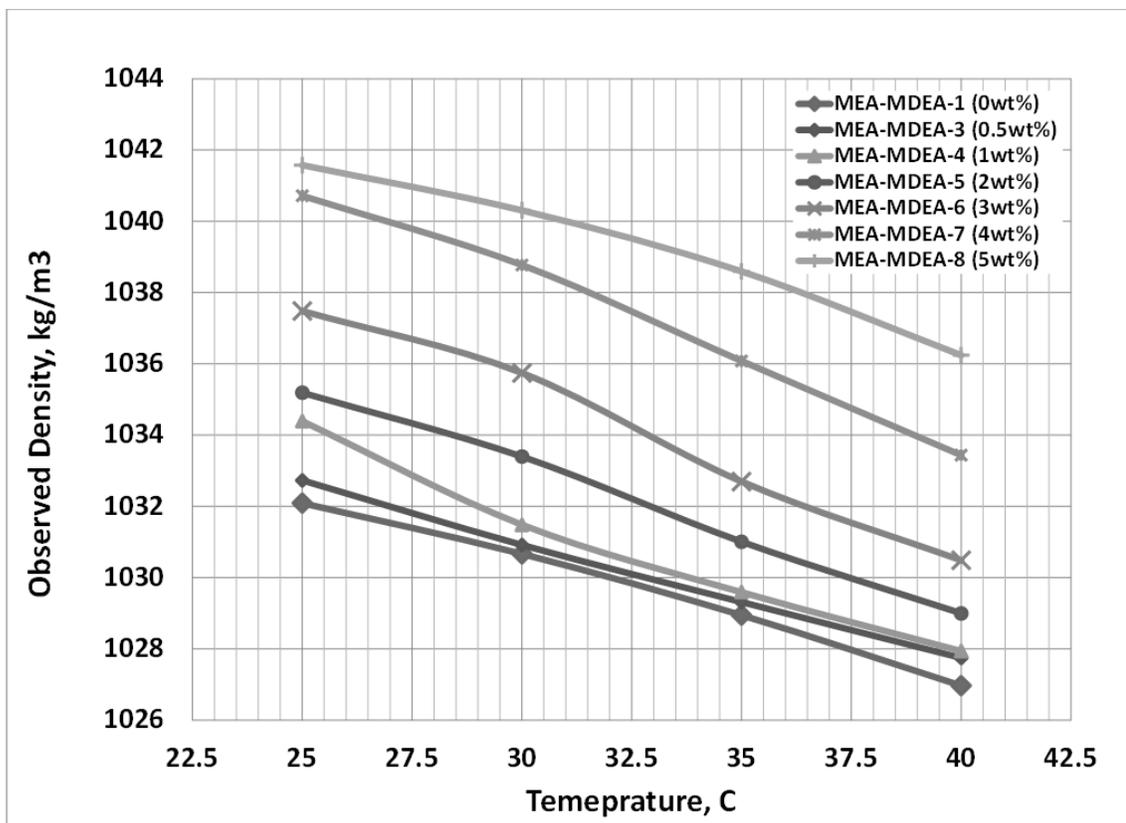


Figure 25 Observed density of 5M MDEA vs. temperature and total degradation product concentration

6.3 Refractive index measurements

Refractive Index is one of the physical properties that can be measured and can indicate the solvent degradation by the change in its value. However, it has been reported by the US Naval Research Laboratory (US NRL) (Blachly et al 1961) that they were looking for an easy, not excessively time consuming, and reliable method to determine the MEA solvent concentration rather than using the colorimetric titration, which takes time and consumes more chemicals. MEA solvents have been used in submarines to purify and control the air inside the submarine from excessive CO₂. However, US NRL has found that refractive index can be changed once the solvent becomes degraded, and this requires correction with solvent titration, which can be conducted one time per day at least to correct refractive index measurements. In this study, measurements of clean and degraded solvent of MEA and MEA/MDEA, which were unloaded by CO₂, were carried out.

In the first part, measurements of the refractive index as a function of solvent concentrations were done for MEA from 0.5 to 9 M and MEA/MDEA from 0.5 to 6M. In the second part, the refractive index measurement of degraded 5M MEA and 5 MEA/MDEA solvents was carried out for different total degradation product concentrations from 0.5 to 5 wt%. It is fair to say that the refractive index, with either the solvent concentration or degradation content, is a linear function. Refractive index measurements were done by using a Reichert r² mini Digital Pocket Refractometer obtained from Cole-Parmer Canada, Montreal, Quebec. All measurements of the refractive index reported in this study were automatically corrected to 20°C by the refractometer device unless otherwise mentioned.

6.3.1 Refractive index of MEA and MEA/MDEA concentrations

Figure 26 illustrates the refractive index as a function of MEA solvent concentration (0.5M to 9M) while Figure 27 illustrates the same data but for MEA/MDEA solvent (0.5M to 6M). In both cases, the refractive index linearly increases with amine solvent concentration. The linear regression of both data sets of MEA and MEA/MDEA give two equations (6.4) and (6.5), which can be used to estimate the solvent concentration just by measuring the refractive index at 20°C. The MEA and MEA/MDEA linear regression coefficient of determinations, R^2 , were 100% and 97.98%, respectively. This indicates good regression results for data for both solvents. It should be kept in mind that the MEA/MDEA blend solvent has been blended at equivalent molarity; however, the equation is not valid for any other different blend ratio between MEA/MDEA unless another set of data and regression are obtained for a new blend.

$$RI_{MEA}^{20^{\circ}C} = 0.0079 \times [MEA] + 1.3330 \quad \text{----- Equation (6.4)}$$

where:

$[MEA]$ = MEA solvent concentration in mole/liter

$RI_{MEA}^{20^{\circ}C}$ = Refractive Index at 20°C for MEA solvent

$$RI_{MEA/MDEA}^{20^{\circ}C} = 0.0136 \times [MEA/MDEA] + 1.3361 \quad \text{----- Equation (6.5)}$$

where:

$[MEA/MDEA]$ = Total MEA/MDEA concentration in mole/liter at 1:1 molar ratio

$RI_{MEA/MDEA}^{20^{\circ}C}$ = Refractive Index at 20°C for MEA/MDEA solvent

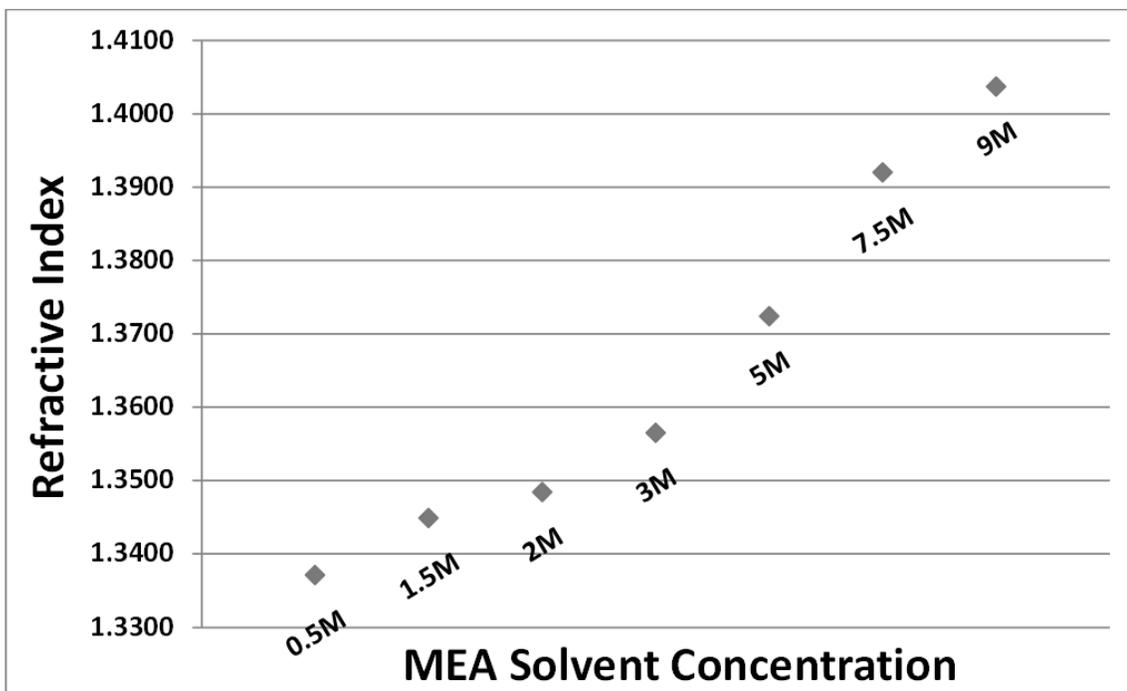


Figure 26 Refractive Index vs. MEA Concentration

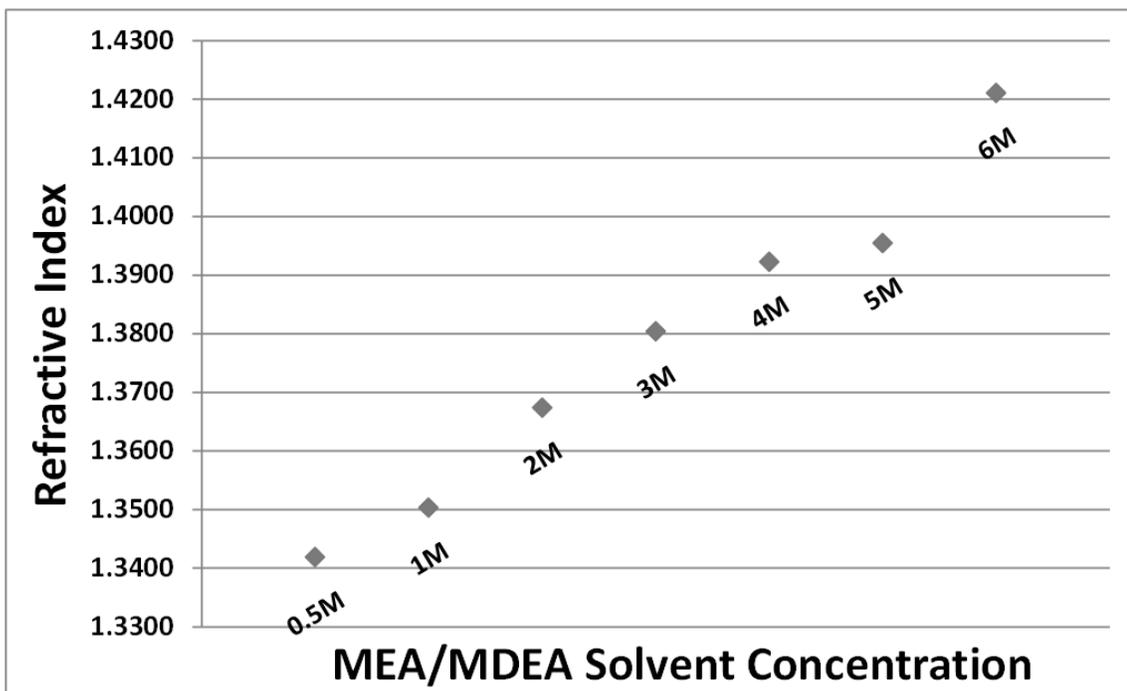


Figure 27 Refractive Index vs. MEA/MDEA Concentration

6.3.2 Refractive index of degraded 5M MEA and 5M MEA/MDEA solvents

The effects of degradation products on amine solvent refractive index are measured and depicted in Figure 28 for 5M MEA and Figure 29 for 5M MEA/MDEA solvents. The total degradation product concentration varies from 0.5 to 5 wt%. The refractive index linearly increases with the increase of the degradation product concentration. The linear regression of both data sets of degraded MEA and MEA/MDEA give two equations, (6.6) and (6.7), which can be used to estimate the total degradation product concentration just by measuring the refractive index at 20°C. The linear regression coefficients of determinations, R^2 , for degraded 5M MEA and 5M MEA/MDEA are 94.74% and 99.98%, respectively.

$$RI_{Deg-MEA}^{20^{\circ}C} = 0.0011 \times [DP_{MEA}] + 1.3721 \quad \text{----- Equation (6.6)}$$

where:

$[DP_{MEA}]$ = Degradation Concentration in wt% for 5M MEA solvent

$RI_{Deg-MEA}^{20^{\circ}C}$ = Refractive Index at 20°C for degraded 5M MEA solvent

$$RI_{Deg-MEA/MDEA}^{20^{\circ}C} = 0.0010 \times [DP_{MEA/MDEA}] + 1.3955 \quad \text{----- Equation (6.7)}$$

where:

$[DP_{MEA/MDEA}]$ = Degradation Concentration in wt% for 5M MEA/MDEA solvent

$RI_{Deg-MEA/MDEA}^{20^{\circ}C}$ = Refractive Index at 20°C for degraded 5M MEA/MDEA solvent

From these two figures, it is possible to construct a reference graph for any solvent in reference status (i.e., free from CO₂) to help understand the solvent degradation progress without the need to do any comprehensive analysis, time consuming, and costly testing. To test the method, 5M MEA and two 5M MEA/MDEA solvents were prepared with random mixes of degradation products. The degraded and unloaded solvents were evaporated in the micro distillate vacuum system to estimate the residue quantity, which is very close to the degradation content in the solvent. The refractive index was measured for the degraded and unloaded solvent. The predictions of degradation content in these three solvents were accomplished by using equations (6.6) and (6.7). Table 14 compares the predicted values of degradation level and the measured amount of heavy materials in the solvents.

Table 14 Predict the degradation content in random prepared amine solvents

| Random Degraded Solvent | Refractive Index | Predicted Degradation content, wt% | Estimated of heavy materials, wt% |
|--------------------------------|-------------------------|---|--|
| 5M MEA – Solvent A | 1.3742 | 1.91 | 2.32 |
| 5M MEA/MDEA – Solvent B | 1.3980 | 2.50 | N/A |
| 5M MEA/MDEA – Solvent C | 1.3989 | 3.40 | 3.96 |

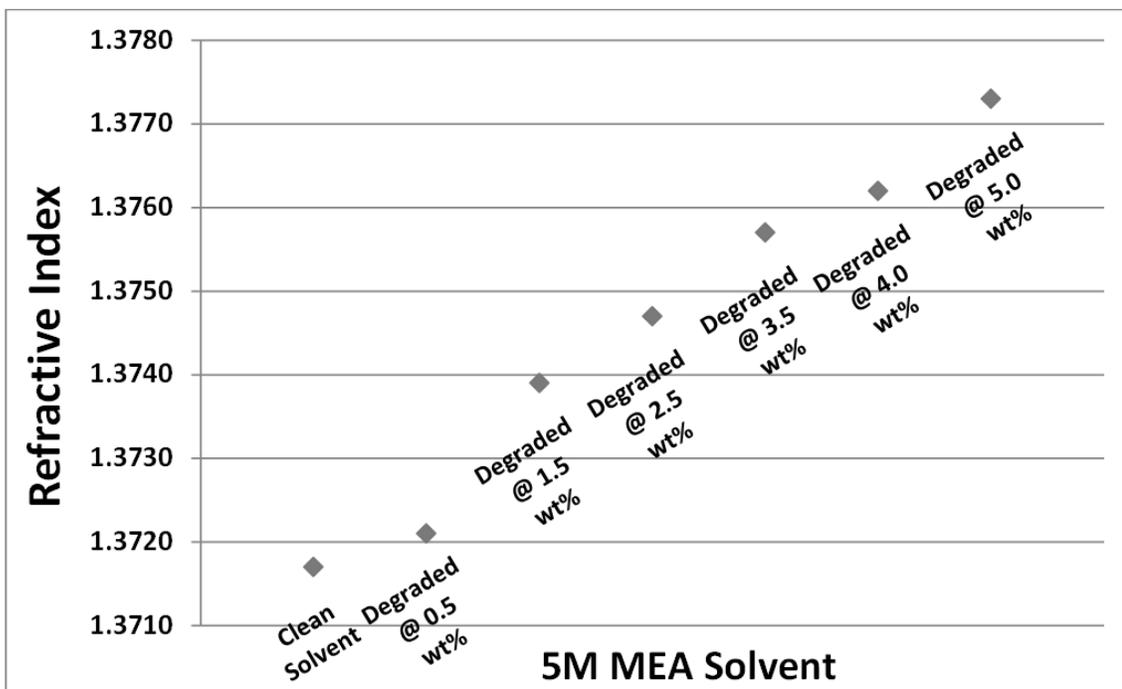


Figure 28 Refractive Index of MEA solvent vs. degradation product concentration

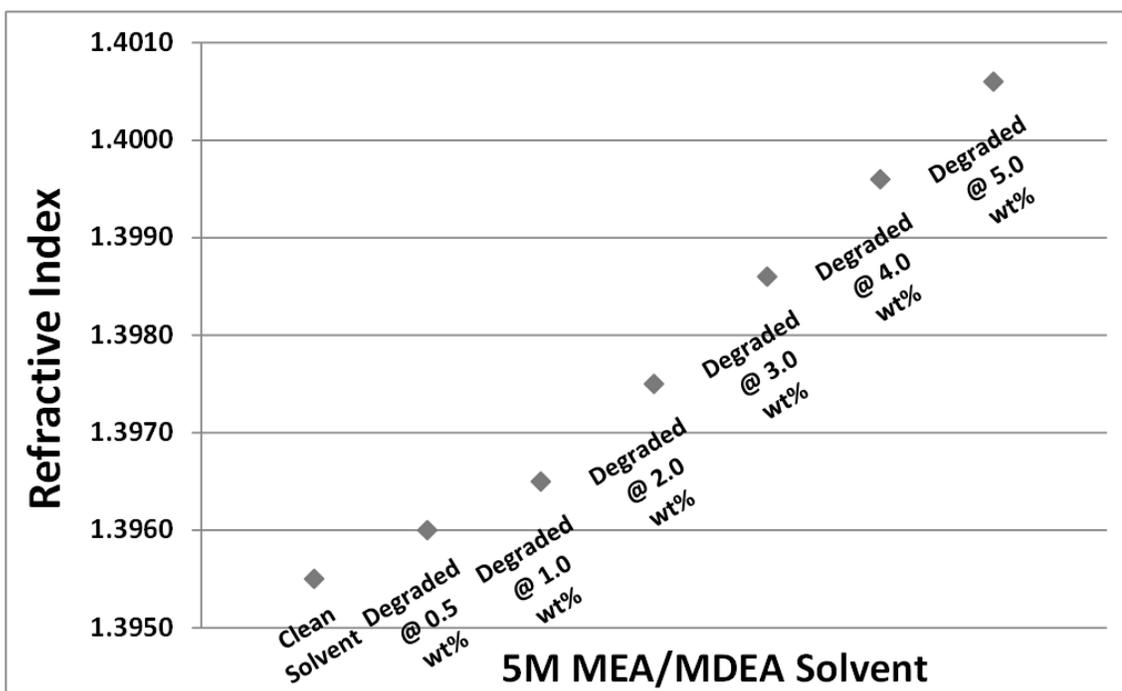


Figure 29 Refractive Index of MEA/MDEA vs. degradation product concentration

6.4 Concluding remarks

- **Solvent density**

1. Density measurement was carried out by using a pycnometer per BS 2000-189/190 British standard method.
2. Three categories of solvents were included for density measurement:
 - Pure MEA and pure MDEA
 - Clean and degraded 5M MEA with degradation ranging from 0.5 to 5wt%.
 - Clean and degraded 5M MEA/MDEA with degradation ranging from 0.5 to 5wt%.
3. Comparison between measured and predicted density by process simulators ProMax and ProTreat was done and found the results were found to be in acceptable agreement for pure and clean solvents of MEA and MEA/MDEA.
4. Solvent density was found to increase as the degradation concentration increased.
5. Two empirical correlations were developed by using non-linear regression for degraded 5M MEA and 5M MEA/MDEA solvents.

- **Solvent refractive index**

1. Refractive index as a function of solvent concentration was measured for MEA and MEA/MDEA and found to follow linear behaviour.
2. Two linear correlations of refractive index versus solvent concentration of MEA and MEA/MDEA were developed.
3. Refractive index was measured and correlated into empirical correlations for degraded 5M MEA and MEA/MDEA solvents. The degradation content varied from 0.5 to 5 wt%.

Chapter 7: Heat Stable Salts and Their Neutralization in Amine Solvents

7.1 Chapter introduction

One type of degradation product formed in amine solvent is heat stable salts (HSSs). The definition of HSSs varies in the literatures, but we consider the best definition of HSS as that provided on the technical bulletin under the title of Amine Glossary on the MPR Services website⁷. Their definition is extensive and new terms are introduced to allow ease of understanding. In the normal absorption process, amine reacts with acid gas, such as CO₂, to form heat unstable salt, which could be reversed back and broken into to CO₂ and amine at high temperature and energy in the stripper. However, if the amine reacts with some of the degradation products, such as organic acids, HSSs are formed and cannot be regenerated in the stripper because the bonds between the acids anions and protonated amines are very strong (MPR Services, 2010). Organic acids, or more specifically carboxylic acids, are usually formed from oxidative degradation reactions, although other pathways can be followed in their formation. Table 15 provides examples of comparisons between HSSs and heat unstable salts. All HSS are water soluble salts.

HSSs can be formed from a reaction between inorganic/organic acids with amine or strong base cations such as sodium or potassium if it exists in the system. If these HSSs form from reactions between amine and organic acid or inorganic acids, which are not carbonate, bicarbonate, sulfide, or bisulfide, then they will be called Heat Stable Amine Salt (HSAS) or protonated amine plus organic/inorganic acid anions. If the HSSs are formed from reactions between strong bases with organic/inorganic acids, then they are

⁷ www.mprservices.com

called high heat stable salts (HHSS). Table 16 generally gives the matrix of possible HSSs formed in amine systems. Also, it is possible to propose equation (7.1) to help define the HSS matrix illustrated in Table 16. In our study, we will consider only the presence of HSSs produced from organic acid.

$$HSS = HSAS + HHSS \text{ ----- Equation (7.1)}$$

Examples of HSS anions formed from the solvent degradation could include acetate, formate, thiosulfate, sulfate, thiocyanate, oxalate, butyrate, and propionate. Other HSS anions introduced to the solvent from water make-up or flue gas are chloride, phosphate, cyanide, and nitrate (Cummings & Mecum, 2000). HSS levels in amine are recommended to be less than 10% of amine concentrations; for instance, 30 wt% MEA should contain a maximum of 3% HSS (Bacon 1987). As a general rule, it is preferred to control concentrations of the HSS and degradation products to less than 3 wt% to avoid operational problems. However, the presence of these products (i.e., HSS and amine degradation products) even in smaller concentrations, is considered undesirable. Therefore, the desired concentration of these contaminants is zero. Further details of these degradation products and their formation paths are extensively reported in the literature (Supap et al., 2011). Table 17 provides the list of organic acids used in this study to create HSSs. Based on Table 17, the selected carboxylic acids have different strengths and pKa values; $pK_a < 0$ is a strong acid, and $pK_a > 0$ is a weak acid (Brown & Poon, 2004). The acid might have two pKa values, which means there are two different strengths for the acid. For instance propionic acid has two pKa values: -6.8, which is a strong acid portion, and 4.88, which is a weak acid portion.

Table 15 Comparison of heat unstable and stable salts (Cummings et al 2007)

| Amine | Absorber | Stripper |
|---|---|--|
| Heat unstable Salts (CO ₂ absorption) | | |
| Secondary | $2R_2NH + CO_2 \longrightarrow R_2NH_2^+ + R_2NCOO^-$ | $R_2NH_2^+ + R_2NCO^- + \Delta \longrightarrow 2R_2NH + CO_2$ |
| Tertiary | $CO_2 + H_2O \longrightarrow H_2CO_3$ \swarrow $H_2CO_3 + R_3N \longrightarrow R_3NH^+ + HCO_3^-$ | $R_3NH^+ + HCO_3^- + \Delta \rightarrow R_3N + H_2CO_3$ \swarrow $H_2CO_3 \rightarrow CO_2 + H_2O$ |
| Heat Stable Salts (formic acid as an example of organic acid) | | |
| Secondary | $R_2NH + CHOOH \longrightarrow R_2NH_2^+ + CHOO^-$ | $R_2NH_2^+ + CHOO^- + \Delta \longrightarrow$ (No Change) |
| Tertiary | $R_3N + CHOOH \longrightarrow R_3NH^+ + CHOO^-$ | $R_3NH^+ + CHOO^- + \Delta \longrightarrow$ (No Change) |
| | $MDEA + CHOOH \rightarrow MDEAH^+ + CHOO^-$ <i>Methyldiethanol ammonium formate</i> | $MDEAH^+ + CHOO^- + \Delta \longrightarrow$ (No Change) |

Table 16 Heat stable salt matrix in amine system

| | Organic Acid | Inorganic Acid |
|-------------|-------------------------------|---|
| Amine | Heat stable amine salt (HSAS) | Heat unstable salts, if anions are carbonate, bicarbonate, sulfide, and bisulfide. Otherwise, it is heat stable amine salts (HSAS). |
| Strong Base | High heat stable salts (HHSS) | High heat Stable Salts (HHSS) |

Table 17 Organic acids selected for formation of HSSs in amine solvents⁸

| | Formic Acid | Acetic Acid | Propionic Acid | Butyric Acid | Glycolic Acid | Oxalic Acid | Lactic Acid | Malonic Acid |
|----------------------------|--------------------------------|--|--|--|--|--|--|--|
| CAS # | 64-18-6 | 64-19-7 | 79-09-4 | 107-92-6 | 79-14-1 | 144-62-7 | 50-21-5 | 141-82-2 |
| Chemical Structure | CH ₂ O ₂ | C ₂ H ₄ O ₂ | C ₃ H ₆ O ₂ | C ₄ H ₈ O ₂ | C ₂ H ₄ O ₃ | C ₂ H ₂ O ₄ | C ₃ H ₆ O ₃ | C ₃ H ₄ O ₄ |
| Form | Clear Liquid | Clear Liquid | Clear Liquid | Clear Liquid | Colorless Crystals | White Crystalline | Liquid | White Powder |
| Mwt | 46.03 | 60.05 | 74.1 | 88.11 | 76.05 | 90.03 | 90.08 | 104.06 |
| pH | 2.2 | 2.4 | 2.5 @ 100 g/l @ 20°C | 3 @ 10 g/lit @ 20°C | 2 | 1.3 | | |
| Melting Point, °C | 8.5 | 16.2 | -24 to -23 | -7 to -5 | 75 | 189.5 | 17 | 132-135 |
| Boiling Point, °C | 100.8 | 117-118 | 141 - 142 | 164 | | 157 | 122 / 15 mmHg | |
| Vapor Pressure, mmHg | 44.8 @ 20°C | 55 @ 50°C 11.4 @ 20°C | 2.4 @ 20°C | 0.43 @ 20°C | 8.1 @ 80°C | <0.01 @ 20°C | | |
| Density, g/cm ³ | 1.2 | 1.05 | 0.992 | 0.958 | 0.6 | 1.9 @ 20°C | 1.209 @ 25°C | 1.6 |
| Water Solubility, g/l | Miscible | Miscible | Soluble | Miscible | 0.1 g/ml | N/A | | N/A |
| Acidity (pKa) ₁ | 3.74 @ 25°C | 4.76 @ 25°C | -6.8 @ 25°C | 2.82 @ 25°C | 3.62 @ 25°C | 1.08 @ 25°C | 3.86 | 2.58 @ 25°C |
| Acidity (pKa) ₂ | | | 4.88 @ 25°C | | | 3.55 @ 25°C | | 5.69 @ 25°C |

⁸Most of the data were extracted from MSDS; however, the remainder were obtained from Armarego and Chai (2009) (those with *Italic* fonts).

7.2 Heat stable salts formation and their neutralization

To create artificial degraded amine solvent with HSS for the study, organic acids were added in the desired concentration (i.e. 1wt %) to the amine solvent. Organic acids are believed to react with the amine to form HSSs, and this practice has been used elsewhere for similar studies (e.g., Rooney et al (1996)). Gas chromatography (GC) analysis for degraded samples shows that some amides are formed relative organic acids, and possibly aldehydes were formed as well, and this will be discussed in this section. To neutralize HSS and free the bonded amine, a strong base is usually added in equivalent amounts to the organic acid “HSSs” (i.e., sodium hydroxide or potassium hydroxide). All sodium salts formed with any carboxylic acids are water soluble (Brown & Poon 2004). Five acids are covered in this subsection: formic acid, acetic acid, glycolic acid, oxalic acid, and malonic acid.

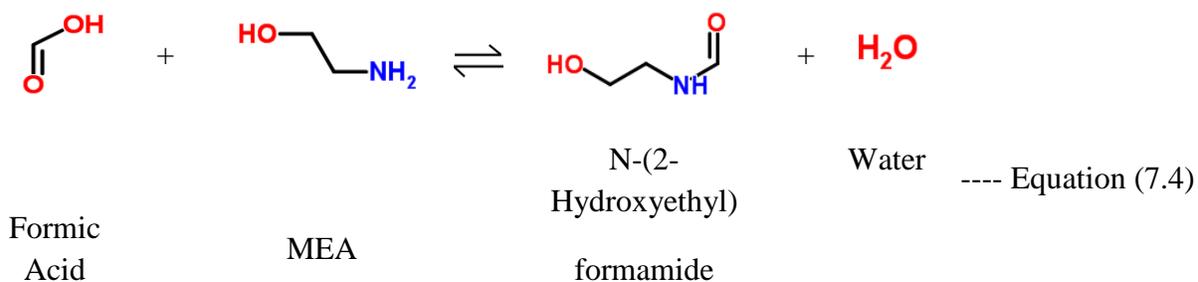
7.2.1 Formic acid addition and neutralization

Formic acid is a weak acid and is the simplest carboxylic acid that can be formed in the amine oxidation reactions. Once the formic acid is formed, it reacts immediately with the amine solvent to form an ammonium formate complex salt that is considered a heat stable salt, and it bonds some of amine, making it inactive for acid gas absorption, as shown in Equation (7.2). Other chemicals that can be formed from the addition of formic acid are formaldehydes and formamides, as shown in equations (7.3) or (7.4).



An example of MEA with formic acid is given in Equation (7.4). As can be seen, the formation reaction of formamide is an equilibrium reaction, and the equilibrium between reactants and

products can be disturbed by changes in the concentration of one of them. For example, if formic acid is removed by a suitable method like neutralization, it will lead to a reduction of formamide formation and reverse equilibrium towards the reactants.



To free amine and neutralize the heat stable salts, addition of a strong base such as sodium hydroxide, NaOH, is used, as shown in Equation (7.5):



However, by thermal distillation, the amine and water is recovered while the neutralized salts and heavy degradation products are left behind. To understand the formation of amides and heat stable salts, samples of MEA with formic acid were prepared and analysed using GC. Figure 30 shows the GC chromatograph before (A) and after addition of formic acid (B) and after addition of 50 wt% NaOH to the samples (C). It was assumed that all formic acid would convert into heat stable salt and amide because of the small concentration of added formic acid (1.0 wt%) compared to the large amount of amine solvent. The high temperature at the injection port in the GC could break the bond between the amine and formate into formic acid and MEA. Before the addition of the formic acid in Figure 30 (A), the GC shows the presence of MEA and H₂O only.

Once the formic acid is added, as in Figure 30 (B), formation of amide appears as well as formic acid. This has been observed elsewhere (Supap et al 2010).

The neutralization of heat stable salt is done by adding equivalent amounts of 50 wt% of NaOH to formic acid. Figure 30 (C) shows the disappearance of both formic acid and N-(2-hydroxyethyl)formamide formed previously. This means that when the strong base is added beyond the required amount to free the heat stable salts, it might reverse the reaction of N-(2-hydroxyethyl)formamide formation, making it disappear, as the formamide is no longer free, and it converts to sodium formate.

Similar to the addition of formic acid to MEA, the acid is added for the blend of MEA/MDEA. Out of the four peaks found in Figure 31, only formamide has been confirmed (last peak). The other three peaks are believed to be other types of amides formed through the reaction between MDEA and formic acid. This requires confirmation by either additional analysis or cross checking with degraded MDEA samples. In addition, when the strong base equivalent to the amount of formic acid is added, all four peaks disappear, confirming that any compounds formed as result from addition of formic acid will be neutralized.

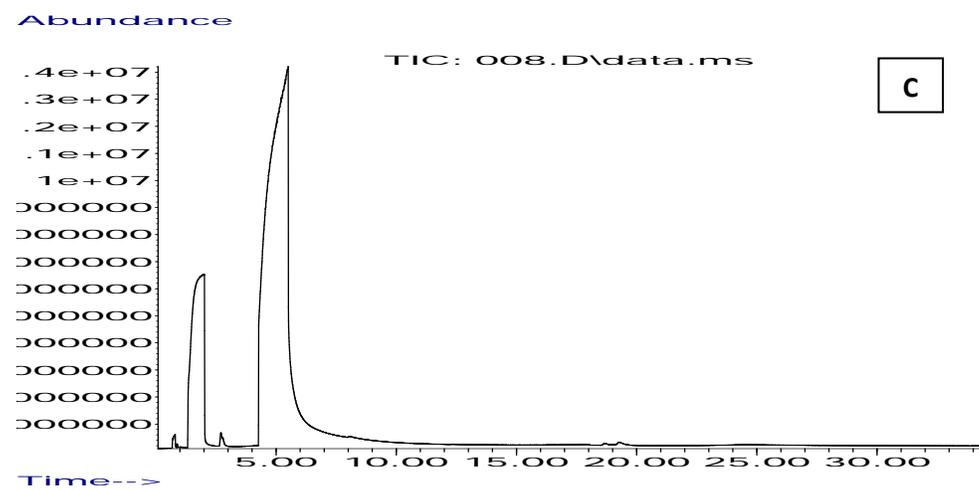
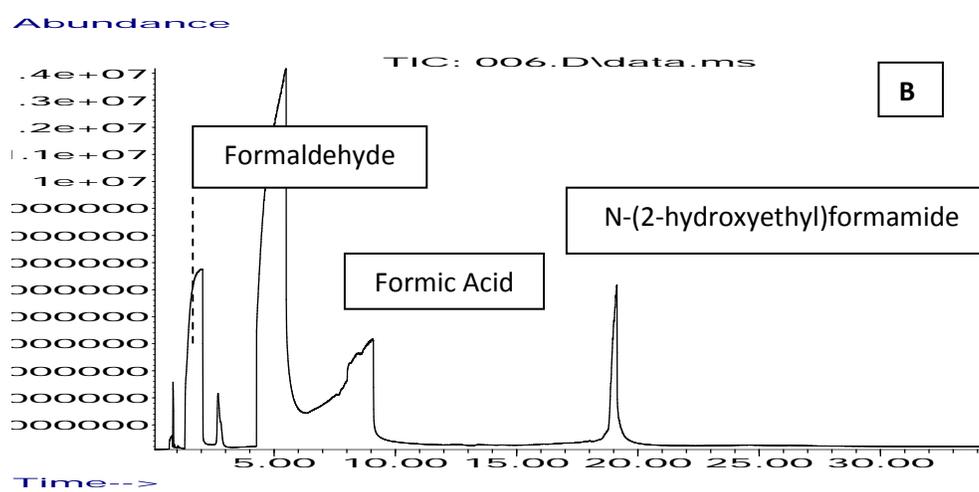
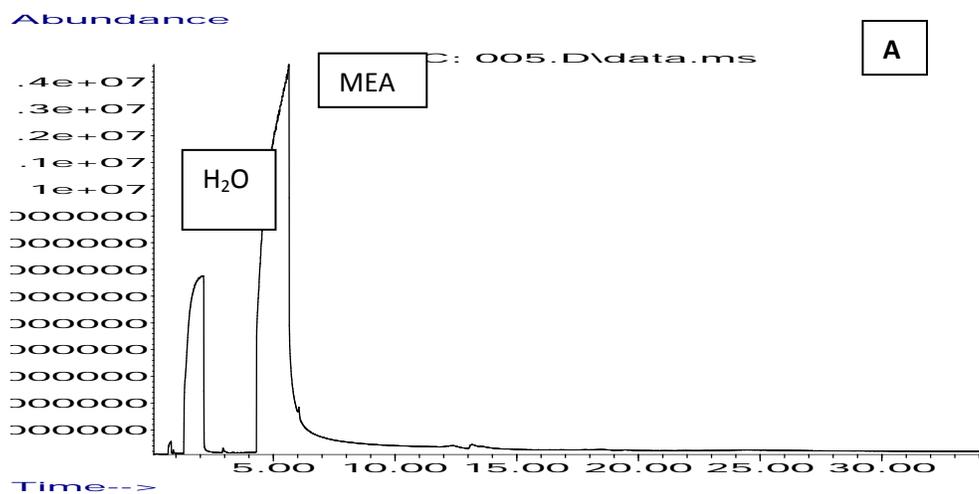


Figure 30 MEA GC Chromatographs of clean solvent (A), solvent with formic acid (B), and neutralized solvent (C)

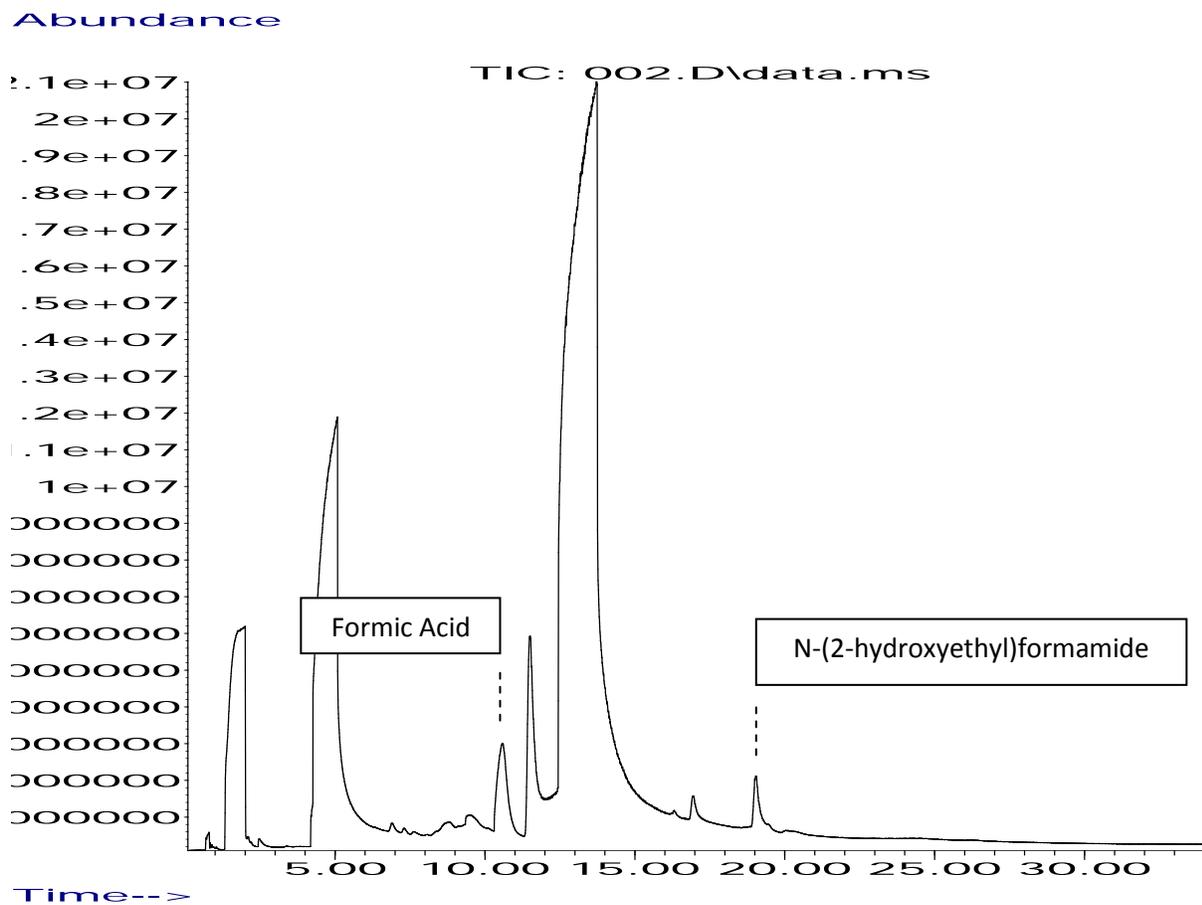


Figure 31 GC Chromatograph for MEA/MDEA with formic acid

7.2.2 Acetic acid addition and neutralization

Acetic acid is a weak acid that was used to simulate the effect of acetate on the solvent strength. Acetic acid results from oxidative degradation of amine solvent. The formation of HSS, acetaldehyde, or acetamide could occur once acetic acid is formed and reacts with amine. Acetic acid will bond some amine and convert it to a complex salt or HSS, see Equation (7.6). Thus, the solvent strength “or concentration” will be reduced. To free the bonded amine, neutralization with addition of a strong base is used, as shown in Equation (7.8). Acetamide is in equilibrium with acetate anions, and removing the acetate with neutralization will lead to reduced acetamide due to reverse equilibrium.



A GC chromatograph of samples after addition of acetic acid is given in Figure 32. There are some new peaks found, including acetaldehyde, acetic acid, and N-(2-hydroxyethyl)acetamide. One peak has not been confirmed as of yet. All new peaks that appeared after addition of acetic acid disappeared when an equivalent amount of 50 wt% NaOH to acetic acid was added. Similar results have been found with a blended MEA/MDEA solvent (Figure 33).

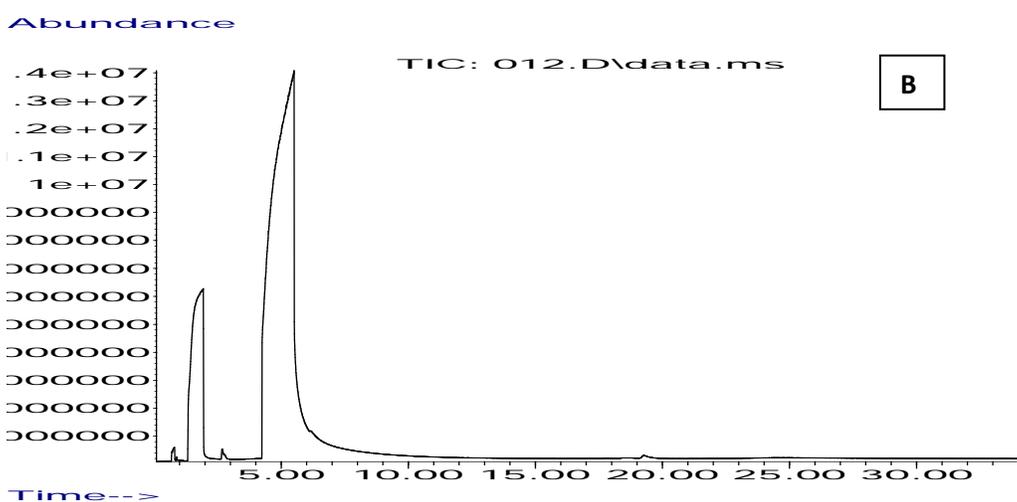
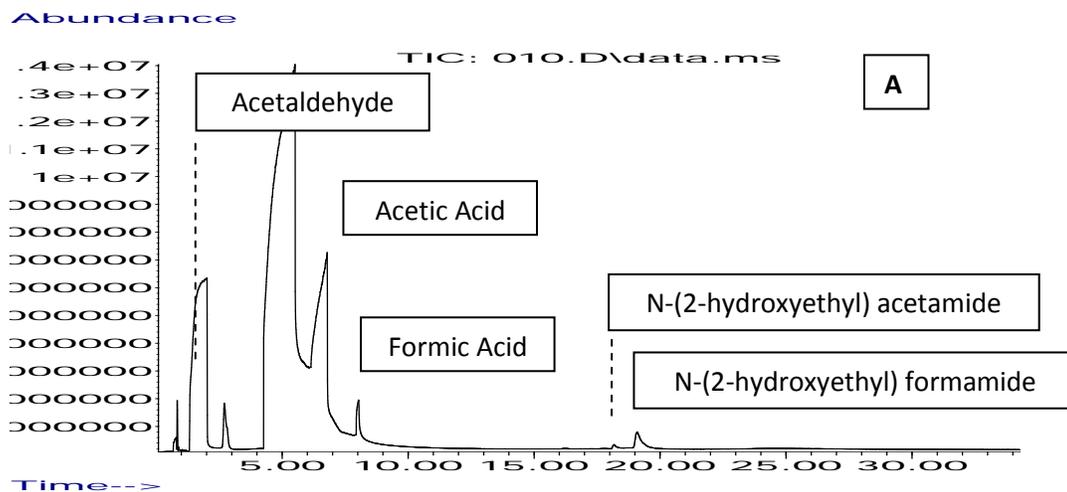


Figure 32 MEA GC Chromatographs with acetic acid before (A) and after neutralization (B)

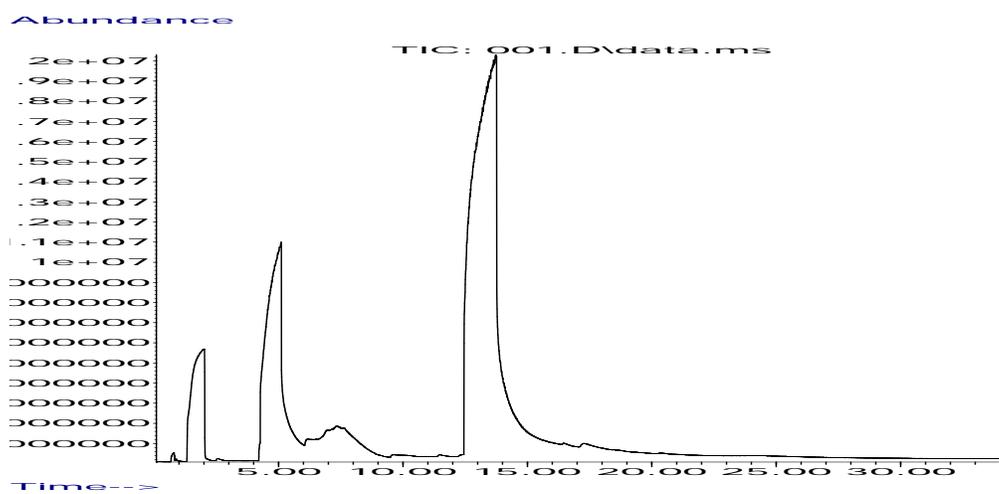


Figure 33 GC Chromatographs for MEA/MDEA with acetic acid

7.2.3 Impact of neutralization on degradation products (None-HSS)

During neutralization of HSSs with strong base, some degradation products might interfere with neutralization, making the objective of neutralization of HSSs incomplete. A blended solvent of MEA/MDEA was prepared, and then, degradation products were added and mixed with an equivalent amount of 50wt% NaOH. From the GC chromatograph, it can be seen that there is some reduction in degradation products. In particular, bicine, which is an amino acid, has completely disappeared, while 1-(2-hydroxyethyl)-2-imidazolidone and N-acetyethanolamine reacted to a certain extent and then reached an equilibrium point. Acetamide and imidazole seem not to be removed significantly.

One explanation of the change of concentration of some degradation products once a strong base is added for neutralization is that some of those degradation products have been converted to sodium salt to a certain extent. In Figure 34, it becomes obvious that by adding NaOH, no new peaks have formed. Reactions of the possible products of neutralization of degradation products are given as follows:

- Acetamide (Unlikely): $C_2H_5NO + NaOH \rightleftharpoons$ (not confirmed)
- Imidazole (Unlikely): $Imidazole + NaOH \rightleftharpoons Imidazole\ Sodium\ Derivative + Water$
- N-Acetyethanolamine (Likely):
 $C_4H_9NO_2 + NaOH \rightleftharpoons C_4H_8NO_2Na$ (N,N-Dimethylglycine sodium) + Water
- Bicine (Likely): $C_6H_{13}NO_4 + NaOH \rightleftharpoons C_6H_{12}NO_4Na$ (Bicine Sodium) + Water
- 1-(2-Hydroxyethyl)-2-Imidazolidinone (Likely)



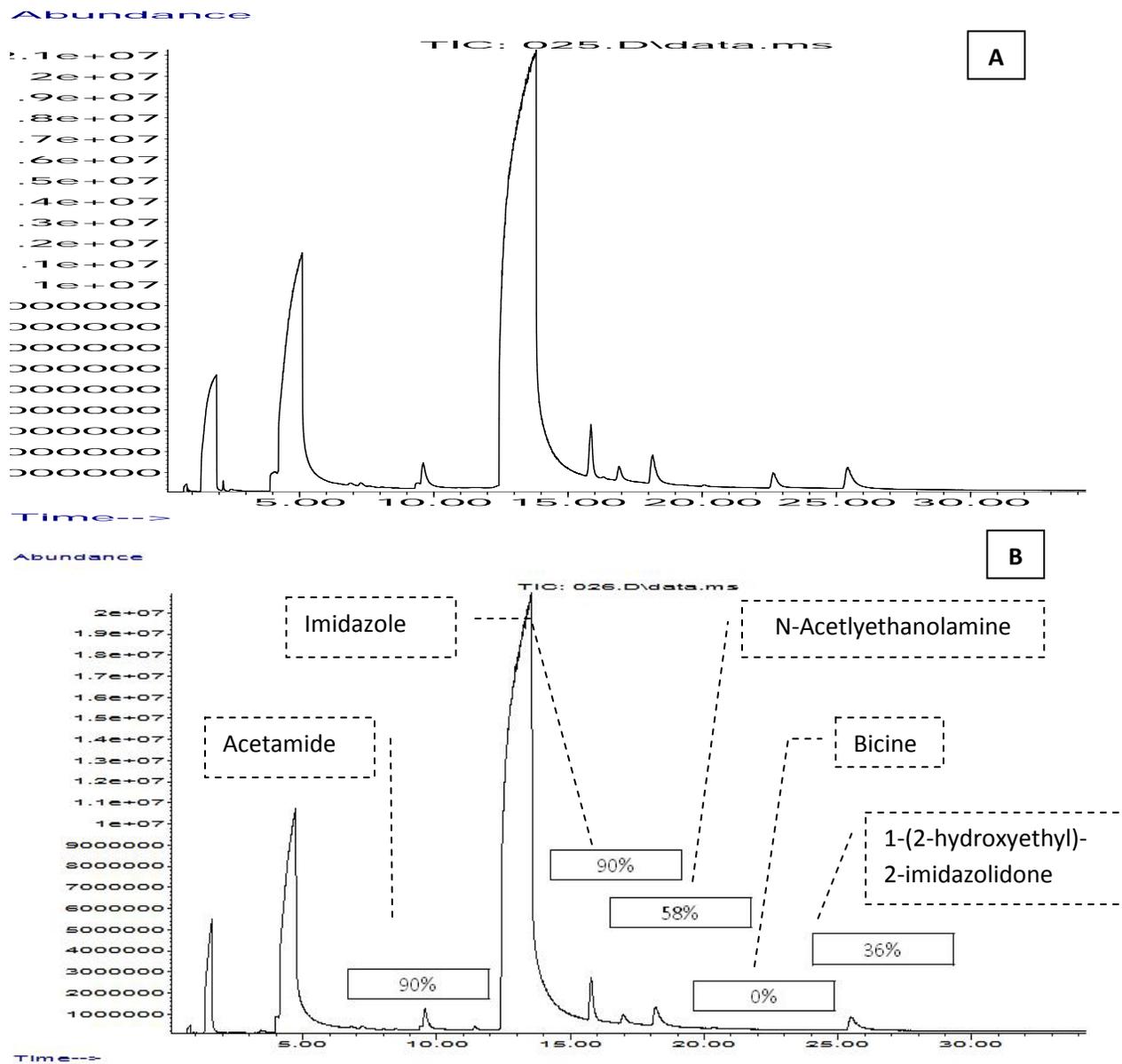


Figure 34 GC chromatograph of degraded MEA/MDEA and impact of the neutralization on degradation products

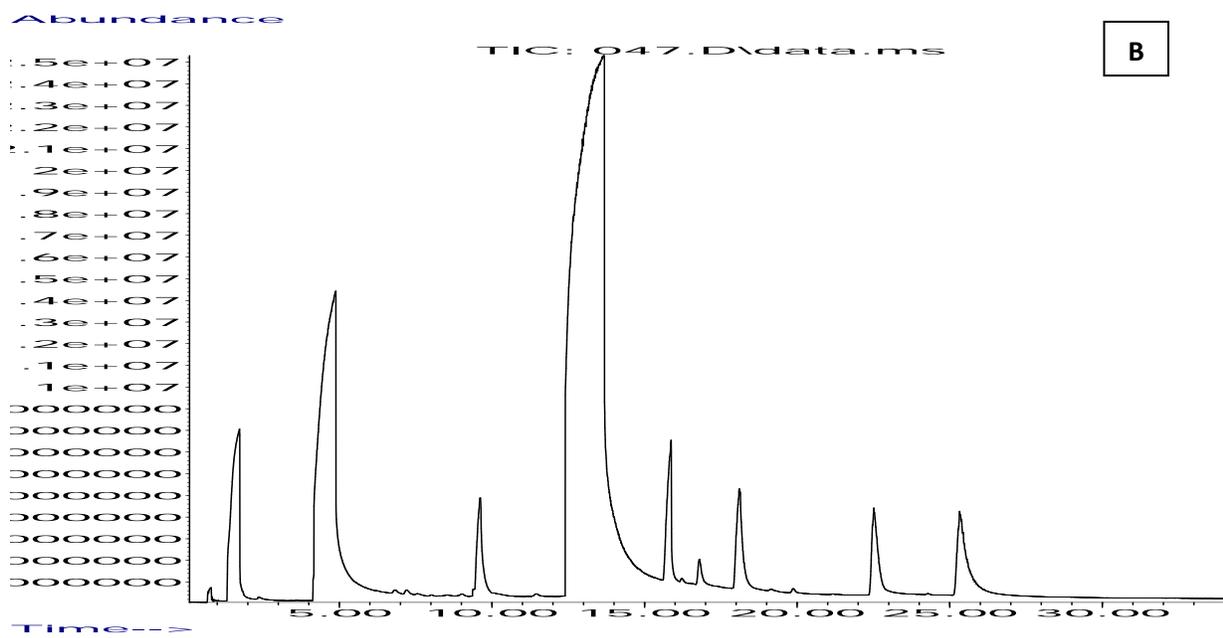
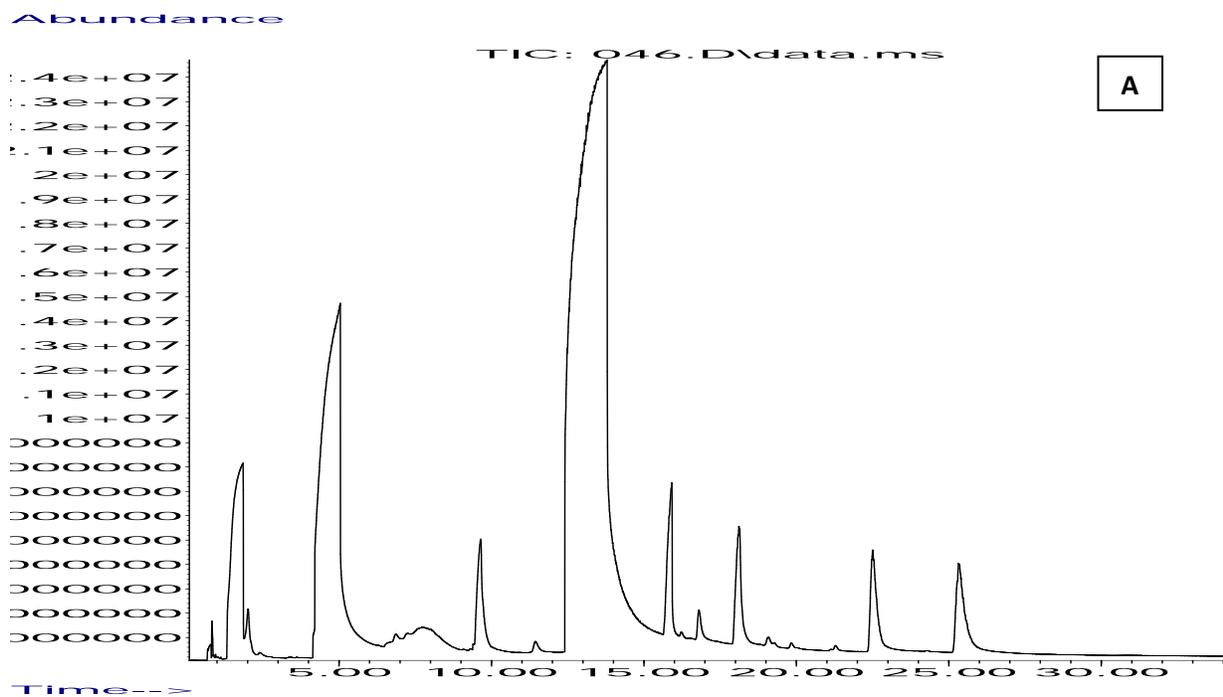


Figure 35 GC chromatograph of neutralization of heat stable salts in a degraded MEA/MDEA solvent

7.2.4 Impact of neutralization of HSS in the presence of degradation products

Degraded solvent was prepared by adding five degradation products and the HSSs mentioned previously in this section. The GC chromatograph obtained for this sample before and after neutralization is shown in Figure 35. The presence of HSSs (organic acids) and amides can be seen in Figure 35 (A). NaOH was added in the equivalent amount to the organic acids in the solvent. It can be clearly seen that all small peaks around the amine peaks and degradation products have disappeared with a slight reduction in bicine concentration, as compared to Figure 35 (A) and (B).

7.3 Degraded 5M MEA with heat stable salts

7.3.1 MEA solvent available and unavailable with HSS

Addition of the HSSs to MEA solvent reduces the amount of amine available for acid gas absorption. To examine this, a number of selected organic acids (HSS) were added to unloaded and clean 5M MEA solvent. All organic acids were added to get 5.0wt% concentration in the amine solvent, with the exception that oxalic acid was 2.7%, which is the saturation solubility in 5M MEA. Analyses were conducted to measure the solvent concentration and the HSS content after the acid addition, and the analyses were based on titration with strong acid (i.e., 1N HCl) for determination of solvent concentration and with strong base (i.e., 0.1N NaOH) for HSS content.

Based on solvent concentration determination by titration, Table 18 gives the solvent concentration before and after the organic acid addition. The strongest organic acid impact is listed on the top while the weaker acids are listed in the bottom. For instance, it is found that the

order of impact is as follows: formic acid > glycolic acid > acetic acid > malonic acid > lactic acid > propionic acid > oxalic acid > butyric acid > bicine. Table 18 also shows the solvent capacity loss in weight percentage and the reduction in solvent capacity in percentage. At the bottom of the table, the overall impact of all HSS added excluding oxalic acid is given.

Table 19 gives the HSS determination, how much solvent is still available for acid gas absorption, the reduction percentage of MEA available for absorption. The table has been organized in the order of the stronger impact acid, formic acid, down to the less impact acid, bicine: formic acid > malonic acid > acetic acid > glycolic acid > propionic acid > oxalic acid > butyric acid > Lactic acid > Bicine. Table 19 shows the overall impact of all HSSs added. It should be mentioned that the bases between Table 18 and 19 are not the same, and Table 19 directly shows the real impact of HSSs on the solvent available for acid gas absorption. Therefore, due to HSS impact on reducing the solvent absorption capacity, it is clear that organic acid or HSS formation should be controlled and/or prevent in the first place if this can be done.

Table 18 Impact of heat stable salts on MEA solvent concentration

| Addition of acid to MEA | | MEA concentration, wt% | Solvent capacity loss, wt% | Reduction of solvent capacity, % |
|-------------------------|-------------|------------------------|----------------------------|----------------------------------|
| Clean Solvent | 0 | 30 | - | - |
| Formic acid | 5 wt% | 23.44 | 6.56 | 21.87 |
| Glycolic acid | 5 wt% | 25.48 | 4.52 | 15.07 |
| Acetic acid | 5 wt% | 26.20 | 3.80 | 12.67 |
| Malonic acid | 5 wt% | 26.32 | 3.68 | 12.27 |
| Lactic acid | 5 wt% | 26.44 | 3.56 | 11.87 |
| Propionic acid | 5 wt% | 27.16 | 2.84 | 9.46 |
| Oxalic acid | 2.7 wt% | 27.52 | 2.48 | 8.26 |
| Butanoic acid | 5 wt% | 28.24 | 1.76 | 5.86 |
| Bicine | 5 wt% | 29.56 | 0.44 | 1.45 |
| All HSS(No oxalic acid) | Total 5 wt% | 26.80 | 3.20 | 10.67 |

Table 19 Determination of heat stable salts on 5M MEA solvent

| Addition of acid to MEA | | HSS as MEA, wt% | MEA available, wt % | Reduction in available MEA, % |
|-------------------------|---------|-----------------|---------------------|-------------------------------|
| Clean Solvent | 0 | - | - | - |
| Formic acid | 5 wt% | 7.93 | 22.07 | 26.44 |
| Malonic acid | 5 wt% | 7.45 | 22.55 | 24.84 |
| Acetic acid | 5 wt% | 6.89 | 23.11 | 22.95 |
| Glycolic acid | 5 wt% | 6.13 | 23.87 | 20.43 |
| Propionic acid | 5 wt% | 6.11 | 23.89 | 20.35 |
| Oxalic acid | 2.7 wt% | 5.01 | 24.99 | 16.71 |
| Butanoic acid | 5 wt% | 4.93 | 25.07 | 16.42 |
| Lactic acid | 5 wt% | 4.29 | 25.71 | 14.30 |
| Bicine | 5 wt% | 3.51 | 26.49 | 11.70 |
| All HSS (No oxalic) | 5 wt% | 6.13 | 23.87 | 20.43 |

7.3.2 Neutralization of heat stable salts in 5M MEA solvent

A study of neutralization of HSS in MEA solvent was carried out. Four different bases were used: NaOH 50wt%, KOH 50wt%, Na₂CO₃ 30wt%, and K₂CO₃ 30wt%. This experiment enabled comparison and evaluation of which base one will be more effective in forming precipitation to easily eliminate the salt from boiling solution, preventing carry over and entrainments, as well as allowing the recovery of clean solvent. All the neutralization tests were done at room temperature, and a magnetic stirrer was used for mixing organic acid with amine. Mixing was carried out for one day or more after which colorimetric titration or GC-MS analyses were carried out. Equation (7.18) shows the general equation of neutralization reaction between the organic acid in amine solvent and strong base. Equation (7.19) illustrates an example of formic acid neutralization with sodium hydroxide:

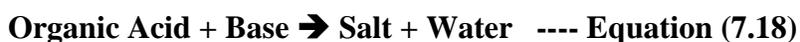


Table 20 provides a comparison of organic acid neutralization with four different bases, which were considered in this study. All neutralization of 5M MEA solvents with organic acid shows that the salts formed are soluble, even with high organic acid (i.e., 7.5 or 5.0 wt%) except in two cases: oxalic acid with NaOH and Na₂CO₃. Oxalic acid is already at the saturation solubility (2.7 wt%) in 5M MEA solvent. Potassium salts are very soluble in amine solvent, and, therefore, this might not be an attractive base to be used in neutralization of HSS. In addition, potassium bases are more expensive than sodium bases. Therefore, KOH and K₂CO₃ were not considered in our selection of the best neutralization agent. The results of these studies suggest that NaOH is the best neutralization agent. Although, 1 mole of Na₂CO₃ could liberate two of bound amine in

HSS, while 1 mole NaOH could liberate only one mole, NaOH has additional merits listed as follows: NaOH is cheaper than Na_2CO_3 , NaOH is a much stronger base than Na_2CO_3 , and NaOH is readily available in large quantities in liquid or pellet form. NaOH is less corrosive than KOH therefore it is more preferable to be utilized (Berlie et al 1965).

Solubility of sodium salts formed from neutralization of oxalic acid with sodium hydroxide showed that sodium salt would be formed even at low concentrations of 2.0 wt%, 1wt%, and 0.5 wt%. Therefore, in any amine system, if oxalic acid or its HSS are found, caution should be taken to prevent the accumulation of this acid due to its low solubility or the consequent formation of salt within the amine system in case there is a leakage of sodium or potassium to the system. However, oxalic acid is expected to be the first HSS removed by neutralization and settle in the reclaimer bottom.

7.4 Degraded 5M MEA/MDEA with heat stable salts

7.4.1 MEA/MDEA solvent available and unavailable with HSS

Addition of HSSs to MEA/MDEA solvent would reduce the amount of amine available for acid gas absorption; therefore, to examine this fact, a number of selected organic acids (HSS) were added to unloaded and clean 5M MEA/MDEA solvent. All organic acids were added to get 5.0wt% concentration, except oxalic acid, which was added at 1.7wt%, its saturation solubility in 5M MEA/MDEA as determined in the laboratory. The analyses were conducted to determine the solvent concentration after the acid addition and the HSS content, and both measurements were based on the colorimetric titration with strong acid (i.e., 1N HCl) for determination of solvent concentration or with strong base (i.e., 0.1N NaOH) for HSS content.

Table 20 Comparing four bases in neutralization of organic acids (or HSS) in 5M MEA

| | | Neutralized salt formation after addition | | | |
|--------------------------|--------------------|---|-------------|---|--|
| Organic Acid | Concentration, wt% | NaOH, 50 wt% | KOH, 50 wt% | Na ₂ CO ₃ , 30wt% | K ₂ CO ₃ , 30wt% |
| Formic Acid | 7.5 | No | No | No | No |
| Formic Acid | 5.0 | No | No | No | No |
| Acetic Acid | 5.0 | No | No | No | No |
| Propionic Acid | 5.0 | No | No | No | No |
| Butyric Acid | 5.0 | No | No | No | No |
| Glycolic Acid | 5.0 | No | No | No | No |
| Malonic Acid | 5.0 | No | No | No | No |
| Lactic Acid | 5.0 | No | No | No | No |
| Oxalic Acid | 2.7* | Yes | No | Yes | No |
| Mixed of all acids above | 5.0 | Yes | No | Yes | No |

* The saturation concentration of oxalic acid in 5M MEA.

Table 21 gives the solvent concentration before and after the organic acid addition. The strongest organic acid impact is listed on the top while the weaker acids are listed in the bottom. For instance, it was found that the order of impact is as follows: formic acid > lactic acid > glycolic acid > malonic acid > propionic acid > butyric Acid > acetic acid > oxalic acid > bicine. Table 21 also shows the solvent capacity loss in weight percentage and the reduction in solvent capacity in percentage. At the bottom of the table, overall impact of all HSS added excluding oxalic acid is given.

Table 22 gives the HSS determination; how much solvent is still available for acid gas absorption, and the reduction percentage of MEA/MDEA available for absorption. The table has been organized in the order of the stronger impact organic acid, formic acid, down to the lowest impact acid, bicine: formic acid > malonic acid > acetic acid > glycolic acid > propionic acid > oxalic acid > butyric acid > lactic acid > bicine. Table 22 shows the overall impact of all HSS added. Table 22 shows the real impact of HSS on the solvent available for acid gas absorption, and the results in Table 21 are not due to the interference of the residual of organic acid or HSS on the colorimetric titration.

As it is difficult to determine which amine in a mixed solvent is actually reacting with organic acid to form HSS by using colorimetric titration, GC-MS chromatographs were used for this. Table 23 provides the MEA or MDEA concentration and loss of concentration. Based on the results from Table 23, it seems MDEA is reduced in a higher ratio than MEA. Sometimes MEA concentration increased, as represented by the negative values in Table 23. This could either mean that more MEA is formed, which is unlikely, or there are by-products formed, and their peak(s) overlap or increase the width of the MEA peaks.

Table 21 Impact of heat stable salt on MEA/MDEA solvent concentration

| Addition of acid to MEA/MDEA | | MEA/MDEA concentration, wt% | Solvent capacity loss, wt% | Reduction of solvent capacity, % |
|------------------------------|-------------|-----------------------------|----------------------------|----------------------------------|
| Clean Solvent | 0 | 45 | - | - |
| Formic acid | 5 wt% | 34.776 | 10.22 | 22.72 |
| Lactic acid | 5 wt% | 39.26 | 5.74 | 12.76 |
| Glycolic acid | 5 wt% | 39.97 | 5.03 | 11.17 |
| Malonic acid | 5 wt% | 40.15 | 4.85 | 10.77 |
| Propionic acid | 5 wt% | 41.59 | 3.41 | 7.58 |
| Butyric Acid | 5 wt% | 41.77 | 3.23 | 7.18 |
| Acetic acid | 5 wt% | 41.77 | 3.23 | 7.18 |
| Oxalic acid | 1.7 wt% | 42.84 | 2.16 | 4.79 |
| Bicine | 5 wt% | 43.56 | 1.44 | 3.20 |
| All HSS (No oxalic) | Total 5 wt% | 39.08 | 5.92 | 13.16 |

Table 22 Determination of heat stable salts in 5M MEA/MDEA solvent

| Addition of acid to MEA/MDEA | | HSS as MEA/MDEA, wt% | MEA/MDEA available, wt % | Reduction in available MEA/MDEA, % |
|------------------------------|---------|----------------------|--------------------------|------------------------------------|
| Clean Solvent | 0 | - | - | - |
| Formic acid | 5 wt% | 6.35 | 38.65 | 14.10 |
| Malonic acid | 5 wt% | 5.59 | 39.41 | 12.42 |
| Acetic acid | 5 wt% | 4.80 | 40.20 | 10.66 |
| Glycolic acid | 5 wt% | 4.21 | 40.79 | 9.35 |
| Propionic acid | 5 wt% | 3.91 | 41.09 | 8.68 |
| Butyric Acid | 5 wt% | 3.39 | 41.61 | 7.53 |
| Lactic acid | 5 wt% | 2.79 | 42.21 | 6.21 |
| Bicine | 5 wt% | 1.75 | 43.25 | 3.90 |
| Oxalic acid | 1.7 wt% | 1.56 | 43.44 | 3.47 |
| All HSS (No oxalic) | 5 wt% | 3.86 | 41.14 | 20.43 |

Table 23 MEA and MDEA content with HSS and their concentration change

| Addition of acid to MEA/MDEA | | MEA, wt% | Δ MEA, wt% | MDEA, wt% | Δ MEA, wt% |
|------------------------------|---------|----------|-------------------|-----------|-------------------|
| Clean Solvent | 0 wt% | 15.00 | 0 | 30.00 | 0 |
| Formic acid | 5 wt% | 13.53 | 1.47 | 25.12 | 4.88 |
| Malonic acid | 5 wt% | 13.53 | 1.47 | 25.88 | 4.12 |
| Acetic acid | 5 wt% | 14.67 | 0.33 | 25.54 | 4.46 |
| Glycolic acid | 5 wt% | 15.73 | -0.73 | 25.06 | 4.94 |
| Propionic acid | 5 wt% | 15.13 | -0.13 | 25.96 | 4.04 |
| Butyric Acid | 5 wt% | 14.91 | 0.09 | 26.70 | 3.30 |
| Lactic acid | 5 wt% | 14.21 | 0.79 | 27.99 | 2.01 |
| Bicine | 5 wt% | 13.83 | 1.17 | 29.42 | 0.58 |
| Oxalic acid | 1.7 wt% | 14.26 | 0.74 | 29.18 | 0.82 |

7.4.2 Neutralization of heat stable salts in MEA/MDEA solvent

A study of neutralization of HSS in MEA/MDEA solvent was carried out. Four different bases were used: NaOH 50wt%, KOH 50wt%, Na₂CO₃ 30wt%, and K₂CO₃ 30wt%. This experiment enabled comparison and determination of which base would be more effective in forming precipitation to easily eliminate the salt from boiling solution, preventing carry over and entrainments, as well as allowing recovery of clean solvent. All the neutralization tests were done at room temperature, and a magnetic stirrer was used for mixing organic acid with amine. The samples were mixed for day or more after which the colorimetric titration or GC-MS analyses were carried out.

Table 24 provides a comparison of organic acid neutralization with the four different bases considered in this study. All neutralization of 5M MEA/MDEA solvents with organic acid show that the salts formed are soluble, even at high organic acid concentrations (i.e., 5.0 wt%) except in one case of oxalic acid with NaOH. Oxalic acid is already at the saturation solubility (1.7 wt%) in 5M MEA/MDEA solvent. Potassium salts are very soluble in amine solvent, and, therefore, this might not be an attractive base to be used in neutralization of HSSs. Solubility studies on sodium salt formation from neutralization of oxalic acid with sodium hydroxide showed that these salts could be formed even at low concentrations of 1.5 wt%, 1wt%, and 0.5 wt%. Therefore, in any amine system, if oxalic acid or its HSS are found, caution should be taken to prevent the accumulation of this acid due to its low solubility or forming of salt within an amine system, in case there is a leakage of sodium or potassium to the system. However, oxalic acid is expected to be the first HSS removed by neutralization, and it would settle down in the reclaimer bottom.

**Table 24 Comparing four bases in neutralization of organic acids (or HSS) in 5M
MEA/MDEA**

| | | Neutralized salt formation after addition | | | |
|-----------------------------|-----------------------|---|----------------|--|---|
| Organic Acid | Concentration, wt% | NaOH, 50 wt% | KOH, 50 wt% | Na ₂ CO ₃ , 30wt% | K ₂ CO ₃ , 30wt% |
| Formic Acid | 7.5 | No | No | No | No |
| Formic Acid | 5.0 | No | No | No | No |
| Acetic Acid | 5.0 | No | No | No | No |
| Propionic Acid | 5.0 | No | No | No | No |
| Butyric Acid | 5.0 | No | No | No | No |
| Glycolic Acid | 5.0 | No | No | No | No |
| Oxalic Acid | 1.7* | Yes | No | No | No |
| Lactic Acid | 5.0 | No | No | No | No |
| Malonic Acid | 5.0 | No | No | No | No |
| Mixed of all acids above | 5.0 | Yes | No | No | No |

* The saturation concentration of oxalic acid in 5M MEA/MDEA.

7.5 Concluding remarks

- 1- HSSs can form from reaction of amine or strong base with organic/inorganic acids. In this study, only HSSs produced from organic acids were considered and with amine only.
- 2- Formation of HSSs can lead to formation of amides and aldehydes of relevant/parental organic acids. However, during the neutralization of HSSs with strong bases, such as NaOH, all HSS, amides, and aldehydes can be neutralized.
- 3- Neutralization of HSS in the presence of other degradation products has minimal impact on degradation product concentration, and, therefore, we consider that it has no impact, except with amino acids such as bicine, which will be neutralized like a HSS.
- 4- HSSs in MEA solvent have different effects on MEA concentration and solvent capacity for CO₂ absorption. It was found that organic acid has a great impact, and the strength of impact can be listed Table 5.
- 5- HSSs in MEA/MDEA solvent have different effects on MEA/MDEA absorption capacity. It was found that organic acid has great impact, and the strength of impact is listed in Table 8.
- 6- For MEA/MDEA, it was found that the most amine disappearing is MDEA more than MEA.
- 7- Four strong bases were selected for neutralization of HSS: 50wt% NaOH, 50% KOH, 30wt% Na₂CO₃, and 30 wt% K₂CO₃. It is desirable to have a strong base that will form insoluble salts with amine to make it easy to separate from the amine in a suitable method like filtration, gravity separation, or distillation. For the best neutralization results, NaOH and Na₂CO₃ at high concentrations are the favoured
- 8- It was found that oxalic acid has lower solubility in amine solvent than other organic acids considered in this research: 2.77 wt% in 5M MEA and 1.70 wt% in 5M MEA/MDEA.

Chapter 8 MEA Solvent Purification by Thermal Distillation

8.1 Chapter introduction

This chapter covers the laboratory work on recovering clean and degraded 5M MEA solvents from their degradation products. The work accomplished is as follows: thermal degradation testing, recovery of MEA solvent (first series), and recovering of MEA solvent (second series). The degradation products used in the preliminary work, series I, might not be the degradation products for a relevant solvent under study, but in the series II, the only possible degradation products formed from the respective solvents were used.

8.2 Thermal degradation studies

The thermal degradation tests were carried out to examine the extent of solvent loss under the effects of temperature for pure MEA solvents. The aim is just to understand the thermal degradation more than an attempt to obtain accurate results at this stage. This is due to the possibility that oxidation of solvents could occur, and, therefore, changes to the solvent could be due to both thermal and oxidative degradation. Each test lasted for 3 hours of continuous heating under specific controlled temperatures, and in some cases, the tests were even run for up to 10 hours. Although these tests were carried out under atmospheric pressure, and this might not be the optimum method to test thermal degradation, it allowed us to study the impact of temperature on the solvent by analysing the degraded solvents in GC-MS and measuring the refractive index. The experiments were carried out in a full reflux distillation set-up shown in Photo 1. The set-up includes hot and stirrer plates with a temperature probe to control the temperature, magnetic

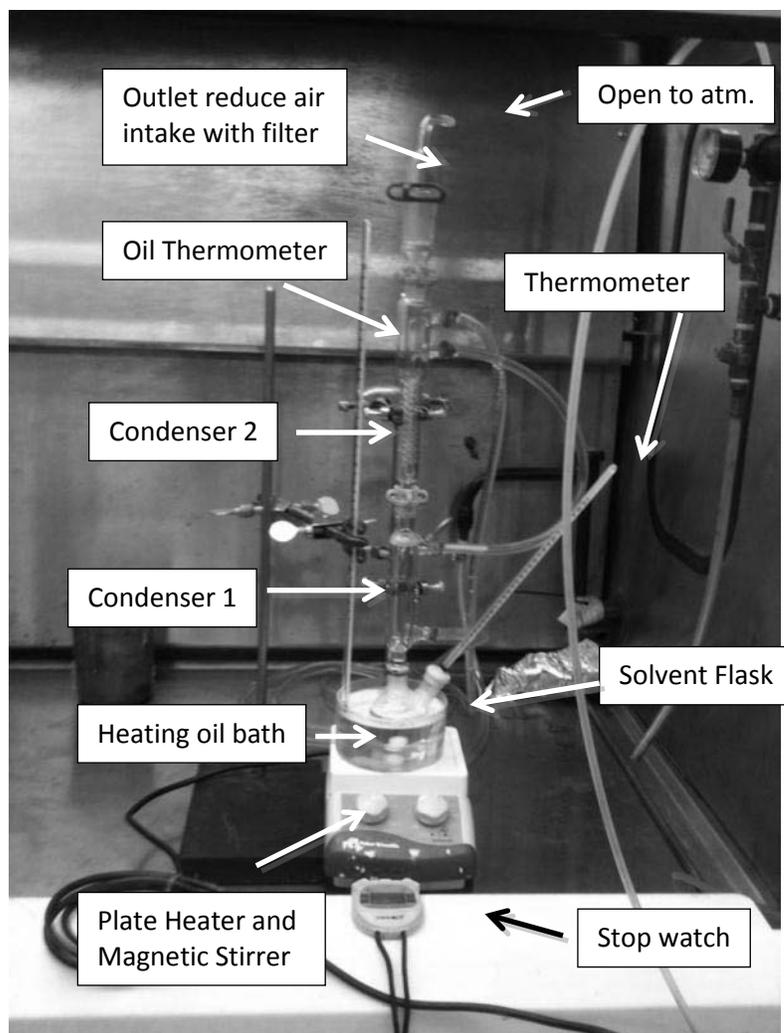


Photo 1 Thermal degradation study set-up, full reflux distillation

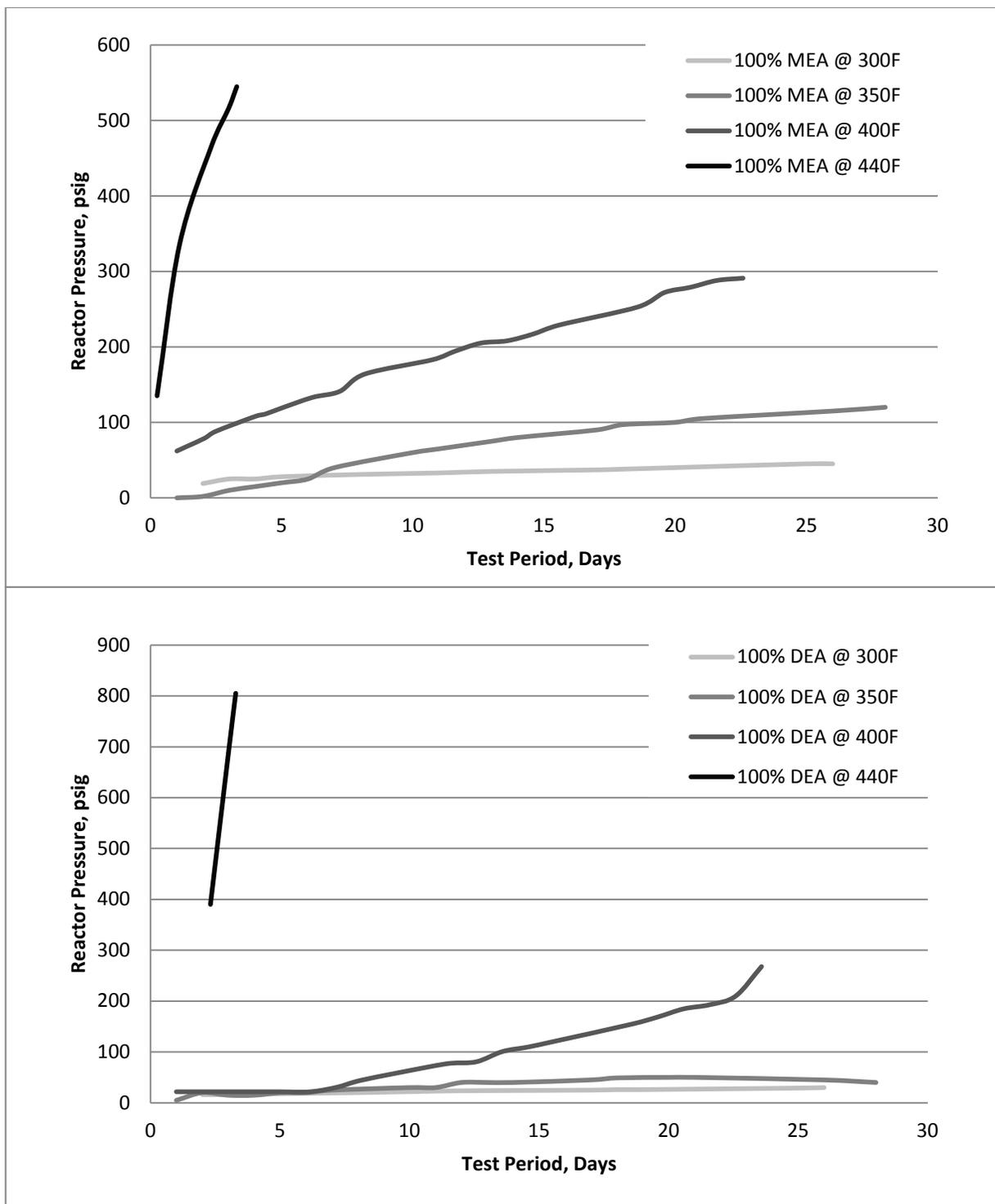


Figure 36 Dow thermal stability tests for MEA and DEA (Dow 1962)

(Used with permission from Dow Chemical Company)

stirrer bar, heating oil in an open glass pan, a thermometer to measure the temperature of the heating oil, a 50 ml distillation flask with two necks in which the test solvent must be put, a second thermometer to measure the temperature of the test solvent, two condensers in series to cool and condense evaporated water and solvent and return them back to the distillation flask, an adapter to facilitate the system operation at atmosphere but at the same time reduce the air flow to the set-up to minimize the possibility of oxidative degradation due to exposure to air (O₂), and, finally, a stop watch. Due to the configuration of the set-up, it was found that the temperature in the distillation flask varied $\pm 1-2^{\circ}\text{C}$ in some cases.

8.2.1 Pure solvent thermal degradation

Pure MEA solvent was tested in the set-up shown in Photo 1. From observation, the solvent is a clear, viscous liquid. The solvent was boiled to reach its normal boiling point in atmospheric pressure to verify whether the amines are thermally stable at or before reaching their normal boiling point (Kohl & Nielsen, 1997). For instance, MEA has been reported to thermally degrade when temperature exceeds 147°C, which is far from its boiling point of 171°C (Dow 1962; Kohl & Nielsen, 1997). Once MEA reached boiling point temperature, it will be left to boil for three hours.

Figure 36 shows the thermal stability tests for MEA and DEA carried out by Dow in a special reactor in which the pressure of the reactor was measured with time and temperature. As can be seen, Dow claimed the MEA and DEA solvents are stable up to 300°F (147°C) and 350°F (176°C), respectively (Dow, 1962, 249). The thermal stability curves of MEA or DEA show that they could be stable for short periods of exposure to

high temperature and then increased a little bit in pressure and stable for the rest of the test period. Dow (1962) also mentioned that diluting the amine solvent with water would enhance thermal stability of amine and reduce its thermal sensitivity. Therefore, a maximum temperature of 147°C was used as a limit for the thermal distillation of single and mixed amine solvent. Table 25 gives the GC-MS analysis of degraded MEA solvent. As can be seen, the pure MEA solvent started degrade at its boiling point.

8.2.2 5M MEA solvent thermal degradation

Clean MEA solvent with a concentration of 5M was prepared in the laboratory for the thermal degradation test. MEA solvent has been reported to start thermal degradation at a temperature of 147°C; therefore, it is a design practise for a CO₂ capture plant with MEA to prevent the temperature of MEA solvent from reaching 147°C at any point. The test was carried out for 8 to 10 hours for each experiment, and temperatures of heating oil were maintained slightly higher than the boiling point of the solvent to achieve the desired temperature. The 5M MEA solvent loss results as determined from GC-MS are shown in Table 26. Also, the table gives the change of solvent concentration as determined by titration with HCl using the methyl orange indicator. As can be seen, the solvent change was first observed as a change in the solvent color, and then and the total solvent loss was 0.8% at 147°C from GC-MS. Refractive index was measured for 5M MEA solvent at 110°C, 120°C, 130°C, 140°C, and 147°C. The results obtained are illustrated in Figure 37, which shows that the solvent was being gradually thermally degraded. However, the solvent concentrations did not show significant changes for tests from 110 to 140°C, so these are not shown.

Table 25 Analysis of degraded pure solvents by GC-MS

| | Pure MEA | Comments |
|---|-------------------------|--|
| Reported normal boiling point, °C | 171.0 | (Kohl and Nielsen 1997) |
| Measured testing temperature, °C | 170.0 | Boiling temperature under test condition |
| Color solvent change (before → after) | Clear → light yellowish | |
| Solvent loss | 7.11 % | Change in Peak Area |

Table 26 Thermal degradation of 5M MEA at different temperature

| | Reference | 147°C |
|--|------------------|-----------------|
| Color solvent appearance | Clear liquid | Light yellowish |
| Solvent concentration, M | 5.00 | 4.96 |
| Solvent concentration change, % | 0 | 0.80 |
| MEA Solvent loss, M | 0 | 0.04 |
| Refractive Index | 1.3717 | 1.3725 |

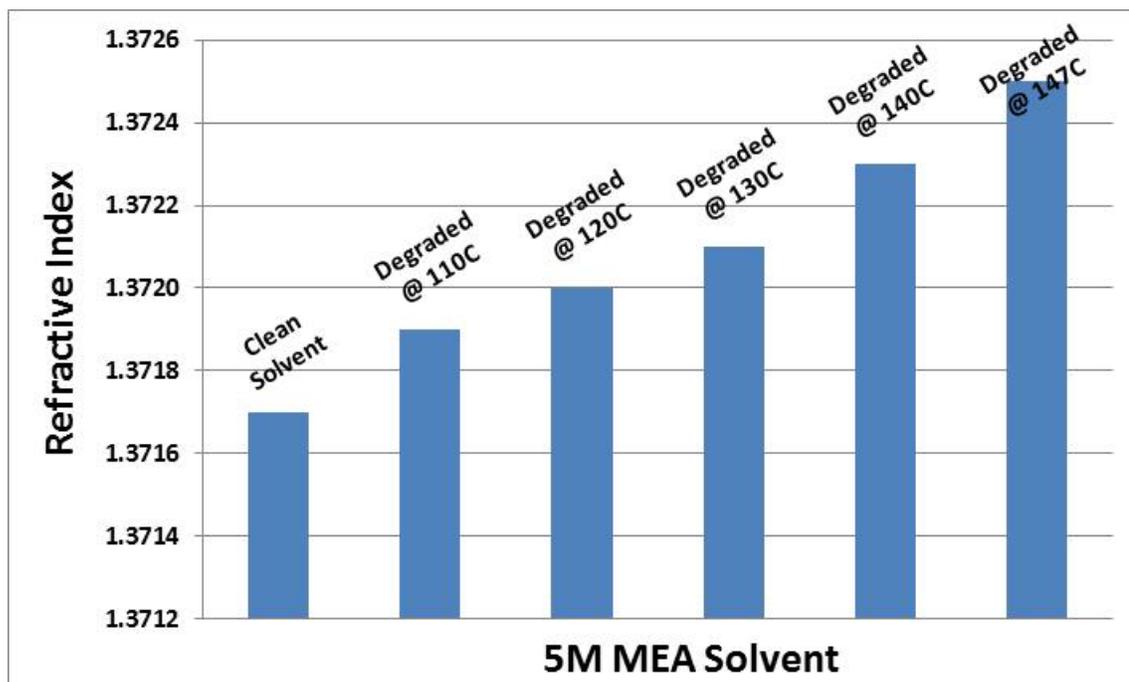


Figure 37 Refractive index for thermally degraded 5M MEA

8.3 Recovery of 5M MEA solvent experiments

Thermal reclamation was tested in atmospheric and vacuum distillation set-ups. In the first campaign of experiments, a variety of MEA solvents was tested, including clean and degraded solvents. The degradation products could be general more than those specifically formed from MEA degradation. The second series of experiments were the same as the preliminary series except that the degradation products are relevant to MEA solvent degradation. In this section, the results of thermal distillation of MEA are given with detailed analysis of the recovery of each solvent.

8.3.1 First series of experiments for MEA solvent purification

The first series covered attempts to recovering clean MEA solvent and search for optimum operating conditions to maximize solvent recovery. Degraded solvent purification was later applied at the optimum operating conditions for one case. Figure 38 provides the list of tests carried out in Series I along with the degradation products used. As explained in Chapter 4, MEA solvent reclamation is commonly used in industry at conditions close to or slightly higher than atmospheric pressure. The claim that the reclaiming of MEA is simple might not be completely accurate, as it might have unacceptable reclamation consumption and costs. By using a simple calculation, it can be easily understood that the MEA vapour pressure at atmospheric pressure is quite low, which means low solvent recovery, and to make MEA reclamation work, intensive reclamation cycles of dilution with water and/or steam directly injected into the reclamation kettle are required to enhance solvent recovery. Also, adding water and then evaporating it using heating steam can be considered a loss of energy. Another issue is

that the solvent temperature is restricted by the maximum allowed temperature of 147°C. MEA will be thermally degraded if the temperature of the reclaimer exceeds 147°C, which is below MEA boiling point of 171°C. Therefore, optimum reclamation with minimum thermal degradation should be achieved before the decomposition temperature. Photo 2 shows the distillation set-up used for series I tests.

8.3.1.1 MEA Recovery at 760 mmHg (MEA-1-760mmHg)

The first test for recovery of MEA was at atmospheric pressure, where the fresh solvent was discharged into the distillation flask and allowed to evaporate under constant heat flux and monitoring of the bottom and top temperature. The vapor-liquid relationship of the binary system of MEA and water is given in Figure 39. This graph is important to assess the progress of distillation of specific concentrations of MEA. As explained in Chapter 4, the equilibrium conditions for maximum recovery of solvent in the reclaimer can be studied with this graph. As can be seen from Figure 39, the maximum possible recovery of solvent is achieved when the solvent concentration in the vapour stream existing in the reclaimer is similar to the feed amine solvent (i.e., 15 w %). At this point, the temperature and solvent concentration of the reclaimer bottom is almost 70 w%. The recovery of pure amine is quite low for each reclamation cycle under this condition (i.e. 2%/cycle). To enhance recovery, water or steam dilutions to reduce the solvent vapour pressure are used. Figure 40 gives the demonstration of water dilution and the number of times this action is to be done, along with number of reclamation cycles. It is not easy to recover the solvent unless many dilution and evaporation cycles are applied (i.e. 85-95 cycles). Unquestionably, this represents excessive consumption of water and energy.

| | Test Code | | | | | | | |
|---|--------------------------------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| | | | | | | | | |
| | | MEA-1-760mmHg | MEA-2-660mmHg | MEA-3-550mmHg | MEA-4-460mmHg | MEA-5-360mmHg | MEA-6-260mmHg | MEA-7-260mmHg |
| | Degradation Level, wt% | 0 | 0 | 0 | 0 | 0 | 0 | 0.63 |
| | CO2 Loading, mol/mol | No |
| Degradation Products | Ammonium Hydroxide | | | | | | | |
| | 2-(Methylamino) Ethanol | | | | | | | |
| | Amino-2-propanol | | | | | | | |
| | 3-Picoline | | | | | | | |
| | Ethylamine | | | | | | | |
| | 1,3-Diaminopropane | | | | | | | |
| | Imidazole | | | | | | | X |
| | Bicine | | | | | | | X |
| | Acetamide | | | | | | | X |
| | N-Acetyethanolamine | | | | | | | X |
| | 1-(2-Hydroxyethyl)-2-Imidazolidinone | | | | | | | X |
| | Monomethylethanolamine | | | | | | | |
| Heat stable salts (HSS) Neutralized or Organic Acids Cause them | Formic Acid | | | | | | | |
| | Acetic Acid | | | | | | | |
| | Propionic Acid | | | | | | | |
| | Butyric Acid | | | | | | | |
| | Lactic Acid | | | | | | | |
| | Malonic Acid | | | | | | | |
| | Glycolic Acid | | | | | | | |
| | Oxalic Acid | | | | | | | |
| | Sodium Thiocyanate | | | | | | | |
| | Sodium Thiosulfate | | | | | | | |

Figure 38 Series I for MEA recovery tests

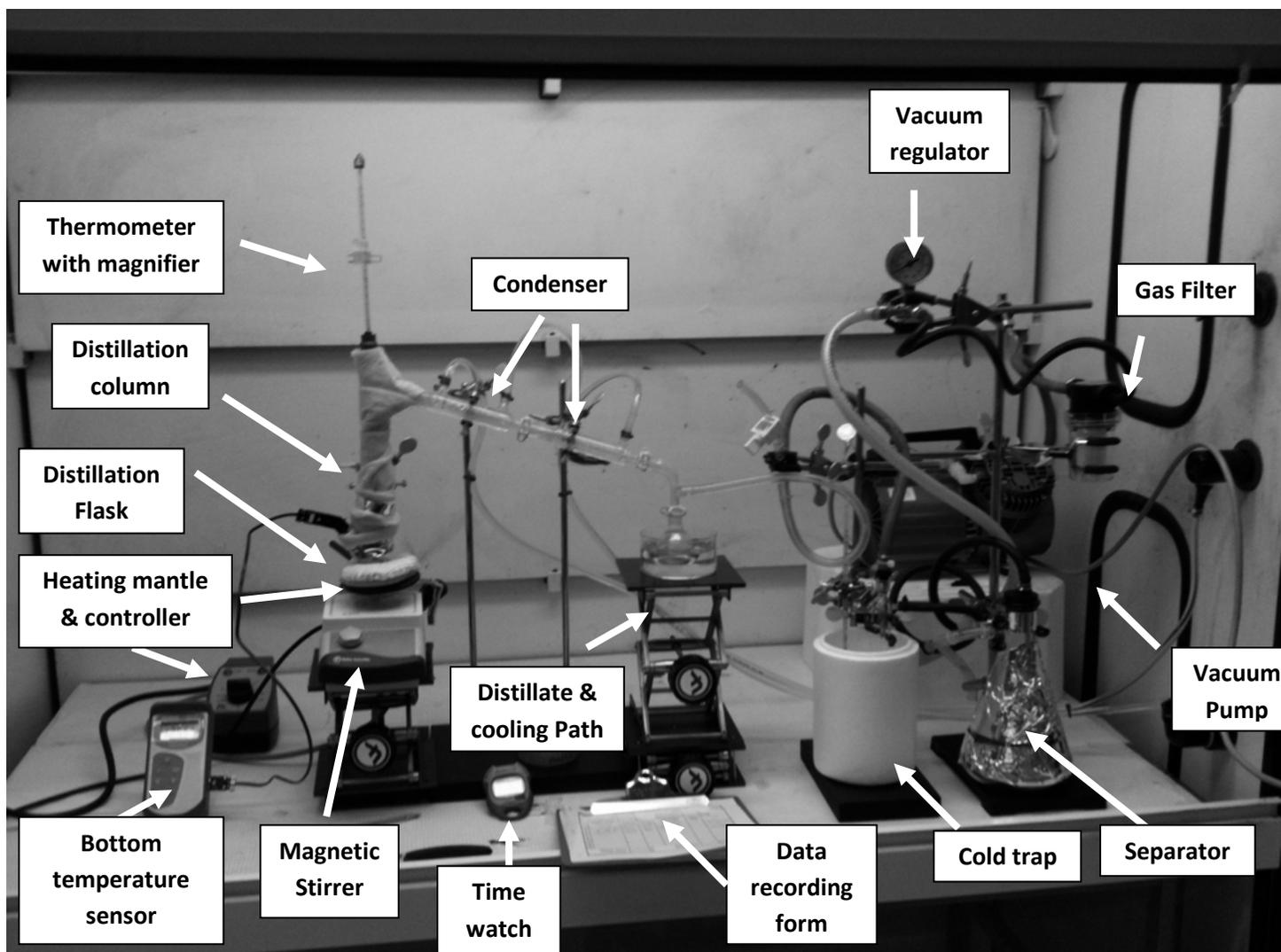


Photo 2 Distillation set-up used for Series I of MEA/MDEA purification

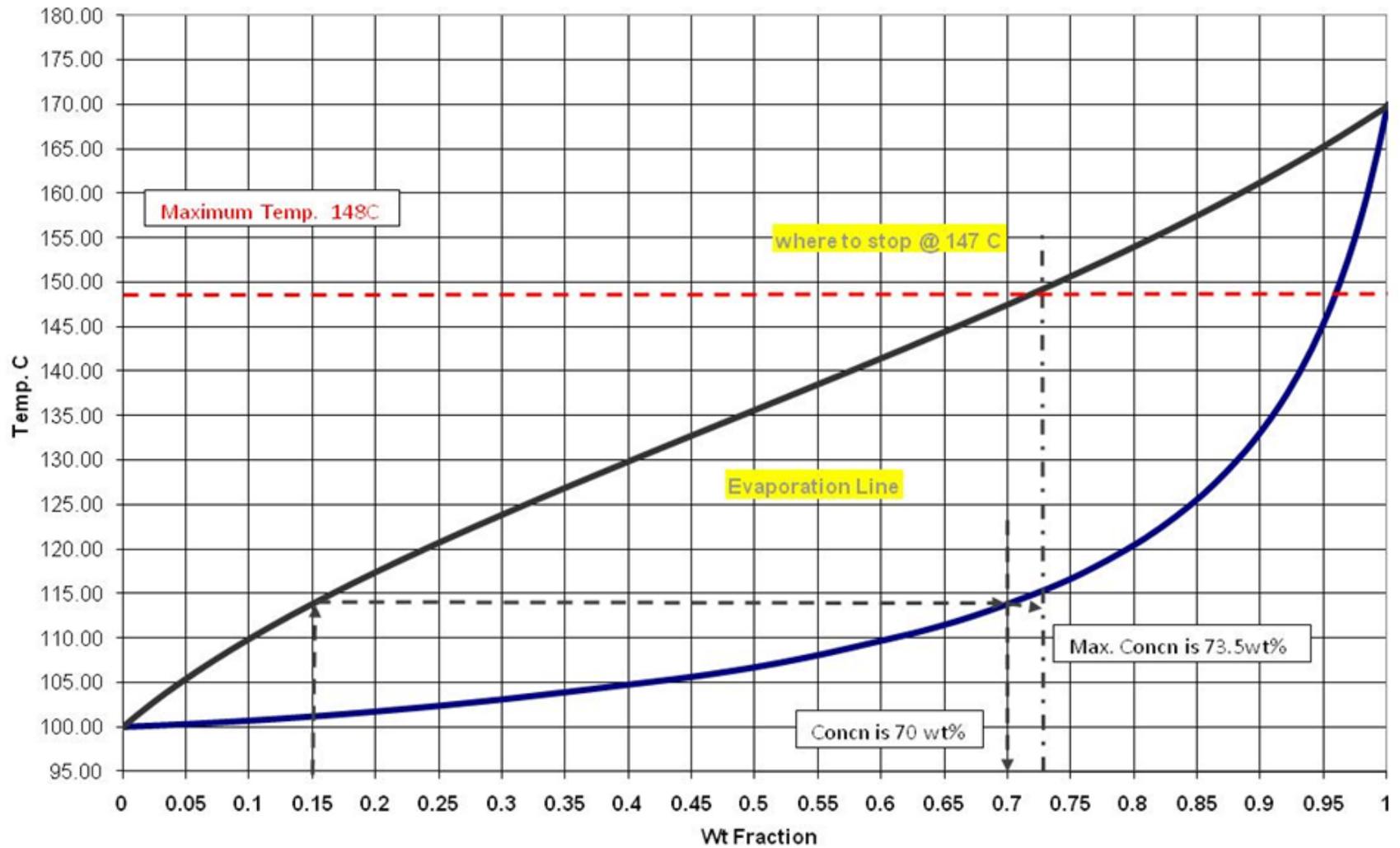


Figure 39 Vapour-liquid relationship for MEA-Water system (MEA-1-760 mmHg)

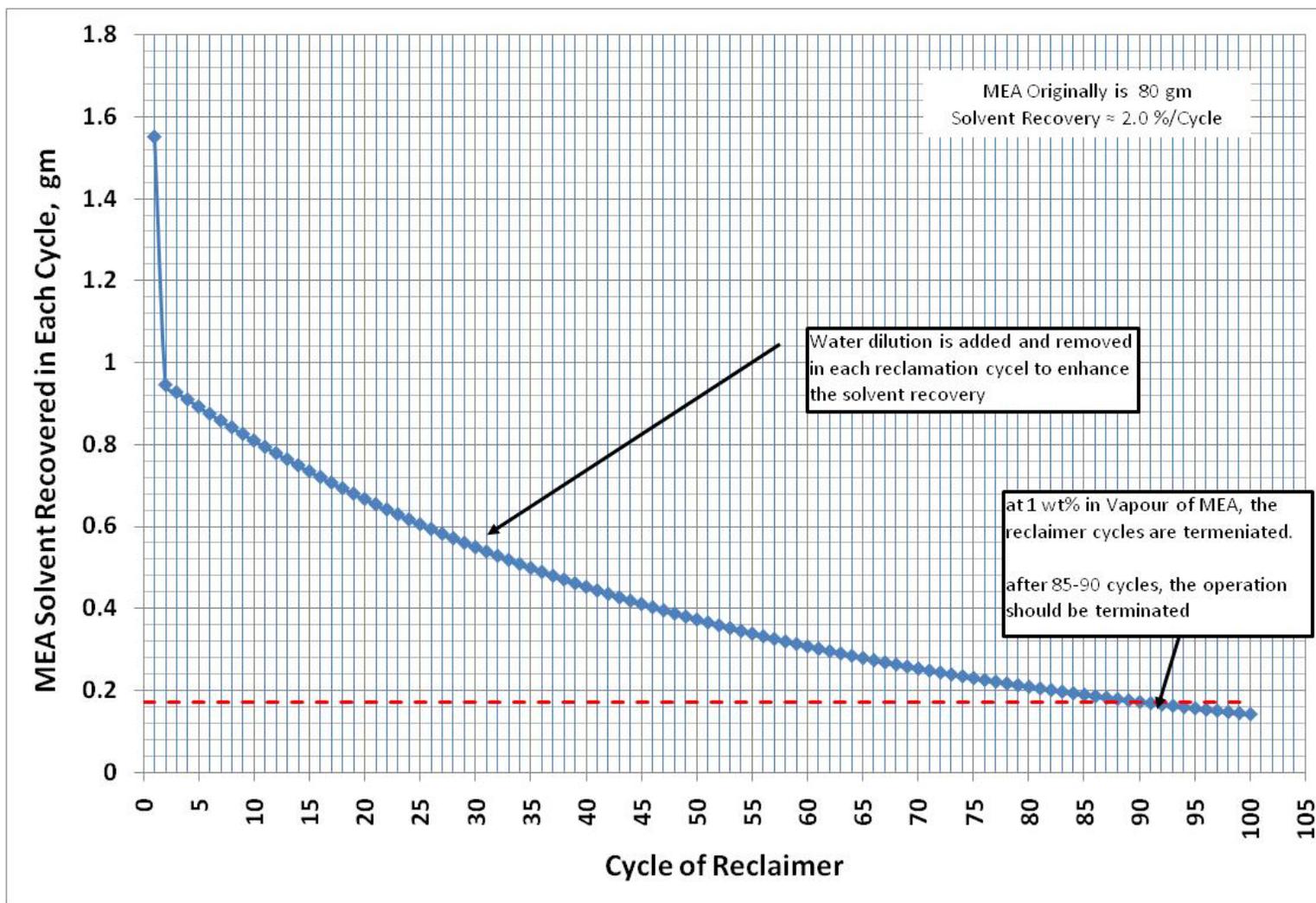


Figure 40 Enhanced recovery of MEA with water dilution vs. dilution and reclamation cycles (MEA-1-760 mmHg)

8.3.1.2 MEA Recovery at 660 mmHg (MEA-2-660mmHg)

The second test series was done at 660 mmHg to test enhancement of solvent recovery by distillation at a pressure lower than atmospheric pressure. The recovery was slightly higher than the results obtained in the 760 mmHg case. Figure 41 illustrates the vapour-liquid equilibrium curve for the MEA-H₂O system. The reduction of operating pressure allows slight enhancement of solvent recovery. The solvent concentration is slightly increased from 70 wt% to 78 wt% in the distillate bottom.

Each reclamation cycle for evaporation of MEA solvent is quite low (~9.3% per cycle) before the solvent in the distillation flask approaches the maximum allowable temperature (147°C). To enhance solvent recovery, water dilution or steam injection could be used. Figure 42 shows the effects of water dilution for enhanced solvent recovery. The use of slight vacuum has a great impact on reclamation cycles, which were reduced from around 85 cycles to between 37-38 cycles.

8.3.1.3 MEA Recovery at 550 mmHg (MEA-3-550mmHg)

The third test campaign was conducted at a pressure of 550 mmHg, and as a result, there was an improvement in the solvent recovery. The degree of solvent concentration in the bottom was about 83%; however, the residue collected was less than in the previous tests. Another notable result was the dilution of water when it was used to enhance solvent recovery: 18.4% per each reclamation cycle. Figure 43 gives the water dilution impact on the solvent recovery. The reclamation cycles could be reduced from 35 to 20 cycles.

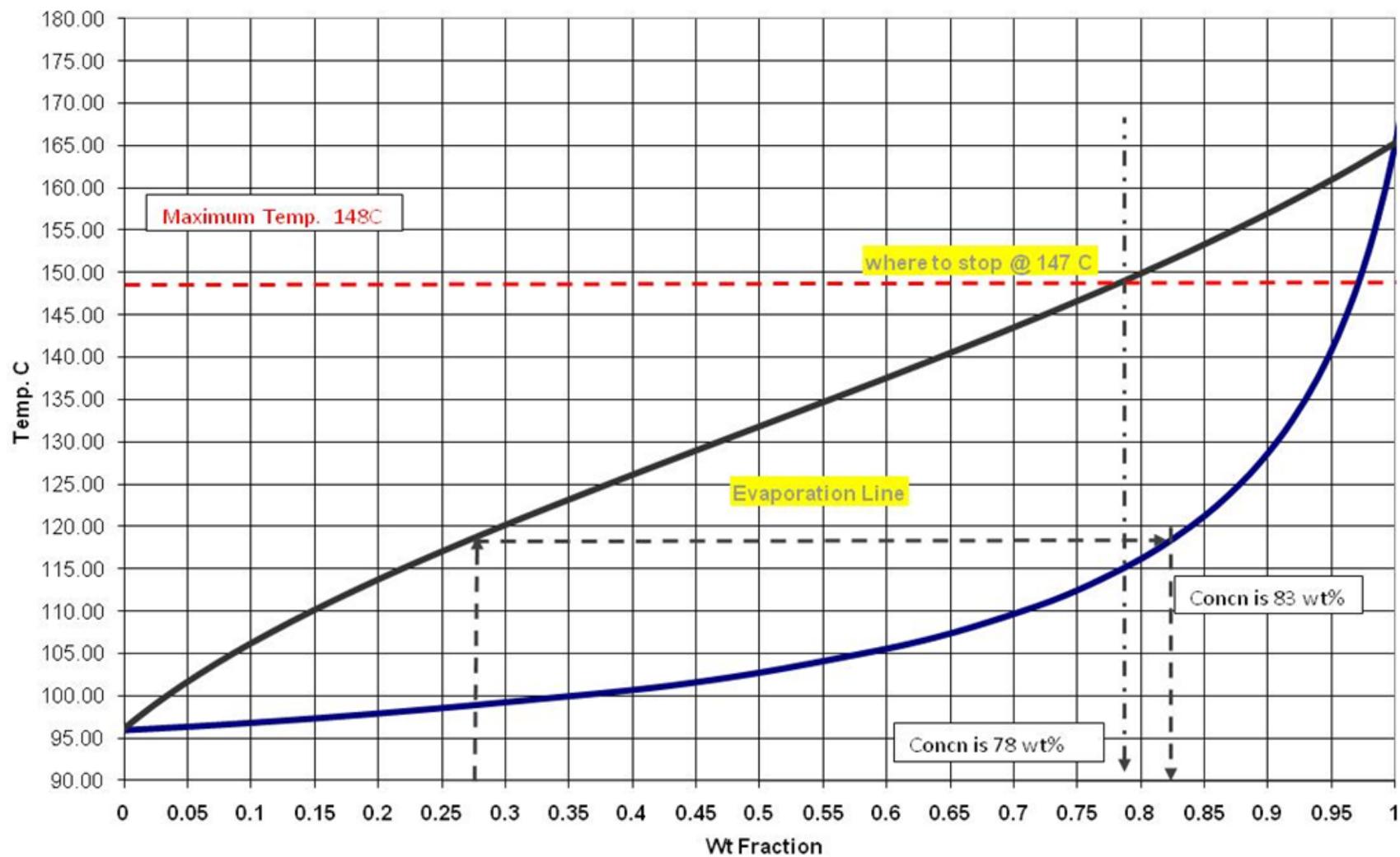


Figure 41 Vapour-liquid relationship for MEA-Water system (MEA-2-660 mmHg)

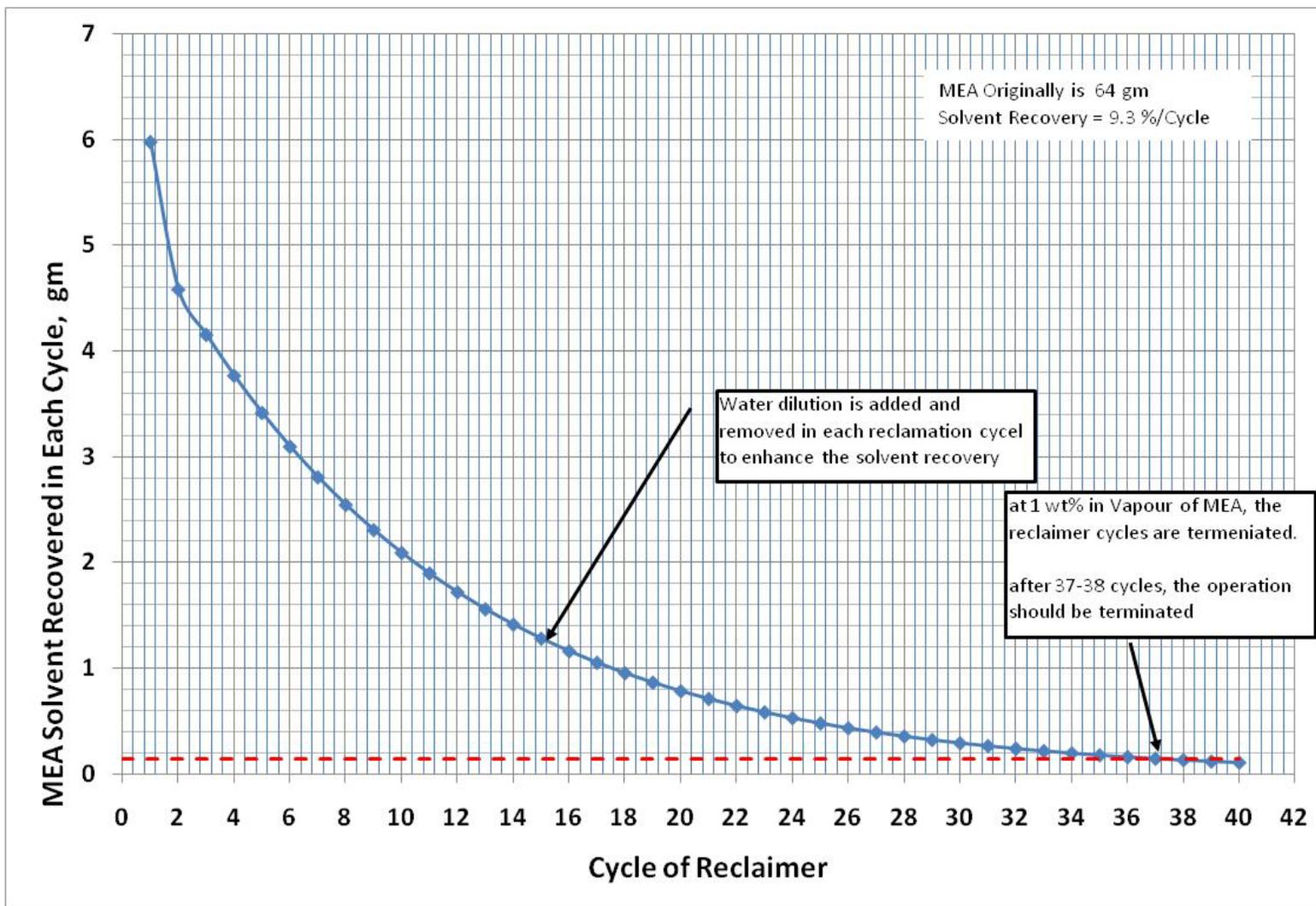


Figure 42 Enhanced recovery of MEA with water dilution vs. dilution and reclamation cycle (MEA-2-660 mmHg)

8.3.1.4 MEA Recovery at 460 mmHg (MEA-4-460mmHg)

The fourth campaign involved running the distillation test at 460 mmHg for solvent concentration of 30wt%. This showed further improvements in solvent recovery. The solvent recovery for one reclamation cycle was 18.66% per cycle. Figure 44 illustrates the water dilution impact on solvent recovery. The reclamation cycles could be 21-22 cycles to recover the solvent.

8.3.1.5 MEA Recovery at 360 mmHg (MEA-5-360mmHg)

The fifth set of tests was at a much lower pressure, 360 mmHg. This led to improved solvent recovery and reduced its loss in the residue. One way to explain this improvement is illustrated in Figure 45 which shows the vapour-liquid equilibrium for the MEA-H₂O system. However, during the test, the total solvent recovery overall was 76%, which is still not sufficient. Water addition can be used to enhance solvent recovery by the effect of dilution, but pure MEA recovery for each cycle was still found to be low (i.e., 23%/cycle). Nevertheless, addition of water reduces the reclamation cycles to 17.

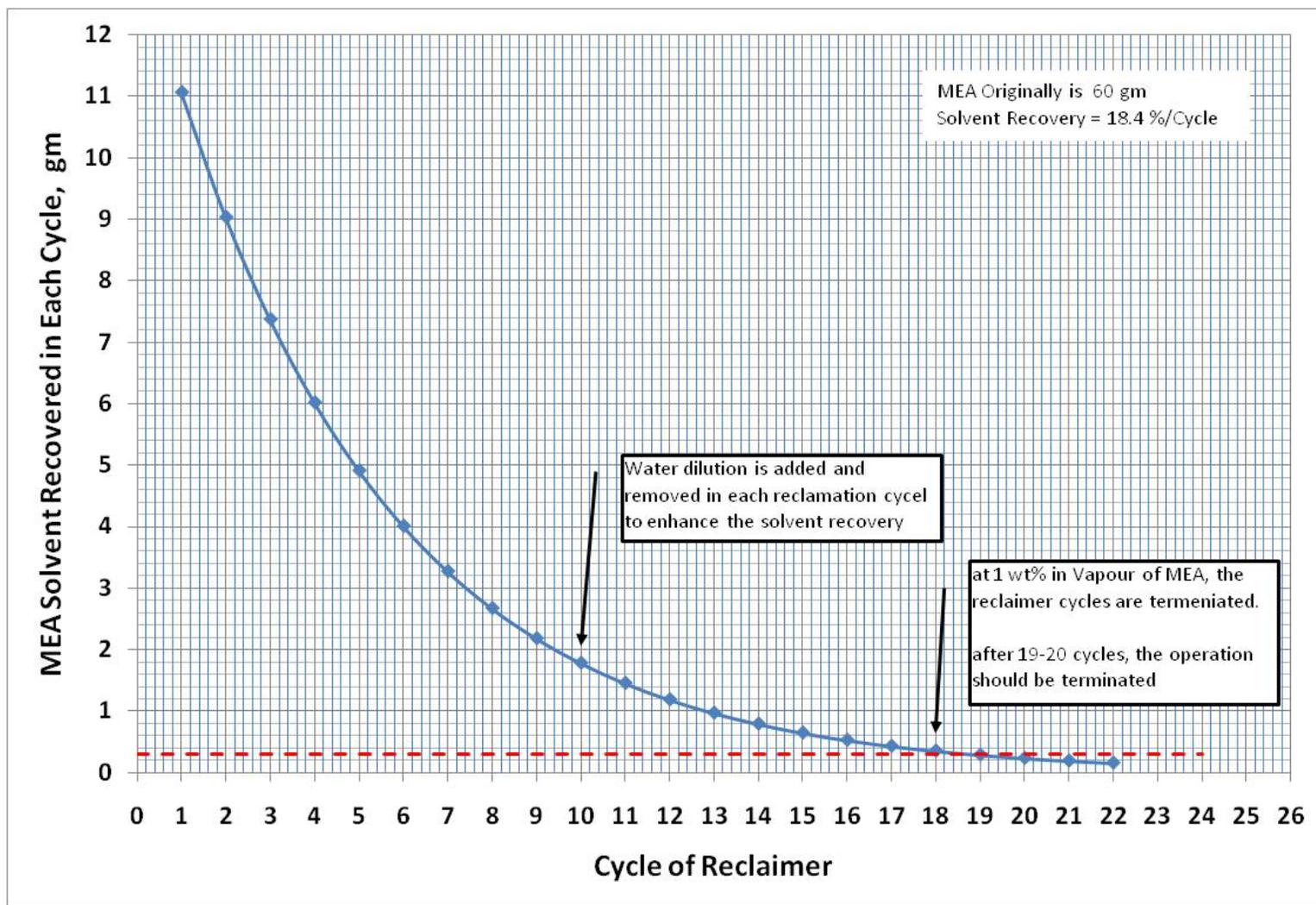


Figure 43 Enhanced recovery of MEA with water dilution vs. dilution and reclamation cycle (MEA-3-550 mmHg)

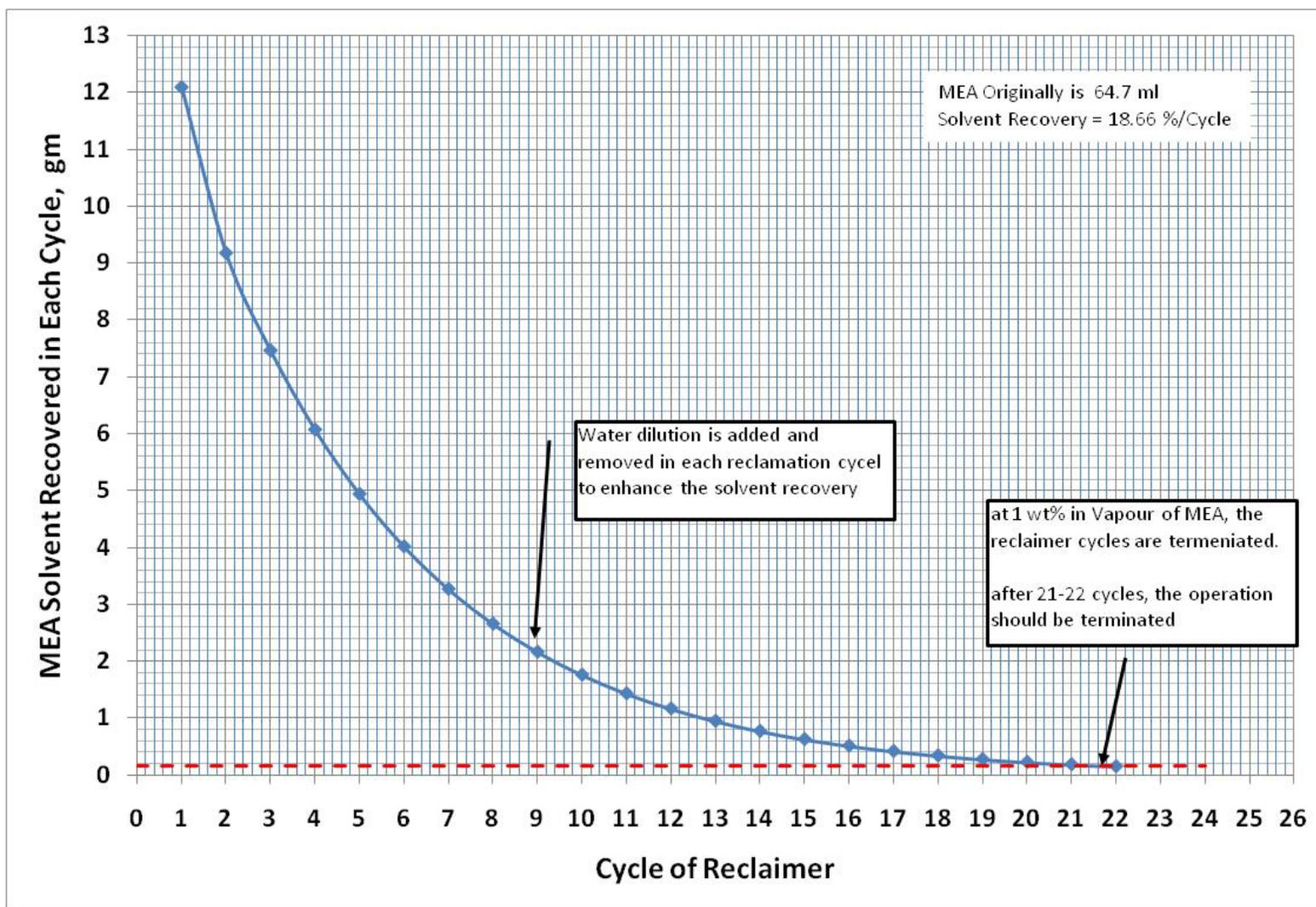


Figure 44 Enhanced recovery of MEA with water dilution vs. dilution and reclamation cycle (MEA-4-460 mmHg)

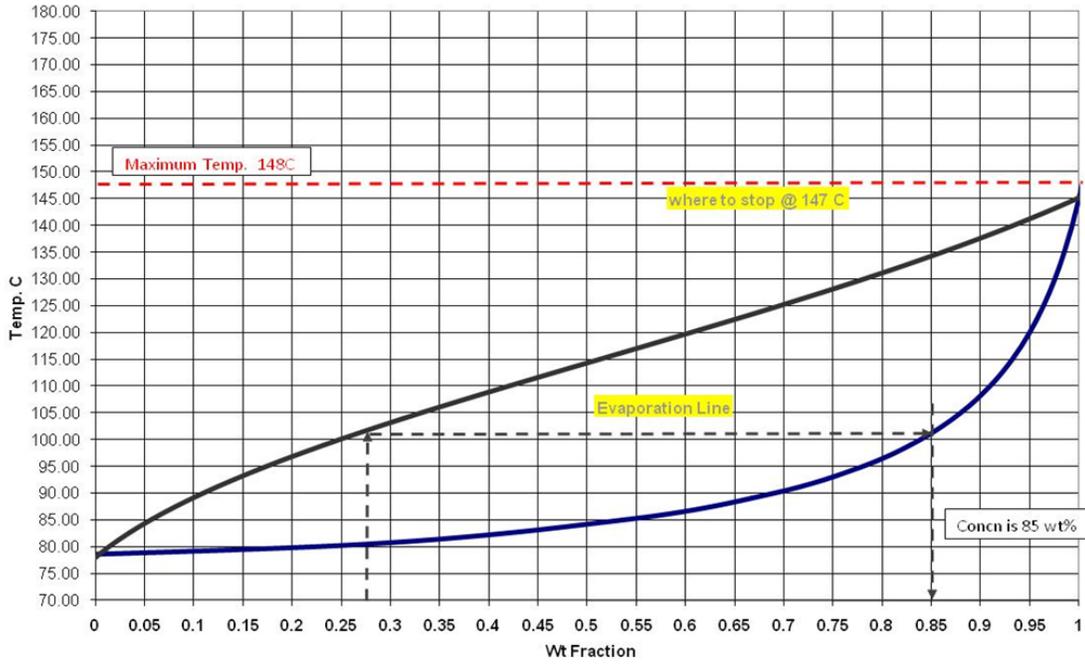


Figure 45 Vapour-liquid relationship for MEA-Water system (MEA-5-360 mmHg)

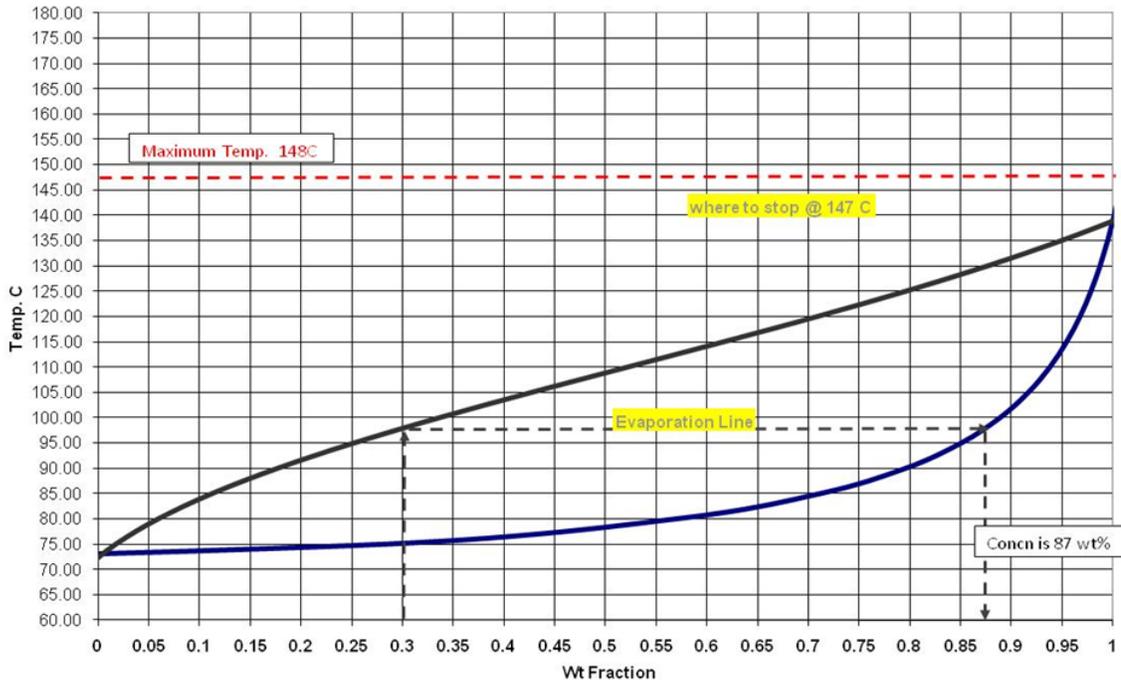


Figure 46 Vapour-liquid relationship for MEA-Water system (MEA-6-260 mmHg)

8.3.1.6 MEA Recovery at 260 mmHg (MEA-6-260mmHg)

The solvent recovery was further improved that reducing the pressure allowed the regions of solvent recovery to increase without exceeding 147°C, Figure 46. This means that all the solvent that can possibly be recovered can be recovered with the lowest energy consumption and fewest water dilutions cycles. The test was terminated once the temperature in the distillation flask approached the maximum allowable temperature (i.e., 147°C) or the liquid level became very low to the point that the distillation process could not proceed any further. The total solvent recovery for the process was 97.8%, while the pure MEA recovery was 94%.

To demonstrate the enhancement in solvent recovery using water dilution, the dilution and reclamation cycles were reduced from 17 cycles in the previous test at 360 mmHg to 4 to 7 cycles, as shown in Figure 47. The pure MEA recovery was quite high for each cycle (94% compared to 76% in the test of 360 mmHg). This means considerable direct savings of water and energy consumption of 95% compared to operation at atmospheric pressure.

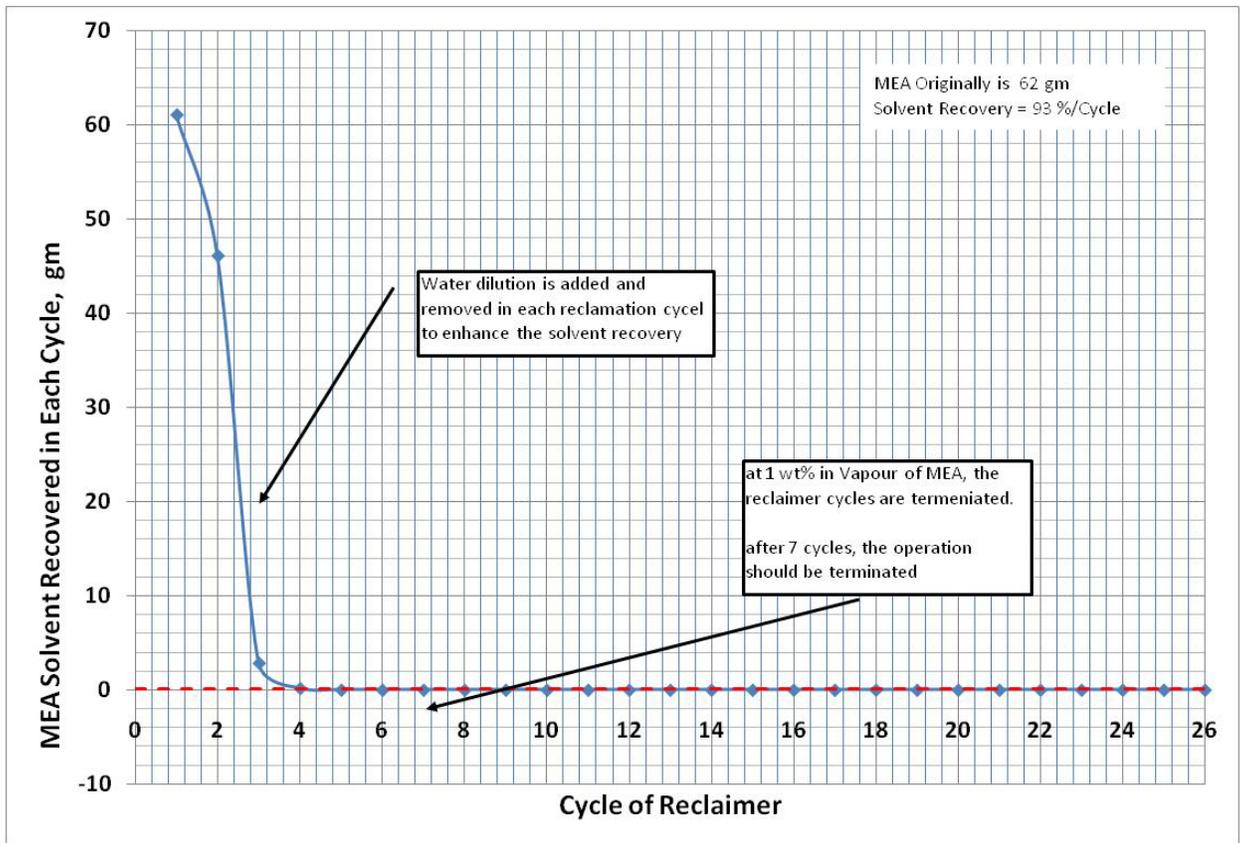


Figure 47 Enhanced recovery of MEA with water dilution vs. dilution and reclamation cycle (MEA-6-260 mmHg)

8.3.1.7 Degraded solvent recovery at 260 mmHg (MEA-7-260mmHg)

A degraded solvent of 5M MEA with five degradation products (each 1,000 ppm, except acetamide 2000 ppm) was prepared and evaporated at the optimum distillation conditions obtained at 260 mmHg. The total solvent recovery was high, at 97.5%, and the pure MEA solvent recovery was 97%. Figure 48 shows the GC chromatographs for the degraded solvent before the test, distillate collected, and the residue. As can be seen, some degradation products, mainly amides (acetamide and N- (2-hydroxyethyl) acetamide) were able to evaporate and contaminate the distillate. However, the others remained in the residue. Table 27 provides the summary for recovery of degraded MEA.

8.3.2 Summary of first series of MEA purification tests

Table 28 gives a summary of tests carried out for MEA recovery. The objective was to maximize solvent recovery with short and quick reclamation cycles. This has been achieved by reducing the operating pressure to what can be considered as optimum conditions to recover MEA. Seven tests are given in Table 28, and some of the tests not reported are those that were repeated to confirm the results. The total solvent recovery increased from 65% at atmospheric pressure (mainly water) to 97% (mainly both water and amine). Figure 49 shows that the solvent recovery maximized as the operating pressure was reduced, and optimum solvent recovery was at 260 mmHg.

Table 27 Summary for recovery of degraded MEA (MEA-7-260mmHg)

| | Initial Fill | | Distillate | | |
|--------------------------------------|--------------|------------|------------|-------------|---------|
| | Concn | Weight | Concn | Weight | |
| | ppm | gm | ppm | gm | |
| Imidazole | 1,053.95 | 0.038186 | 0.00 | 0 | |
| Bicine | 1,051.91 | 0.038112 | 0.00 | 0 | |
| Acetamide | 2,118.12 | 0.076358 | 178.47 | 0.0063 | |
| N-acetyethanolamine | 1,044.81 | 0.037666 | 0.00 | 0 | |
| 1-(2-hydroxyethyl)-2-imidazolidinone | 1,045.40 | 0.037687 | 0.00 | 0 | |
| | | | | | |
| | Initial Fill | Distillate | Residue | | |
| Volume, ml | 35.00 | 34.20 | 0.80 | Recovery, % | 97.71 |
| Solvent wt% | 29.71 | 26.68 | 45.14 | Recovery, % | 87.7549 |
| Water, wt% | 69.65 | 73.30 | 34.94 | Recovery, % | 102.83 |
| Others, wt% | 0.63 | 0.02 | 19.92 | | |

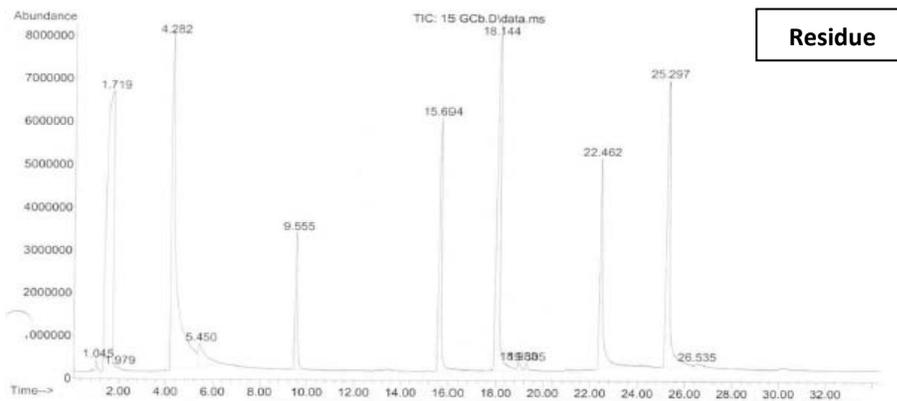
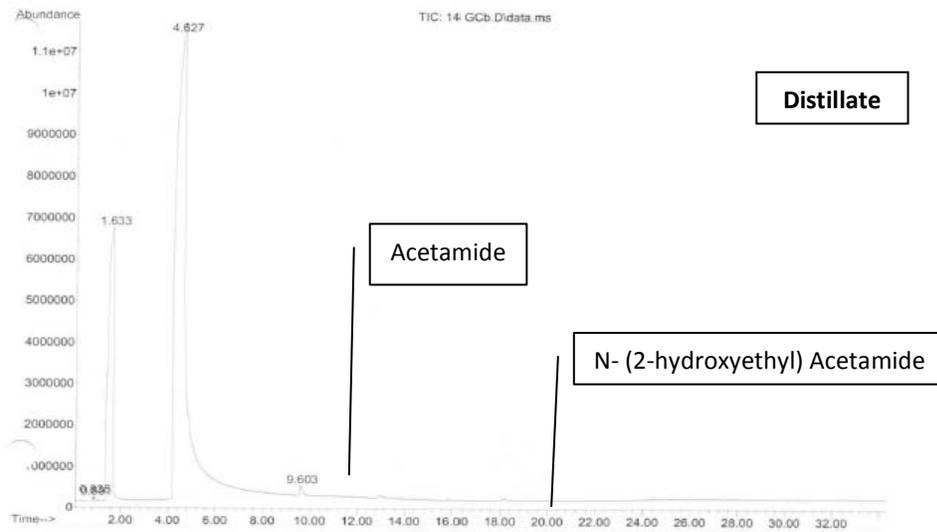
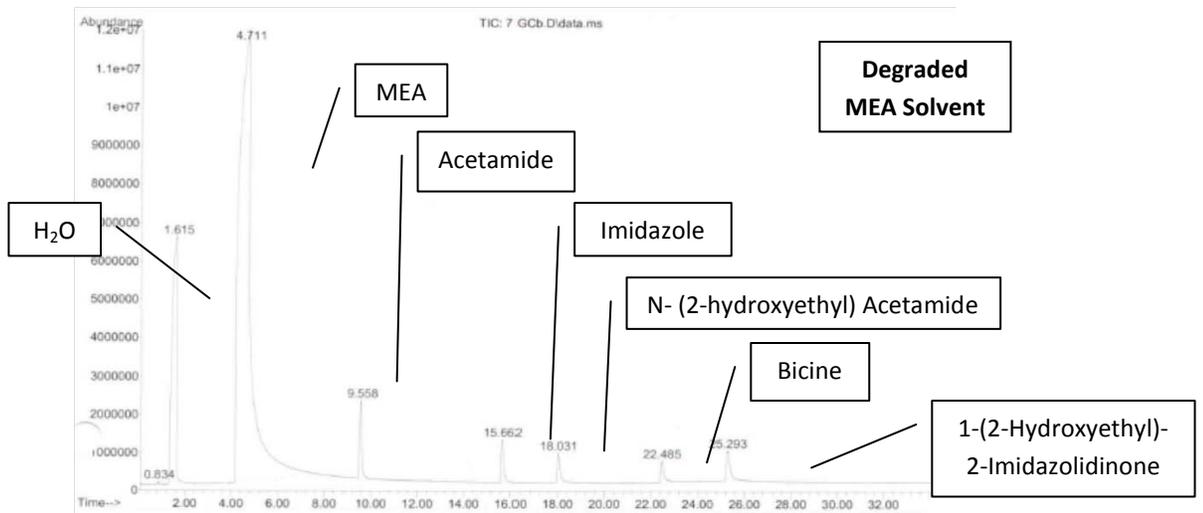


Figure 48 GC chromatograph of MEA, distillate, and residue (MEA-7-260mmHg)

Table 28 Series I summary of MEA reclamation

| Test | Pressure | MEA | Distillate | Residue | Loss | Top temperature @ test end | Bottom temperature @ test end | Solvent content in residue | Amine recovery | |
|------|----------------------------------|-----|------------|---------|--------|----------------------------|-------------------------------|----------------------------|----------------|-----|
| | mmHg | M | % | % | % | °C | °C | % | % | |
| 1 | Test MEA-1 | 760 | 2.5 | 64.83% | 35.17% | N/A | 110.5 | 151 | 92.07% | N/A |
| 2 | Test MEA-2 | 660 | 5 | 72.55% | 27.45% | N/A | N/A | 148 | 94.38% | 10% |
| 3 | Test MEA-3 | 550 | 5 | 74.07% | 23.86% | 2.07% | 148 | 157 | 89.42% | 24% |
| 4 | Test MEA-4 | 460 | 5 | 75.51% | 23.79% | 0.70% | 135 | 148 | 93.18% | 22% |
| 5 | Test MEA-5 | 360 | 5 | 76.17% | 22.50% | 1.33% | 138 | 145 | 95.08% | 27% |
| 6 | Test MEA-6 | 260 | 5 | 97.86% | 1.91% | 0.23% | 135 | 141-145 | 92.05% | 94% |
| 7 | Test MEA-7 (Degraded Solvent) | 260 | 5 | 97.57% | 2.29% | 0.14% | 138 | N/A | 44.40% | 97% |

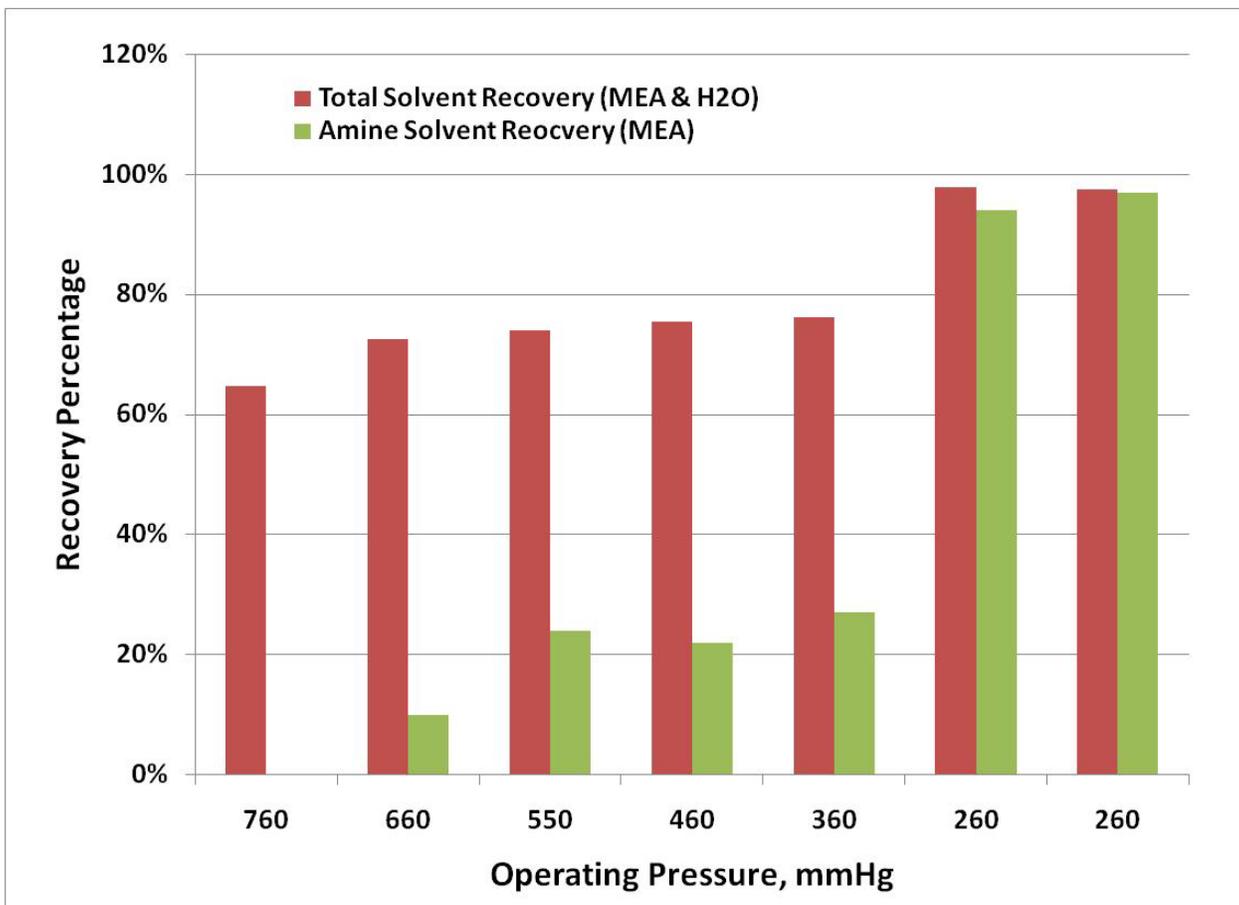


Figure 49 Summary of total solvent and pure MEA recoveries for Series I

8.3.3 Second series of experiments for MEA solvent purification

8.3.3.1 Introduction

CO₂ loaded 5 mole/L MEA solvents with and without degradation products and/or HSSs were thermally recovered under vacuum to evaluate solvent recovery under the conditions in test Series II (described below). The clean or degraded solvent was prepared in the laboratory as shown in the flow chart in Figure 50 by adding the degradation products at desired concentrations and/or by increasing loading of the solvent with CO₂. The samples were prepared prior the test one day or two and allowed to mix with continuous magnetic stirring. The samples collected were analysed with GC and titration to determine the solvent concentration, CO₂ loading, and heat stable salt (HSS) content. A total of 8 tests was conducted for Series II, and the degradation products and HSS added are given in Figure 51. A test code was assigned for each test to help track samples and results. For example, MEA-3-0.50%-210 mmHg means the test was for recovery of MEA solvent, the test number was 3, the degradation level was 0.5 wt%, and it was under a vacuum pressure of 190 mmHg. Each test and its results will be briefly discussed separately, and then overall results will be given at the end of this section.

8.3.3.2 Thermal reclamation of MEA-1-0.00%-190mmHg

Thermal reclamation of MEA solvent with 0.00 wt% degradation products was carried out at 190 mmHg vacuum. The clean solvent was prepared and then loaded with CO₂ through sparging the CO₂ into the solvent for some time. Table 29 gives the analysis summary for the feed solvent charged to the distillation flask, the collected distillate, and the residue. As can be seen, the clean solvent has a low content of non-volatile and

unidentified products, which was determined to be 0.06 wt.% (Figure 25). The distillate recovered was 96.60% of the charged amine, and loading was almost 50% the feed charge solvent; the rest of CO₂ was lost. The residue was mainly MEA, and it could not be recovered due to the deficiencies inherent in the batch distillation set-up. More details on the distillation results are given in Figure 52. Photo 1 in Chapter 9 shows the distillation set-up used for experiments of series II.



Figure 50 Procedure for test solvent preparation

| | Test Code | MEA-1-0.00%-190mmHg & MEA-2-0.00%-90mmHg MEA-3-0.50%-210mmHg MEA-4-1.50%-180mmHg MEA-5-2.50%-180mmHg MEA-6-3.50%-180mmHg MEA-7-4.00%-190mmHg MEA-8-5.00%-180mmHg | | | | | | |
|---|--------------------------------------|---|-----|-----|-----|-----|-----|-----|
| | | Degradation Level, wt% | 0 | 0.5 | 1.5 | 2.5 | 3.5 | 4 |
| | CO ₂ Loading, mol/mol | Yes | Yes | Yes | Yes | Yes | Yes | Yes |
| Degradation Products | Ammonium Hydroxide | | X | X | X | X | X | X |
| | 2-(Methylamino) Ethanol | | | | | | | |
| | Amino-2-propanol | | | | | | | |
| | 3-Picoline | | | | | | | |
| | Ethylamine | | X | X | X | X | X | X |
| | 1,3-Diaminopropane | | | | | | | |
| | Imidazole | | X | X | X | X | X | X |
| | Bicine | | X | X | X | X | X | X |
| | Acetamide | | X | X | X | X | X | X |
| | N-Acetyethanolamine | | X | X | X | X | X | X |
| | 1-(2-Hydroxyethyl)-2-Imidazolidinone | | X | X | X | X | X | X |
| | Monomethylethanolamine | | | | | | | |
| Heat stable salts (HSS) Neutralized or Organic Acids Cause them | Formic Acid | | X | X | X | X | X | X |
| | Acetic Acid | | X | X | X | X | X | X |
| | Propionic Acid | | X | X | X | X | X | X |
| | Butyric Acid | | X | X | X | X | X | X |
| | Lactic Acid | | X | X | X | X | X | X |
| | Malonic Acid | | X | X | X | X | X | X |
| | Glycolic Acid | | X | X | X | X | X | X |
| | Oxalic Acid | | X | X | X | X | X | X |
| | Sodium Thiocyanate | | X | | | | | |
| | Sodium Thiosulfate | | X | | | | | |

Figure 51 Series II for MEA recovery tests

Table 29 Analysis summary of MEA-1-0.00%-190mmHg samples

| | Loaded lean amine | Distillate amine | Residue |
|--|------------------------------|-----------------------------|----------------|
| Solvent Concentration, wt% | 30.24* | 28.45 | 94.85 |
| CO₂ Loading, mol/mol | 0.097 | 0.040 | - |
| HSS, wt% as MEA | 0.00 | - | - |
| Solvent Recovery, % | - | 96.60% | - |
| Total Non-volatile Content, wt% | 0.06 | - | 5.15 |

*Solvent concentration before adding the degradation products and CO₂

| Reclaimer Research: Small Set-Up Distillation Form | | | | | | |
|--|---|--------|-----|--|----------|------|
| 1 | Distillation Test Code | MEA-1 | | Date | 1.4.2011 | |
| 2 | Solvent type | MEA | | Time | | |
| 3 | Solvent Conc | 30.24 | wt% | Mode Operation: | Vacuum | |
| 4 | Degradation Level | 0.00 | wt% | Room Temp. = | 21.00 | C |
| 5 | Heat Set # = | 9.00 | | Room pressure = | | kpa |
| 6 | Cooling temp. = | 10.00 | C | Set-up pressure = | | mmHg |
| 7 | Trap one temp. = | 1.80 | C | Set-up pressure = | 190.00 | mmHg |
| 8 | Trap two temp. = | 3.90 | C | Cooling bath | 1.40 | |
| 9 | Distillation Flask | | | | | |
| 10 | Distillation Flask = | 160.09 | gm | Stirrer Bar = | 1.45 | gm |
| 11 | Yellow Cover 1 = | 9.05 | gm | with grease = | 0.05 | gm |
| 12 | Yellow Cover 2 = | 9.01 | gm | with grease = | 0.03 | gm |
| 13 | Solvent Added = | 145.81 | gm | HSS as solvent = | 0.00 | gm |
| 14 | Pure NaOH needed = | 0.00 | gm | NaOH 50wt% = | 0.00 | gm |
| 15 | NaOH 50wt% = | 0.00 | ml | Total solution with NaOH = | 145.81 | gm |
| 16 | Distillate Flask | | | | | |
| 17 | Distillate flask = | 103.93 | gm | Stirrer Bar = | 1.44 | gm |
| 18 | Distillate Flask (flask + distillate + bar) = | 244.77 | gm | Distillate = | 139.40 | gm |
| 19 | Solvent Recovery = | 95.60 | % | Total Loss = | 6.41 | gm |
| 20 | Solvent Loss = | 4.40 | % | Amine in distillate = | 28.45 | wt% |
| 21 | Amine in distillate = | 39.66 | gm | Pure solvent recovery = | 89.94 | % |
| 22 | Residue Flask | | | | | |
| 23 | Residue Flask (flask + residue + bar+cover) = | 181.43 | gm | Water Dilution for Residue = | 20.03 | gm |
| 24 | Residue (without NaOH) = | 1.75 | gm | Residue + Water = | 21.78 | gm |
| 25 | Residue to Total Loss = | 27.30 | % | Amine in residue = | 7.64 | wt% |
| 26 | Amine in residue = | 1.66 | gm | Pure solvent loss = | 1.14 | % |
| 27 | What left in heavy residue = | 0.09 | gm | What left in Heavy residue = | 0.06 | % |
| 28 | Washing Run | | | | | |
| 29 | Distillate flaks = | 209.68 | gm | Stirrer Bar = | 1.46 | gm |
| 30 | | | | | | |
| 31 | Distillation Flask = | 140.36 | gm | Stirrer Bar = | 1.43 | gm |
| 32 | Water added = | 330.40 | gm | | | |
| 33 | | | | | | |
| 34 | Distillate Flask + water + bar = | 431.80 | gm | Wash water left = | 250.62 | gm |
| 35 | Recovered water and amine in Distillate = | 220.66 | gm | Left water and amine in Distillation Flask = | 108.83 | gm |
| 36 | Amine in distillate = | 0.23 | wt% | Amine in left water = | 0.86 | wt% |
| 37 | amine in distillate = | 0.51 | gm | amine in distillate = | 0.94 | gm |
| 38 | | | | | | |
| 39 | Recoverable Pure solvent = | 41.10 | gm | Recoverable Pure solvent = | 93.22 | % |
| 40 | Recoverable solvent = | 140.84 | gm | Recoverable solvent = | 96.59 | % |

Figure 52 Distillation evaluation sheet of MEA-1-0.00%-190mmHg

8.3.3.3 Thermal reclamation of MEA-2-0.00%-90mmHg

A second thermal reclamation test of clean MEA solvent was carried out, but this time at a deeper vacuum to enhance solvent recovery and avoid formation of thermal degradation products. Table 30 summarises the test results, and as can be seen, the solvent recovery was 97.63%, which is higher than the previous run of 96.60% at 190 mmHg. The total non-volatile compounds in the clean amine solvent were determined to be 0.06 wt%, similar to the amount determined in the previous test. The GC-MS analysis of the residue revealed the presence of degradation products or contaminants that originally existed in the solvent, as shown in Figure 53. The peak that appeared at a retention time of 20.022 minutes could be N-ethylacetamide (CAS: 625-580-3).

8.3.3.4 Thermal Reclamation of MEA-3-0.50%-210mmHg

The total concentration of degradation products and heat stable salts was 0.50 wt%. The solvent concentration was determined by titration with HCl with a pH meter. The laboratory determination of HSS could not be performed, as the test fail due to the pH of the sample being higher than the end-point pH. Therefore, titration with strong caustic soda 0.1N was not feasible. The high pH was likely due to contribution of some degradation products, such as ammonium hydroxide, to the solvent pH. The HSS data given in Table 31 are based on the solvent preparation. The distillate was contaminated with an unknown degradation product, which was not one of degradation products added. The new peak at the retention time of 2.286 min, as shown in Figure 54, is likely formed after the addition of degradation products and/or heat stable salts.

Table 30 Analysis summary of MEA-2-0.00%-90mmHg samples

| | Loaded lean amine | Distillate amine | Residue |
|--|--------------------------|-------------------------|----------------|
| Solvent Concentration, wt% | 30.24* | 29.02 | 94.96 |
| CO₂ Loading, mol/mol | 0.134 | 0.084 | - |
| HSS, wt% as MEA | 0.0 | - | - |
| Solvent Recovery, % | - | 97.63% | - |
| Total Non-volatile Content, wt% | 0.06 | - | 5.04 |

*Solvent concentration before adding the degradation products and CO₂

Table 31 Analysis summary of MEA-3-0.50%-210mmHg samples

| | Loaded lean amine | Distillate amine | Residue |
|--|--------------------------|-------------------------|----------------|
| Solvent Concentration, wt% | 30.24* | 27.90 | 82.27 |
| CO₂ Loading, mol/mol | 0.208 | 0.077 | - |
| HSS, wt% as MEA | (As mixed 0.294 wt%) | - | - |
| Solvent Recovery, % | - | 96.38% | - |
| Total Non-volatile Content, wt% | 0.46 | - | 17.72 |

*Solvent concentration before adding the degradation products and CO₂

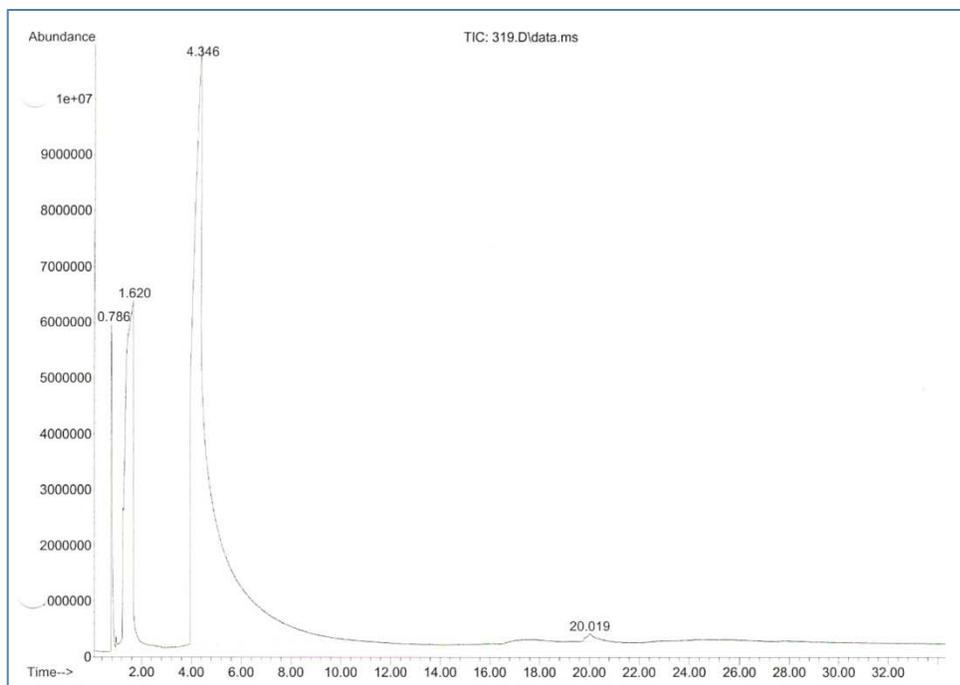


Figure 53 GC chromatograph of residue MEA-2-0.00%-90mmHg

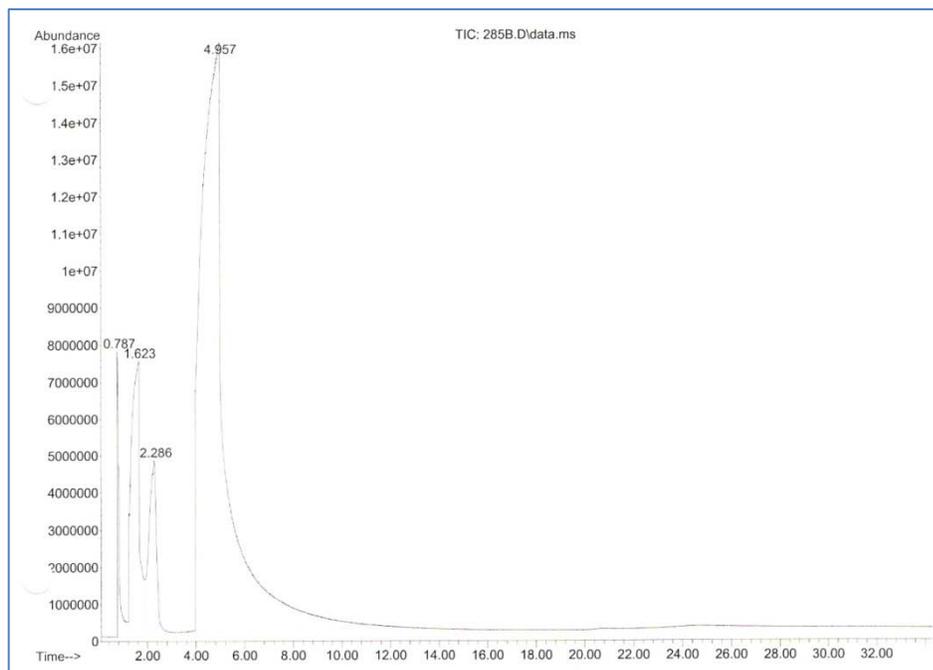


Figure 54 GC chromatograph of distillate of MEA-3-0.50%-210mmHg

8.3.3.5 Thermal Reclamation of MEA-4-1.50%-180mmHg

The total concentration of degradation products and heat stable salts was around 1.50 wt%. The laboratory determination of HSS could not be done, as the test failed due to the pH of sample being higher than the end-point pH. Alternatively, the HSS data given in Table 32 are based on the solvent preparation. Distillate was found to be contaminated with an unknown degradation product, which was not one of degradation products added, similar to the one shown in Figure 54 in the previous test: MEA-3-0.50%-210mmHg.

8.3.3.6 Thermal Reclamation of MEA-5-2.50%-180mmHg

The total concentration of degradation products and heat stable salts was around 2.50 wt%. The laboratory determination of HSS could not be done, as the test failed due to the pH of the sample being higher than the end-point pH. Alternatively, the HSS data given in Table 33 are based on the solvent preparation. Distillate was found to be contaminated with an unknown degradation product, which was not one of degradation products added, similar to the one shown in Figure 54 in the previous test: MEA-3-0.50%-210mmHg.

8.3.3.7 Thermal reclamation of MEA-6-3.50%-180mmHg

The total concentration of degradation products and heat stable salts was around 3.50 wt%. The laboratory determination of HSS could not be done due to the pH of the sample being higher than the end-point pH. Alternatively, the HSS data given in Table 34 are based on the solvent preparation. Distillate was found to be contaminated with two unknown degradation products that appeared at a retention time of 1.074 and 2.337 minutes that might not be one of degradation products added, as shown in Figure 55.

Table 32 Analysis Summary of MEA-4-1.50%-180mmHg Samples

| | Loaded lean amine | Distillate amine | Residue |
|--|--------------------------|-------------------------|----------------|
| Solvent Concentration, wt% | 30.24* | 28.50 | 69.35 |
| CO₂ Loading, mol/mol | 0.217 | 0.107 | - |
| HSS, wt% as MEA | (As mixed 0.660 wt%) | - | - |
| Solvent Recovery, % | - | 93.55% | - |
| Total Non-volatile Content, wt% | 1.99 | - | 30.64 |

*Solvent concentration before adding the degradation products and CO₂

Table 33 Analysis summary of MEA-5-2.50%-180mmHg samples

| | Loaded lean amine | Distillate amine | Residue |
|--|--------------------------|-------------------------|----------------|
| Solvent Concentration, wt% | 30.24* | 27.40 | 60.44 |
| CO₂ Loading, mol/mol | 0.221 | 0.110 | - |
| HSS, wt% as MEA | (As mixed 1.330 wt%) | - | - |
| Solvent Recovery, % | - | 93.67% | - |
| Total Non-volatile Content, wt% | 2.80 | - | 39.55 |

*Solvent concentration before adding the degradation products and CO₂

Table 34 Analysis summary of MEA-6-3.50%-180mmHg samples

| | Loaded lean amine | Distillate amine | Residue |
|--|--------------------------|-------------------------|----------------|
| Solvent Concentration, wt% | 30.24* | 27.30 | 54.08 |
| CO₂ Loading, mol/mol | 0.181 | 0.118 | - |
| HSS, wt% as MEA | (As mixed 1.86wt%) | - | - |
| Solvent Recovery, % | - | 92.44% | - |
| Total Non-volatile Content, wt% | 3.90 | - | 45.92 |

*Solvent concentration before adding the degradation products and CO₂

Table 35 Analysis Summary of MEA-7-4.0%-190mmHg Samples

| | Loaded lean amine | Distillate amine | Residue |
|--|--------------------------|-------------------------|----------------|
| Solvent Concentration, wt% | 30.24* | 27.30 | |
| CO₂ Loading, mol/mol | 0.132 | 0.058 | - |
| HSS, wt% as MEA | (As mixed 2.133wt%) | - | - |
| Solvent Recovery, % | - | 92.12% | - |
| Total Non-volatile Content, wt% | 4.91 | - | |

*Solvent concentration before adding the degradation products and CO₂

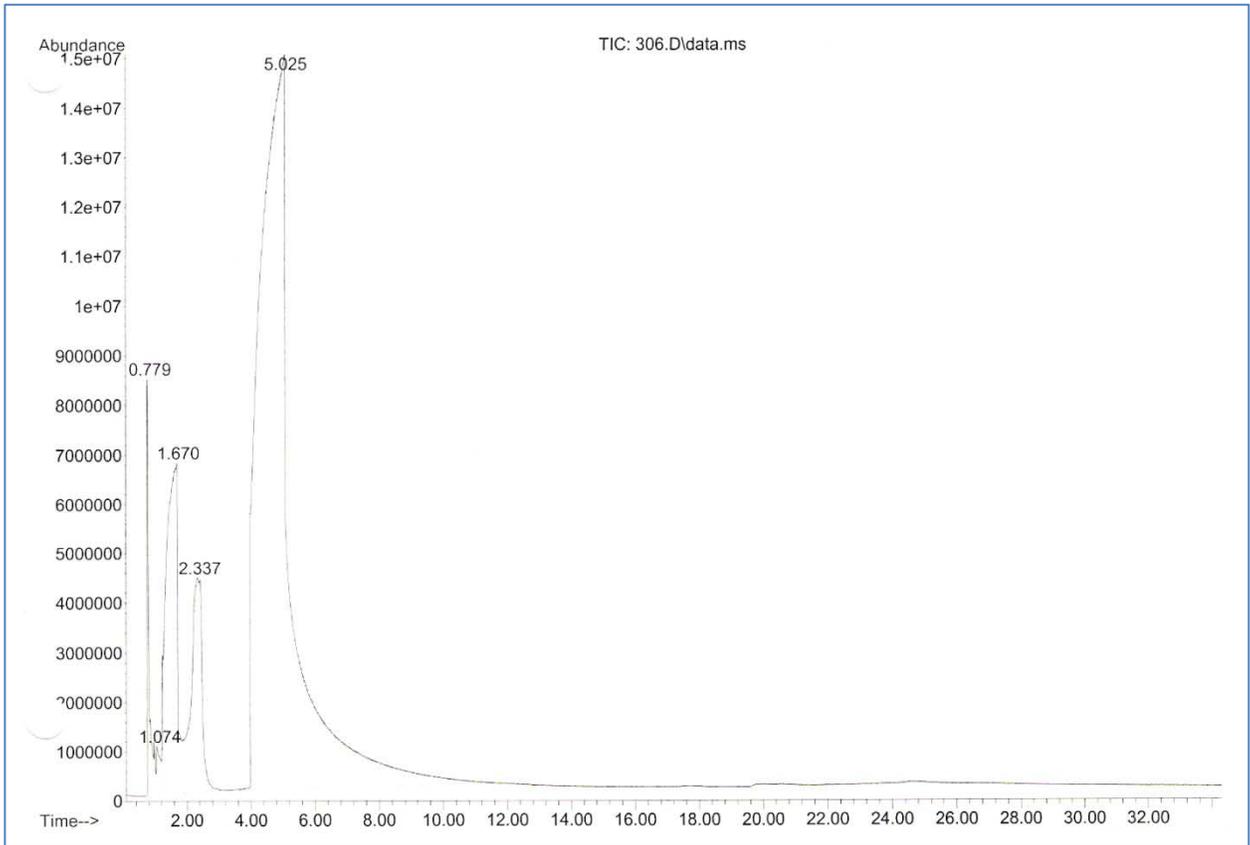


Figure 55 GC chromatograph of distillate of MEA-6-3.50%-180mmHg

8.3.3.8 Thermal Reclamation of MEA-7-4.0%-190mmHg

Degraded solvent loaded with CO₂ was prepared and thermally reclaimed. The total concentration of degradation products and heat stable salts was around 4.0 wt%. The laboratory determination of HSS could not be done, as the test failed due to the pH of the sample being higher than the end-point pH. Alternatively, the HSS data given in Table 35 are based on the solvent preparation. Distillate was found to be contaminated with a number of unknown degradation products. The two degradation products reported previously that appeared at retention times of 1.074 (at lower concentration) and 2.337 minutes are major degradation products (Figure 56). Based on GC-MS evaluation and injection of standard solutions, it appears that the peak at 1.074 min is ethylamine and the peak at 2.337 min is unknown. This will be discussed in the summary results at the end of this section. Table 36 shows the summary of these degradation products and what they could be based on GC-MS evaluation; however, some GC-MS judgments on the identification might not be correct. For instance, a peak that appeared at 2.320 minute is given by GC-MS as CO₂ but it is well known that the CO₂ peak should be at 0.787 minutes, and this is ethylamine, which was confirmed with a standard injection test. GC-MS evaluation is looking to evaluate all the output of analysis, like matching the peak with peaks in the chemical database. For instance, consider Figure 57, which shows the evaluation table of GC-MS for the peak that appeared at the retention time of 11.088 min in Figure 56. The best peak matching is listed from top (more likely) to bottom (less likely).

Table 36 GC-MS identification for chemicals found in distillate of MEA-7-4.0%-190mmHg

| Degradation Product | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|------------------------|-------------------|-------------|-------------------------------------|-----------------------------|--------------------|-------------------------------|------------|
| Retention Time, Minute | 0.800 (not shown) | 1.074 | 2.317 | 2.447 | 11.027 | 12.763 | 24.617 |
| Possible Chemical | Ammonia* | Ethylamine* | Carbamic Acid, Mono ammonium Salt** | N-Methyl-1-3-Propanediamine | N,N'-dimethyl Urea | Methyl diethanol amine (MDEA) | Ethyl Urea |

* Confirmed peaks

** This is an associated peak appeared after adding ammonium hydroxide

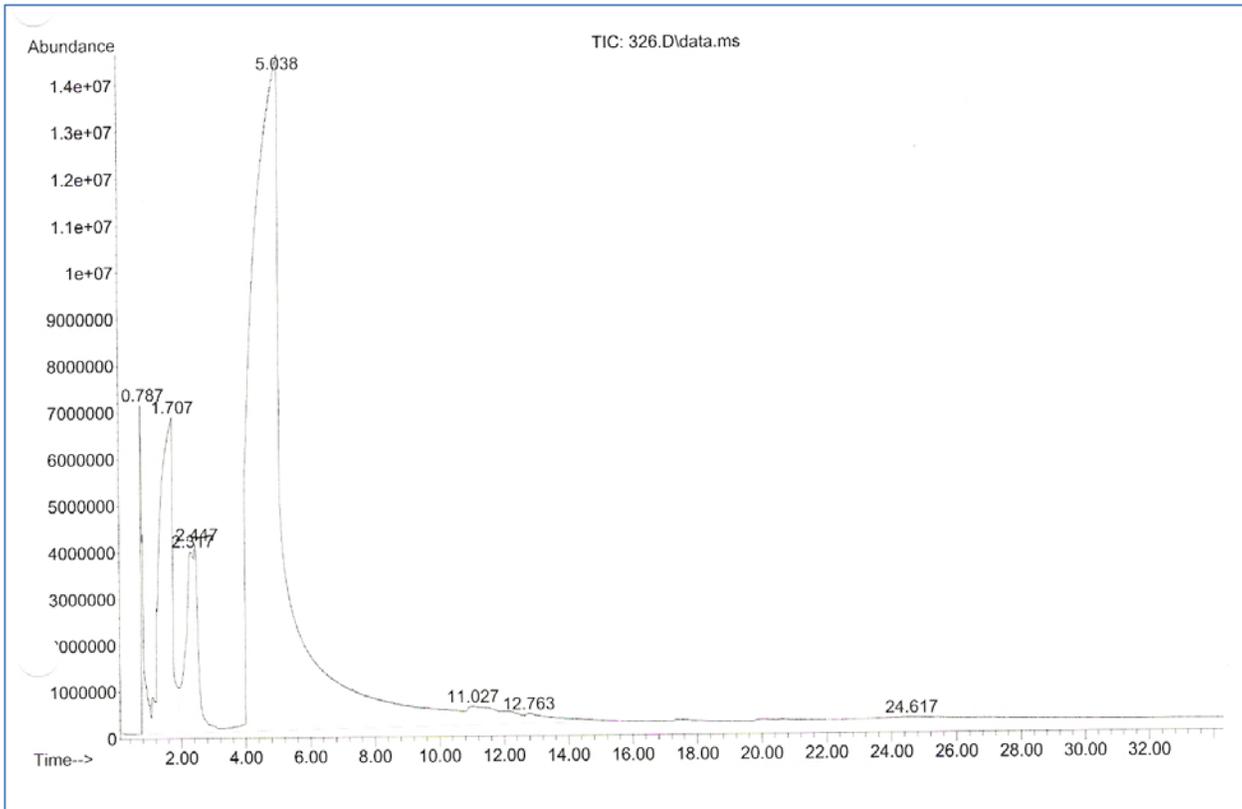


Figure 56 GC chromatograph of distillate of MEA-7-4.0%-190mmHg

Scan 1790 (11.088 min): 326.D\data.ms
distillate - MEA -6

| Ra Name | MW | Formula | Qu | M | CAS # | Ref # | K | dK | F1 | % | Co | C1 | Ti | Re | XCORR |
|--|-----|----------|----|---|-------------|--------|----|----|----|----|----|----|----|----|-------|
| 1 2-Amino-2-ethyl-1,3-propanediol | 119 | C5H13NO2 | 53 | | 000115-70-8 | 35775 | 43 | 57 | 3 | 74 | 30 | 28 | 19 | 41 | 6681 |
| 2 Urea, N,N'-dimethyl- | 88 | C3H8N2O | 50 | * | 000096-31-1 | 108256 | 37 | 49 | 2 | 99 | 34 | 25 | 0 | 39 | 8828 |
| 3 Methyl-diethanolamine | 119 | C5H13NO2 | 47 | | 000105-59-9 | 117019 | 45 | 41 | 1 | 60 | 39 | 20 | 12 | 41 | 7081 |
| 4 Urea, N,N-dimethyl- | 88 | C3H8N2O | 43 | * | 000598-94-7 | 110630 | 47 | 47 | 3 | 62 | 43 | 18 | 17 | 40 | 6697 |
| 5 Methyl-diethanolamine | 119 | C5H13NO2 | 43 | * | 000105-59-9 | 117018 | 49 | 41 | 1 | 69 | 49 | 18 | 0 | 44 | 6995 |
| 6 Methyl-diethanolamine | 119 | C5H13NO2 | 43 | * | 000105-59-9 | 35678 | 57 | 30 | 1 | 69 | 49 | 18 | 0 | 47 | 6974 |
| 7 1-Hexanol, 6-amino- | 117 | C6H15NO | 22 | * | 004048-33-3 | 786 | 36 | 36 | 2 | 99 | 64 | 5 | 0 | 39 | 7082 |
| 8 2-Propanol, 1-amino- | 75 | C3H9NO | 22 | * | 000078-96-6 | 108169 | 36 | 33 | 0 | 83 | 65 | 5 | 0 | 41 | 7003 |
| 9 1-Propanamine | 59 | C3H9N | 22 | * | 000107-10-8 | 108233 | 45 | 22 | 0 | 67 | 61 | 5 | 15 | 40 | 7186 |
| 10 D-Aspartic acid | 133 | C4H7NO4 | 17 | | 001783-96-6 | 35770 | 41 | 60 | 3 | 66 | 52 | 3 | 0 | 29 | 6374 |
| 11 Ethylenediamine | 60 | C2H8N2 | 14 | * | 000107-15-3 | 667 | 40 | 30 | 0 | 78 | 66 | 2 | 0 | 39 | 7055 |
| 12 1-Propanol, 3-amino- | 75 | C3H9NO | 14 | | 000156-87-6 | 675 | 44 | 24 | 1 | 77 | 66 | 2 | 0 | 39 | 7222 |
| 13 5-Aminovaleric acid | 117 | C5H11NO2 | 12 | | 000660-88-8 | 784 | 39 | 39 | 3 | 99 | 61 | 2 | 0 | 33 | 7291 |
| 14 Acetamide, 2-amino-N-(1-methylethyl)- | 116 | C5H12N2O | 12 | | 067863-05-2 | 709 | 41 | 42 | 3 | 83 | 65 | 2 | 0 | 33 | 7501 |
| 15 Monoethanolamine | 61 | C2H7NO | 12 | * | 000141-43-5 | 665 | 30 | 34 | 1 | 97 | 64 | 2 | 0 | 33 | 7048 |
| 16 Monoethanolamine | 61 | C2H7NO | 10 | | 000141-43-5 | 108157 | 41 | 24 | 1 | 73 | 66 | 1 | 0 | 33 | 7008 |
| 17 2-Butanamine | 73 | C4H11N | 10 | * | 013952-84-6 | 10458 | 35 | 38 | 1 | 61 | 80 | 1 | 0 | 39 | 5026 |
| 18 Methyl-diethanolamine | 119 | C5H13NO2 | 10 | * | 000105-59-9 | 117020 | 35 | 41 | 1 | 36 | 77 | 1 | 0 | 41 | 7005 |
| 19 5-Aminovaleric acid | 117 | C5H11NO2 | 10 | * | 000660-88-8 | 108156 | 30 | 42 | 2 | 82 | 66 | 1 | 0 | 33 | 7089 |
| 20 Acetic acid, [(aminocarbonyl)amino]oxo- | 132 | C3H4N2O4 | 10 | | 000585-05-7 | 110533 | 48 | 34 | 2 | 51 | 77 | 1 | 19 | 41 | 4481 |

Figure 57 GC-MS chemical identification of peak 11.088 min in distillate MEA-7-4.0%-190mmHg

8.3.3.9 Thermal reclamation of MEA-8-5.0%-180mmHg

Degraded solvent loaded with CO₂ was prepared and thermally reclaimed. Table 37 gives the summary of the analysis of samples obtained from the test. The total concentration of degradation products and heat stable salts was around 4.0 wt%. The laboratory determination of HSS was done and showed that HSS is 1.055 wt% as MEA; however, HSS added was 2.66 wt%. The temperature profile for the test is given in Figure 58. Details of the distillation records are given in Figure 59.

Distillate was found to be contaminated with a number of unknown degradation products. The three degradation products reported previously that had appeared at retention times of 0.969, 1.095, and 2.287 minutes are the major degradation products (Figure 60). Table 38 shows the summary of these degradation products and what they could be based on GC-MS evaluation or our confirmation with standard injection. The chemicals expected are similar to the previous test MEA-7-4.0%-190mmHg except that some new peaks were not seen previously at the retention times of 17.625 and 20.526 minutes. The chemical identification of peak 17.581 min is given in Figures 61.

Table 37 Analysis Summary of MEA-8-5.0%-180mmHg Samples

| | Loaded lean amine | Distillate amine | Residue |
|--|-------------------------------------|-----------------------------|----------------|
| Solvent Concentration, wt% | 30.24* | 27.72 | 52.85 |
| CO₂ Loading, mol/mol | 0.130 | 0.055 | - |
| HSS, wt% as MEA | 1.055 (As mixed 2.660wt%) | - | - |
| Solvent Recovery, % | - | 91.27% | - |
| Total Non-volatile Content, wt% | 5.31 | - | 47.14 |

*Solvent concentration before adding the degradation products and CO₂

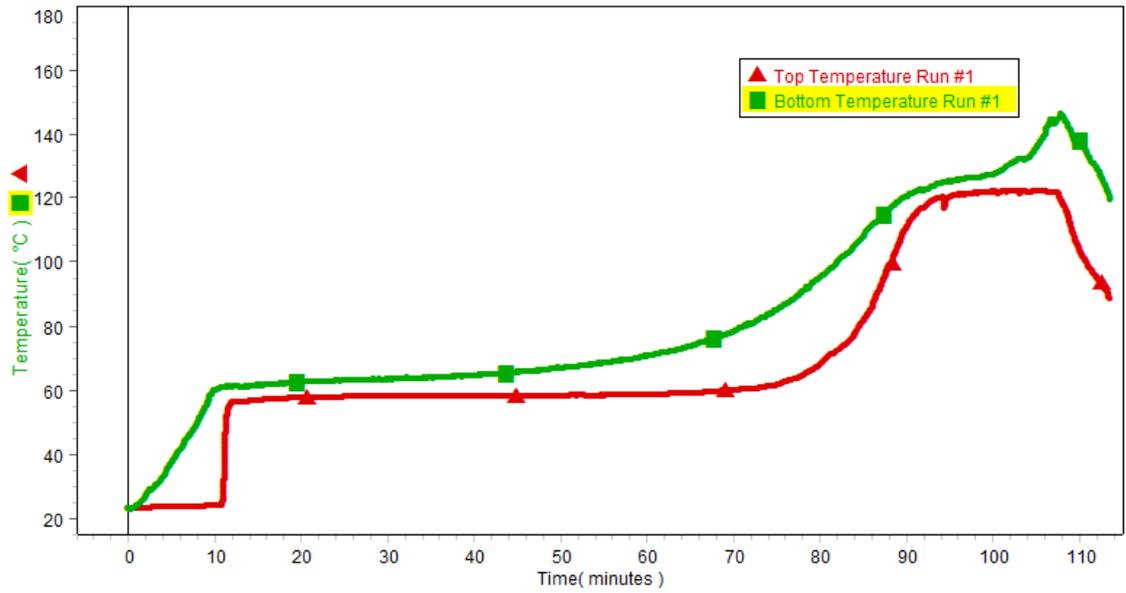


Figure 58 Top and bottom temperature profiles for MEA-8-5.0%-180mmHg

| Reclaimer Research: Small Set-Up Distillation Form | | | | | | |
|--|---|--------|-----|--|------------|------|
| 1 | Distillation Test Code | MEA-8 | | Date | 17.10.2011 | |
| 2 | Solvent type | MEA | | Time | 1:47 hr | |
| 3 | Solvent Conc | 31.20 | wt% | Mode Operation: | Vacuum | |
| 4 | Degradation Level | 5.00 | wt% | Room Temp. = | 21.10 | C |
| 5 | Heat Set # = | 8.50 | | Room pressure = | | kpa |
| 6 | Cooling temp. = | 10.00 | C | Set-up pressure = | | mmHg |
| 7 | Trap one temp. = | 1.60 | C | Set-up pressure = | 180.00 | mmHg |
| 8 | Trap two temp. = | 1.70 | C | Cooling bath | 2.00 | |
| 9 Distillation Flask | | | | | | |
| 10 | Distillation Flask = | 154.47 | gm | Bar = | 1.47 | gm |
| 11 | Yellow Cover 1 = | 9.03 | gm | with grease = | 0.05 | gm |
| 12 | Yellow Cover 2 = | 8.98 | gm | with grease = | 0.03 | gm |
| 13 | Solvent Added = | 231.00 | gm | HSS as solvent = | 5.08 | gm |
| 14 | Pure NaOH needed = | 3.33 | gm | NaOH 50wt% = | 6.66 | gm |
| 15 | NaOH 50wt% = | 4.36 | ml | Total solution with NaOH = | 237.66 | gm |
| 16 Distille Flask | | | | | | |
| 17 | Distillate flask = | 142.49 | gm | Bar = | 1.42 | gm |
| 18 | Distillate Flask (flask + distillate + bar) = | 353.91 | gm | Distillate = | 210.00 | gm |
| 19 | Solvent Recovery = | 88.36 | % | Total Loss = | 27.66 | gm |
| 20 | Solvent Loss = | 11.64 | % | Amine in distillate = | 27.72 | wt% |
| 21 | Amine in distillate = | 58.21 | gm | Pure solvent recovery = | 78.51 | % |
| 22 Residue Flask | | | | | | |
| 23 | Residue Flask (flask + residue + bar) = | 206.74 | gm | Water Dilution for Residue = | 50.46 | gm |
| 24 | Residue (without NaOH) = | 26.05 | gm | Residue + Water = | 76.51 | gm |
| 25 | Residue to Total Loss = | 94.21 | % | Amine in residue = | 18.00 | wt% |
| 26 | Amine in residue = | 13.77 | gm | Pure solvent loss = | 5.80 | % |
| 27 | What left in heavy residue = | 12.28 | gm | What left in Heavy residue = | 5.32 | % |
| 28 Washing Run | | | | | | |
| 29 | Distillate flaks = | 209.70 | gm | bar = | 1.46 | gm |
| 30 | | | | | | |
| 31 | Distillation Flask = | 140.38 | gm | bar = | 1.45 | gm |
| 32 | Water added = | 399.79 | gm | | | |
| 33 | | | | | | |
| 34 | Distillate Flask + water + bar = | 551.01 | gm | Wash water left = | 200.86 | gm |
| 35 | Recovered water and amine in Distillate = | 339.85 | gm | Left water and amine in Distillation Flask = | 59.03 | gm |
| 36 | Amine in distillate = | 0.15 | wt% | Amine in left water = | 0.55 | wt% |
| 37 | amine in distillate = | 0.51 | gm | amine in distillate = | 0.32 | gm |
| 38 | | | | | | |
| 39 | Recoverable Pure solvent = | 59.05 | gm | Recoverable Pure solvent = | 81.93 | % |
| 40 | Recoverable solvent = | 210.83 | gm | Recoverable solvent = | 91.27 | % |

Figure 59 Distillation evaluation sheet of MEA-8-5.0%-180mmHg

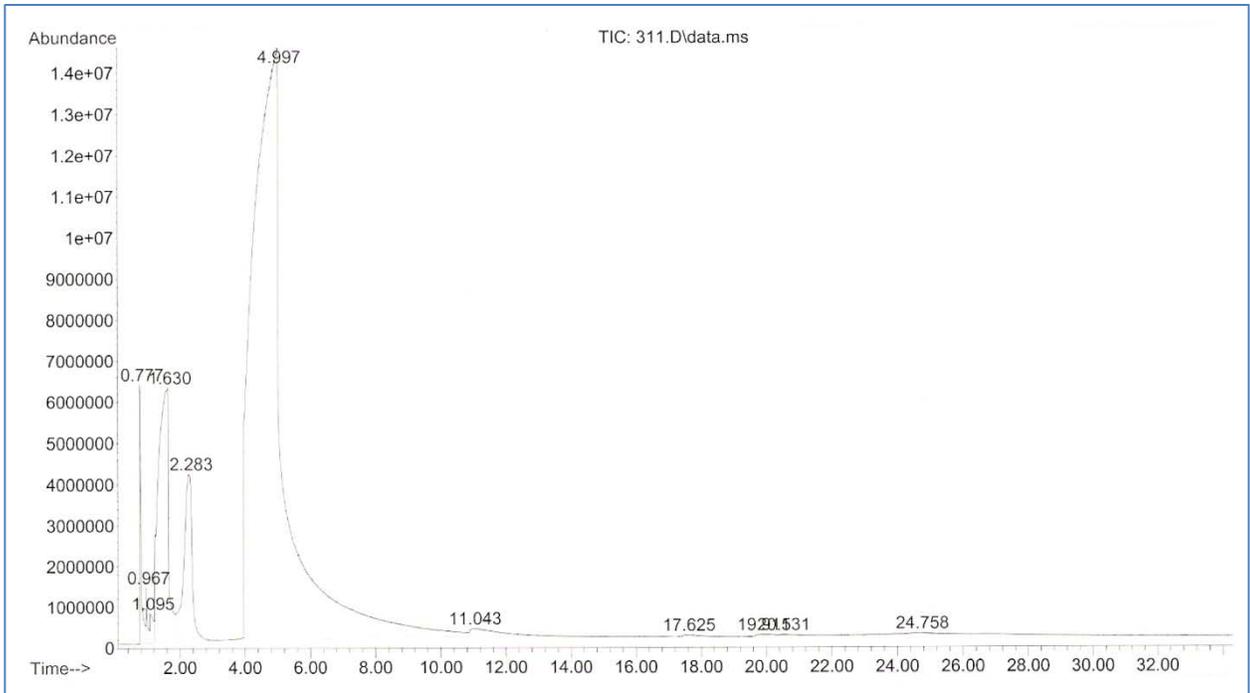


Figure 60 GC chromatograph of distillate of MEA-8-5.0%-180mmHg

| Ra | Name | MW | Formula | Qu | M | CAS # | Ref # | K | dk | Fl | % | Co | Cl | Ti | Re | XCORR |
|----|-----------------------------------|-----|----------|----|---|-------------|--------|----|----|----|----|----|----|----|----|-------|
| 1 | Monoethanolamine | 61 | C2H7NO | 58 | * | 000141-43-5 | 108157 | 44 | 21 | 1 | 99 | 29 | 32 | 0 | 44 | 9749 |
| 2 | dl-4-Amino-3-hydroxybutyric acid | 119 | C4H9NO3 | 53 | | 000352-21-6 | 683 | 39 | 36 | 2 | 85 | 29 | 28 | 17 | 39 | 9716 |
| 3 | Ethylenediamine | 60 | C2H8N2 | 47 | * | 000107-15-3 | 667 | 48 | 22 | 1 | 95 | 36 | 20 | 0 | 39 | 9640 |
| →4 | 1,4-Butanediamine | 88 | C4H12N2 | 47 | * | 000110-60-1 | 739 | 45 | 25 | 0 | 69 | 40 | 20 | 22 | 43 | 9715 |
| 5 | 1-Propanol, 3-amino- | 75 | C3H9NO | 47 | | 000156-87-6 | 675 | 41 | 32 | 2 | 80 | 40 | 20 | 6 | 39 | 9681 |
| 6 | 1-Propanamine, 2-methyl- | 73 | C4H11N | 47 | * | 000078-81-9 | 677 | 39 | 28 | 1 | 94 | 36 | 20 | 0 | 39 | 9665 |
| 7 | 1-Butanamine, 2-methyl- | 87 | C5H13N | 43 | * | 000096-15-1 | 698 | 41 | 22 | 2 | 84 | 42 | 18 | 17 | 39 | 9652 |
| 8 | 2-Fluoro-.beta.-alanine | 107 | C3H6FNO2 | 40 | | 003821-81-6 | 736 | 38 | 44 | 2 | 87 | 31 | 16 | 9 | 31 | 9776 |
| 9 | Ethanol, 2-(2-aminoethoxy)- | 105 | C4H11NO2 | 40 | | 000929-06-6 | 771 | 38 | 46 | 3 | 99 | 33 | 16 | 0 | 33 | 9758 |
| 10 | Propanoic acid, 3-amino-2-methyl- | 103 | C4H9NO2 | 38 | | 000144-90-1 | 687 | 33 | 38 | 2 | 88 | 38 | 14 | 6 | 31 | 9671 |
| 11 | 4-Amino-1-butanol | 89 | C4H11NO | 37 | * | 013325-10-5 | 783 | 39 | 30 | 1 | 99 | 42 | 13 | 0 | 35 | 9652 |
| 12 | 2-Propanol, 1-amino- | 75 | C3H9NO | 36 | | 000078-96-6 | 710 | 41 | 33 | 2 | 99 | 29 | 12 | 0 | 28 | 9738 |
| 13 | Monoethanolamine | 61 | C2H7NO | 33 | * | 000141-43-5 | 665 | 29 | 35 | 1 | 99 | 33 | 10 | 0 | 29 | 9745 |
| 14 | Guanidine, methyl- | 73 | C2H7N3 | 33 | * | 000471-29-4 | 108192 | 23 | 60 | 3 | 80 | 35 | 10 | 2 | 23 | 8115 |
| 15 | Aminocaproic Acid | 131 | C6H13NO2 | 28 | | 000060-32-2 | 108209 | 37 | 32 | 2 | 93 | 38 | 8 | 0 | 25 | 9660 |
| 16 | Aminocaproic Acid | 131 | C6H13NO2 | 28 | | 000060-32-2 | 790 | 34 | 44 | 3 | 68 | 40 | 8 | 0 | 21 | 9641 |
| 17 | Ethylamine | 45 | C2H7N | 28 | | 000075-04-7 | 108213 | 35 | 42 | 3 | 95 | 36 | 8 | 0 | 22 | 9730 |
| 18 | 1-Heptanamine | 115 | C7H17N | 25 | | 000111-68-2 | 766 | 33 | 38 | 1 | 67 | 42 | 7 | 2 | 22 | 9662 |
| 19 | 3,3-Dimethylbutylamine | 101 | C6H15N | 25 | | 015673-00-4 | 722 | 37 | 27 | 3 | 97 | 42 | 7 | 0 | 25 | 9648 |
| 20 | S-(-)-2-Methylbutylamine | 87 | C5H13N | 25 | | 020626-52-2 | 720 | 36 | 29 | 2 | 99 | 42 | 7 | 0 | 25 | 9646 |

Figure 61 GC-MS chemical identification of peak 17.581 min of distillate (MEA-8-5.0%-180mmHg)

Table 38 GC-MS identification for degradation products found in distillate (MEA-7-4.0%-190mmHg)

| Degradation Product | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|------------------------|----------|-------------|-------------------------------------|--------------------|-------------------------|-------------------|------------|
| Retention Time, Minute | 0.969 | 1.095 | 2.287 | 11.035 | 17.625 | 20.526 | 24.617 |
| Possible Chemical | Ammonia* | Ethylamine* | Carbamic Acid, Mono ammonium Salt** | N,N'-dimethyl Urea | 1-Butanamine, 2-Methyl- | 1,4-Butanediamine | Ethyl Urea |

* Confirmed peaks

** This is an associated peak that appeared after addition of ammonium hydroxide.

8.3.3.10 Identification of major chemicals contaminating the MEA distillate

It has been seen with all cases of degraded amine solvents that the distillate is contaminated with three major peaks, as shown in Figure 60. The first peak partially overlaps the CO₂ peak and appeared at 0.850 min. The second peak appeared at 1.000 min, which is clearly between the CO₂ and water peaks. The third peak was at 2.200 min, after the water peak. GC-MS suggested that the first two peaks could be due to the presence of ethylamine and ammonia, while the third one is ammonium carbamate (CAS: 1111-78-0). To make sure that these peaks belong to these chemicals, standard chemicals were used to match the peak retention time and spectrum.

In order to check the chemical matching with the peaks, we prepared clean MEA solvent and added only the expected degradation chemical. For instance, the first peak was expected to be ammonia from GC-MS evaluation, so degraded MEA solvent was prepared by mixing ammonium hydroxide and MEA, and Figure 62 shows the chromatograph of this sample. As can be seen, there are two new peaks formed at the retention times of 0.762 and 2.428 minutes. Figure 63 shows the GC-MS evaluation of the first peak, and Figure 64 shows the spectrum obtained for this peak, which is obviously ammonia. The other unknown peak was also evaluated and seems to be ammonium carbamate as shown in Figure 65. The second unknown peak could be ethylamine based on GC-MS evaluations. We prepared a standard ethylamine dissolved in clean and unloaded MEA solvent, and the GC chromatograph is shown in Figure 66. Only one new peak was found at a retention time of 0.917 minute. The GC-MS evaluation, as shown in Figure 67, confirmed ethylamine, as can be clearly seen in Figure 68, which shows the spectrum of the 0.917 minute peak.

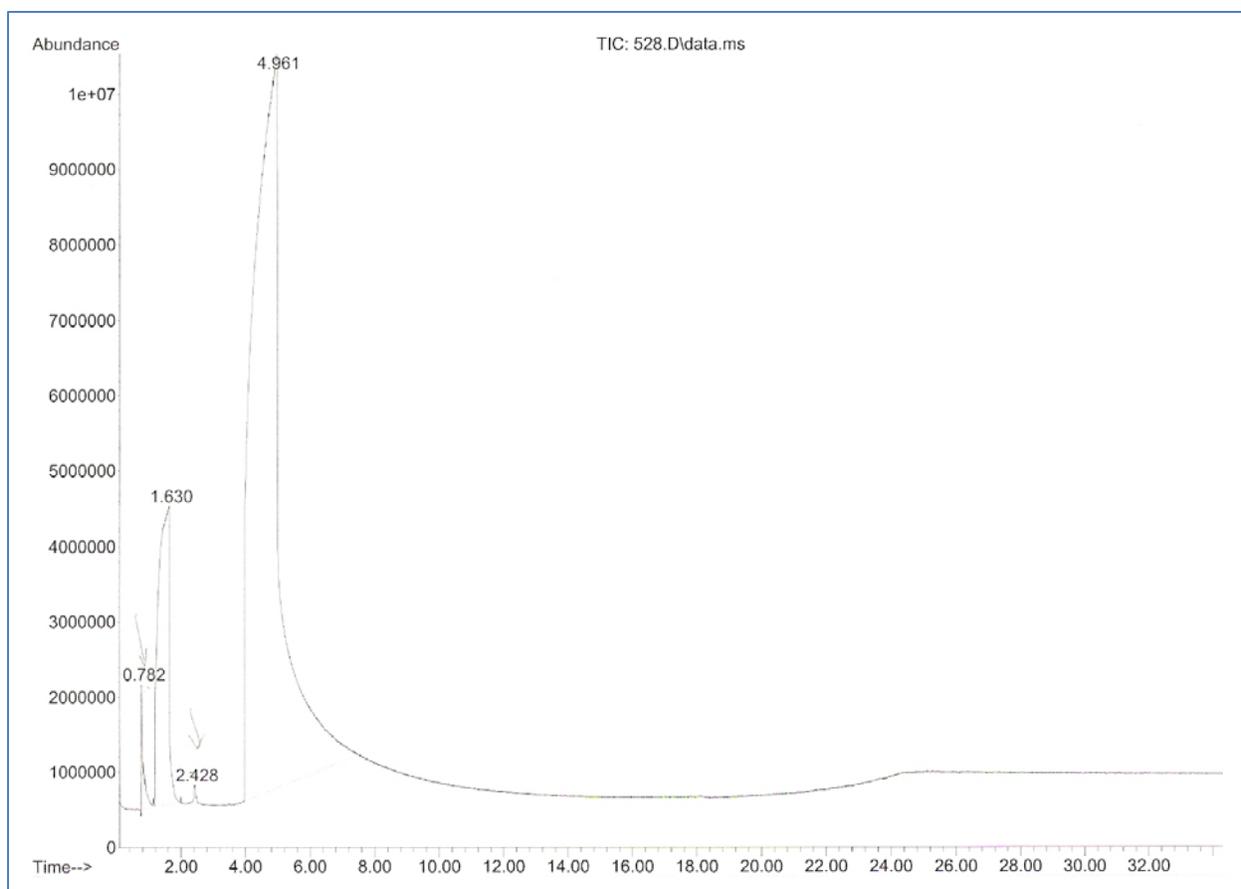


Figure 62 GC chromatograph of MEA-Ammonium hydroxide system

| Ra Name | MW | Formula | Qu | M | CAS # | Ref # | K | dK | F1 | % | Co | C1 | Ti | Re | XCORR |
|------------------------------------|-----|----------|----|---|-------------|--------|----|----|----|----|----|----|----|----|-------|
| 1 Ammonia | 17 | H3N | 7 | * | 007664-41-7 | 19 | 22 | 4 | 0 | 84 | 10 | 1 | 0 | 7 | 9982 |
| 2 Carbamic acid, monoammonium salt | 78 | CH6N2O2 | 4 | | 001111-78-0 | 107903 | 26 | 31 | 2 | 73 | 10 | 1 | 0 | 4 | 8301 |
| 3 Methane | 16 | CH4 | 3 | * | 000074-82-8 | 107901 | 12 | 21 | 1 | 75 | 54 | 1 | 0 | 3 | 5177 |
| 4 Methane | 16 | CH4 | 2 | * | 000074-82-8 | 107902 | 7 | 30 | 2 | 75 | 57 | 1 | 0 | 2 | 4959 |
| 5 Methane | 16 | CH4 | 2 | * | 000074-82-8 | 18 | 7 | 33 | 2 | 75 | 56 | 1 | 0 | 2 | 4924 |
| 6 Manganese, pentacarbonylmethyl- | 210 | C6H3MnO5 | 1 | | 013601-24-6 | 107939 | 12 | 10 | 3 | 55 | 54 | 1 | 0 | 1 | 4660 |
| 7 water | 18 | H2O | 1 | | 007732-18-5 | 22 | 7 | 9 | 0 | 99 | 52 | 1 | 0 | 1 | 8217 |
| 8 Oxygen | 32 | O2 | 1 | | 007782-44-7 | 1145 | 7 | 0 | 0 | 75 | 54 | 1 | 0 | 1 | 5985 |
| 9 Carbon monoxide | 28 | CO | 1 | | 000630-08-0 | 107937 | 5 | 22 | 2 | 20 | 57 | 1 | 0 | 1 | 5610 |

Figure 63 GC-MS evaluation of first unknown peak (Ammonia) MEA-NH₄OH system

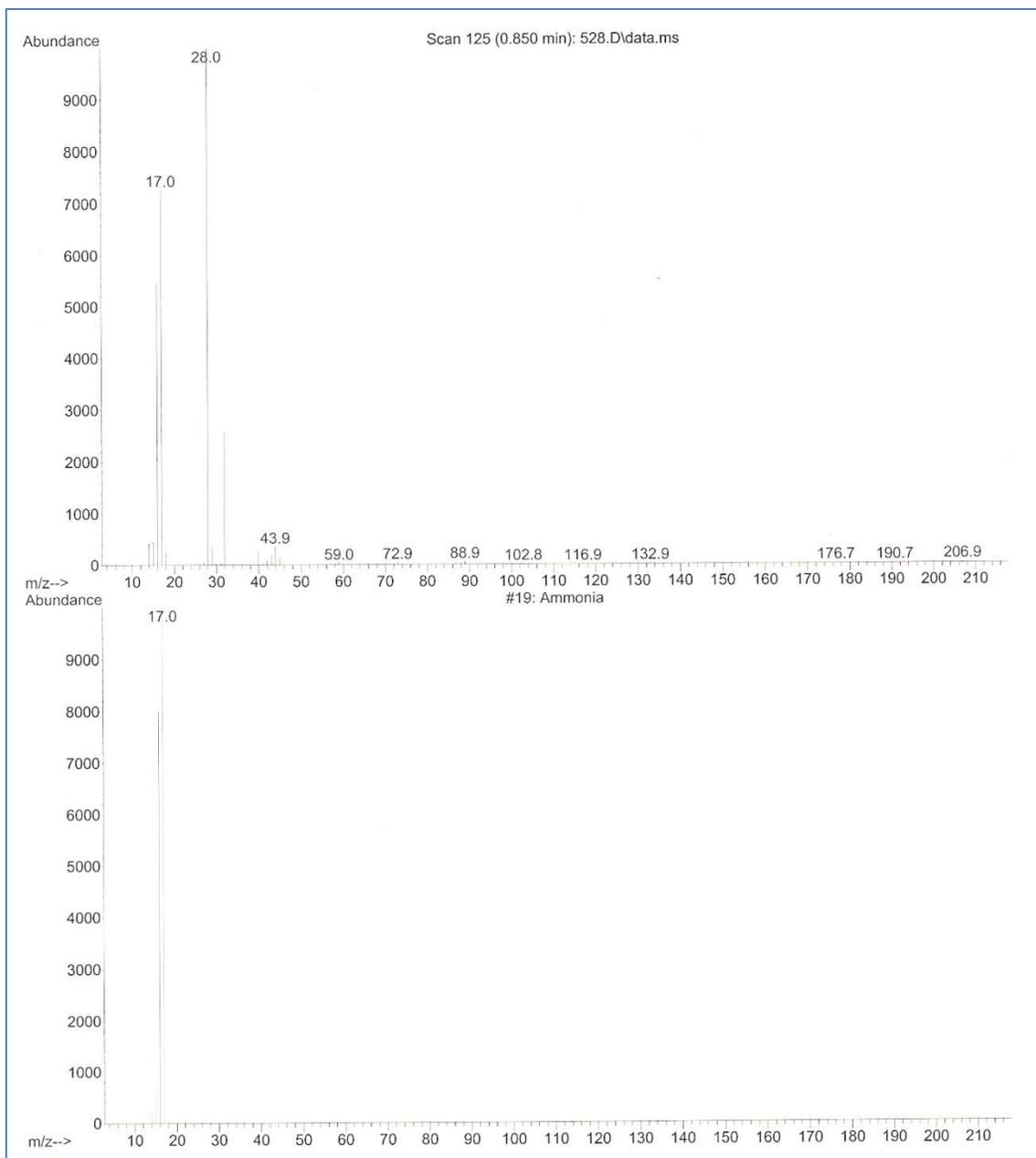


Figure 64 Spectrum of ammonia of MEA-Ammonium hydroxide system

| MEA+NH3 clean unload | | | | | | | | | | | | | | | | |
|----------------------|---------------------------|-----|----------|----|---|-------------|--------|----|----|----|------|----|----|----|-------|------|
| Ra | Name | MW | Formula | Qu | M | CAS # | Ref # | K | dK | F1 | % Co | C1 | Ti | Re | XCORR | |
| 1 | 2-Butanamine, 3-methyl- | 87 | C5H13N | 5 | * | 000598-74-3 | 10776 | 19 | 32 | 1 | 28 | 80 | 1 | 0 | 5 | 9962 |
| 2 | Carbon dioxide | 44 | CO2 | 5 | * | 000124-38-9 | 10466 | 17 | 8 | 1 | 78 | 16 | 1 | 0 | 5 | 9971 |
| 3 | 2-Butanamine | 73 | C4H11N | 4 | * | 013952-84-6 | 10458 | 15 | 58 | 3 | 72 | 27 | 1 | 0 | 4 | 9962 |
| 4 | 2-Propanamine, 1-methoxy- | 89 | C4H11NO | 4 | * | 037143-54-7 | 10462 | 15 | 55 | 3 | 96 | 23 | 1 | 0 | 4 | 9962 |
| 5 | 2-Aminononadecane | 283 | C19H41N | 4 | * | 031604-55-4 | 10636 | 15 | 59 | 1 | 25 | 78 | 1 | 0 | 4 | 9962 |
| 6 | Ethyne, fluoro- | 44 | C2HF | 4 | * | 002713-09-9 | 10511 | 14 | 39 | 2 | 99 | 27 | 1 | 0 | 4 | 9962 |
| 7 | 2-Hexanamine, 4-methyl- | 115 | C7H17N | 4 | * | 000105-41-9 | 110664 | 24 | 21 | 1 | 72 | 15 | 1 | 0 | 4 | 9962 |
| 8 | Carbon dioxide | 44 | CO2 | 3 | * | 000124-38-9 | 110470 | 12 | 20 | 2 | 99 | 25 | 1 | 0 | 3 | 9958 |
| 9 | 2-Pentanamine | 87 | C5H13N | 3 | * | 000625-30-9 | 110491 | 12 | 54 | 3 | 51 | 57 | 1 | 0 | 3 | 9962 |
| 10 | Nitrous Oxide | 44 | N2O | 3 | * | 010024-97-2 | 110482 | 12 | 19 | 2 | 70 | 22 | 1 | 0 | 3 | 9910 |
| 11 | Nitrous Oxide | 44 | N2O | 3 | * | 010024-97-2 | 10492 | 12 | 19 | 2 | 87 | 22 | 1 | 0 | 3 | 9951 |
| 12 | Ethyl oxamate | 117 | C4H7NO3 | 3 | * | 000617-36-7 | 110480 | 11 | 58 | 3 | 34 | 80 | 1 | 0 | 3 | 9950 |
| 13 | Tuaminoheptane | 115 | C7H17N | 3 | * | 000123-82-0 | 110648 | 9 | 25 | 1 | 22 | 78 | 1 | 0 | 3 | 9962 |
| 14 | 2-Butanamine, (S)- | 73 | C4H11N | 3 | * | 000513-49-5 | 10463 | 9 | 37 | 1 | 21 | 80 | 1 | 0 | 3 | 9962 |
| 15 | 2-Hexanamine, 4-methyl- | 115 | C7H17N | 3 | * | 000105-41-9 | 10457 | 9 | 40 | 2 | 31 | 80 | 1 | 0 | 3 | 9962 |
| 16 | 2-Pentanamine | 87 | C5H13N | 3 | * | 000625-30-9 | 110483 | 9 | 63 | 3 | 59 | 63 | 1 | 0 | 3 | 9962 |
| 17 | 2-Hexanamine, 4-methyl- | 115 | C7H17N | 3 | * | 000105-41-9 | 110485 | 9 | 29 | 1 | 21 | 80 | 1 | 0 | 3 | 9962 |
| 18 | 2-Propanamine | 59 | C3H9N | 2 | * | 000075-31-0 | 10459 | 21 | 50 | 2 | 99 | 22 | 1 | 0 | 2 | 9971 |
| 19 | Tuaminoheptane | 115 | C7H17N | 2 | * | 000123-82-0 | 10500 | 8 | 45 | 1 | 27 | 80 | 1 | 0 | 2 | 9962 |
| 20 | L-Alanine, ethyl ester | 117 | C5H11NO2 | 2 | * | 003082-75-5 | 110479 | 21 | 39 | 2 | 59 | 55 | 1 | 0 | 2 | 9962 |

Figure 65 GC-MS evaluation of second unknown peak (ammonium carbamate) MEA-NH₄OH System

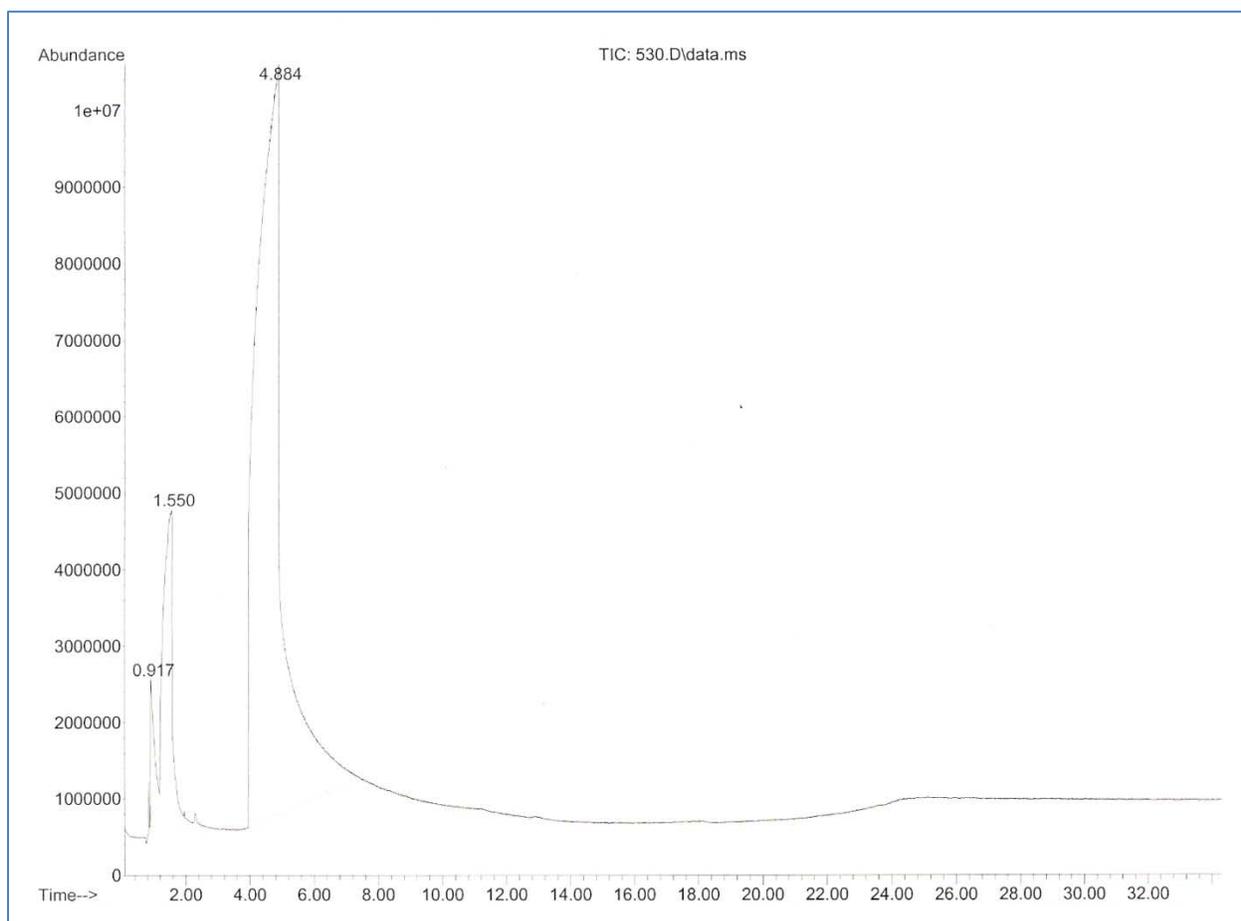


Figure 66 GC chromatograph of MEA-Ethylamine system

| Ra Name | Mw | Formula | Qu | M | CAS # | Ref # | K | dK | F1 | % | Co | C1 | Ti | Re | XCORR |
|-------------------------------|-----|----------|----|---|-------------|--------|----|----|----|----|----|----|----|----|-------|
| 1 Ethylamine | 45 | C2H7N | 91 | * | 000075-04-7 | 108212 | 76 | 4 | 0 | 94 | 4 | 62 | 2 | 66 | 9976 |
| 2 Ethylamine | 45 | C2H7N | 91 | * | 000075-04-7 | 108213 | 70 | 7 | 0 | 92 | 4 | 62 | 0 | 76 | 9978 |
| 3 Ethylamine | 45 | C2H7N | 90 | * | 000075-04-7 | 108211 | 68 | 6 | 1 | 96 | 6 | 59 | 17 | 66 | 9904 |
| 4 Ethanol, 2-(2-aminoethoxy)- | 105 | C4H11NO2 | 72 | | 000929-06-6 | 771 | 41 | 41 | 1 | 90 | 11 | 42 | 14 | 39 | 9890 |
| 5 1-Amino-2-butanol | 89 | C4H11NO | 53 | * | 013552-21-1 | 706 | 42 | 34 | 1 | 99 | 29 | 28 | 0 | 39 | 8925 |
| 6 2-Propanol, 1-amino- | 75 | C3H9NO | 40 | | 000078-96-6 | 108205 | 37 | 60 | 3 | 68 | 14 | 16 | 0 | 25 | 9839 |
| 7 3-Aminopropionitrile | 70 | C3H6N2 | 40 | | 000151-18-8 | 108159 | 36 | 28 | 1 | 95 | 32 | 16 | 5 | 30 | 8913 |
| 8 3-Aminopropionitrile | 70 | C3H6N2 | 40 | | 000151-18-8 | 680 | 35 | 33 | 2 | 99 | 35 | 16 | 5 | 30 | 8908 |
| 9 1-Butanamine | 73 | C4H11N | 40 | | 000109-73-9 | 108149 | 41 | 26 | 2 | 97 | 35 | 16 | 0 | 33 | 8906 |
| 10 1,3-Propanediamine | 74 | C3H10N2 | 39 | | 000109-76-2 | 108229 | 36 | 42 | 3 | 99 | 19 | 15 | 0 | 25 | 9569 |
| 11 1,3-Propanediamine | 74 | C3H10N2 | 38 | | 000109-76-2 | 108228 | 42 | 33 | 2 | 95 | 22 | 14 | 0 | 29 | 9439 |
| 12 1-Pentanamine | 87 | C5H13N | 36 | | 000110-58-7 | 671 | 33 | 37 | 1 | 96 | 29 | 12 | 0 | 25 | 9141 |
| 13 4-Amino-1-butanol | 89 | C4H11NO | 9 | * | 013325-10-5 | 108210 | 26 | 36 | 2 | 81 | 37 | 1 | 0 | 9 | 9074 |
| 14 1-Propanamine | 59 | C3H9N | 9 | | 000107-10-8 | 108234 | 28 | 42 | 1 | 94 | 33 | 1 | 0 | 9 | 8898 |
| 15 1-Propanamine | 59 | C3H9N | 9 | | 000107-10-8 | 689 | 28 | 33 | 2 | 99 | 35 | 1 | 0 | 9 | 8873 |
| 16 1-Propanol, 3-amino- | 75 | C3H9NO | 9 | | 000156-87-6 | 675 | 32 | 37 | 2 | 99 | 29 | 1 | 0 | 9 | 9132 |
| 17 Ethylamine | 45 | C2H7N | 9 | | 000075-04-7 | 684 | 31 | 50 | 3 | 78 | 25 | 1 | 0 | 9 | 9763 |
| 18 Monoethanolamine | 61 | C2H7NO | 9 | | 000141-43-5 | 108158 | 32 | 46 | 1 | 76 | 30 | 1 | 0 | 9 | 9079 |
| 19 1-Butanamine, 3-methyl- | 87 | C5H13N | 9 | | 000107-85-7 | 670 | 30 | 40 | 2 | 84 | 35 | 1 | 0 | 9 | 9007 |
| 20 1-Hexanamine | 101 | C6H15N | 9 | | 000111-26-2 | 108144 | 29 | 37 | 2 | 99 | 37 | 1 | 0 | 9 | 8966 |

Figure 67 GC-MS evaluation of unknown peak MEA-Ethylamine system

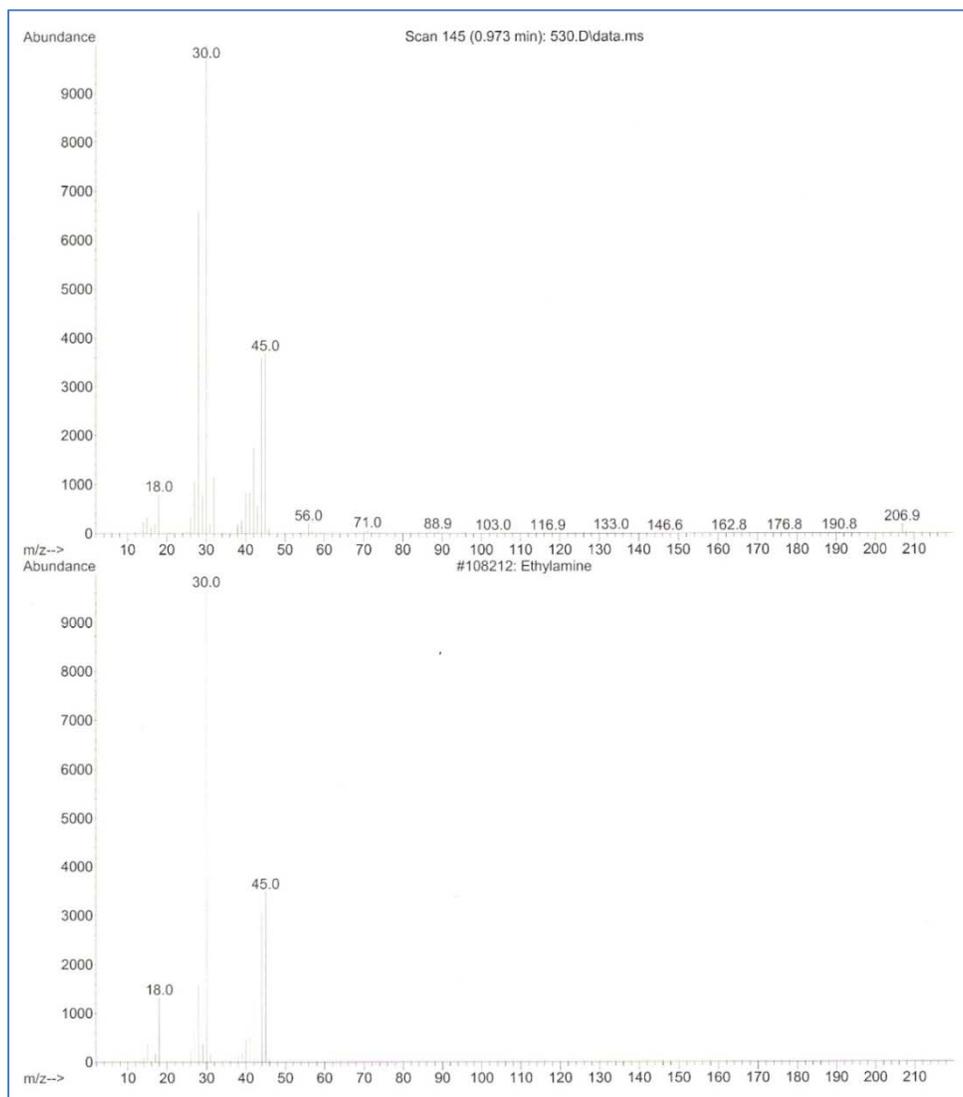


Figure 68 Spectrum of Ethylamine of MEA-Ethylamine system

8.3.4 Summary of Second Series of MEA Solvent Purification

A number of clean and degraded MEA solvents were thermally reclaimed. The number of degradation products formed in the MEA system in post-combustion are fewer than with blended amine, and they have a merit that most of the MEA degradation products would not contaminate the distillate and will be left behind in the residue, with the exception of ammonia and ethylamine. The reclaimer solvent under vacuum would reduce the reclamation cycles and the need for water for dilution. This would enhance solvent recovery so as to be similar to the traditional MEA reclaimer.

A summary of solvent recovery (specific and overall) is given in Figure 69, excluding the solvent recovered from washing the apparatus after the test was concluded. Figure 70 shows the solvent recovery including the recovered solvent from washing. The latter gives the net solvent recovery. Washing of the reclaimer equipment will be carried out at the end of the reclamation cycle, so the washed amine should be accounted for.

The solvent recovery of MEA could be enhanced at vacuum pressure. However, the recovery was reduced as the degradation product concentration increased. Although the residual content of amine was reduced, in reality, the quantity of residue was significantly increased. The solvent amount in terms of percentage in residue, which is considered as loss of solvent, is also illustrated in Figure 69 and 70.

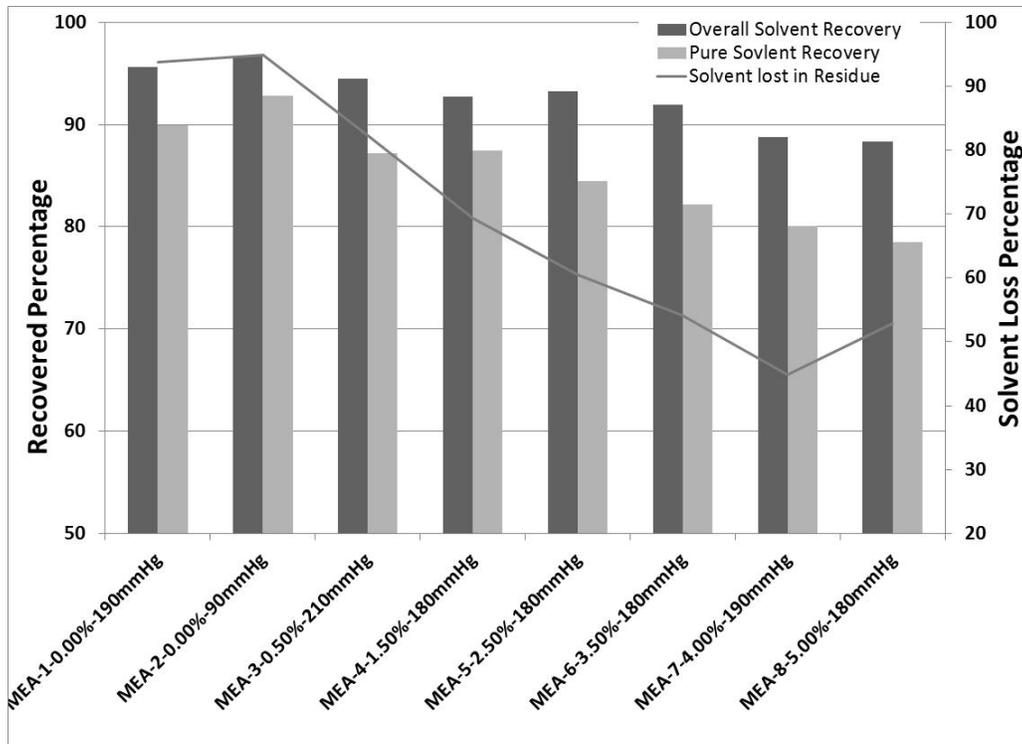


Figure 69 MEA solvent recovery for 8 tests excluding solvent recovered by washing

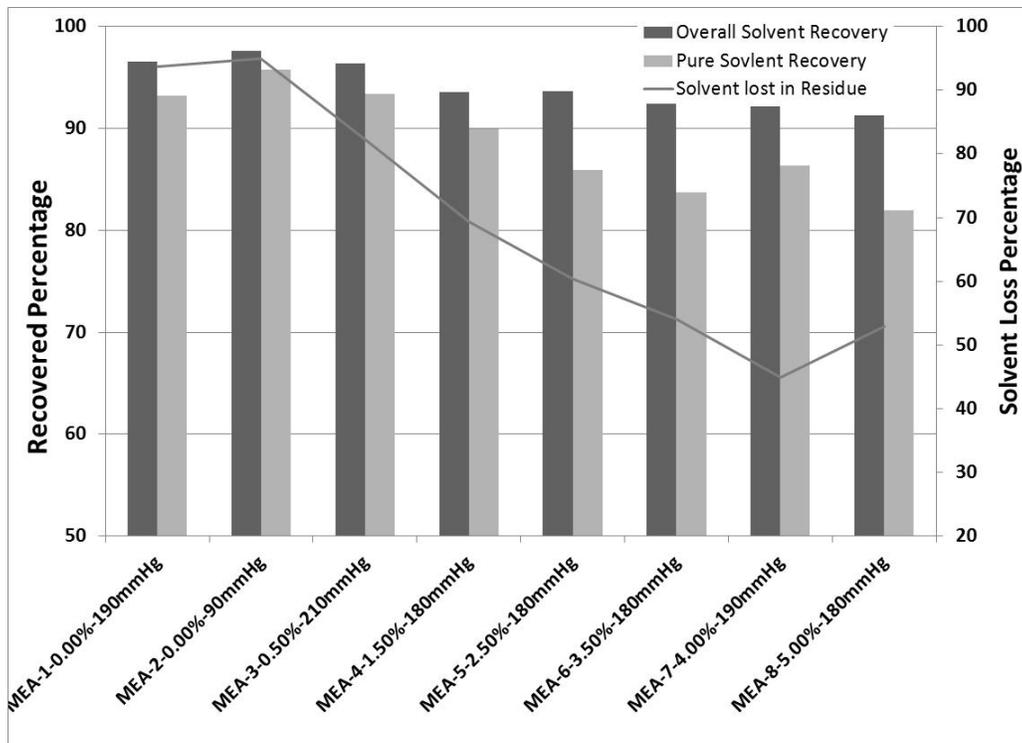


Figure 70 MEA solvent recovery for 8 tests including solvent recovered by washing

8.4 Concluding Remarks

- 1 Traditional MEA reclamation seems an unattractive option to purify degraded solvent due to its long reclamation time and excessive consumption of utilities.
- 2 Thermal stability of MEA, whether in pure form or solvent, at a concentration of 5M was tested. MEA solvent was found to be very sensitive to temperature when approaching 147°C, which is in agreement with what has been reported in the literature. Identification of this effect was accomplished by measuring the change of solvent concentration and refractive index.
- 3 The aim in the first series of tests was to find the optimum operating conditions for purifying clean and degraded MEA solvent. Simple and fraction distillation set-up configurations were used, and thermometers were used to measure temperature.
 - 3.1 MEA solvent recovery was improved as the vacuum increased. The optimum condition was at 260 mmHg for clean or low degraded solvents. The preliminary optimum solvent recovery was around 97% for both cases.
 - 3.2 Increased vacuum also reduced the need for long solvent reclamation cycles and cut water dilution and energy consumption by at least 95%.
- 4 In the second series of tests, the effect of degradation product concentrations on solvent recovery was examined at the new optimum operating conditions with respect to purifying clean, degraded, and CO₂ loaded MEA solvents. The fractionation distillation set-up was improved by using thermocouples to measure temperature and integrating these measurements with data collector and analyser software. Solvent loss was minimized, and enhanced cooling equipment was used.

- 4.1 Degradation products and heat stable salts that were expected to form from MEA degradation were selected and mixed with amine to create degraded MEA solvent. Total degradation product content was varied from 0.5 to 5 wt%. HSSs neutralization with 50% NaOH was applied prior the test.
- 4.2 To improve solvent recovery for degraded and CO₂ loaded solvents, new optimum conditions are recommended, specifically a lower vacuum pressure (i.e., 210 to 180 mmHg) than the previously considered optimum (i.e., 260 mmHg). One case of deeper vacuum of 90 mmHg was tested just to investigate the MEA recovery in blended amine that requires deeper vacuum.
- 4.3 MEA recovery reduced as degradation product content increased. At degradation content of 1.5 wt%, total solvent recovery was 93.55% and amine concentration in distillate was 90%. For 5 wt% degradation content, total solvent recovery was 91.27% and amine concentration in distillate was 82%.
- 4.4 High degradation content means difficult solvent reclamation and higher solvent loss in the reclaimer waste; therefore, solvent degradation should not be allowed to exceed 1.5 wt%.
- 4.5 It is concluded that two degradation products are likely to contaminate the recovered MEA solvent: ammonia and ethylamine. All other degradation products and neutralized HSSs did not appear in any distillate collected. There is a need to remove these contaminants in the solvent.

Chapter 9 MEA/MDEA Solvent Purification by Thermal Distillation

9.1 Chapter introduction

This chapter covers the laboratory work on recovery of 5M MEA/MDEA solvents from their degradation products. The laboratory work is split into three stages: thermal degradation study, recovery of MEA/MDEA solvent (first series), and recovery of MEA/MDEA solvent (second series). The degradation products used in the preliminary work might not be the specific degradation products for a relevant solvent under study, but in the final work, the only possible degradation products formed from the respective solvents were used. Degradation contents were varied from a few thousand ppm to 5 wt.

9.2 Thermal degradation studies

The thermal degradation tests were carried out to examine the extent of solvent loss under the effect of temperature for pure MDEA solvent or MEA/MDEA blend. The approach is just to help understand the thermal degradation more than an attempt to obtain an accurate result. The aim is just to understand the thermal degradation more than an attempt to obtain accurate results at this stage. This is due to the possibility that oxidative of solvents could occur, and, therefore, changes to the solvent could be due to both thermal and oxidation degradation. Each test lasted for 3 hours of continuous heating under specific controlled temperatures, and in some cases, the tests were even run for up to 10 hours, such as in the 147°C case. Although these tests were carried out under atmospheric pressure, and this might not be the optimum method to test thermal degradation, it allowed us to study the impact of temperature on the solvent by analysing

the degraded solvents in GC-MS and measuring the refractive index. The experiments were carried out in a full reflux distillation set-up, shown in Photo 1 in Chapter 8.

9.2.1 Pure solvent thermal degradation

Thermal stability of pure MDEA solvent was tested. The observations of the solvent shows that pure MDEA is more viscous than MEA. Its appearance is a clear liquid with a light yellowish color. It is known that amines can be thermally degraded before reaching their relevant normal boiling point at atmospheric pressure (Kohl and Nielsen 1997). MDEA has been thermally degraded at 360°F or 182°C (S. A Bedell et al. 2010) while its boiling temperature is 247°C; thus, this temperature should be avoided in the reclamation of a single MDEA solvent. In the case of blended solvent, the lighter amine should be considered the limit for reclamation. For instance, in the blend of MEA/MDEA, MEA thermally degrades before MDEA.

Table 39 gives the GC-MS analysis of degraded solvents. As can be seen, the pure MDEA solvent was degraded at a higher rate than pure MEA. This means MDEA tertiary amine solvent could be more sensitive to temperature than MEA. This conclusion is also supported by the overall percentage increase in peaks, which are not solvent peaks. Unfortunately, we could not measure the refractive index for clean and degraded MEA and MDEA solvent because their refractive indices were out of range of our measuring device, a Digital Refractometer (1.3300 – 1.4488), with the exception of the clean MEA.

9.2.2 5M MEA/MDEA solvent thermal degradation

Similar to the 5M MEA experiments, blended solvent of 2.5M MEA/2.5M MDEA was thermally tested under the same conditions and up to 147°C, which is the restricted temperature for MEA solvent. Table 42 summarizes the results from GS-MS analysis, titration, and refractive index measurements. The solvent loss for MEA in the blend was more than the loss in the single solvent. The MEA loss was about 1.80% while MDEA loss was 1.40%. Overall, the MEA/MDEA solvent loss is 1.60%, while in the case of MEA alone, it was only 0.80%.

Figure 71 gives the change of the refractive index at different boiling temperatures of 5M MEA/MDEA. It was found that the blended solvent has more sensitivity to temperature than the single solvent, as can be observed in the sharp change of the blended solvent's refractive index compared to the MEA solvent alone, where the change quite gradually developed.

Table 39 Analysis of Degraded Pure Solvents by GC-MS

| | Pure MEA | Pure MDEA | Comments |
|--|-------------------------|---------------------|--|
| Reported normal boiling point, °C | 171.0 | 247.2 | (Kohl and Nielsen 1997) |
| Measured testing temperature, °C | 170.0 | 246.0 | Boiling temperature under test condition |
| Color solvent change (before → after) | Clear → light yellowish | Clear → Dark Yellow | |
| Solvent loss | 7.11 % | 12.10 % | Change in Peak Area |

Table 40 Thermal Degradation of 5M MEA/MDEA at Different Temperature

| | Reference | 147°C |
|--|-----------------|----------------|
| Color solvent appearance | Light yellowish | Dark yellowish |
| Solvent concentration, mole/L | 5.00 | 4.92 |
| Solvent concentration change, % | 0 | 1.60 |
| MEA Solvent loss, M | 0 | 0.045 |
| MDEA Solvent loss, M | 0 | 0.035 |
| Refractive Index | 1.3957 | 1.3969 |

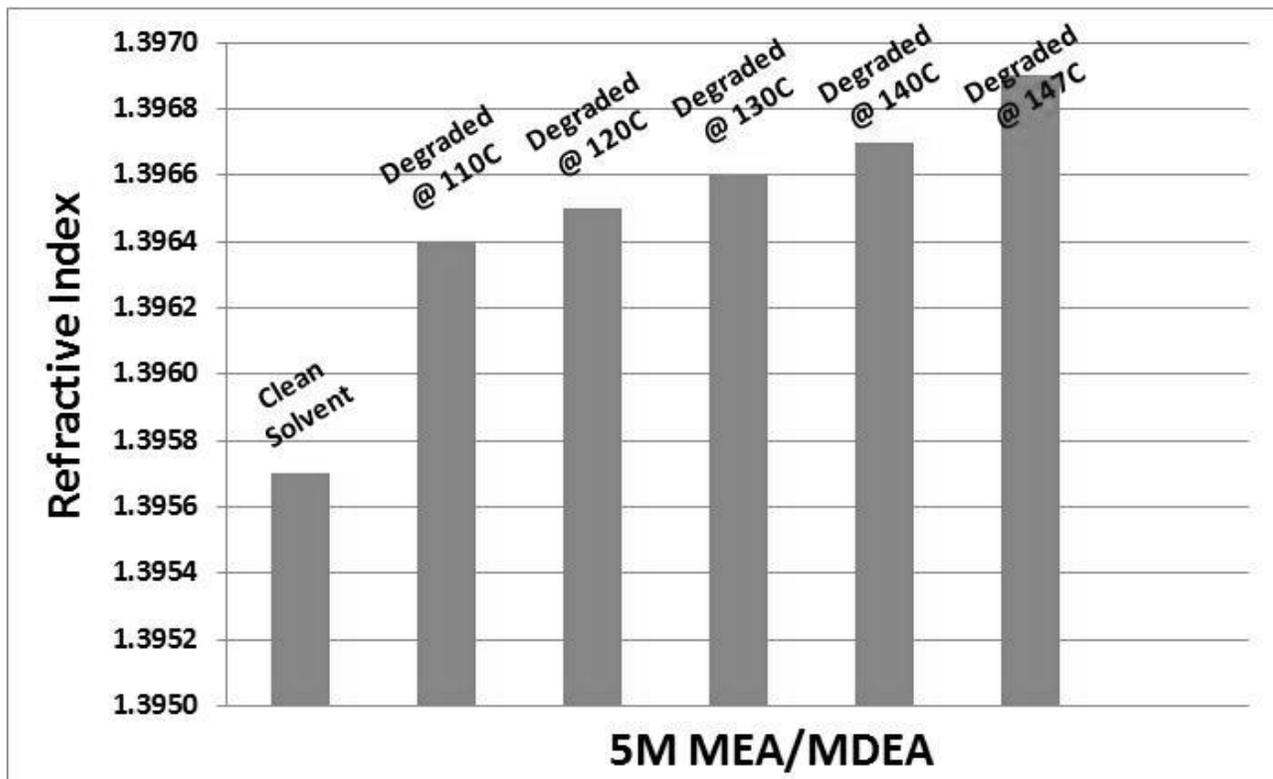
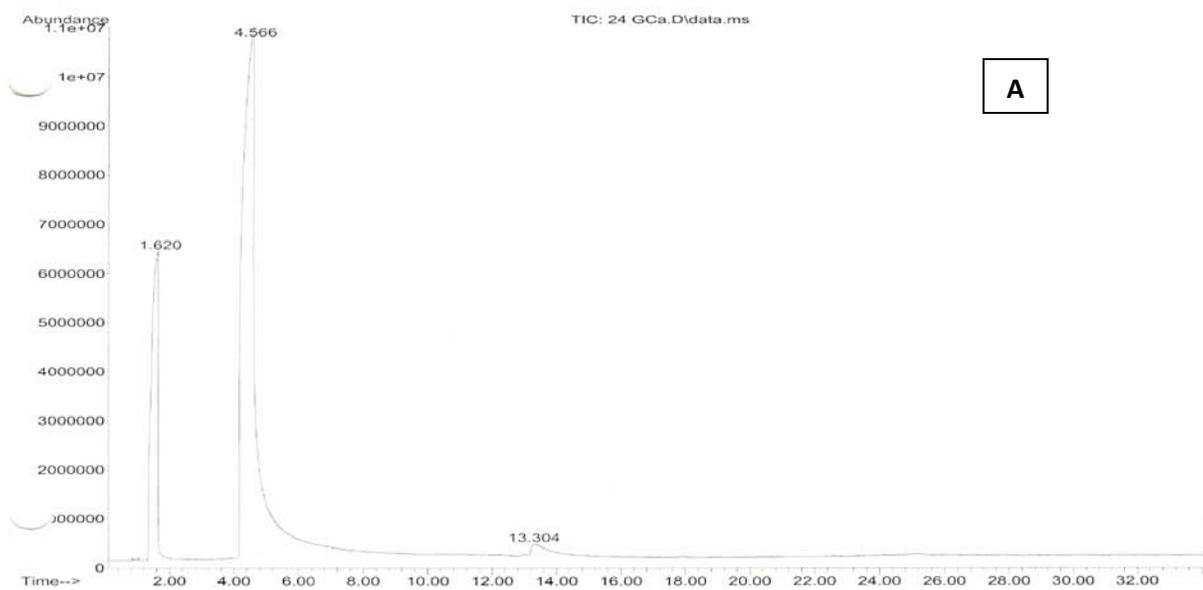
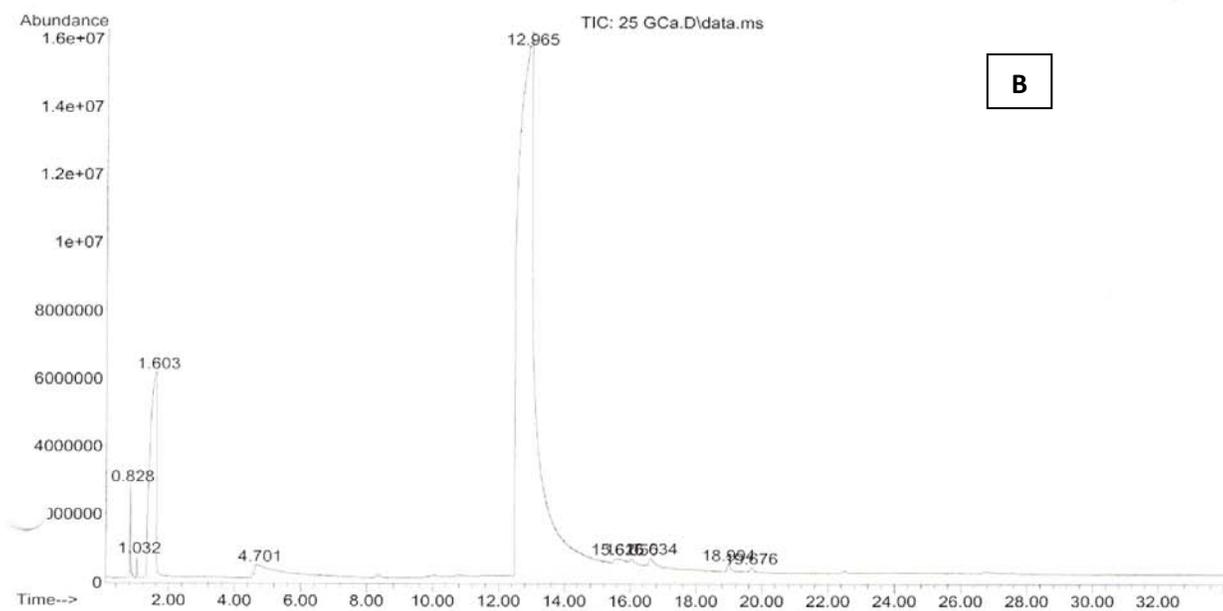


Figure 71 Refractive index for thermally degraded 5M MEA/MDEA



A



B

Figure 72 GC chromatograph for distillate (A) and residue (B) of MEA/MDEA-1-160mmH

9.3 Recovery of 5M MEA/MDEA solvent experiments

Thermal reclamation was tested in atmospheric and vacuum distillation set-ups. In the first series of experiments, a variety of MEA/MDEA solvents was tested, including clean and degraded solvents. The degradation products could be generally selected more than specifically formed from MEA/MDEA degradation. The second series of experiments was like the preliminary series except the degradation products were relevant to the specific MEA/MDEA solvent degradation. In this section, results of thermal distillation of MEA/MDEA are given with detailed analysis of the recovery of each solvent.

9.3.1 First series of experiments for MEA/MDEA solvent purification

A blend of MEA and MDEA was tested in the second test series to investigate recovery of blended solvent under the most favourable operating conditions. This section presents the results of 7 tests of recovery of solvent with different conditions and composition for degradation products and heat stable salts. Most tests were carried with a fixed total amine solvent concentration of 5M with a molar ratio of 2.5/2.5 between MEA and MDEA. It should be emphasised that this is not the only test conducted; many more have been done either to confirm the results of a test or to explore different operating conditions. The screening process for the recovery of blended solvent showed that the solvent could be recovered with more success at vacuum pressures much lower than was found in MEA reclamation (i.e., <260 mmHg). Figure 73 summarized the Series I tests and degradation products selected for each test. Monomethylethanolamine (MMEA) was used only for two tests.

9.3.1.1 MEA/MDEA recovery at 160 mmHg (MEA/MDEA-1-160mmHg)

The first test for clean MEA/MDEA blended solvent was carried out at a vacuum of 160 mmHg. The total solvent concentration was 5.5 M at a molar ratio of 5/0.5. The evaporation was carried out at a constant pressure of 160 mmHg. It began at room temperature and was terminated when the distillation flask temperature approached 147°C. The solvent recovery was quite high at 96.41%, while the pure MEA recovery was 90%, Figure 72 (A). A very small amount of solvent, mainly MDEA, which is the higher boiling point amine, was left behind in the residue, as shown in Figure 72 (B).

9.3.1.2 MEA/MDEA recovery at 110-160 mmHg (MEA/MDEA-2-110/160mmHg)

The second test involved degraded MEA/MDEA amine. The total solvent concentration was 5M at a molar ratio of 2.5/2.5, and the concentration of five degradation products was 2,000 ppm each (total of 10,000 ppm or 1 wt%). The evaporation was carried out at a constant pressure of 160 mmHg. It started at room temperature and terminated when the distillation flask temperature approached 147°C. Then, the evaporation started again at a much deeper vacuum of 110 mmHg to maximize the heavy portion of solvent recovery (i.e., MDEA). The total solvent recovery was high at 97.5%, as shown in Table 9. The distillate chromatograph shows the high recovery of water, MEA, and MDEA achieved; however, the penalty of that high recovery is that the distillate was contaminated with all the degradation products in different levels. The degradation products found in the distillate are imidazole, acetamide, and bicine, but in general, all five degradation products were found in the distillate. To explain this, there is a possibility that the entrainment was due to aggressive evaporation. Table 41 gives more details on degradation product concentration.

| | Test Code | | | | | | | |
|---|--------------------------------------|--------------------|------------------------|------------------------|-----------------------|-----------------------|-------------------|-----------------------|
| | | MEA/MDEA-1-160mmHg | MEA/MDEA-2-110/160mmHg | MEA/MDEA-3-100/160mmHg | MEA/MDEA-4-70/130mmHg | MEA/MDEA-5-60/260mmHg | MEA/MDEA-6-65mmHg | MEA/MDEA-7-70/205mmHg |
| | Degradation Level, wt% | 0 | 1 | 1 | 1.5 | 0.6 | 0.6 | 4.75 |
| | CO2 Loading, mol/mol | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Degradation Products | Ammonium Hydroxide | | | | | | | |
| | 2-(Methylamino) Ethanol | | | | | | | |
| | Amino-2-propanol | | | | | | | |
| | 3-Picoline | | | | | | | |
| | Ethylamine | | | | | | | |
| | 1,3-Diaminopropane | | | | | | | |
| | Imidazole | | X | X | X | X | X | X |
| | Bicine | | X | X | X | X | X | X |
| | Acetamide | | X | X | X | X | X | X |
| | N-Acetyethanolamine | | X | X | X | X | X | X |
| | 1-(2-Hydroxyethyl)-2-Imidazolidinone | | X | X | X | X | X | X |
| | Monomethylethanolamin | | | | | X | X | |
| Heat stable salts (HSS) Neutralized or Organic Acids Cause them | Formic Acid | | | | | | | X |
| | Acetic Acid | | | | | | | X |
| | Propionic Acid | | | | | | | |
| | Butyric Acid | | | | | | | |
| | Lactic Acid | | | | | | | |
| | Malonic Acid | | | | | | | X |
| | Glycolic Acid | | | | | | | X |
| | Oxalic Acid | | | | | | | X |
| | Sodium Thiocyanate | | | | | | | |
| | Sodium Thiosulfate | | | | | | | |

Figure 73 Series I for MEA/MDEA recovery tests

Table 41 Distribution of degradation products for MEA/MDEA-2-110/160mmHg

| | Initial Fill | | Distillate | | Residue | |
|---|-----------------|---------------|-----------------|---------------|-------------------|---------------|
| | Concn, ppm | Weight, gm | Concn, ppm | Weight, gm | Concn, ppm | Weight, gm |
| Imidazole | 2,026.0 | 0.0745 | 1,156.7 | 0.0413 | 94,857.14 | 0.0332 |
| Bicine | 2,051.0 | 0.0741 | 780.45 | 0.0279 | 130,000.0 | 0.0462 |
| Acetamide | 1,975.7 | 0.0714 | 1,319.63 | 0.0472 | 96,142.86 | 0.0242 |
| N-Acetyethanolamine | 1,908.8 | 0.069 | 406.31 | 0.0145 | 155,714.29 | 0.0545 |
| 1-(2-Hydroxyethyl)-2-Imidazolidinone | 1,981.25 | 0.0716 | 451.75 | 0.0161 | 158,571.43 | 0.0555 |

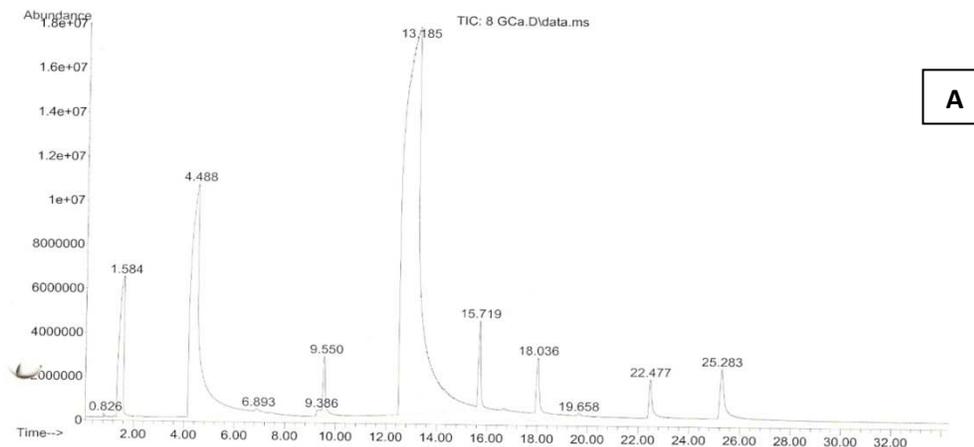
Table 42 Distribution of degradation products for MEA/MEA-3-110/160mmHg

| | Initial Fill | | Distillate | | Residue | |
|---|--------------|----------------|--------------|---------------|----------------|---------------|
| | Concn, ppm | Weight, gm | Concn, ppm | Weight, gm | Concn, ppm | Weight, gm |
| Imidazole | 2,051 | 0.07581 | 1,144 | 0.041 | 57,063 | 0.0342 |
| Bicine | 1,908 | 0.07054 | 104 | 0.004 | 111,271 | 0.0668 |
| Acetamide | 2,062 | 0.07583 | 1,550 | 0.056 | 32,949 | 0.0198 |
| N-Acetyethanolamine | 1,975 | 0.07265 | 673.9 | 0.0244 | 80,474 | 0.0483 |
| 1-(2-Hydroxyethyl)-2-Imidazolidinone | 1,981 | 0.07285 | 147.6 | 0.0053 | 112,527 | 0.0675 |

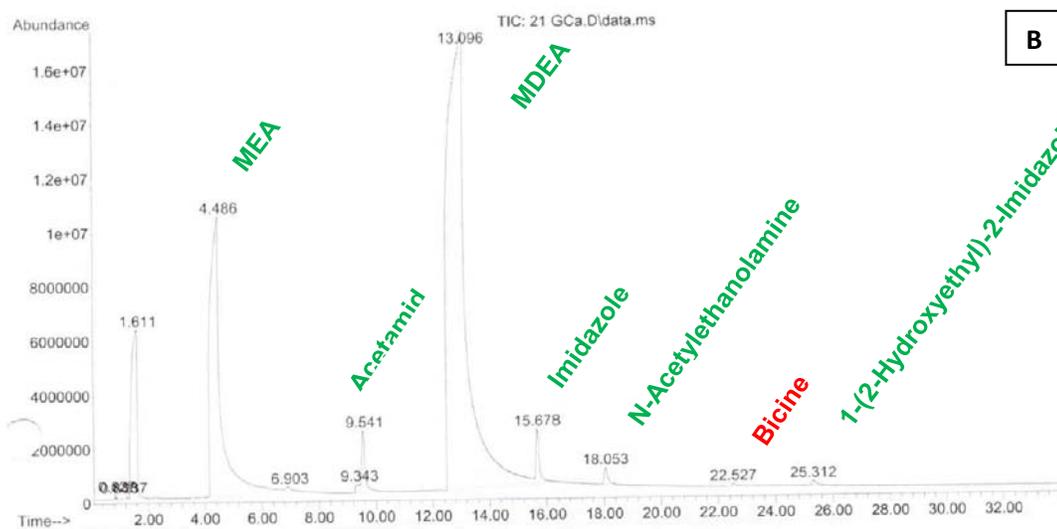
9.3.1.3 MEA/MDEA recovery at 100-160 mmHg (MEA/MDEA-3-100/160mmHg)

The objective was to repeat the test of MEA/MDEA-2-110/160mmHg but under more controlled evaporation to determine the extent of degradation products that could contaminate the recovered solvent distillate. The third test involved degraded MEA/MDEA amine with a total solvent concentration of 5M and a molar ratio of 2.5/2.5. The concentration of the five degradation products was 2,000 ppm each (total of 10,000 ppm). The evaporation was carried out at a constant pressure of 160 mmHg. It began at room temperature and was terminated when the distillation flask temperature approached 147°C. Then, the evaporation was started again at a much deeper vacuum of 100 mmHg to maximize the solvent recovery.

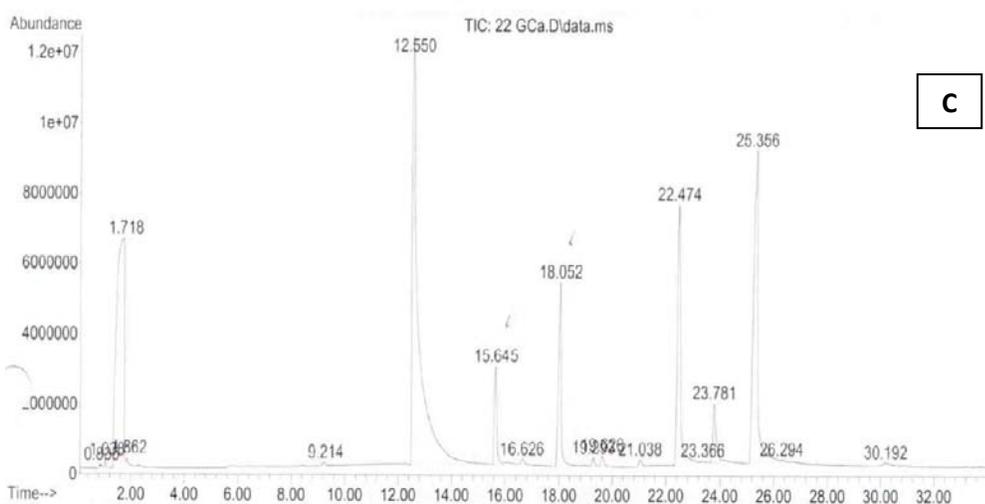
Figure 74 provides the GC chromatograph of the samples obtained from this test, the original solvent before the distillation, the distillate, and the residue. The solvent recovery was high at 98%. The degradation products were again found in the distillate and now in different intensities despite the fact that aggressive evaporation was prevented by careful control of the distillation process. The major degradation products found in the distillate were acetamide, imidazole, and N-acetylethanoamine. In the residue, as shown in Figure 42 (C), the degradation products were found in significant amounts, except for acetamide, of which it is believed that it most likely travelled with the solvent. Surprisingly, a new peak was found at the retention point 6.9. This new chemical is believed to have formed due to MEA degradation during the reclamation, which was allowed to proceed at temperatures beyond 147°C. Table 42 provides the details of degradation product distribution in the solvent, distillate, and residue of the test.



A



B



C

Figure 74 GC chromatograph of degraded solvent (A), distillate (B), and residue (C) (MEA/MDEA-3-100/160mmHg)

9.3.1.4 MEA/MDEA recovery at 70-130 mmHg (MEA/MDEA-4-70/130mmHg)

This experiment tested the reclamation of 5M MEA/MDEA (molar ratio of 2.5/2.5). The total degradation product level was 1.5wt% (each degradation product was 3,000 ppm). The objective was to observe the extent of solvent recovery when the degradation level was 1.5 wt% with gradual reduction in operating vacuum. The distillation process was carried out by decreasing the vacuum starting at 130 mmHg, and then the pressure was reduced gradually to 110, 105, 100, 90, and 70 mmHg. The process was terminated due to very low levels of liquid in the distillation flask at 70 mmHg and 137°C. The solvent recovery was 94.86%, which was lower than the previous tested system of 1 wt% degradation products. The systematic reduction of the vacuum was used to enhance solvent recovery; this means that when the degradation level is high, the recovery of solvent becomes difficult despite vacuum reduction control. Some of the heavier portions of the MDEA solvent were trapped in the residue, and there was no way that they could be recovered without dilution with water.

Although four degradation products were found to be concentrated in the residue, all degradation products were found at different concentrations, except acetamide, which was found in higher concentrations in the distillate than in the residue. In the residue, very small amounts of MEA were found in low concentrations of 0.48 wt%. It is obvious that the continuous reclamation at higher temperatures can degrade this MEA, but this might be an acceptable penalty in order to recover the heavier and more expensive MDEA. Table 43 provides the distribution of degradation products in the solvent, distillate, and residue.

Table 43 Distribution of degradation products for MEA/MEA-4-70/130mmHg

| | Initial Fill | | Distillate | | Residue | |
|---|-----------------|----------------|-----------------|---------------|------------------|---------------|
| | Concn, ppm | Weight, gm | Concn, ppm | Weight, gm | Concn, ppm | Weight, gm |
| Imidazole | 2,923.80 | 0.10593 | 1,502.37 | 0.0516 | 30,166.36 | 0.0543 |
| Bicine | 3,015.74 | 0.10926 | 803.46 | 0.0276 | 45,361.42 | 0.0817 |
| Acetamide | 3,276.33 | 0.11811 | 2,119.78 | 0.0725 | 25,346.46 | 0.0456 |
| N-Acetyethanolamine | 3,032.27 | 0.10931 | 1,242.11 | 0.0425 | 37,132.32 | 0.0668 |
| 1-(2-Hydroxyethyl)-2-Imidazolidinone | 3,029.18 | 0.1092 | 864.66 | 0.0296 | 44,241.14 | 0.0796 |

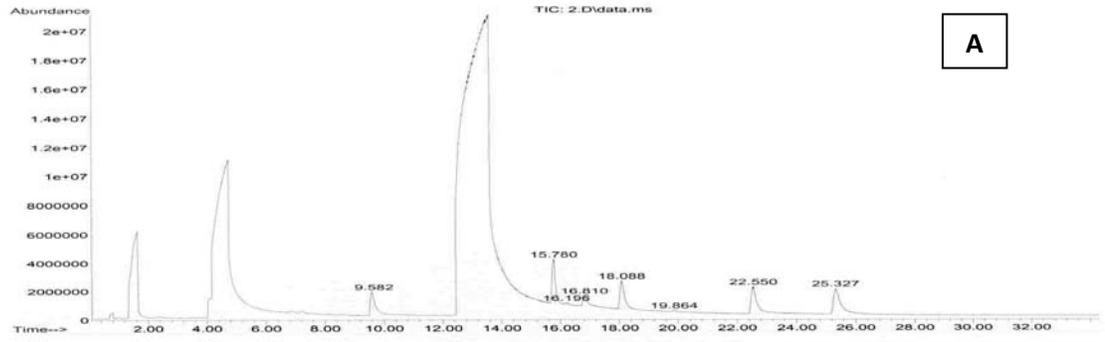
Table 44 Distribution of degradation products for MEA/MEA-5-60/260mmHg

| | Initial Fill | | Distillate | | Residue | |
|---|--------------|----------------|-----------------|---------------|------------------|---------------|
| | Concn, ppm | Weight, gm | Concn, ppm | Weight, gm | Concn, ppm | Weight, gm |
| Imidazole | 1,130 | 0.03931 | 134.94 | 0.0045 | 39,139.55 | 0.0348 |
| Bicine | 1,045 | 0.03636 | 0.0 | 0.0 | 40,848.93 | 0.0364 |
| Acetamide | 912 | 0.03173 | 437.90 | 0.0145 | 19,319.64 | 0.0172 |
| N-Acetyethanolamine | 1,000 | 0.03479 | 264.78 | 0.0088 | 29,215.73 | 0.0260 |
| 1-(2-Hydroxyethyl)-2-Imidazolidinone | 750 | 0.02609 | 0.0 | 0.0 | 29,317.42 | 0.0261 |
| MMEA | 980 | 0.03409 | 1,027.24 | 0.034 | 0.0 | 0.0 |

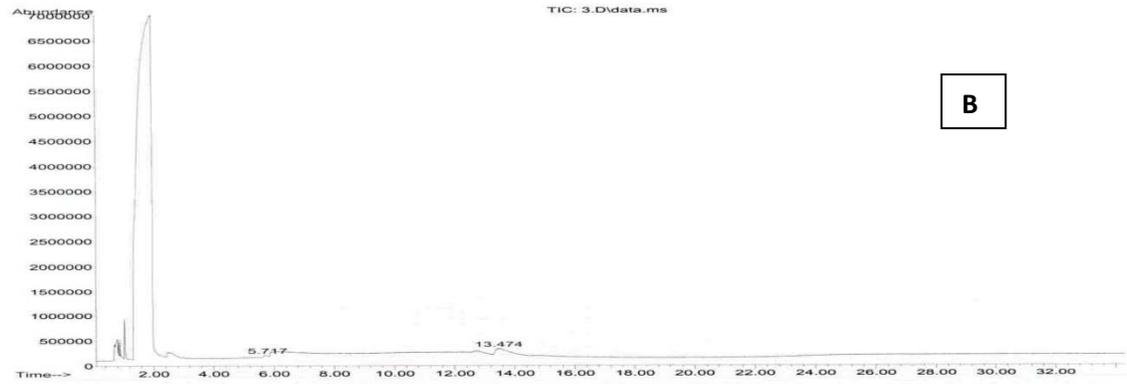
9.3.1.5 MEA/MDEA recovery at 60-260 mmHg (MEA/MDEA-5-60/260mmHg)

Reclamation of degraded 5M MEA/MDEA solvent was carried out (molar ratio of 2.5/2.5). The six degradation products used in this solvent were at concentrations of 1,000 ppm each. The five degradation products were the same as those reported in previous tests; however, a new degradation product added here was MMEA. The distillation process was carried out at step one to recover MEA and water, while the second step was to recover MDEA. The residue collected was a very dark brown. The total solvent recovery was 97.44%. The recovery of solvent occurs in two steps: recovery of water and MEA (at 260 mmHg), and recovery MDEA (at 60 mmHg).

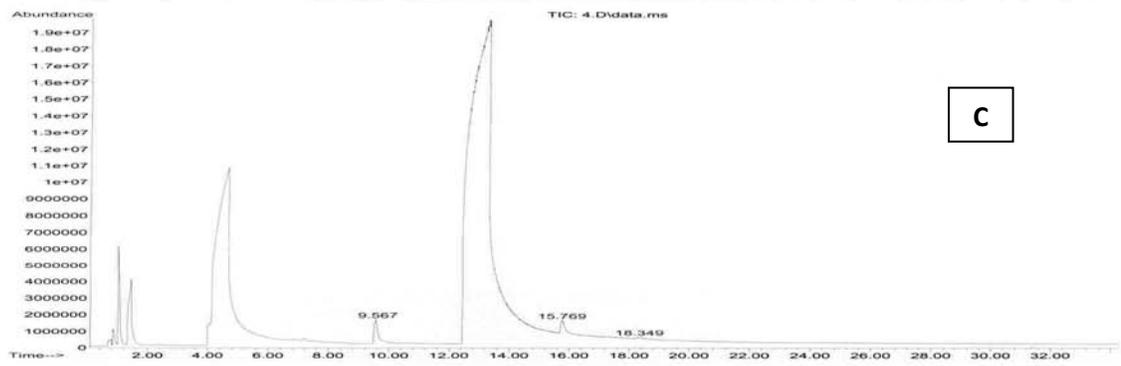
Four samples obtained from the tests were analysed using GC-MS. These samples were solvent, Distillate I, Distillate II, and residue. GC chromatographs generated by GC-MS are given in Figure 75. As can be seen, Distillate B was mainly water with traces of MEA and MDEA. In the second round of distillation, Distillate C was expected to contain recovered amines, but based on the results, some degradation products were found (only three), along with MMEA, in contrast with the previous tests, where the whole set of degradation products could be found in the distillate collected. The whole MMEA and most of the acetamide were found in the distillate, as seen in Figure 75 (C). Regarding the residue, it had all other degradation products, but surprisingly, two new peaks were seen, suggesting thermal degradation occurred. They most likely came from the decomposition of MEA. The residue sample was diluted with water to make it possible to extract and analyse its components. The distribution of degradation products is given in Table 44.



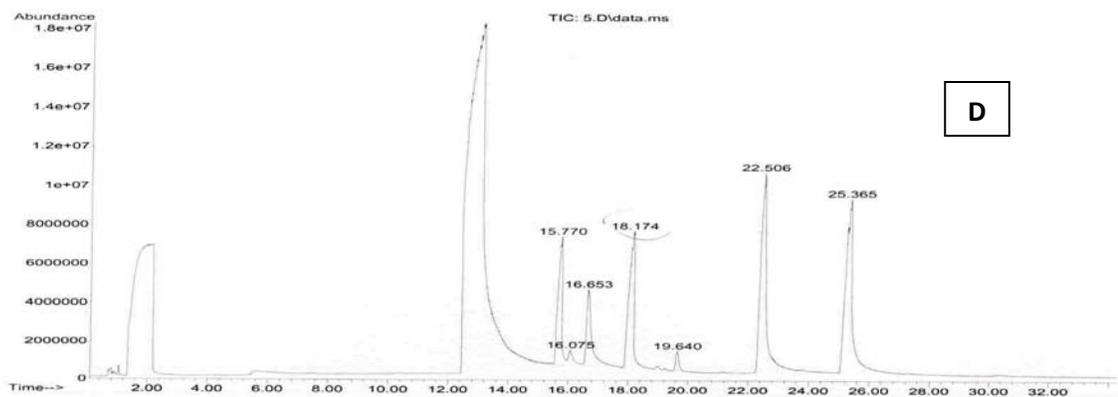
A



B



C



D

Figure 75 GC chromatograph for solvent (A), distillates (B & C), and residue (D)
(MEA/MDEA-5-60/260mmHg)

9.3.1.6 MEA/MDEA recovery at 65 mmHg(MEA/MDEA-6-65mmHg)

The same solvent, degradation products and concentrations used in the previous test have been utilized here as well. The distillation process was carried out at a fixed vacuum pressure starting at 65 mmHg and at room temperature. The new operation philosophy shows that it is possible to recover the whole solvent in just one operating vacuum at moderate temperatures. Samples of distillate were collected four times during the distillation and were analysed using GC-MS.

Figure 76 shows the temperature profiles for the distillation flask as well as the temperature at the top, just at the entrance of the condenser. Three distinctive phases of recovery of water, then MEA, and then MDEA were very clear with stable temperature for some time in each stage of recovery. The samples obtained were analysed, and Figure 77 shows the solvent after adding degradation products (A), the distillates (B,C,D,E) and the residue (F). In Distillate I (B), most of the water was recovered, and Distillate II consists of some water and some MEA with traces of MMEA degradation product, which were found in Distillate II (C) only. Distillate III (D) is mainly MEA and MMEA with small traces of MDEA and acetamide. Regarding Distillate IV (E), the major portion of this cut was MDEA with the presence of MEA, acetamide, imidazole, and N-acetyethanolamine. The collected residue (F) has the largest portion of the degradation products and at a higher concentration. A new peak was found, possibly due to the thermal degradation of MEA. Table 45 provides the concentration distribution for the degradation products as obtained from the calibration curves.

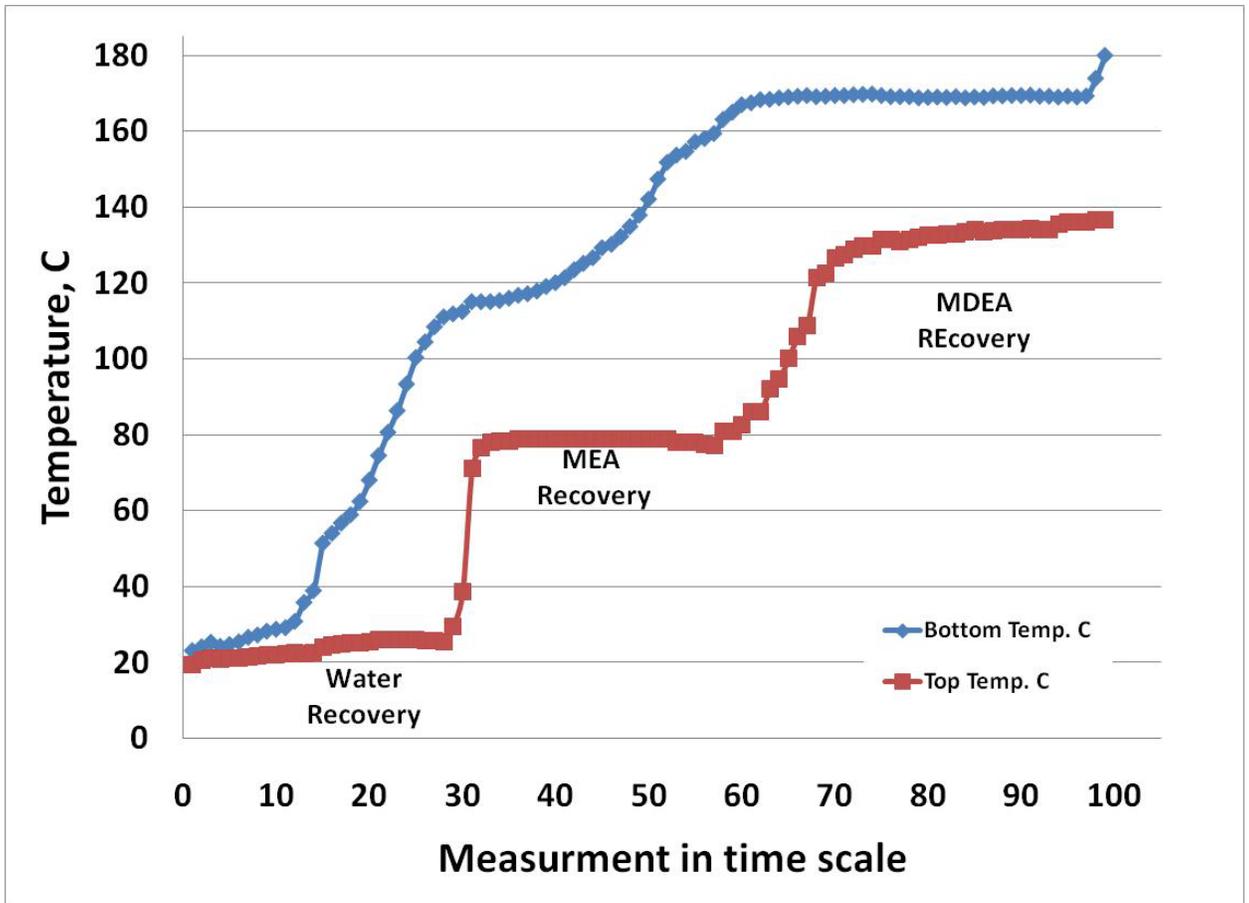


Figure 76 Temperature profiles of top and bottom (MEA/MDEA-6-65mmHg)

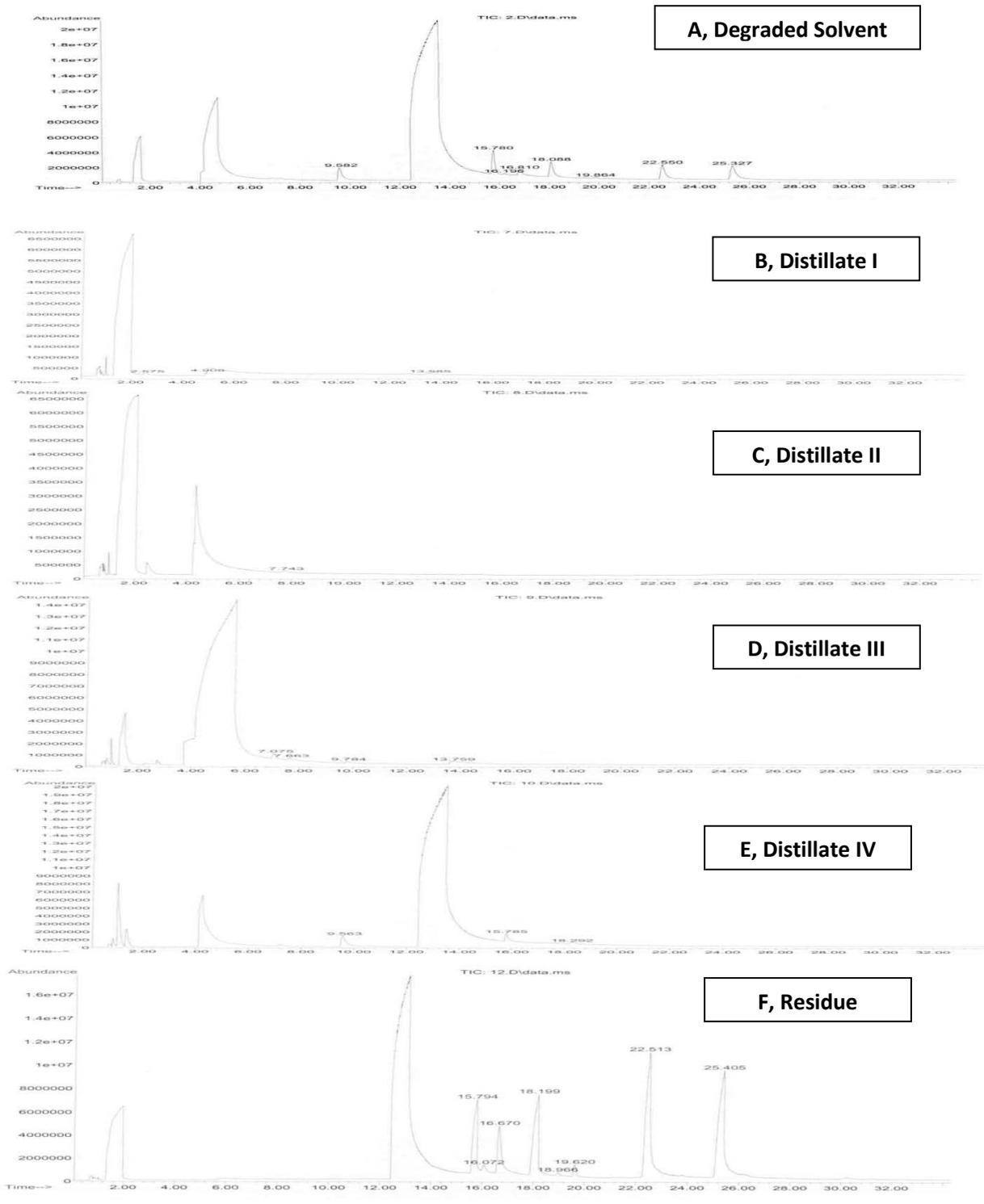


Figure 77 GC chromatograph for solvent (A), distillates (B,C,D,E), and residue (F) (MEA/MDEA-6-65mmHg)

Table 45 Distribution of degradation products for MEA/MDEA-6-65mmHg

| | Initial Fill | | Distillate | | Residue | |
|---|--------------|----------------|---------------|----------------|------------------|----------------|
| | Concn, ppm | Weight, gm | Concn, ppm | Weight, gm | Concn, ppm | Weight, gm |
| Imidazole | 1,130 | 0.04161 | 100 | 0.0036 | 67,822.50 | 0.03801 |
| Bicine | 1,045 | 0.03848 | 0.0 | 0.0 | 68,708.8 | 0.03848 |
| Acetamide | 912 | 0.03358 | 913.9 | 0.03358 | 0.0 | 0.0 |
| N-Acetyethanolamine | 1,000 | 0.03682 | 30 | 0.0011 | 63,807.5 | 0.03572 |
| 1-(2-Hydroxyethyl)-2-Imidazolidinone | 750 | 0.02762 | 0.0 | 0.0 | 49,312.5 | 0.02762 |
| MMEA | 980 | 0.03608 | 995.14 | 0.03608 | 0.0 | 0.0 |

Table 46 Distribution of degradation products for MEA/MDEA-7-70/205mmHg

| | Initial Fill | | Distillate | | Residue | |
|---|----------------|----------------|-----------------|---------------|------------------|---------------|
| | Concn, ppm | Weight, gm | Concn, ppm | Weight, gm | Concn, ppm | Weight, gm |
| Imidazole | 4,787.0 | 0.1634 | 6,022.13 | 0.1634 | 0.0 | 0.0 |
| Bicine | 7,704.0 | 0.16055 | 0.0 | 0.0 | 22,935.36 | 0.1605 |
| Acetamide | 4,184.0 | 0.1428 | 1,754.15 | 0.0476 | 13,601.42 | 0.0952 |
| N-Acetyethanolamine | 4,803.0 | 0.16393 | 1,490.97 | 0.0405 | 17,639.48 | 0.1235 |
| 1-(2-Hydroxyethyl)-2-Imidazolidinone | 3,584.0 | 0.12232 | 0.0 | 0.0 | 14,474.56 | 0.1223 |
| Sodium formate | 4,702.0 | 0.16048 | 0.0 | 0.0 | 22,925.61 | 0.1605 |
| Sodium acetate | 4,769.0 | 0.16277 | 0.0 | 0.0 | 23,252.28 | 0.1628 |
| Sodium malonate | 4,763.0 | 0.16256 | 0.0 | 0.0 | 23,223.03 | 0.1626 |
| Sodium glycolate | 4,639.0 | 0.15833 | 0.0 | 0.0 | 22,618.44 | 0.1583 |
| Sodium oxalate | 4,811.0 | 0.1642 | 0.0 | 0.0 | 23,457.06 | 0.1642 |

9.3.1.7 MEA/MDEA recovery at 70-205 mmHg (MEA/MDEA-7-70/205mmHg)

A degraded solvent of MEA/MDEA was prepared. Total solvent concentration was 5M with a molar ratio of a blend of 2.5/2.5. This solvent is a mixture of five degradation products and five organic acids (heat stable salts) with 4,000 ppm added for each. Neutralization with 50 wt% NaOH was added in an equivalent amount to the organic acids added previously. The distillation recovery process was carried out in two stages at two vacuum values of 205 mmHg first (recovery of water) and then at 70 mmHg (recovery of MEA and MDEA). The heating intensity was at a medium level to produce a gentle boiling.

Temperature profiles for the experiment during the 205 mmHg and then 70 mmHg periods are given in Figure 78. The first part of the temperature profile shows the water recovery. Once most of the water was removed and MEA recovery began, a short drop in temperature in the top section of the distillation set-up occurred, indicating that the water cut was completed and the second chemical vapour had started. At this point, the distillation process can be terminated, mainly to collect the distillation cut of water. The second part of the profiles of the deeper vacuum shows the same trend, where MEA recovery is likely ending when there is a drop in the top temperature and then a gradual increase in temperature occurs. After this, MDEA recovery began, and there was a clear indication when the top and bottom distillation temperature are quite fixed over a certain time until the distillation process is finished.

The collected samples from this experiment were neutralized and degraded solvent, distillate cut 1 (water recovery), distillate cut 2 (MEA recovery), distillate cut 3 (MDEA recovery), and residue. Figure 79 (B) mainly shows the presence of water with no traces

of MEA or MDEA. For recovery of MEA, GC chromatograph in Figure 79 (C) shows the presence of water, MEA (most), MDEA, and acetamide. The presence of acetamide shows that it will travel during MEA recovery in all scenarios tested for recovering MEA or MEA/MDEA solvents.

Distillate III, for recovery of MDEA, consists of water, MEA, an unknown new peak, acetamide, MDEA (most), imidazole and N-acetyethanolamine. The new degradation product peak is believed to be an amide formed from the addition of organic acids (heat stable salts). Residue was formed from water, MDEA, imidazole, N-acetyethanolamine, bicine, and 1-(2-hydroxyethyl)-2-imidazolidinone. The distillation was carried out to high temperatures (159°C) in the distillation flask. This might lead to the decomposition of MEA and possibly of MDEA as well; however, five new peaks were found in the residue sample (E). These new peaks are possibly organic acids or amides of organic acids, which were used to create heat stable salts. Table 8 provides the distribution of degradation products and naturalized heat stable salts. As can be see, all heat stable salts after neutralization accumulated in the residue.

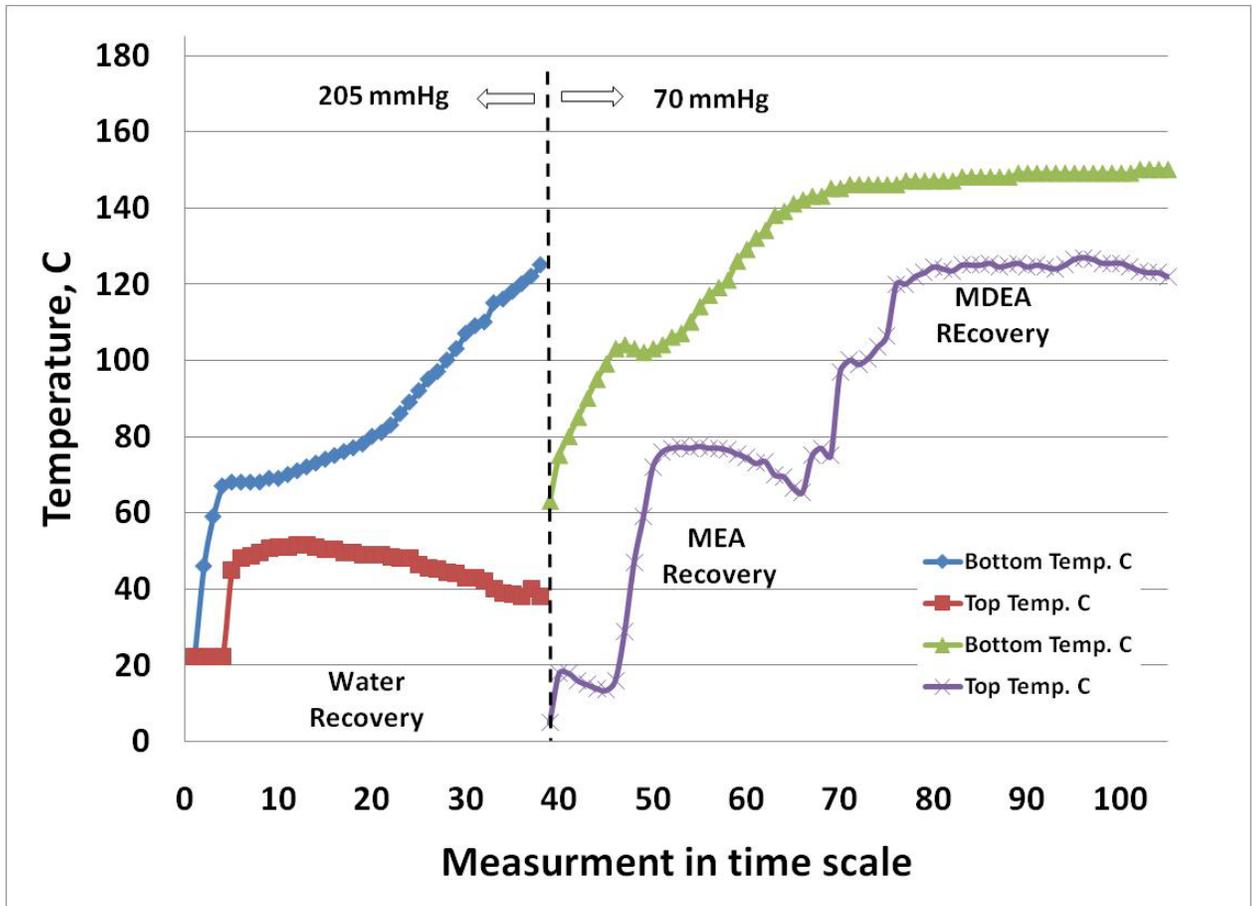


Figure 78 Temperature profiles of top and bottom (MEA/MDEA-7-70/205mmHg)

**A, Neutralized
Degraded Solvent**

B, Distillate I

C, Distillate II

D, Distillate III

E, Residue

**Figure 79 GC chromatograph for solvent (A), distillates (B,C,D), and residue
(E)(MEA/MDEA-7-70/205mmHg)**

9.3.2 Summary of first series of MEA/MDEA purification

The presence of degradation products makes the recovery of blended amine much more difficult and further lowering of vacuum is needed, as shown in Table 47, which gives the summary of the MEA/MDEA recovery tests. The solvent recovery was high and loss was minimized when the major impurities in the solvent were degradation products, but when there was a combination of degradation products and heat stable salts, it was likely that the solvent recovery would not be as high due to the fact that most of the amine was trapped in the distillation process residue, unless water dilution and re-evaporation were used. Further details and information are given for each experiment in this section.

The degradation product level was found to impact solvent recovery to a great extent. At higher degradation levels, recovery would become difficult even when allowing increase of distillation temperature or reducing the pressure further. Figure 80 shows the relationship between the degradation level and solvent recovery. Although the results were not achieved under the same operating conditions, this graph can help demonstrate that it is not easy to recover solvent that is already highly degraded (i.e., 4.7wt%) compared to a lesser degraded solvent (i.e., 1wt%).

Table 47 Summary of MEA/MDEA reclamation series

| Test | Pressure | MEA/MDEA | | | Distillate | | | Residue | | | Loss |
|------|----------|-------------|------------|---------------------------|------------|--------------|---------------------------|---------|--------------|---------------------------|-------|
| | mmHg | Solvent wt% | Mole ratio | Degradation products, wt% | % | Solvent, wt% | Degradation Products, wt% | % | Solvent, wt% | Degradation Products, wt% | % |
| 1 | 160 | 36.50% | 5.0/0.5 | 0.00% | 96.34% | 35.00% | - | 0.03% | 98.00% | - | 0.30% |
| 2 | 110-160 | 45.00% | 2.5/2.5 | 1.00% | 97.00% | 43.51% | 0.41% | 1.50% | 39.49% | 61.02% | 0.50% |
| 3 | 100-160 | 45.00% | 2.5/2.5 | 1.00% | 98.00% | 44.00% | 0.36% | 1.70% | 37.00% | 40.00% | 0.30% |
| 4 | 70-130 | 45.00% | 2.5/2.5 | 1.50% | 94.86% | 42.77% | 0.65% | 4.29% | 51.31% | 18.22% | 0.44% |
| 5 | 60-260 | 45.00% | 2.5/2.5 | 0.60% | 97.44% | 43.00% | 0.19% | 2.55% | 26.26% | 16.00% | 0.52% |
| 6 | 65 | 45.00% | 2.5/2.5 | 0.60% | 98.48% | 43.00% | 0.14% | 1.52% | 39.00% | 30.00% | 0.25% |
| 7 | 70-205 | 42.00% | 2.5/2.5 | 4.70% | 79.49% | 38.76% | 0.93% | 20.51% | 50.96% | 18.71% | 0.98% |

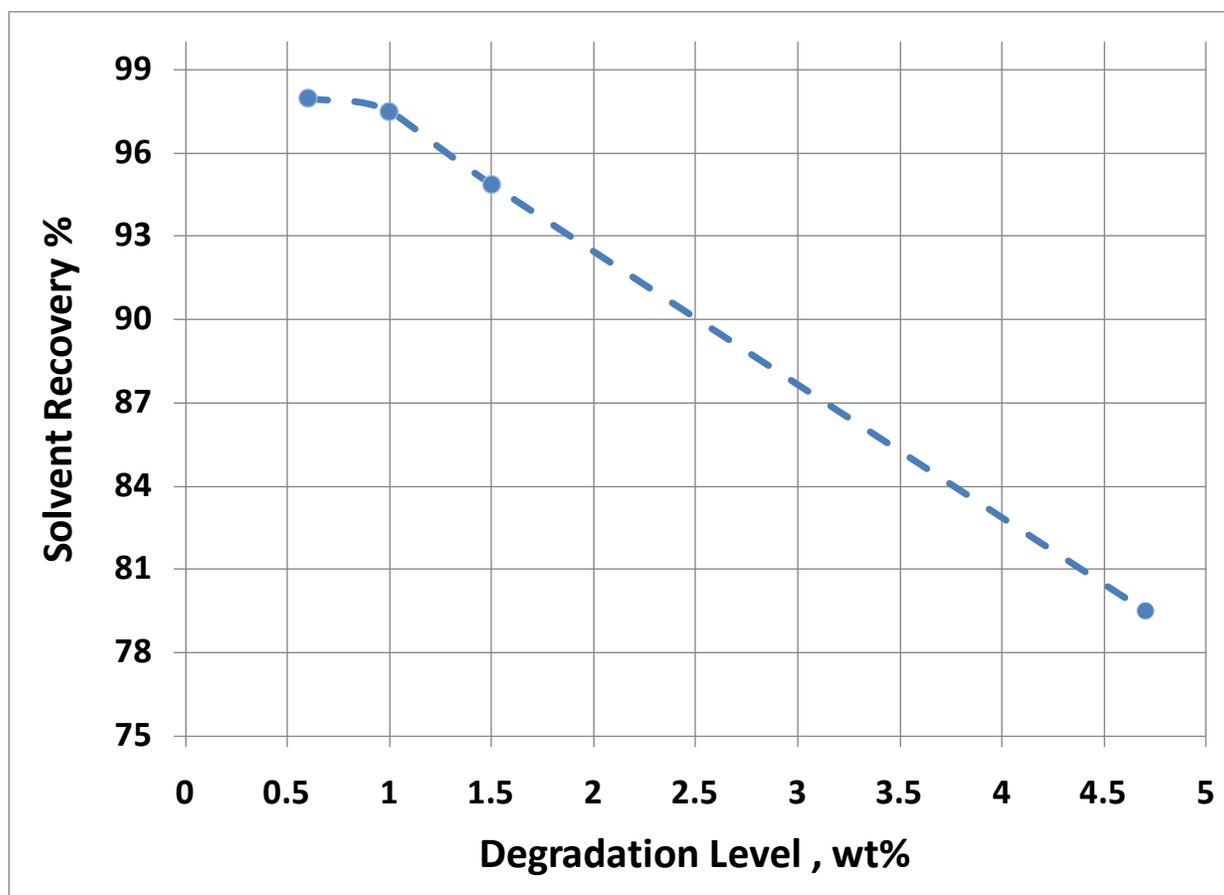


Figure 80 MEA/MDEA solvent recovery vs. degradation level

9.3.3 Second Series of Experiments for MEA/MDEA Solvent Purification

Loaded with CO₂ 5M MEA/MDEA (1:1 molar ratio) solvents with/without degradation products and/or HSS were thermally recovered under vacuum to evaluate solvent recovery under the Series II test conditions. The clean or degraded solvent was prepared in laboratory, as shown in the flow chart in Figure 81, by loading the solvent with CO₂ and then adding the degradation product at desired concentrations. The samples were prepared prior the test by one day or two and allowed to mix with continuous magnetic stirring. It should be mentioned that whenever any amine solvent bottle is open in the lab, nitrogen displacement is used to remove air in the bottle and to prevent solvent oxidation.

The samples collected were analysed with GC and titration to determine the solvent concentration, CO₂ loading, and heat stable salts (HSSs) content. A total of 8 tests was conducted for Series II, and the selected degradation products and HSSs added are given in Figure 82. A test code was assigned for each test to help track follow-up testing and results. For example, MEA/MDEA-3-0.50%-70mmHg means the test solvent is for recovery of mixed solvent of MEA and MDEA, the test number is 3, the total degradation product concentration is 0.50wt%, and it is under vacuum pressure of 70 mmHg. Each test and its results will be discussed separately and then overall results will be given at the end of this section. Photo 3 shows the distillation set-up used in Series II for MEA/MDEA purification.



Figure 81 Test Solvent Preparation Procedure for MEA/MDEA Solvent

| | Test Code | Degradation Level, wt% | | | | | | |
|---|--------------------------------------|------------------------|-----|---|---|---|---|---|
| | | 0 | 0.5 | 1 | 2 | 3 | 4 | 5 |
| | | CO2 Loading, mol/mol | | | | | | |
| Degradation Products | Ammonium Hydroxide | | | | X | X | X | X |
| | 2-(Methylamino) Ethanol | | X | X | X | X | X | X |
| | Amino-2-propanol | | | | X | X | X | |
| | 3-Picoline | | X | X | X | X | X | X |
| | Ethylamine | | X | X | X | X | X | X |
| | 1,3-Diaminopropane | | | | | | | |
| | Imidazole | | | | | | | |
| | Bicine | | X | X | X | X | X | X |
| | Acetamide | | | | | | | |
| | N-Acetyethanolamine | | X | X | X | X | X | X |
| | 1-(2-Hydroxyethyl)-2-Imidazolidinone | | X | X | X | X | X | X |
| | Monomethylethanolamine | | | | | | | |
| Heat stable salts (HSS) Neutralized or Organic Acids Cause them | Formic Acid | | X | X | X | X | X | X |
| | Acetic Acid | | X | X | X | X | X | X |
| | Propionic Acid | | X | X | X | X | X | X |
| | Butyric Acid | | X | X | X | X | X | X |
| | Lactic Acid | | X | X | X | X | X | X |
| | Malonic Acid | | X | X | X | X | X | X |
| | Glycolic Acid | | X | X | X | X | X | X |
| | Oxalic Acid | | X | X | X | X | X | X |
| | Sodium Thiocyanate | | | | | | | |
| | Sodium Thiosulfate | | | | | | | |

Figure 82 Series II Tests and Degradation Products/HSS Used for MEA/MDEA

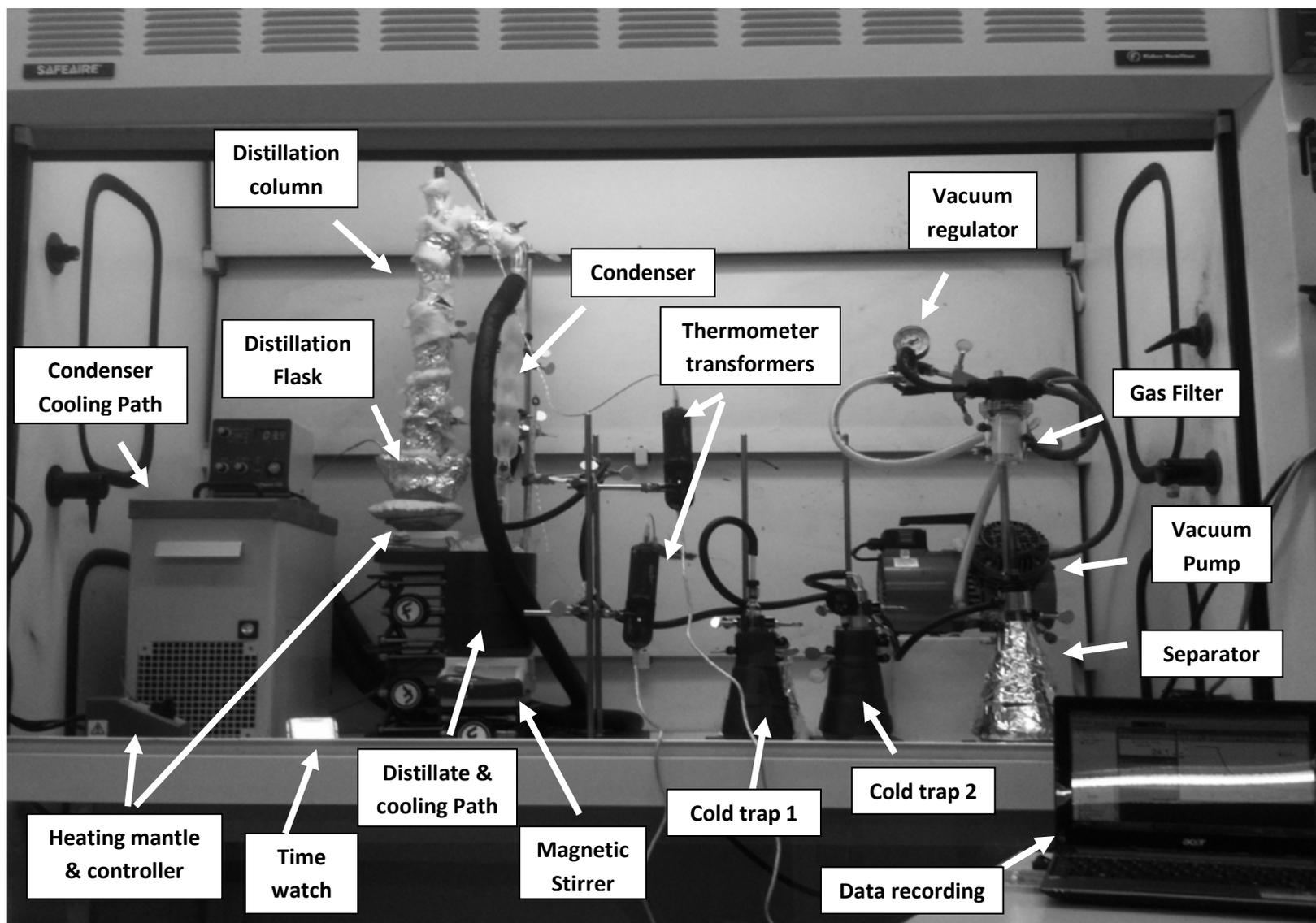


Photo 3 Distillation set-up used for Series II of MEA/MDEA purification

9.3.3.1 Thermal reclamation of MEA/MDEA-1-0.0%-70mmHg

Thermal reclamation of MEA/MDEA solvent with 0.0 wt% degradation products was carried out at 70 mmHg vacuum. The clean solvent was prepared and then loaded with CO₂ through bubbling the CO₂ into the solvent for some time. Table 48 gives the analysis summary for the feed solvent charged to the distillation flask, the collected distillate, and the residue. As can be seen, the clean solvent has low levels of non-volatile and unidentified content, which was determined to be 0.25 wt. %. The distillate recovered is 95.12% of the charged amine, the loading is almost 80% the feed charge solvent, and the remainder of the CO₂ was lost. The residue is mainly MDEA solvent and some water. MDEA in residue could not be recovered, as the process proved infeasible.

9.3.3.2 Thermal reclamation of MEA/MDEA-2-0.0%-75mmHg

The second thermal reclamation of clean MEA/MDEA solvent was carried out, but this time at 75 mmHg. Table 49 summarises the test results, and, as can be seen, the solvent recovery was 95.54% while the pure recovery was 96.68%. The distillation process was terminated when the temperature in the bottom of the distillation flask rose suddenly while the top temperature prior to the condenser dropped. The total non-volatile compounds in the clean amine solvent were determined to be 0.37 wt%.

Table 48 Analysis Summary of MEA/MDEA-1-0.0%-70mmHg Samples

| | Loaded lean amine | Distillate amine | Residue |
|--|--------------------------|-------------------------|----------------|
| Solvent Concentration, wt% | 45.97* | 46.51 | 73.76 |
| CO₂ Loading, mol/mol | 0.121 | 0.022 | - |
| HSS, wt% as MEA | 0.00 | - | - |
| Solvent Recovery, % | - | 95.12% | - |
| Total Non-volatile Content, wt% | 0.25 | - | 26.24 |

*Solvent concentration before adding the degradation products and CO₂

Table 49 Analysis Summary of MEA/MDEA-2-0.0%-75mmHg Samples

| | Loaded lean amine | Distillate amine | Residue |
|--|--------------------------|-------------------------|----------------|
| Solvent Concentration, wt% | 46.51* | 46.69 | 80.19 |
| CO₂ Loading, mol/mol | 0.066 | 0.024 | - |
| HSS, wt% as MEA | 0 | - | - |
| Solvent Recovery, % | - | 95.54 | - |
| Total Non-volatile Content, wt% | 0.37 | - | 19.81 |

*Solvent concentration before adding the degradation products and CO₂

9.3.3.3 Thermal reclamation of MEA/MDEA-3-0.5%-75mmHg

The total concentration of degradation products and heat stable salts was 0.50 wt%. The solvent concentration was determined by titration with HCl with a pH meter. The laboratory determination of HSS could not be performed, as the test failed due to the pH of the sample being higher than the end-point pH, and, therefore, titration with strong caustic soda 0.1N was not feasible. The high pH is likely due to contribution of some degradation products to the solvent pH. Alternatively, the HSSs given in Table 50 are based on the solvent preparation.

GC-MS analysis shows that the distillate was contaminated with some degradation products added to the solvent. Off course, the blended amine even contains some impurities that should be considered if they are not similar to the degradation products added to the solvent. For the sake of clarification, CG chromatographs for the degraded blended solvent and distillate are given in Figure 83. The peak identification for the added or found degradation products in the distillate is given in Table 51. Some degradation chemicals were found in the distillate as well. Based on the degradation products added to the solvent, only four out of six added degradation products caused the distillate contamination, as shown in Table 51 (bold). It seems all these four degradation products left the residue or heavy liquid in the distillation flask.

Table 50 Analysis Summary of MEA/MDEA-3-0.5%-75mmHg Samples

| | Loaded lean amine | Distillate amine | Residue |
|--|--------------------------|-------------------------|----------------|
| Solvent Concentration, wt% | 45.43* | 45.06 | 64.85 |
| CO₂ Loading, mol/mol | 0.052 | 0.025 | - |
| HSS, wt% as MEA | (As mixed 0.2857wt%) | - | - |
| Solvent Recovery, % | - | 96.85 | - |
| Total Non-volatile Content, wt% | 0.59 | - | 35.15 |

*Solvent concentration before adding the degradation products and CO₂

**Table 51 GC-MS identification for degradation products found in distillate
(MEA/MDEA-3-0.5%-75mmHg)**

| Degradation Product | Retention Time, min | Possible Chemical | Comments |
|----------------------------|----------------------------|---|-----------------------------|
| 1 | 1.059 | Ethylamine | Degradation Products |
| 2 | 2.258 | <u>Carbamic acid, 2-dimethylamino ethyl ester</u> | <u>Impurities in MDEA</u> |
| 3 | 2.916 | 3-Picoline | Degradation Products |
| 4 | 6.329 | <u>1-Amino-2-Propanol</u> | <u>Impurities in MDEA</u> |
| 5 | 7.097 | 2-Ethylamino-Ethanol | Degradation Products |
| 6 | 7.749 | 2-(isopropylamino)ethanol* | Impurities in MDEA |
| 7 | 9.046 | Diethylenetriamine* | Impurities in MDEA |
| 8 | 9.507 | N,N' dimethyl-1,2-Ethanediamine* | Impurities in MDEA |
| 9 | 19.173 | N-Acetyl ethanolamine | Degradation Products |

* GC-MS prediction for peak identification

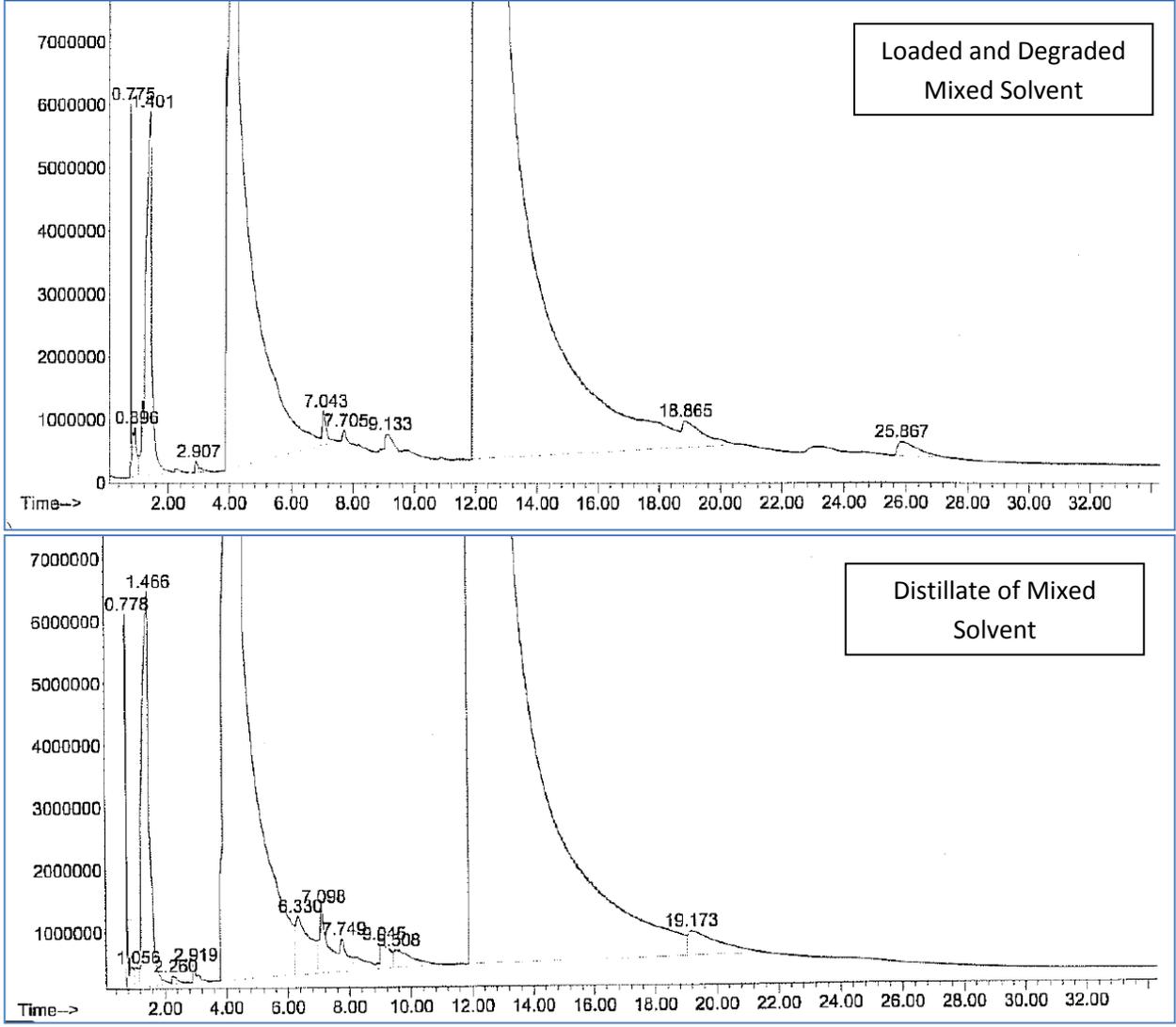


Figure 83 Chromatograph of loaded and degraded mixed solvent and distillate of MEA/MDEA-3-0.5%-75mmHg

9.3.3.4 Thermal reclamation of MEA/MDEA-4-1.0%-70mmHg

Degraded solvent loaded with CO₂ was prepared and thermally reclaimed. The total concentration of degradation products and heat stable salts was around 1.0 wt%. The laboratory determination of HSS could not be done as the test failed due to the pH of the sample being higher than the end-point pH. Alternatively, the HSSs given in Table 14 are based on the solvent preparation. Figure 52 shows the identification of peaks found in loaded and degraded blended solvent. It is also the first time new peaks or chemicals were identified as secondary degradation products, which could be formed by addition of the degradation products selected for this test. Table 53 shows the distillate peaks as they appear in Figure 84. Distillate was found to be contaminated with degradation product as well as impurities similarly to the previous test (MEA/MDEA-3-0.5wt%-75mmHg).

9.3.3.5 Thermal reclamation of MEA/MDEA-5-2.0%-75mmHg

The total concentration of degradation products and heat stable salts, including ammonia, was around 2.0 wt%. The summary of the reclamation test is given in Table 54, and solvent recovery was 94.09%, which is close to the previous test of MEA/MDEA-4-1.0%-70mmHg. Chromatographs of the degraded unloaded solvent and distillate are given in Figure 85. Distillate was found to be contaminated with degradation products and impurities that existed in the MDEA solvent, as well as the new, unknown degradation products, which seemed to form during the solvent preparation, as shown in Figure 20. We tried to use GC-MS evaluation to identify the chemicals in the distillate as given in Table 55. Some peaks are not known; even the GC-MS evaluation looks inaccurate for some of them.

Table 52 Analysis Summary of MEA/MDEA-4-1.0%-70mmHg Samples

| | Loaded lean amine | Distillate amine | Residue |
|--|-----------------------------|-------------------------|----------------|
| Solvent Concentration, wt% | 45.50* | 46.33 | 49.00 |
| CO₂ Loading, mol/mol | 0.083 | 0.038 | - |
| HSS, wt% as MEA | 0.55 (As mixed 0.57 wt%) | - | - |
| Solvent Recovery, % | - | 94.04 | - |
| Total Non-volatile Content, wt% | 1.47 | - | 51.00 |

*Solvent concentration before adding the degradation products and CO₂

**Table 53 GC-MS Identification for Degradation Products Added/Found in Distillate
MEA/MDEA-4-1.0%-70mmHg**

| Degradation Product | Retention Time, min. | Possible Chemical | Comments |
|----------------------------|-----------------------------|---|-----------------------------|
| 1 | 0.900 | Ethylamine | Degradation Products |
| 2 | 2.258 | <u>Carbamic acid, 2-dimethylamino ethyl ester</u> | <u>Impurities in MDEA</u> |
| 3 | 2.910 | 3-Picoline | Degradation Products |
| 4 | 6.329 | <u>1-Amino-2-Propanol</u> | <u>Impurities in MDEA</u> |
| 5 | 7.085 | 2-Ethylamino-Ethanol | Degradation Products |
| 6 | 7.737 | 2-(isopropylamino)ethanol* | Impurities in MDEA |
| 7 | 9.034 | N,N'-Dimethyl-1,2-ethanediamine* | Impurities in MDEA |
| 8 | 19.198 | N-Acetyethanolamine | Degradation Products |

* GC-MS prediction for peak identification

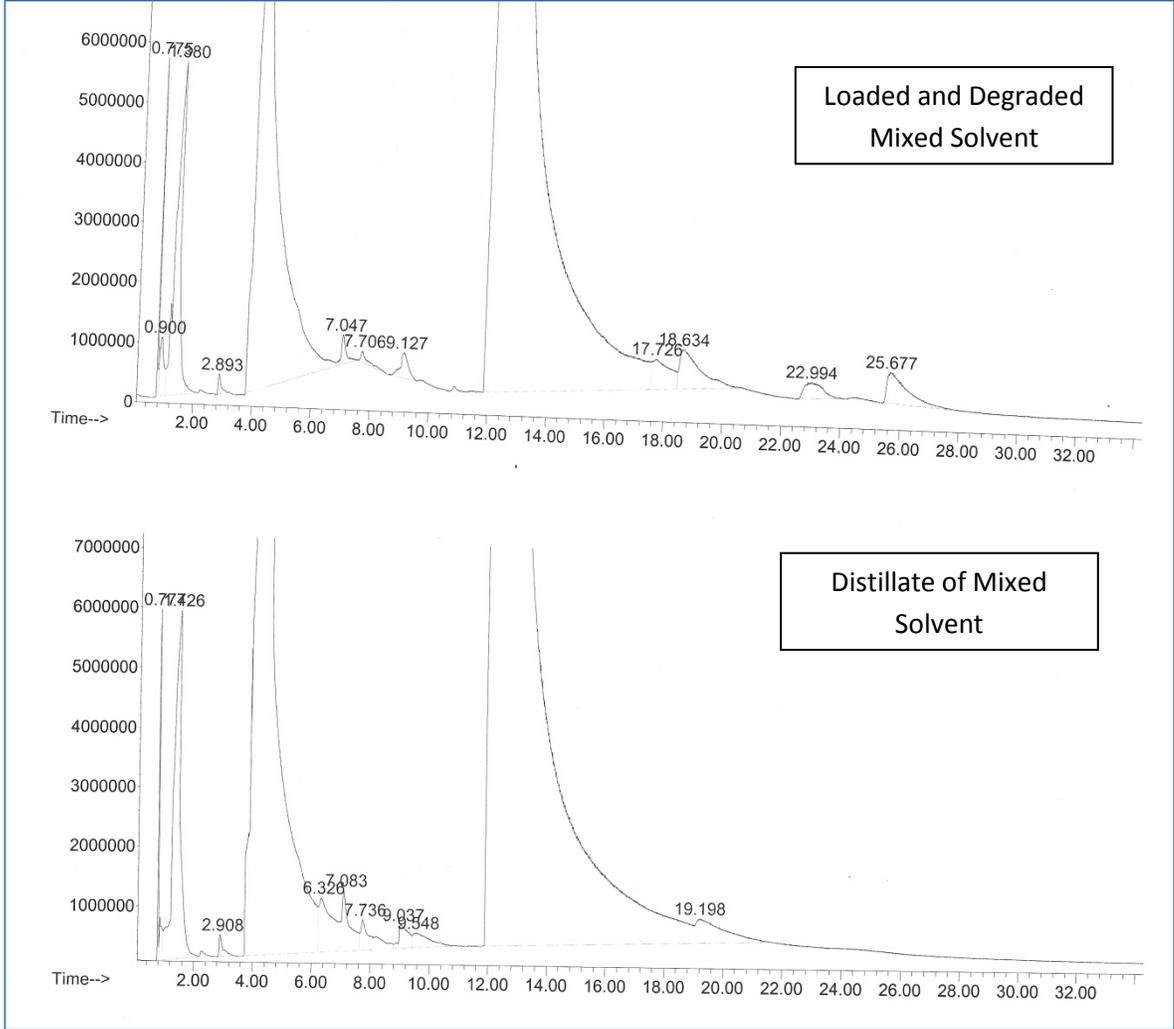


Figure 84 Chromatograph of loaded and degraded mixed solvent and distillate of MEA/MDEA-4-1.0%-70mmHg

Table 54 Analysis summary of MEA/MDEA-5-2.0%-75mmHg samples

| | Loaded lean amine | Distillate amine | Residue |
|--|------------------------------|-------------------------|----------------|
| Solvent Concentration, wt% | 45.43* | 46.03 | 33.25 |
| CO₂ Loading, mol/mol | 0.135 | 0.063 | - |
| HSS, wt% as MEA | 0.88 (As mixed 1.066 wt%) | - | - |
| Solvent Recovery, % | - | 94.09 | - |
| Total Non-volatile Content, wt% | 2.18 | - | 66.75 |

*Solvent concentration before adding the degradation products and CO₂

Table 55 GC-MS Identification for degradation products added/found in distillate

MEA/MDEA-5-2.0%-75mmHg

| Degradation Product | Retention Time, min. | Possible Chemical | Comments |
|----------------------------|-----------------------------|---|--|
| 1 | 0.885 | Ethylamine | Degradation Products |
| 2 | 2.258 | <u>Carbamic acid, 2-dimethylamino ethyl ester</u> | <u>Impurities in MDEA</u> |
| 3 | 2.866 | 3-Picoline | Degradation Products |
| 4 | 7.040 | 2-Ethylamino-Ethanol | Degradation Products |
| 5 | 7.716 | N,N'-Diisopropyl ethylene diamine * | Impurities in MDEA |
| 6 | 9.104 | Pentanoic acid* | 2nd Degradation Products |
| 7 | 17.845 | ? | 2nd Degradation Products |
| 8 | 18.663 | N-Acetyl ethanolamine | Degradation Products |
| 9 | 19.487 | ? | 2nd Degradation Products |

* GC-MS prediction for peak identification

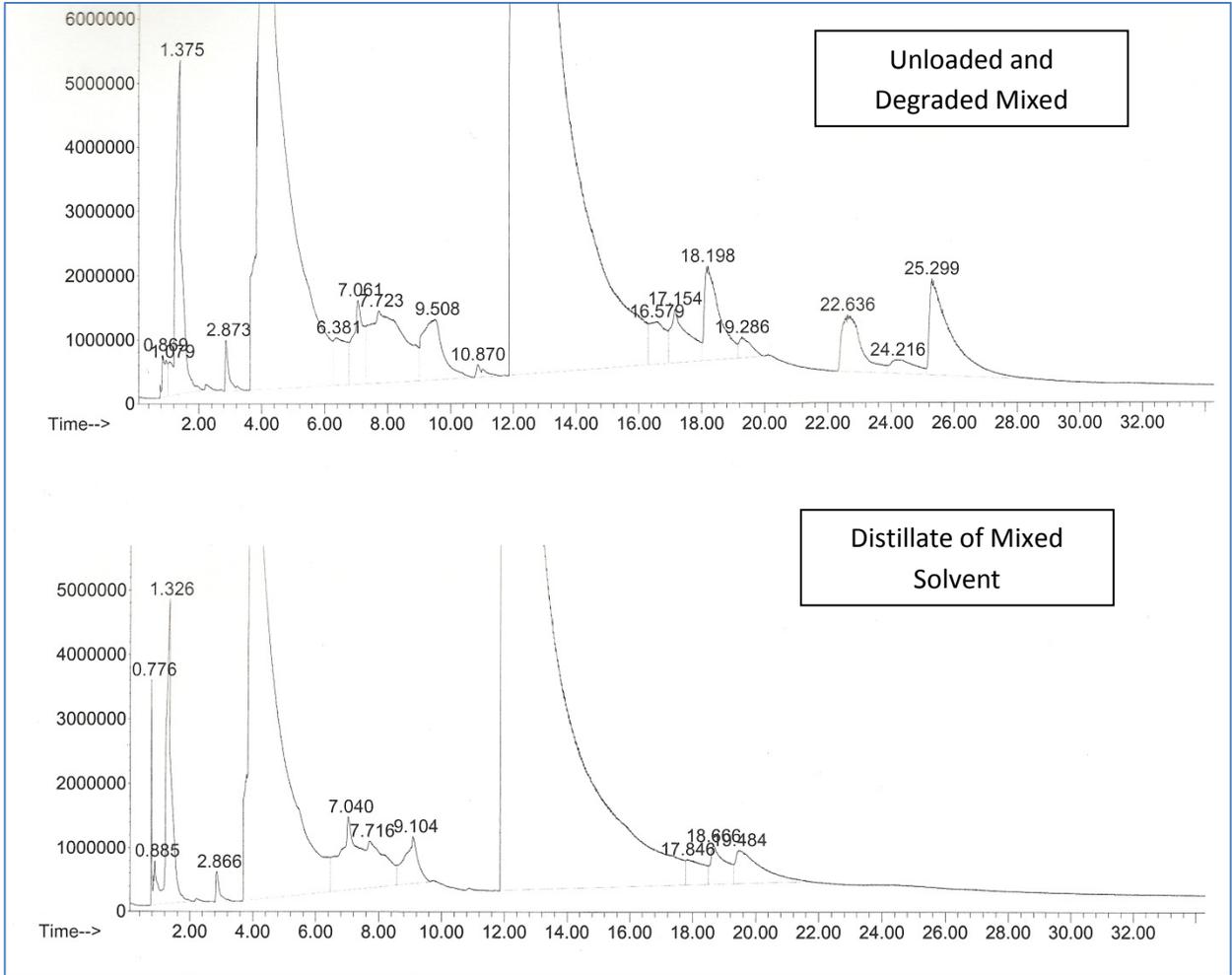


Figure 85 Chromatograph of unloaded and degraded mixed solvent and distillate of MEA/MDEA-5-2.0%-75mmHg

9.3.3.6 Thermal reclamation of MEA/MDEA-6-3.0%-75mmHg

Degraded solvent and solvent loaded with CO₂ was prepared and thermally reclaimed. The total concentration of degradation products and heat stable salts was around 3.50 wt%. Also, ammonia was added to the degraded solvent. Table 56 provides a summary of the results of this test, and solvent recovery was 93.59%. Laboratory determination of HSS was done, and the total HSS added is given in Table 56. Figure 86 provides the chromatographs of the degraded solvent and distillate. The chemical identifications of the peaks, either based on the standard injection or GC-MS evaluation, are given in Table 58. Distillate was found to be contaminated with some degradation products and some impurities, while no trace of ammonia was observed.

9.3.3.7 Thermal reclamation of MEA/MDEA-7-4.0%-75mmHg

Degraded solvent loaded with CO₂ was prepared and thermally reclaimed. The total concentration of degradation products and heat stable salts was around 4.0 wt%. A summary of the distillate results is given in Table 57, and solvent recovery was 91.72%. Figure 87 provides the chromatographs of the degraded solvent and distillate. The chemical identifications of the peaks, either based on the standard injection or GC-MS evaluation, are given in Tables 59. Distillate was found to be contaminated with some degradation products and some impurities. It seems that as the degradation product concentration increased, many secondary degradation products formed.

Table 56 Analysis summary of MEA/MDEA-6-3.0%-75mmHg samples

| | Loaded lean amine | Distillate amine | Residue |
|--|----------------------------|-------------------------|----------------|
| Solvent Concentration, wt% | 46.51* | 45.25 | 30.38 |
| CO₂ Loading, mol/mol | 0.125 | 0.060 | - |
| HSS, wt% as MEA | 1.90 (As mixed 1.60wt%) | - | - |
| Solvent Recovery, % | - | 93.59 | - |
| Total Non-volatile Content, wt% | 3.24 | - | 69.62 |

*Solvent concentration before adding the degradation products and CO₂

Table 57 Analysis summary of MEA/MDEA-7-4.0%-75mmHg samples

| | Loaded lean amine | Distillate amine | Residue |
|--|------------------------------|-------------------------|----------------|
| Solvent Concentration, wt% | 46.18* | 45.61 | 46.36 |
| CO₂ Loading, mol/mol | 0.110 | 0.046 | - |
| HSS, wt% as MEA | 2.220 (As mixed 2.285wt%) | - | - |
| Solvent Recovery, % | - | 91.72 | - |
| Total Non-volatile Content, wt% | 4.21 | - | 53.64 |

*Solvent concentration before adding the degradation products and CO₂

Table 58 GC-MS identification for degradation products added/found in distillate

MEA/MDEA-5-2.0%-75mmHg

| Degradation Product | Retention Time, min. | Possible Chemical | Comments |
|----------------------------|-----------------------------|---|--|
| 1 | 0.985 | Ethylamine | Degradation Products |
| 2 | 2.240 | <u>Carbamic acid, 2-dimethylamino ethyl ester</u> | <u>Impurities in MDEA</u> |
| 3 | 2.885 | 3-Picoline | Degradation Products |
| | 3.562 | 2-methylamino ethanol* | 2nd Degradation Products |
| | 6.316 | <u>1-Amino-2-Propanol*</u> | <u>Impurities in MDEA</u> |
| 4 | 7.085 | 2-Ethylamino-Ethanol | Degradation Products |
| 5 | 7.730 | 2-(isopropylamino)ethanol* | Impurities in MDEA |
| 6 | 9.009 | 2-Propanamine* | 2nd Degradation Products |
| 7 | 17.845 | ? | 2nd Degradation Products |
| 8 | 18.607 | N-Acetyl ethanolamine | Degradation Products |

* GC-MS prediction for peak identification

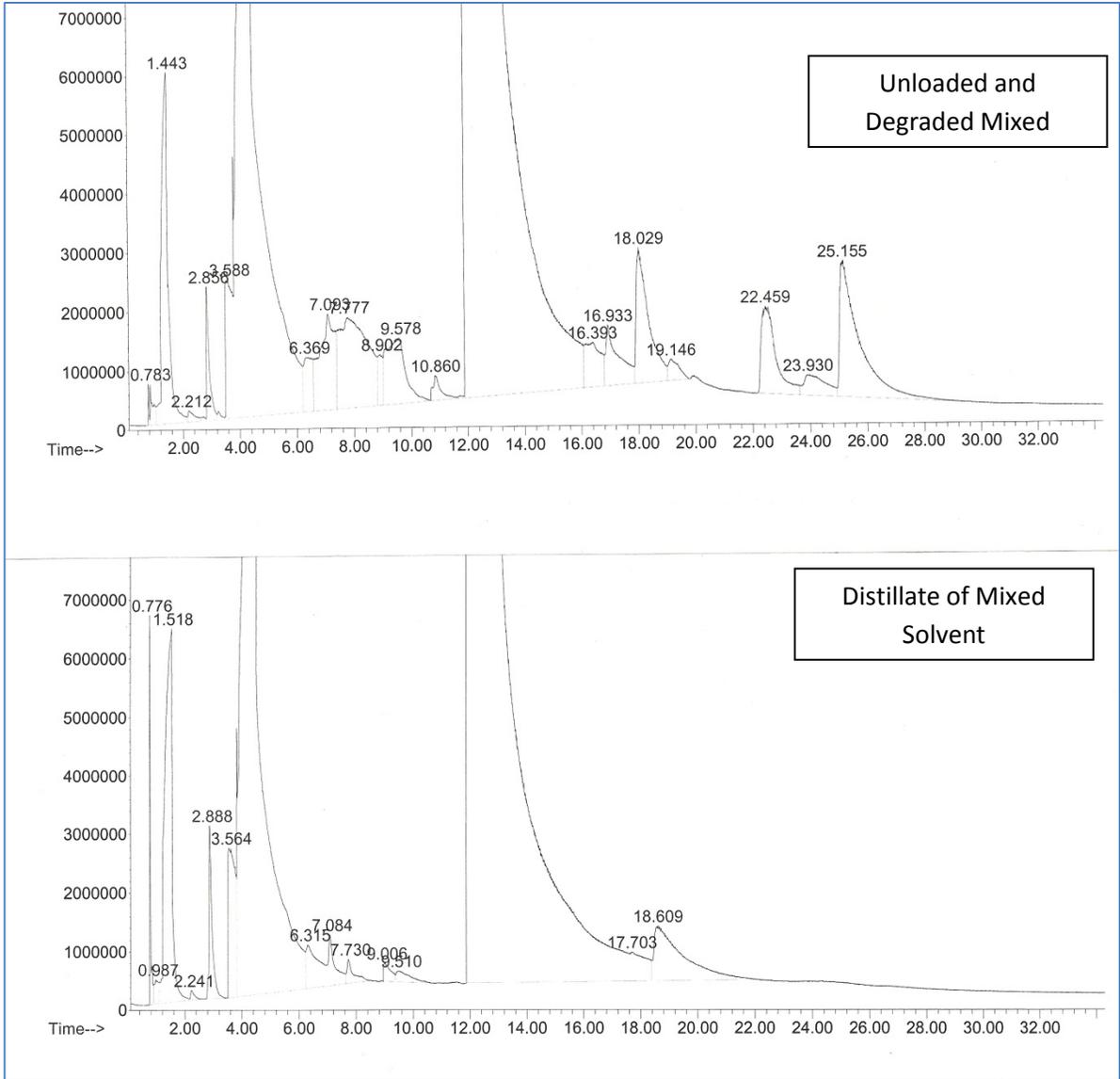


Figure 86 Chromatograph of unloaded and degraded mixed solvent and distillate of MEA/MDEA-6-3.0%-75mmHg

Table 59 GC-MS identification for degradation products added/found in distillate

MEA/MDEA-7-4.0%-75mmHg

| # | Retention Time, min. | Possible Chemical | Comments |
|----|----------------------|---|--|
| 1 | 0.776 | Ammonia | Degradation Products |
| 2 | 0.910 | Ethylamine | Degradation Products |
| 3 | 1.500 | Carbamic acid, monoammonium salt | Degradation Products |
| 4 | 2.246 | <u>Carbamic acid, 2-dimethylamino ethyl ester</u> | <u>Impurities in MDEA</u> |
| 5 | 2.738 | 3-Picoline | Degradation Products |
| 6 | 2.916 | ? | 2nd Degradation Products |
| 7 | 3.549 | 2-methylamino ethanol* | 2nd Degradation Products |
| 8 | 3.765 | 1,3-Propanediamine | 2nd Degradation Products |
| 9 | 6.353 | 1-Amino-2-Propanol | Degradation Products |
| 10 | 7.109 | 2-Ethylamino-Ethanol | Impurities in MDEA |
| 11 | 7.749 | 2-(isopropylamino)ethanol* | Impurities in MDEA |
| 12 | 8.972 | ? | 2nd Degradation Products |
| 13 | 9.409 | N,N'-dimethyl-1,2-Ethandiamine* | 2nd Degradation Products |
| 14 | 17.362 | ? | 2nd Degradation Products |
| 15 | 18.325 | N-Acetyl ethanolamine | Degradation Products |

* GC-MS prediction for peak identification

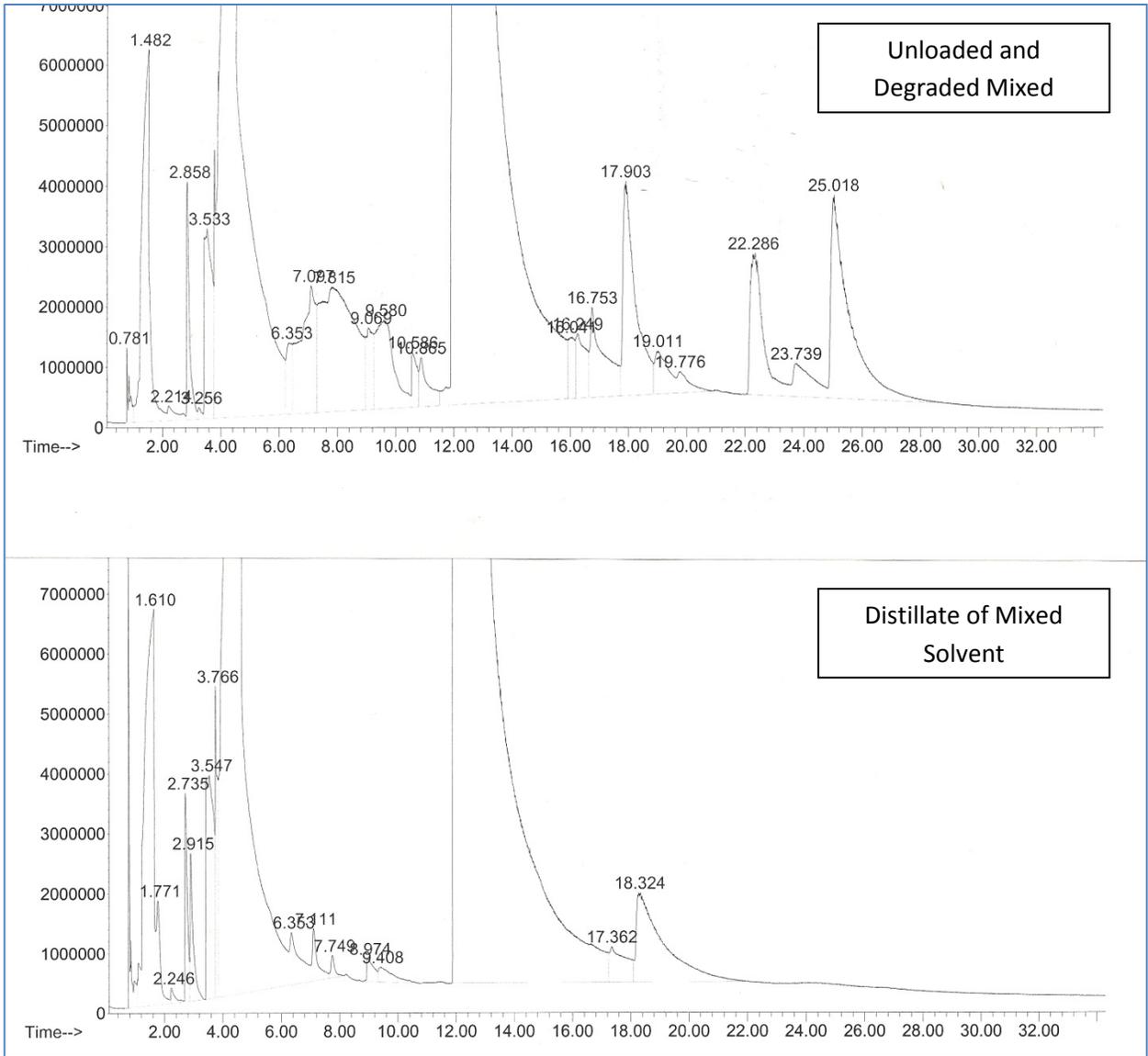


Figure 87 Chromatograph of unloaded and degraded mixed solvent and distillate of MEA/MDEA-7-4.0%-75mmHg

9.3.3.8 Thermal reclamation of MEA/MDEA-8-5.0%-70mmHg

Degraded solvent loaded with CO₂ was prepared and thermally reclaimed. Table 60 gives a summary of the analysis of samples obtained from the test. The total concentration of degradation products and heat stable salts was around 5.0 wt%. The laboratory determination of HSS was done and showed that HSS was 3.1 wt% as MEA; however, HSS added was 2.857 wt%. The temperature profile for the test is given in Figure 88. Details of the distillation records are given in Figure 89.

Figure 90 provides the chromatographs of the degraded solvent and distillate. Distillate was found to be contaminated with a number of degradation products and impurities. The chemical identifications of the peaks, either based on the standard injection or GC-MS evaluation, are given in Tables 61 and 62. It seems that the high concentration of degradation products led to the formation of a number of secondary degradation products, as shown in Tables 61 and 62.

Table 60 Analysis Summary of MEA/MDEA-8-5.0%-70mmHg Samples

| | Loaded lean amine | Distillate amine | Residue |
|--|------------------------------------|-----------------------------|----------------|
| Solvent Concentration, wt% | 44.94* | 44.89 | 30 |
| CO₂ Loading, mol/mol | 0.181 | 0.050 | - |
| HSS, wt% as MEA/MDEA | 3.10 (As mixed 2.857wt%) | - | - |
| Solvent Recovery, % | - | 88.95 | - |
| Total Non-volatile Content, wt% | 6.22 | - | 70 |

*Solvent concentration before adding the degradation products and CO₂

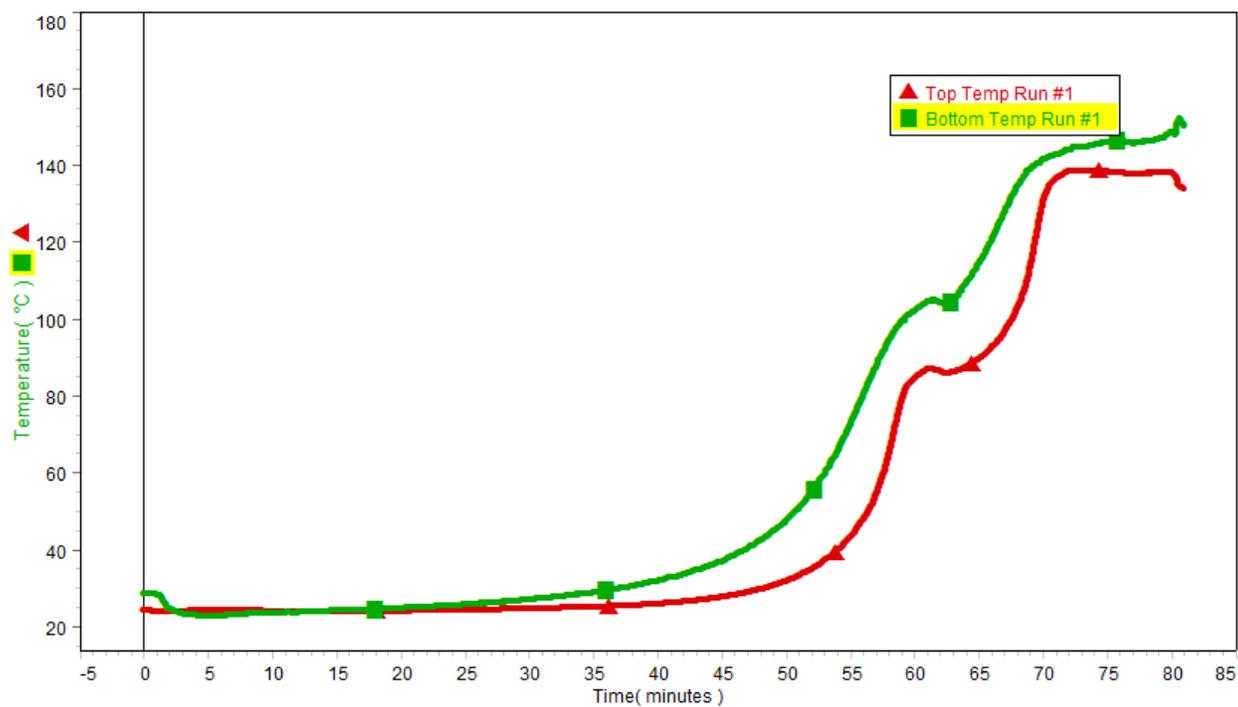


Figure 88 Top and Bottom Temperature Profiles for MEA/MDEA-8-5.0%-70mmHg

| Reclaimer Research: Small Set-Up Distillation Form | | | | | | |
|--|---|------------|-----|--|---------|------|
| 1 | Distillation Test Code | MEA-MDEA-8 | | Date | 18.8.11 | |
| 2 | Solvent type | MEA/MDEA | | Time | | |
| 3 | Solvent Conc | 44.94 | wt% | Mode Operation: | Vacuum | |
| 4 | Degradation Level | 5.00 | wt% | Room Temp. = | 21 | C |
| 5 | Heat Set # = | 9 | | Room pressure = | | kpa |
| 6 | Cooling temp. = | 10 | C | Set-up pressure = | | mmHg |
| 7 | Trap one temp. = | 3 | C | Set-up pressure = | 70.00 | mmHg |
| 8 | Trap two temp. = | 1.8 | C | Cooling bath | 2.00 | |
| 9 | Distillation Flask | | | | | |
| 10 | Distillation Flask = | 154.48 | gm | Bar = | 1.46 | gm |
| 11 | Yellow Cover 1 = | 8.98 | gm | with grease = | 0.04 | gm |
| 12 | Yellow Cover 2 = | 8.97 | gm | with grease = | 0.04 | gm |
| 13 | Solvent Added = | 235.35 | gm | HSS as solvent = | 5.91 | gm |
| 14 | Pure NaOH needed = | 3.87 | gm | NaOH 50wt% = | 7.74 | gm |
| 15 | NaOH 50wt% = | 4.98 | ml | Total solution with NaOH = | 243.09 | gm |
| 16 | Distille Flask | | | | | |
| 17 | Distillate flask = | 209.69 | gm | Bar = | 1.43 | gm |
| 18 | Distillate Flask (flask + distillate + bar) = | 418.30 | gm | Distillate = | 207.18 | gm |
| 19 | Solvent Recovery = | 88.03 | % | Total Loss = | 35.91 | gm |
| 20 | Solvent Loss = | 11.97 | % | Amine in distillate = | 44.89 | wt% |
| 21 | Amine in distillate = | 92.99 | gm | Pure solvent recovery = | 87.92 | % |
| 22 | Residue Flask | | | | | |
| 23 | Residue Flask (flask + residue + bar+cover) = | 202.62 | gm | Water Dilution for Residue = | 77.11 | gm |
| 24 | Residue (without NaOH)= | 20.91 | gm | Residue + Water = | 98.02 | gm |
| 25 | Residue to Total Loss = | 58.25 | % | Amine in residue = | 6.40 | wt% |
| 26 | Amine in residue = | 6.27 | gm | Pure solvent loss = | 2.58 | % |
| 27 | What left in heavy residue = | 14.64 | gm | What left in Heavy residue = | 6.22 | % |
| 28 | Washing Run | | | | | |
| 29 | Distillate flaks = | 140.38 | gm | bar = | 1.46 | gm |
| 30 | | | | | | |
| 31 | Distillation Flask = | 204.16 | gm | bar = | 1.46 | gm |
| 32 | Water added = | 348.92 | gm | | | |
| 33 | | | | | | |
| 34 | Distillate Flask + water + bar = | 370.17 | gm | Wash water left = | 325.71 | gm |
| 35 | Recovered water and amine in Distillate = | 228.33 | gm | Left water and amine in Distillation Flask = | 120.09 | gm |
| 36 | Amine in distillate = | 0.64 | wt% | Amine in left water = | 0.59 | wt% |
| 37 | amine in distillate = | 1.46 | gm | amine in distillate = | 0.71 | gm |
| 38 | | | | | | |
| 39 | Recoverable Pure solvent = | 95.16 | gm | Recoverable Pure solvent = | 89.97 | % |
| 40 | Recoverable solvent = | 209.35 | gm | Recoverable solvent = | 88.95 | % |

Figure 89 Distillation experiment calculation sheet of MEA/MDEA-8-5.0%-

70mmHg

**Table 61 GC-MS Identification for Degradation Products Added/Found in Blended
Solvent MEA/MDEA-7-4.0%-75mmHg**

| # | Retention Time, min. | Possible Chemical | Comments |
|----|----------------------|--|--------------------------------------|
| 1 | 0.782 | ammonia | Degradation Products |
| 2 | 1.000 | Ethylamine | Degradation Products |
| 3 | 1.500 | Carbamic acid, monoammonium salt | Degradation Products |
| 4 | 2.203 | <u>Carbamic acid, 2-dimethylamino ethyl ester*</u> | <u>Impurities in MDEA</u> (HSS) |
| 5 | 2.856 | 3-Picoline | Degradation Products |
| 6 | 3.260 | ? | 2 nd Degradation Products |
| 7 | 3.525 | 2-methylamino ethanol | Degradation Products |
| 8 | 3.700 | 1,3-Propanediamine | Degradation Products |
| 9 | 7.097 | 2-Ethylamino-Ethanol | Impurities in MDEA |
| 10 | 7.816 | 1,2-Dimethyl hydrazine* | Impurities in MDEA |
| 11 | 8.837 | Pentanoic acid* | 2 nd Degradation Products |
| 12 | 9.372 | Butanoic acid | Degradation Products (HSS) |
| 13 | 10.343 | Formic acid | Degradation Products (HSS) |
| 14 | 10.866 | Allantoin* | 2 nd Degradation Products |
| 15 | 15.988 | ? | 2 nd Degradation Products |
| 16 | 16.160 | ? | 2 nd Degradation Products |
| 17 | 16.658 | ? | 2 nd Degradation Products |
| 18 | 17.839 | N-Acetyl ethanolamine | Degradation Products |
| 19 | 18.884 | ? | 2 nd Degradation Products |
| 20 | 19.646 | ? | 2 nd Degradation Products |
| 21 | 22.284 | Bicine | Degradation Products |
| 22 | 23.932 | N-(2-Hydroxyethyl) Lactamide* | 2 nd Degradation Products |
| 23 | 25.156 | 1-(2-Hydroxyethyl)-2-Imidazolidinone | Degradation Products |

* GC-MS prediction for peak identification

**Table 62 GC-MS Identification for Degradation Products Added/Found in Distillate
MEA/MDEA-7-4.0%-75mmHg**

| # | Retention Time, min. | Possible Chemical | Comments |
|----|-----------------------------------|---|--|
| 1 | 0.776 | Ammonia | Degradation Products |
| 2 | 1.102 | Ethylamine | Degradation Products |
| 3 | 1.500 (cover by H ₂ O) | Carbamic acid, monoammonium salt | Degradation Products |
| 4 | 2.221 | <u>Carbamic acid, 2-dimethylamino ethyl ester</u> | <u>Impurities in MDEA</u> |
| 5 | 2.725 | 3-Picoline | Degradation Products |
| 6 | 2.885 | ? | 2nd Degradation Products |
| 7 | 3.512 | 2-methylamino ethanol | Degradation Products |
| 8 | 3.765 | 1,3-Propanediamine | Degradation Products |
| 9 | 6.322 | ? | 2nd Degradation Products |
| 10 | 7.085 | 2-Ethylamino-Ethanol | Impurities in MDEA |
| 11 | 7.730 | 2-(isopropylamino)ethanol* | Impurities in MDEA |
| 12 | 8.978 | ? | 2nd Degradation Products |
| 13 | 9.415 | N,N'-dimethyl-urea* | 2nd Degradation Products |
| 14 | 17.587 | ? | 2nd Degradation Products |
| 15 | 18.503 | N-Acetyl ethanolamine | Degradation Products |

* GC-MS prediction for peak identification

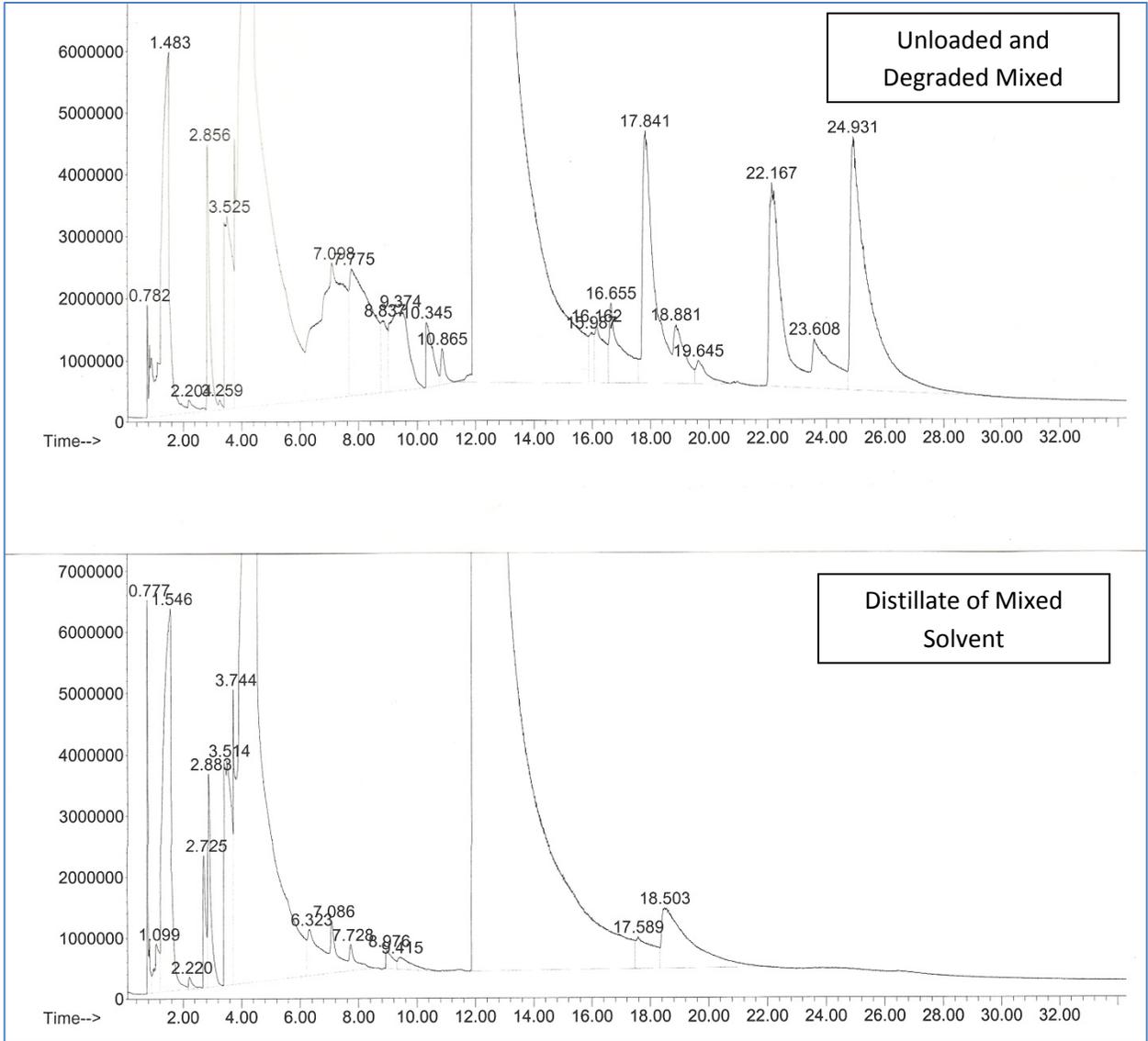


Figure 90 Chromatograph of Unloaded and Degraded Mixed Solvent and Distillate of MEA/MDEA-8-5.0%-70mmHg

9.3.4 Summary of Second Series of MEA/MDEA Solvent Purification

A number of clean and degraded MEA/MDEA solvents were thermally reclaimed. The amounts of degradation products formed in a blended MEA/MDEA system are greater than in single MEA solvents. Most of the MEA/MDEA system degradation products would contaminate the distillate, although some of them would be left behind in the residue. Reclaiming solvent under vacuum would reduce the reclamation cycles and the need to use water for dilution, and it would enhance solvent recovery.

A summary of the solvent recovery, individually and overall, is given in Figure 91, excluding the solvent recovered from washing the apparatus after the test concluded. Figure 92 shows the solvent recovery including the solvent recovered from washing. The second graph gives the net solvent recovered. Washing of the reclaimer equipment is carried out at the end of the reclamation cycle. As can be seen in Figure 91, the solvent recovery is reduced as the degradation product concentration increases, although the content of the amine in the residue is reduced. In reality, the residue quantity, as well as the solvent loss, is significantly increased whenever the degradation product concentration increases.

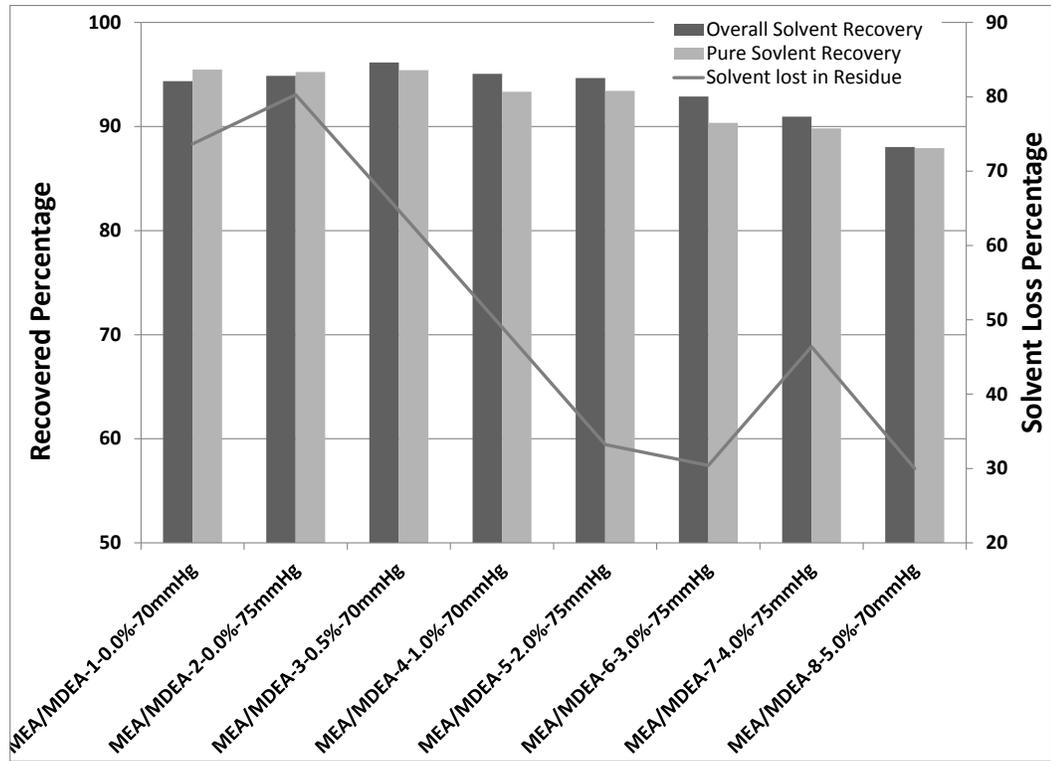


Figure 91 MEA/MDEA recovery tests excluding the solvent recovered by washing.

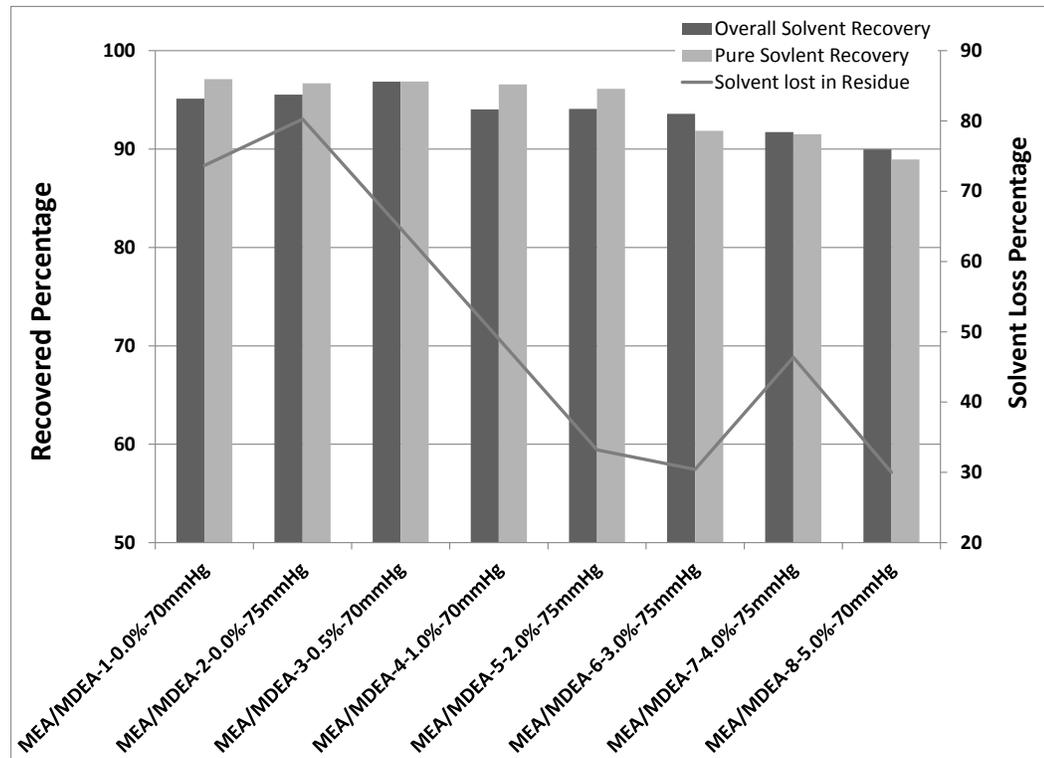


Figure 92 MEA/MDEA recovery tests including the washing solvent recovered.

9.4 Concluding Remarks

- 1 Recovery of clean and degraded MEA/MDEA solvents was studied by using thermal distillation at atmospheric pressure and under vacuum down to 70 mmHg. Two test series of recovery of MEA/MDEA solvents were completed to identify the optimum conditions for recovery of blended solvent and the impact of the degradation products on solvent recovery
- 2 Thermal stability of MEA/MDEA, whether in pure form or solvent at concentration of 5M, was tested. Identification of the effect of temperature was accomplished by measuring the change of solvent concentration and refractive index. 5M MEA/MDEA solvent concentration losses totalled 1.60% in which loss of MEA and MDEA, individually, was 0.88 and 0.72%, respectively.
- 3 The aim of the first series was to find the optimum operating conditions for purifying clean and degraded MEA/MDEA solvent with the objective of minimizing solvent loss in residue. The fraction distillation set-up was used under deep vacuum.
 - 3.1 MEA/MDEA solvent recovery improved as the vacuum was increased. Increasing the vacuum reduced the need for longer solvent reclamation cycles and cut water dilution and energy consumption.
 - 3.2 Different scenarios were considered in which two modes of operation were tested: two different vacuum pressures to recover MEA and MDEA, respectively, and one vacuum pressure mode to achieve recovery of both amines in one operation step.
 - 3.3 The lighter portion of amine, MEA, could be recovered in deep vacuum of around 130-260 mmHg in the scenario with two vacuum pressures while in the

single pressure scenario, MEA could be completely recovered in very deep vacuum of 60-110 mmHg.

3.4 The heavier amine could only be recovered at very deep vacuum of 60-70 mmHg for both two or one vacuum pressure(s).

3.5 It was found that as the degradation product level increased, deeper vacuum was required for the recovery of blended solvent; however, solvent loss in residue or waste increased.

3.6 The optimum recovery of clean and low degraded blended solvent is around 97%; however, the solvent is losing 4.28% for every 1wt% of degradation products.

4 In the second series, the effect of degradation product concentration on solvent recovery was examined under the new optimum operating conditions of purifying the clean, degraded, and CO₂ loaded MEA/MDEA solvents. The fractionation distillation set-up was improved by using thermocouples to measure temperature and integrating these measurements with a data collector and analysis software, minimization of solvent loss, and enhanced cooling equipment.

4.1 Degradation products and heat stable salts expected to form from MEA/MDEA degradation were selected and mixed with amine to create degraded MEA/MDEA solvent. Total degradation product content varied from 0.5 to 5 wt%. Neutralization of HSS with 50% NaOH was applied to the solvent prior to the test.

- 4.2 To improve solvent recovery of MEA/MDEA for degraded and CO₂ loaded solvents, the optimum conditions recommended are a deeper vacuum (i.e., 70-75 mmHg) and one vacuum pressure mode.
- 4.3 MEA/MDEA recovery was reduced as degradation product content increased. At a degradation content of 0.5 wt%, total solvent recovery was 94.88% and amine concentration in distillate was 96.87%. For 5 wt% degradation content, total solvent recovery was 88% and amine concentration in distillate was 90%.
- 4.4 High degradation content results in difficult solvent reclamation and higher solvent loss in the reclaimer waste; therefore, solvent degradation should not be allowed to exceed 1.0wt%.
- 4.5 It is concluded that six out of eight degradation products are likely to contaminate the recovered MEA/MDEA solvent; they are ammonia, ethylamine, 3-Picoline, 2-Methylamino ethanol, 1,3-Propanediamine, and N-Acetyethanolamine. All other degradation products and neutralized HSSs did not appear in any distillate collected.

Chapter 10 Purifying Solvent Distillates by Activated Carbon Adsorption

10.1 Chapter introduction

From previous work on thermal distillation in chapters 8 and 9, it was concluded that the recovered solvent or distillate could be contaminated with some degradation products. The contamination in MEA/MDEA distillates is much higher than MEA distillates, and this is simply due to the blended solvent generating more complex degradation products than single solvents. For instance, MEA could be contaminated by two degradation products: ammonia and ethylamine. In the case of MEA/MDEA solvents, however, recovered solvent could be contaminated by six degradation products: ammonia, ethylamine, 3-Picoline, 2-Methylamino ethanol, 1,3-Propanediamine, and N-Acetyethanolamine. It is not acceptable to return these degradation products back to amine system; therefore, they should be removed by an additional, suitable method. Estimated molecular size for these degradation products is given in Table 63.

It is proposed to treat distillates of both solvent MEA and MEA/MDEA with activated carbon. Activated carbon is well known to remove contamination from wastewater streams and is used to treat amine solvent to remove activate agents and hydrocarbons that can cause foaming (Kohl and Nielsen 1997). Three types of commercial activated carbon were obtained from Calgon Carbon Corporation⁹, Pittsburgh, PA, and Norit America Inc.¹⁰, Marshall, TX. Table 64 shows the summary of properties and specifications of these three activated carbons.

⁹ www.calgoncarbon.com

¹⁰ www.norit-americas.com

Evaluation of the contaminant adsorption from distillate or partially degraded, prepared distillate of MEA or MEA/MDEA was carried out into two steps: isotherm adsorption in batches and dynamic adsorption in a small carbon column. Isotherm adsorption was used to obtain information on the ability of the activated carbon to remove contaminants from amine solvent and how much carbon is needed for purification. Dynamic adsorption was used to obtain information on the amount of liquid that could be treated before the carbon column capacity was consumed. The results were transferred to a graphical representation called breakthrough curves.

Activated carbons can be used in their dry form, but it is advisable to wet the carbon with water before use in treatment. This helps remove air pockets inside the carbon pores to maximize utilization of all surface area on the carbon and to facilitate the adsorption process for contaminants. New wettability procedures for activated carbon were introduced in this study, along with the technique of using clean amine solvent to wet the carbons. It was believed that this would enhance the removal of contaminants from the solvent and reduce the solvent loss overall compared to water wetting.

Table 63 Estimated molecular size based on chemicalize.org

| Geometry | Volume, Å³ | Projection area (Min/Max), Å² | Minimum Z length (Min/Max), Å |
|------------------------------|------------------------------|---|--------------------------------------|
| Ammonia | 22.86 | 8.39 / 10.96 | 3.88 / 3.21 |
| Ethylamine | 57.10 | 10.61 / 22.47 | 6.53 / 5.05 |
| 3-Picoline | 94.65 | 19.07 / 37.34 | 8.00 / 4.06 |
| 2-Methylamino ethanol | 83.22 | 18.31 / 31.68 | 8.87 / 5.78 |
| N-Acetyethanolamine | 101.41 | 22.46 / 37.16 | 9.04 / 5.14 |

Table 64 Activated carbon characteristics selected for this study

| Activated Carbon | Norit GAC 830 (M-1731) | PetroDraco 8×30 (M-1657) | SGL 8×30 | |
|---|-------------------------------|---------------------------------|-----------------|-----|
| Source | Bituminous coal | Lignite coal | Bituminous coal | |
| Activation method | Steam | Steam | Steam | |
| Product Specifications | | | | |
| Iodine number, mg/g | 920 min. | | 900 min | |
| Molasses number, - | 210 min. | 85 min. | 200 min. | |
| Abrasion number (AWWA) | 75 min. | | 75 min. | |
| Moisture, % | 2 max. | 12 max. | 2 max. | |
| Mesh size (US Sieve series) | | | | |
| Greater than 8 mesh (2.36 mm), % | 8 max. | 5 max. | 15 max. | |
| Less than 30 mesh (0.60 mm), % | 4 max. | 5 max. | 4 max. | |
| Ash, % by weight | | | 10 max. | |
| Typical Properties | | | | |
| Apparent density, g/ml | 0.50 | 0.39 | 0.48 | |
| Surface area, m²/g | | 650 | | |
| Total pore volume, ml/g | | 0.95 | | |
| Effective size, mm | 1.00 | | 1.50-1.70 | |
| Uniformity coefficient | 1.70 | | | |
| pH, water extract | | 4.50 | | |
| Micropores, Pore Volume | ml/g | 0.30 | 0.12 | N/A |
| | % | 37.97 | 11.76 | N/A |
| Mesopores, Pore Volume | ml/g | 0.22 | 0.49 | N/A |
| | % | 27.84 | 48.04 | N/A |
| Macropores, Pore Volume | ml/g | 0.25 | 0.30 | N/A |
| | % | 31.64 | 29.41 | N/A |

10.2 Purifying of MEA distillates

It was found that MEA solvent recovered via thermal distillation is contaminated with ammonia and ethylamine. Here, the contaminated distillate was treated with activated carbon. Distillates used for the artificial-type activated carbon treatment were obtained by mixing the amine solvent with contaminants. Three types of carbons were used, as shown in Table 64, each in three different forms: dry, wetted with water, and wetted with amine solvent. The first step in the evaluation of the capability of carbons to remove degradation products is determining the wettability capacity of carbons for water and amine solvent. Then, isotherm or batch adsorption experiments and, finally, the dynamic adsorption experiments could be carried out.

10.2.1 Wettability of Activated Carbon

Before conducting the adsorption tests, it was important to measure the wettability of activated carbon with both water and 5M MEA solvent. The three activated carbons were weighed and placed in three flasks each, and then water or amine solvent was added to two of the three flasks to a point just higher than the top of the carbons. The carbons were left for a week or so, occasionally opened and manually shaken to remove air pockets. Table 65 gives the measurements of wettability of the three carbons. Measurements of the change of solvent concentration were carried out and are reported in Table 65.

Table 65 Wettability of activated carbons with water and MEA solvent

| Activated Carbon | Water wetting, gm water / gm dry carbon | MEA solvent wetting | |
|-------------------------|--|---|-------------------------------|
| | | gm amine solvent / gm dry carbon | MEA concentration, wt% |
| Reference | - | - | 30.00 |
| Calgon SGL | 1.4948 | 1.445 | 29.32 |
| Norit M-1657 | 1.8992 | 1.9604 | 29.93 |
| Norit M-1731 | 1.5536 | 1.7212 | 28.96 |

10.2.2 Isothermal tests to treat MEA distillates

Isotherm tests for artificially contaminated distillates were prepared at a total concentration of 0.5 wt%, in which each degradation product, ammonia and ethylamine, contributed 0.25 wt% to the total concentration. The experiments involved weighing a specific amount of carbon, which was then placed in a 60 ml vial and a specific amount of contaminated distillate was added to each vial. Then, the vials were placed in a shaking machine for more than 48 hours. After that, samples were taken to analyse with GC-MS.

10.2.2.1 SGL activated carbon treatment

Three activated carbon forms were tested; dry, wetted with water, and wetted with MEA solvent. Figure 93 gives the degradation products and other specific distributions before and after treatment with dry SGL. As can be seen from Figure 93, ammonia and ethylamine concentrations were not reduced as the carbon dosage increased, suggesting that they are adsorbed and desorbed or have low adsorption tendency. Figure 94 gives the degradation products and other species distribution before and after treatment with water wetted SGL. It can be seen from Figure 94 that ammonia was adsorbed at the first carbon dosage, but no change in concentration was observed for ethylamine, so it is unlikely to be adsorbed. Figure 95 gives the degradation products and other species distribution with the SGL wetted with MEA. From Figure 95, ammonia concentration is slightly reduced with increase of the carbon dosage, but this does not reflect the good adsorption. Ethylamine showed poor adsorption. Figure 96 summaries the SGL adsorption tests, and it can be safely concluded that the ammonia and ethylamine had low or no adsorption tendency.

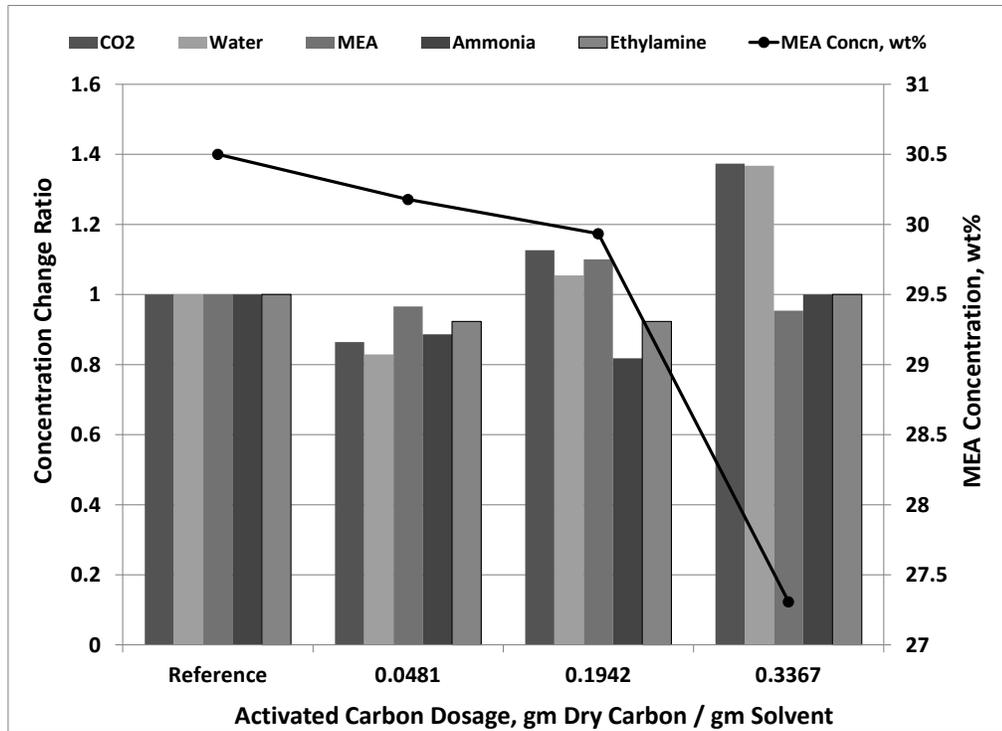


Figure 93 Isotherm of dry SGL for contaminants and others species in MEA

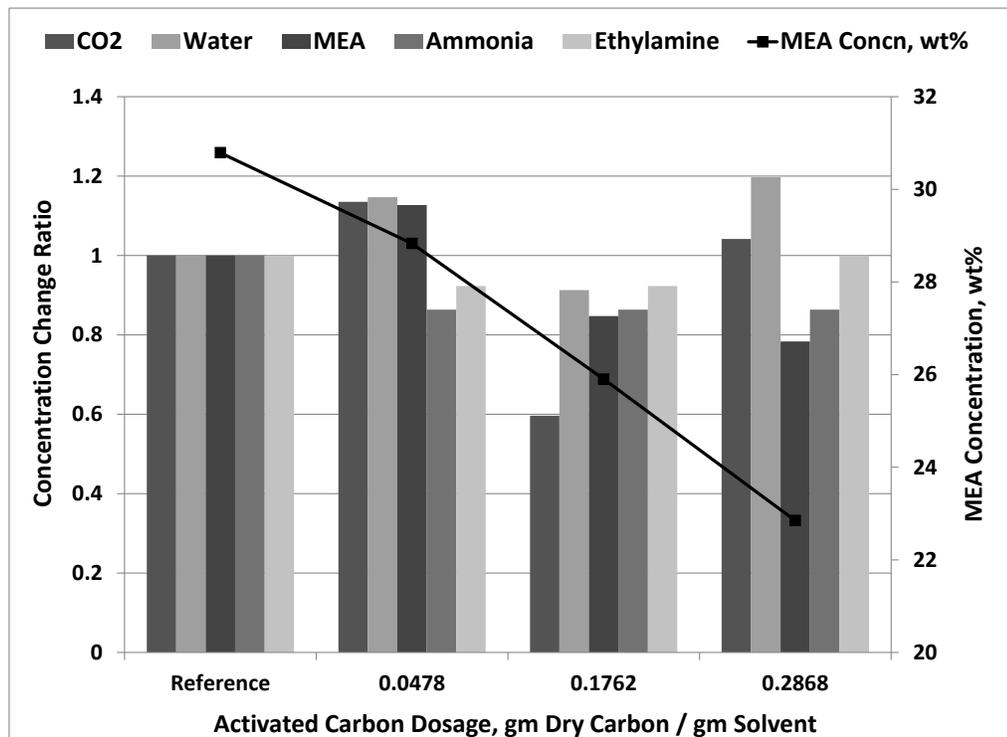


Figure 94 Isotherm of water wetted SGL for contaminants and others species in MEA

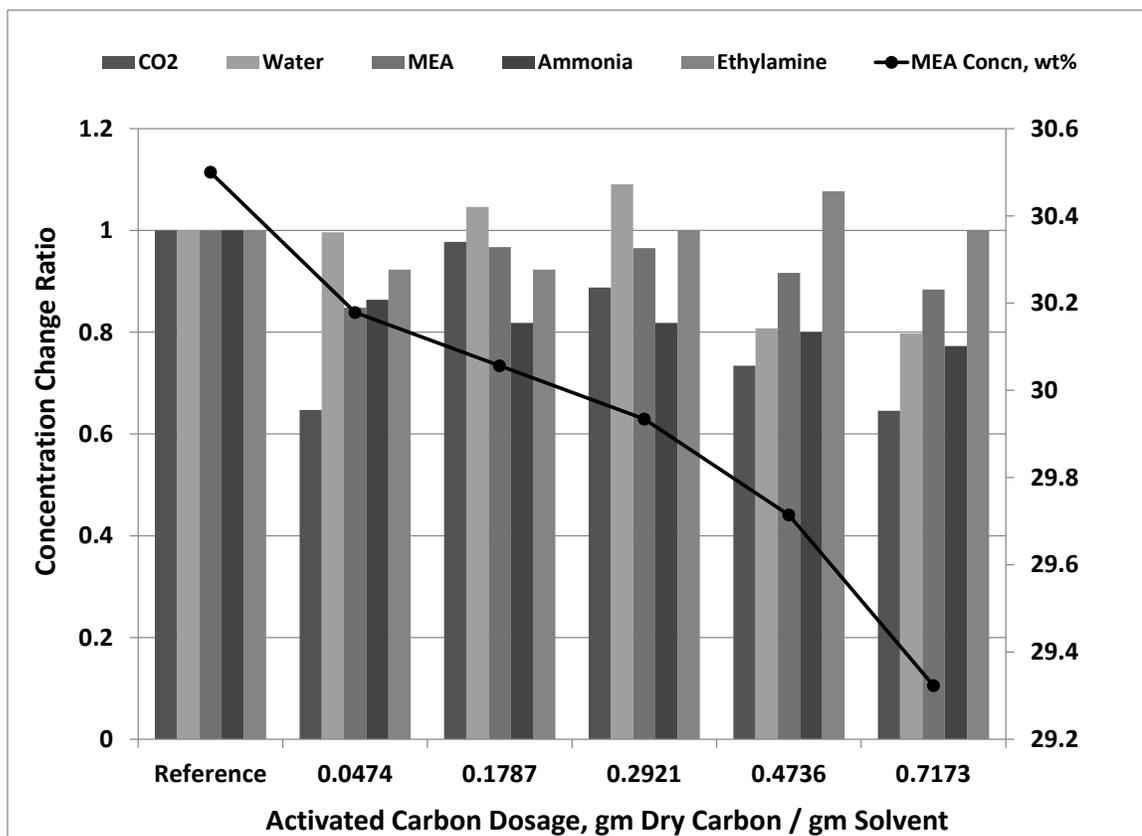


Figure 95 Isotherm of water wetted SGL for contaminants and others species in MEA

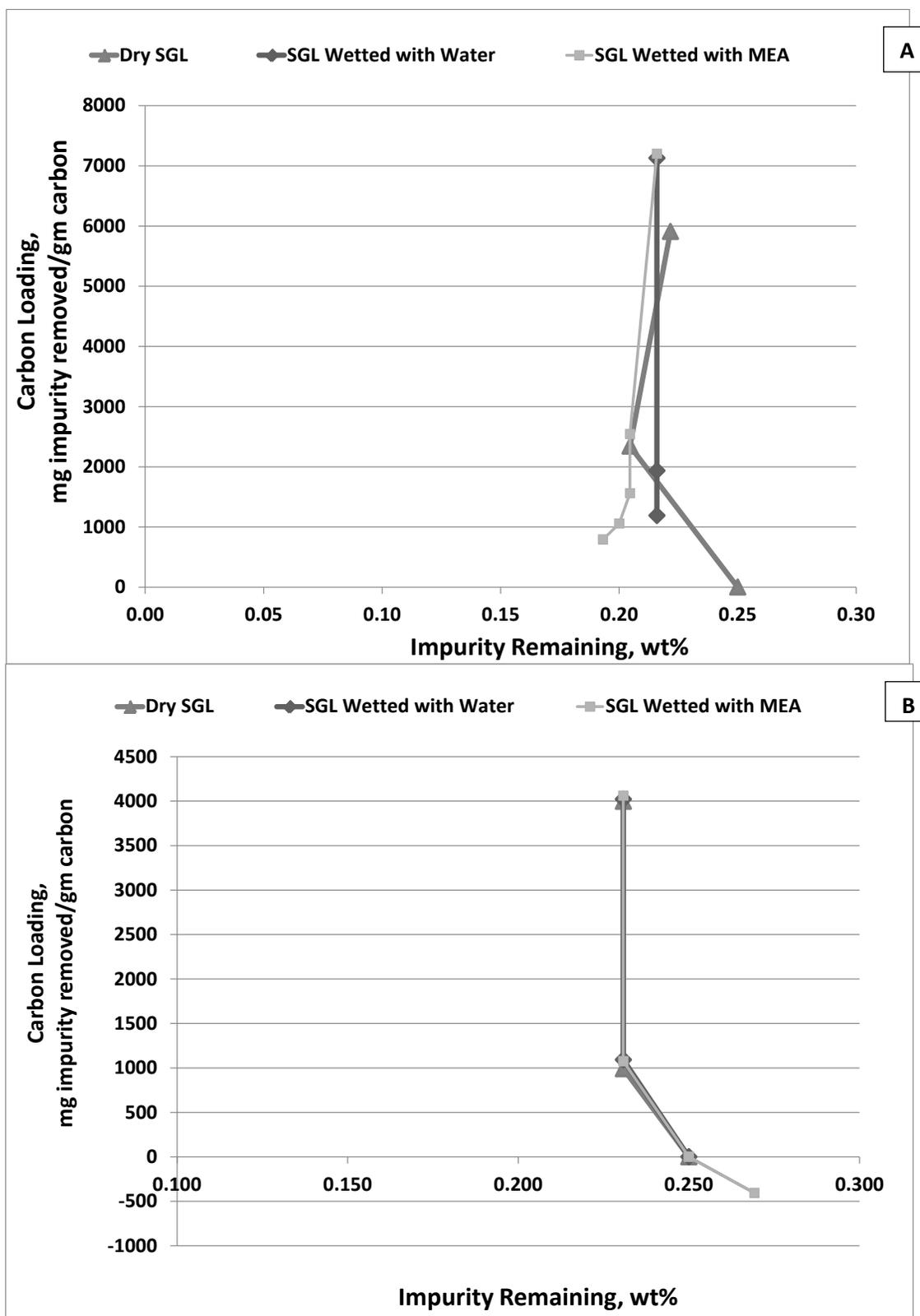


Figure 96 Isotherm SGL for removing ammonia (A) and ethylamine (B) in MEA

10.2.2.2 M-1657 activated carbon treatment

Three activated carbon forms were tested: dry, wetted with water, and wetted with MEA solvent. Figures 97, 98, and 99 give the degradation products distribution before and after treatment with dry M-1657. It can be seen from Figure 97 that ammonia and ethylamine concentrations were not reduced as the carbon dosage increased, indicating that they were not adsorbed by the carbon. Wetting the M-1657 with water or MEA did not help remove ammonia or ethylamine, as shown in Figures 98 and 99; therefore, it can be concluded that M-1657 has a very weak adsorption tendency with respect to ammonia and ethylamine.

10.2.2.3 M-1731 activated carbon treatment

Three activated carbon forms were tested: dry, wetted with water, and wetted with MEA solvent. Figure 100 gives the degradation products and other species distribution before and after treatment with M-1731. It can be seen from Figure 100 that ammonia and ethylamine concentrations were not reduced as the carbon dosage increased, indicating that they are not adsorbed by the carbon. The M-1731 wetted with water or MEA did not help remove ammonia or ethylamine, as shown in Figures 101 and 102; therefore, it can be concluded that M-1657 has weak adsorption tendency with respect to ammonia and ethylamine.

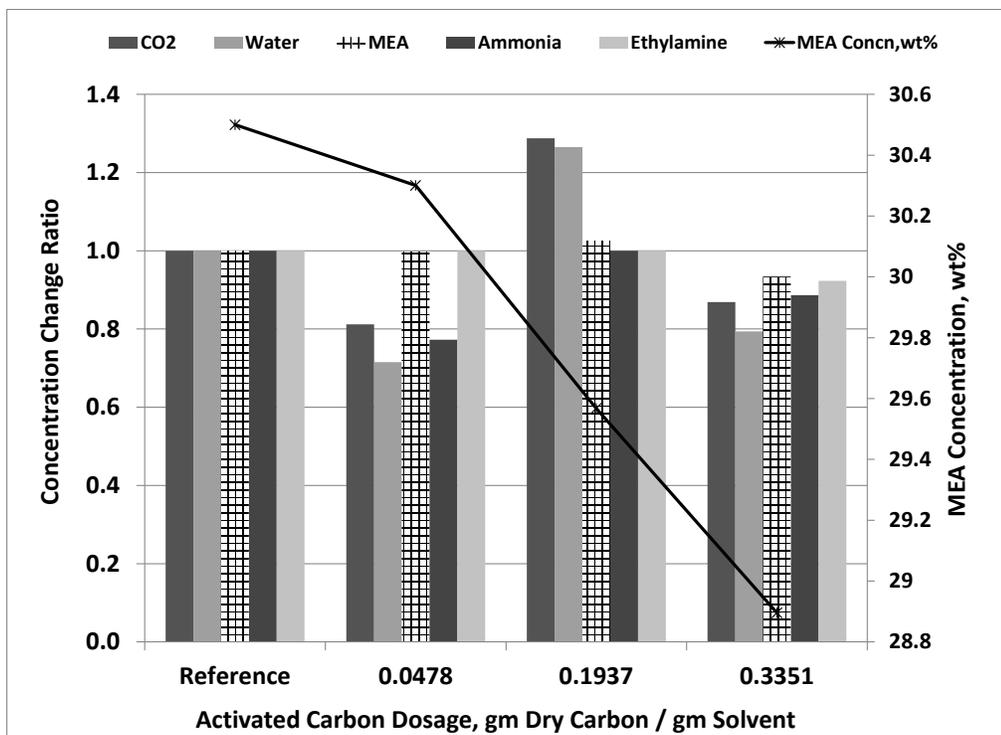


Figure 97 Isotherm of dry M-1657 for contaminants and others species in MEA

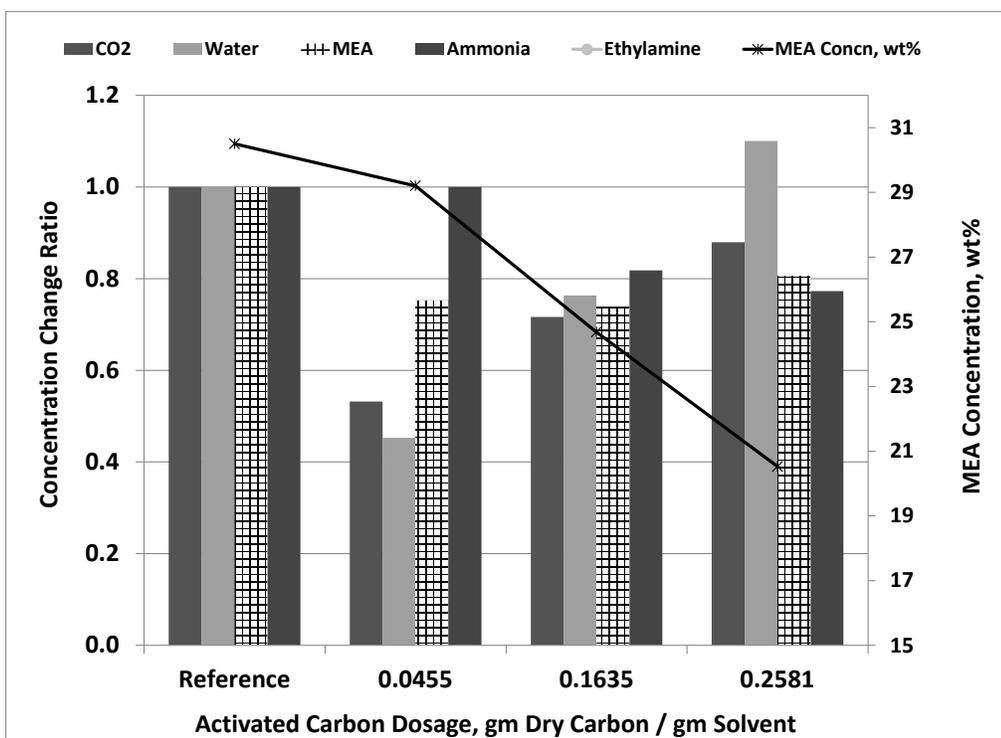


Figure 98 Isotherm of water wetted M-1657 for contaminants and others species in MEA

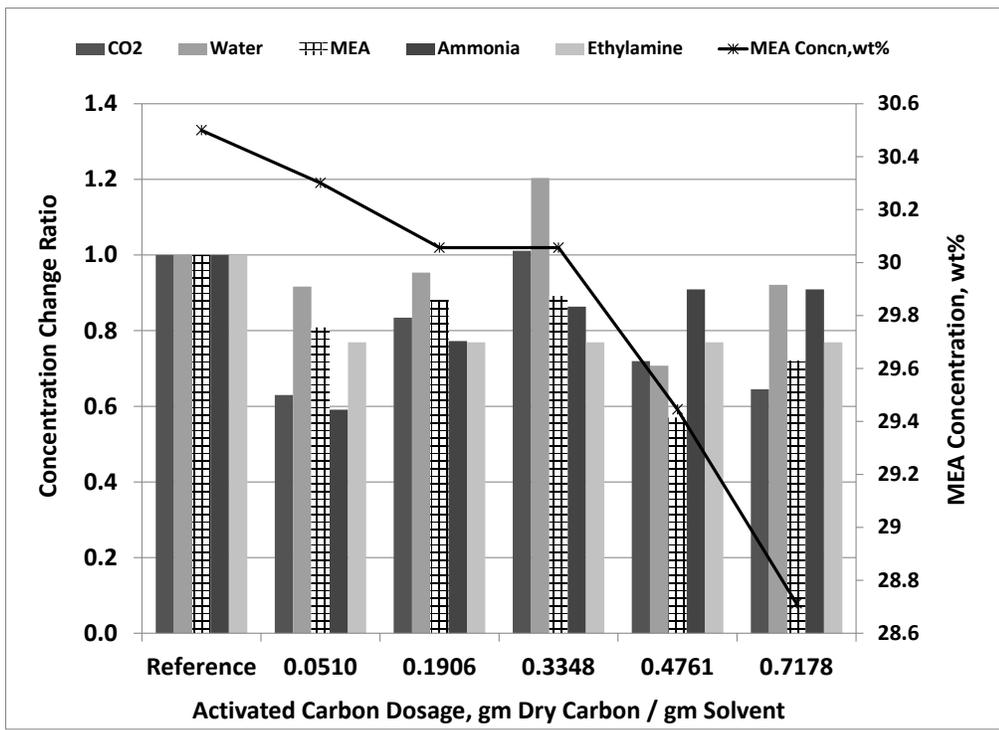


Figure 99 Isotherm of MEA wetted M-1657 for species in MEA solvent

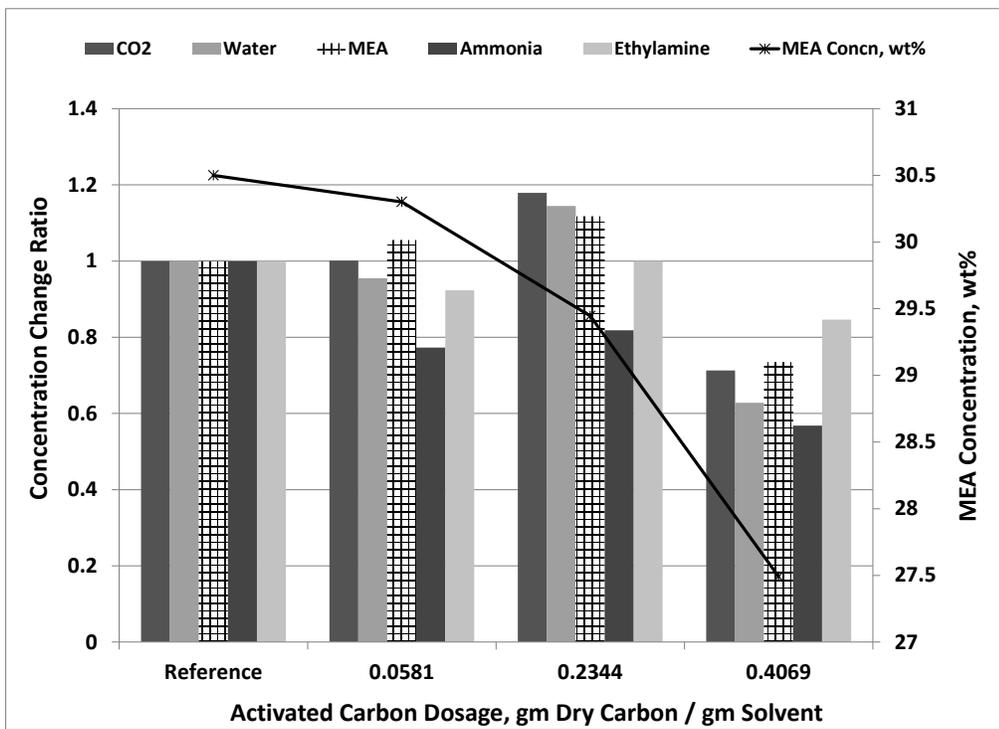


Figure 100 Isotherm of dry M-1731 for species in MEA solvent

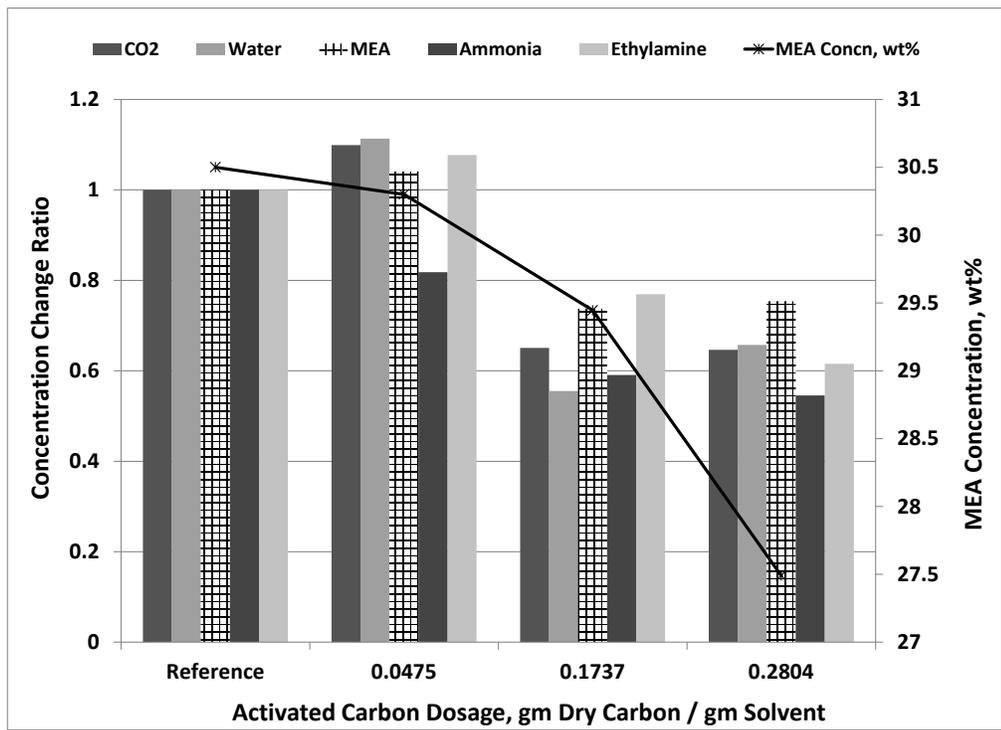


Figure 101 Isotherm of water wetted M-1731 for species in MEA solvent

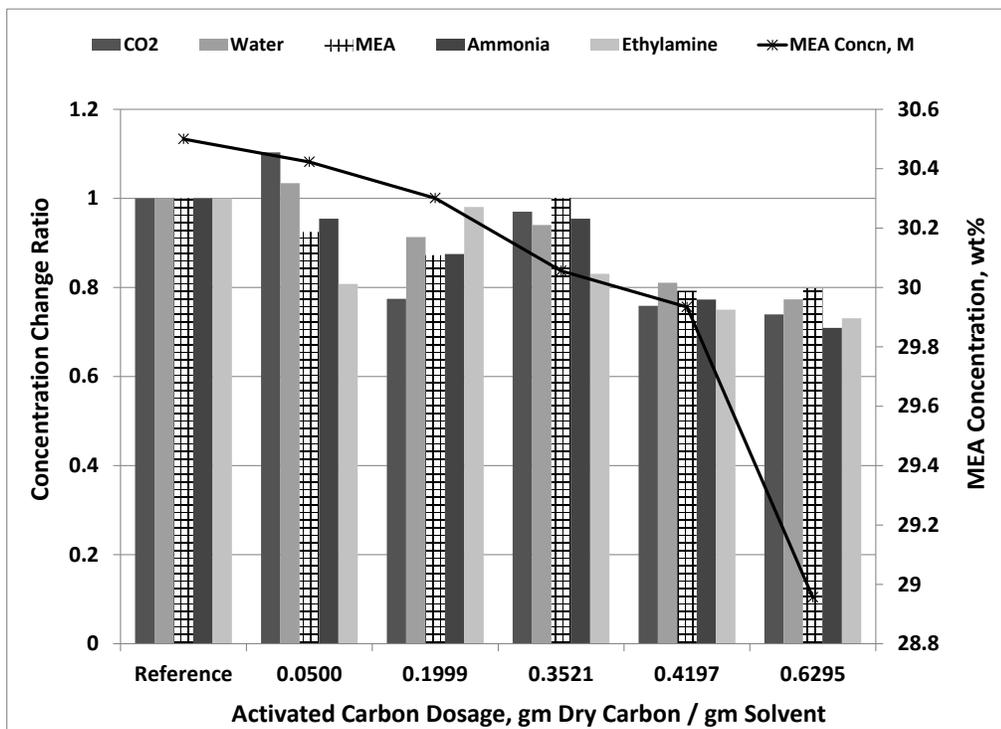


Figure 102 Isotherm of MEA wetted M-1731 for species in MEA solvent

10.2.3 Dynamic adsorption of 5M MEA distillates

Two types of dynamic adsorption experiments were carried out. The first was a closed-loop process wherein the treated amine after treatment in the carbon bed, was returned to the feed tank. The objective is to show if any of the degradation products, ammonia or ethylamine, would be reduced when small amounts of degraded solvent are treated. The second configuration is a typical dynamic adsorption system, where the amine is passed once through the carbon column. The second test is more dynamic and closer to the real adsorption capacity of such columns.

10.2.3.1 Closed-loop dynamic adsorption

A degraded MEA solvent was prepared for the dynamic adsorption tests. The solvent was not loaded with CO₂ to allow better determination of the ammonia and ethylamine chromatograph peaks. The concentration of ammonia and ethylamine was 0.25 wt% each. This test was conducted using two forms of SGL activated carbon to check if any degradation products could be removed by treating the degraded distillate in an activated carbon column. The two forms were: SGL activated carbon wetted with water and wetted with MEA solvent, respectively. Both types of carbons were wetted for two days or more in sealed beakers.

A schematic diagram of the closed-loop configuration of the activated carbon dynamic test is given in Figure 103. It consisted of feed and washing tanks, a liquid pump, a flow meter, the activated carbon column, a sampling port, and a return line for the treated amine to return to the feed tank. The experimental procedures were as follows:

1. At start-up, the wetted activated carbon was loaded into the column. The column of activated carbon was compressed manually to remove air. Glass fibres were used at the top and bottom of the activated carbon column to prevent small particles from exiting column and to hold the column of carbon. The column was filled with water wetted SGL in the first run, while in the second run, the column was filled with MEA wetted SGL. The activated carbon column size was in 35 cm in length with a diameter of 2 cm; therefore the total activated column volume is 110 cm³.
2. The set-up was washed with water, in the case of water wetted SGL, from the water tank (T-03) or with clean and unloaded solvent, in the case of amine wetted SGL, from a pre-washing solvent tank (T-01) to flush the lines and equipment. Then, the washing solutions were drained as waste.
3. Each run was started by allowing the degraded solvent to flow from the degraded solvent tank (T-02) to the liquid pump (P-01), a flow meter (F-01), and then to the carbon column. The time was measured from the beginning of the run, and from time to time, samples were taken for GC-MS analysis. The treated amine was returned back to the feed tank, which was opened to the atmosphere with only a needle.
4. The total flow rate as measured with the flow meter (F-01), which was calibrated for solvent at 3.0 gph. The flow rate for the second test was higher than that, 4.0 gph.
5. After the whole degraded solvent was treated with carbon, the run was and lines and the equipment was flushed with water in preparation for cleaning. Then, the set-up was disassembled for further cleaning and drying.

The samples obtained from the experiment were analysed with GC-MS. The variation of the amine solvent concentration is illustrated in Figures 104 and 105 for water wetted

SGL and MEA wetted SGL, respectively. These breakthrough curves of the degradation products, ammonia and ethylamine, do not show that ammonia and ethylamine are adsorbed by activated carbon in either case, as suggested by the fluctuation of the degradation product concentration. In the case of MEA wetted SGL, the slight reduction in the ammonia could be due to adsorption, while the reduction of ethylamine concentration could mean evaporation loss has occurred or the carbon has a very low adsorption capacity that is reached as soon as the degraded solvent begins treatment.

10.2.3.2 Open-loop dynamic adsorption

This test was done by using two types of activated carbon that were wetted with MEA; they are SGL and M-1731. The objective was to see if degradation products could be removed by treating the degraded distillate. The experimental set-up was very similar to the closed-loop set-up in Figure 103 except there is no return stream to the feed tank and all treated solvent is collected in the waste tank. The steps given in the previous section are applicable to this experiment as well. The results from this experiment are illustrated in Figures 106 and 107. The trend of the concentration determined over the test period suggests that ammonia and ethylamine are not adsorbed in either carbon (SGL and M-1731). Therefore, it is concluded that ammonia and ethylamine have very poor adsorption tendency or they cannot be removed from contaminated distillates, and an alternative method should be investigated.

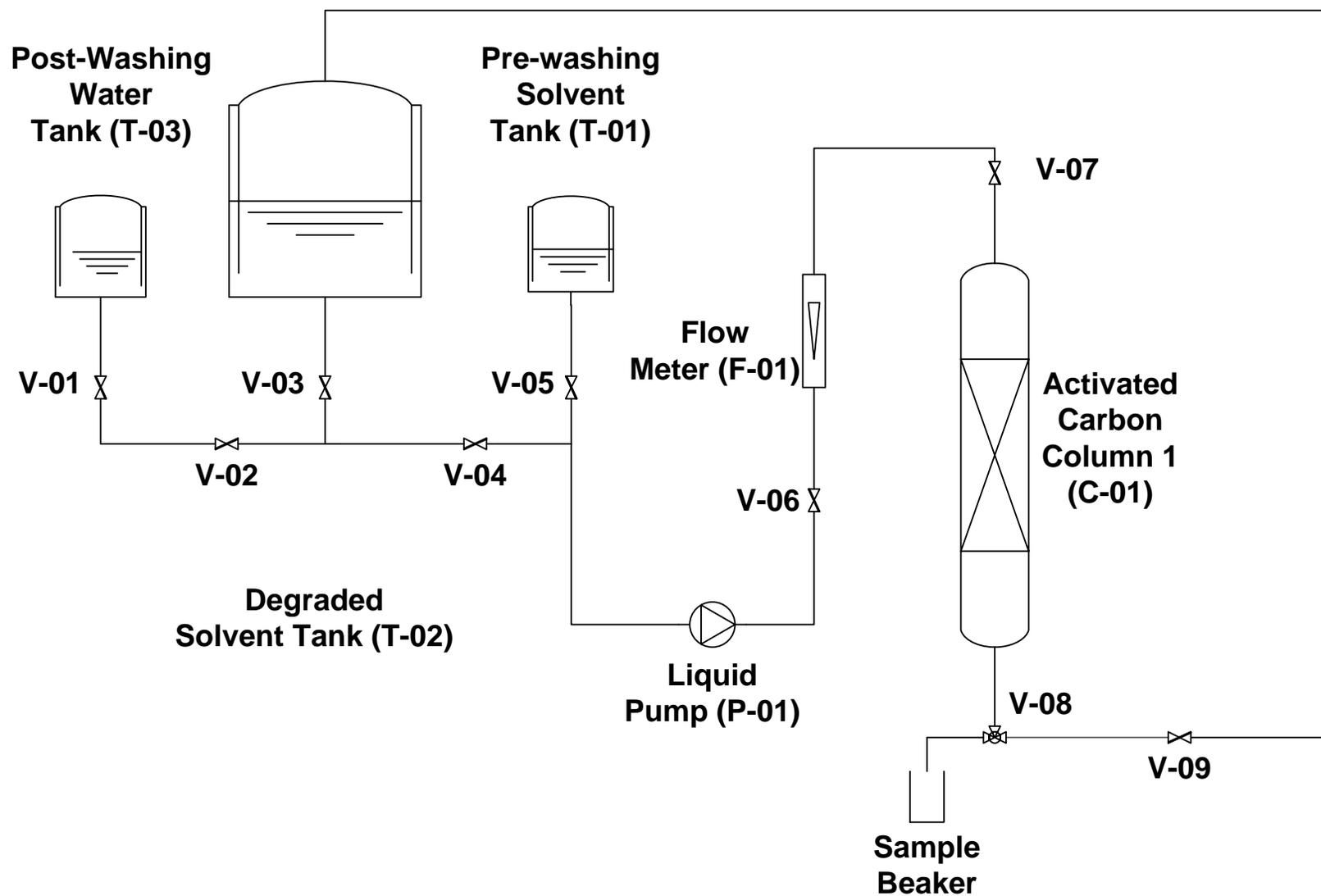


Figure 103 Schematic diagram of closed-loop activated carbon dynamic adsorption test – MEA solvent

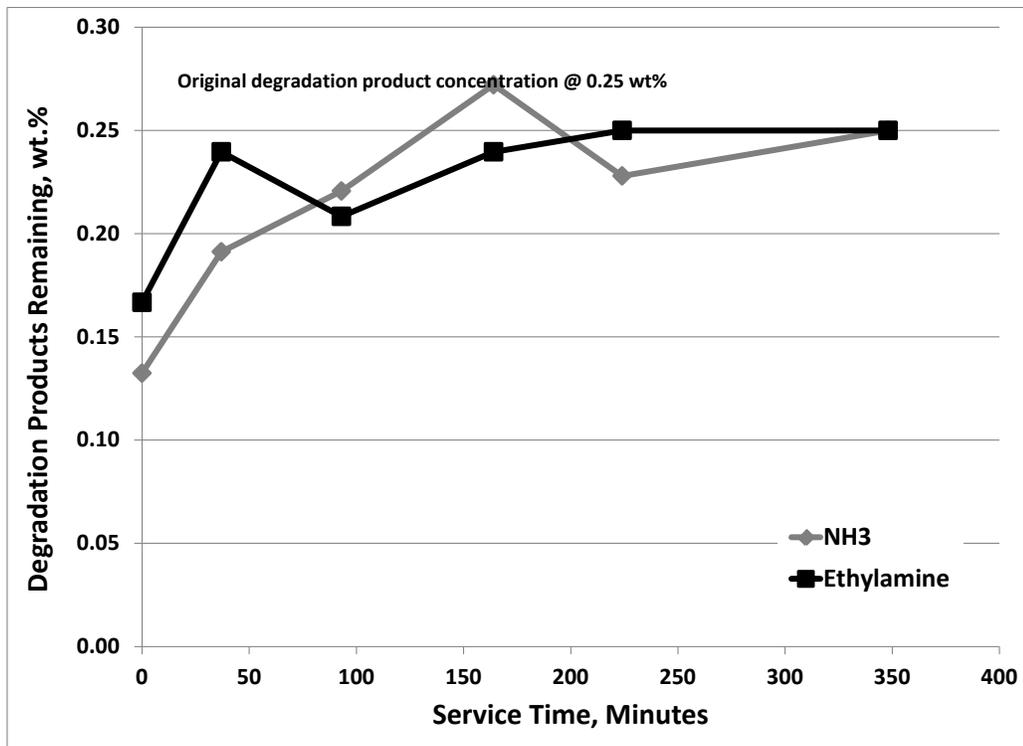


Figure 104 Closed-loop dynamic adsorption curves of water wetted SGL with water

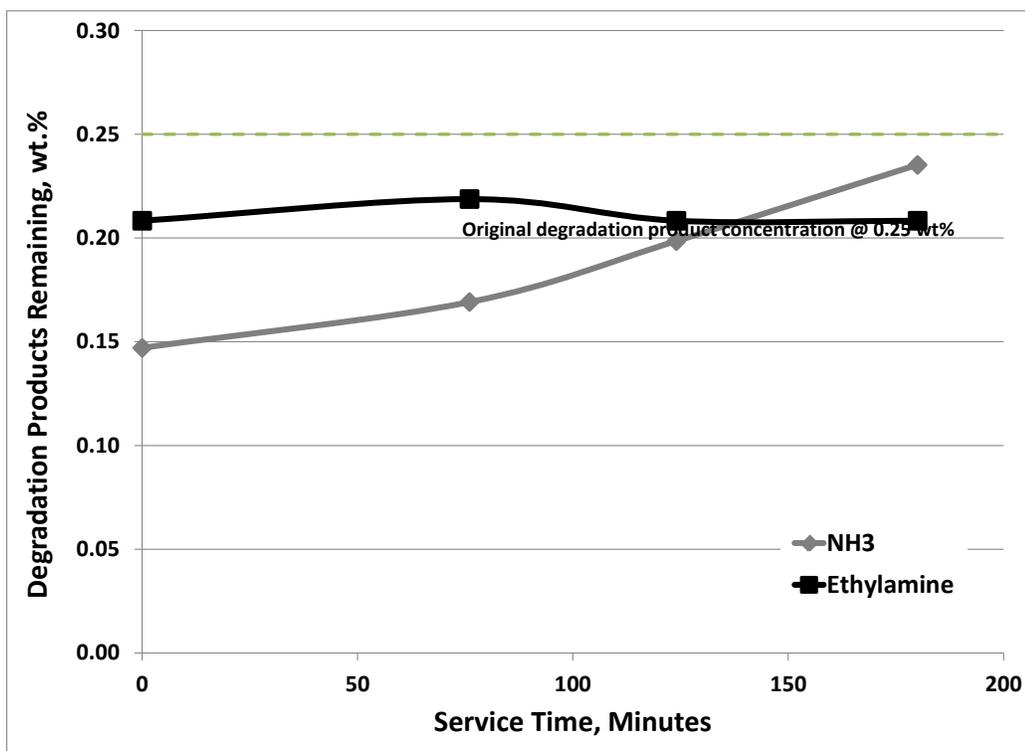


Figure 105 Closed-loop dynamic adsorption curves of MEA wetted SGL with MEA

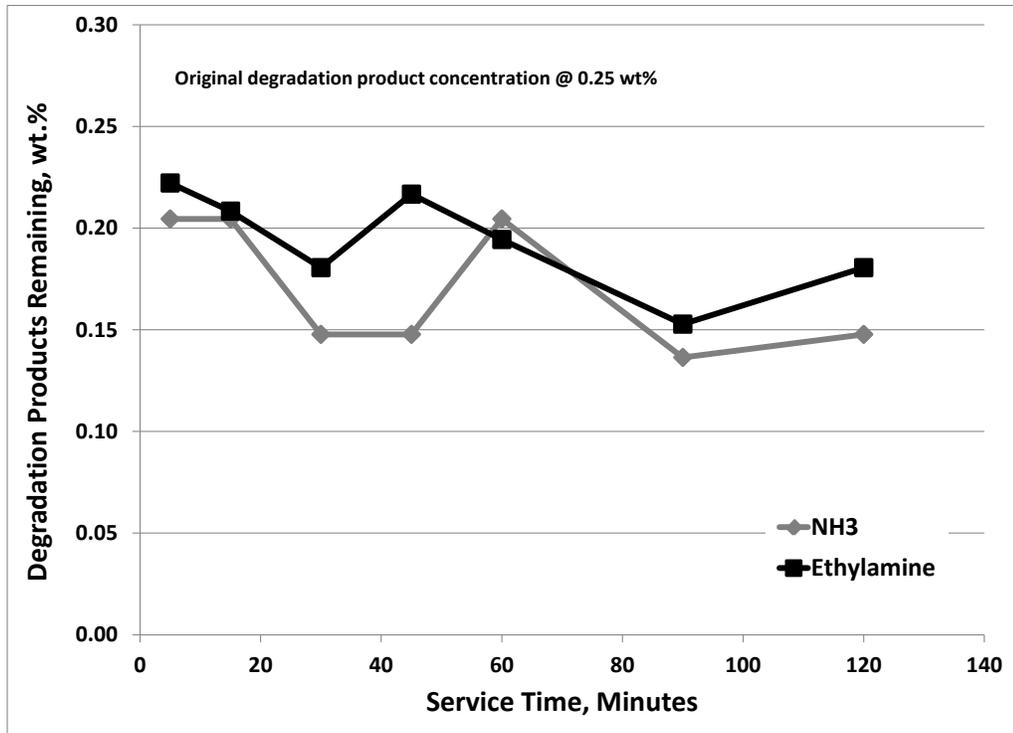


Figure 106 Open-loop dynamic adsorption curves of MEA wetted SGL with MEA

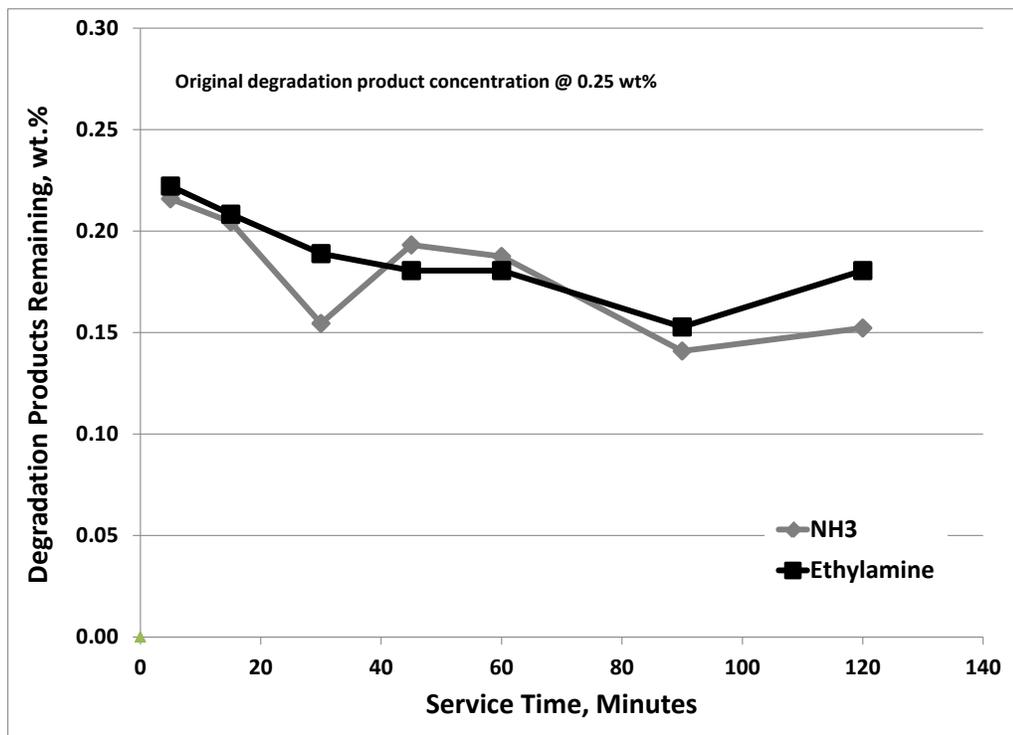


Figure 107 Open-loop dynamic adsorption curves of MEA wetted M-1731 with MEA

10.3 Purifying of MEA/MDEA Distillates

It was found that MEA/MDEA solvent recovered by thermal distillation is contaminated with some degradation products: ammonia, ethylamine, 3-Picoline, 2-Methylamino ethanol, 1,3-Propanediamine, and N-Acetyethanolamine. The contaminated distillate was treated with activated carbon. Two types of contaminated distillates were used: one obtained from the thermal distillation tests if their amount was sufficient for testing or artificial distillates that are mixed with contaminants.

The three types of carbon used were: SGL, M1653, and M-1731. The carbons were used in three different forms: dry, wetted with water, and wetted with amine solvent. The first step in evaluation of the capability of carbons to remove degradation products was to determine the wettability capacity of the carbons with water and amine solvent. Then, isotherm or batch adsorption experiments were conducted, and, finally, the dynamic adsorption experiments were run.

10.3.1 Wettability of Activated Carbon

Before conducting the adsorption tests, it was important to obtain the wettability of activated carbon with both water and 5M MEA/MDEA solvent. The three activated carbons were weighed and placed in three flasks for each carbon, and then water or amine solvent were added to a point that higher than the top of the carbons in two of the three flasks for each carbon, respectively. The carbon was left for a week or so and was occasionally opened and manually shaken to remove air pockets. Table 4 gives the measurements of wettability of the three carbons. Measurements of change of solvent concentration were carried out and are reported in Table 66.

Table 66 Wettability of activated carbons with water and MEA/MDEA solvent

| Activated Carbon | Water wetting, (gm water / gm dry carbon) | MEA/MDEA solvent wetting | |
|------------------|--|------------------------------------|-----------------------------|
| | | (gm amine solvent / gm dry carbon) | MEA/MDEA concentration, wt% |
| Reference | - | - | 45.00 |
| Calgon SGL | 1.4948 | 1.5061 | 44.46 |
| Norit M-1657 | 1.8992 | 1.9603 | 44.82 |
| Norit M-1731 | 1.5536 | 1.7052 | 43.92 |

10.3.2 Isothermal adsorption to treat MEA/MDEA distillates

Isotherm tests for artificially contaminated distillates were prepared at a total concentration of 1.5 wt%, in which each degradation product contributes 0.3 wt%. The experiments involved weighing a specific amount of carbon, which was placed in a 60 ml vial, and then a specific amount of contaminated distillate was added to each vial. Then the vials were placed in a shaking machine for more than 48 hours. After that, samples were taken to be analyzed with GC-MS to determine the chemical distribution and concentration as well as the total solvent concentration, which was determined with HCl titration.

10.3.2.1 SGL activated carbon treatment

Three activated carbon forms were tested: dry, wetted with water, and wetted with MEA/MDEA solvent. Figure 108 gives the degradation products and other specific distribution before and after treatment with the dry SGL. It can be seen from Figure 16 that some degradation product concentrations were reduced as the carbon dosage increased, reflecting that they were adsorbed by the carbon. 3-picoline completely disappeared from the treated sample after a dosage of 0.05 gm carbon/gm solvent. Ammonia, ethylamine, and N-(2-hydroxyethyl) ethanol were gradually adsorbed at different rates. It seems that only 2-methylamino ethanol would not adsorb or had very low adsorption tendency. Figure 109 gives the degradation products and other species distribution before and after treatment with water wetted SGL. It can be seen from Figure 109 that some degradation product concentrations were reduced as the carbon dosage increased, reflecting that they were adsorbed by the carbon and the adsorption was improved compared to the dry SGL case. 3-picoline completely disappeared from treated

sample after a dosage of 0.05 gm carbon/gm solvent. Ammonia, ethylamine, and N-(2-hydroxyethyl) ethanol were gradually adsorbed at different rates. It seems only 2-methylamino ethanol would not adsorb. Figure 110 gives the degradation products and other species distribution before and after treatment with blended amine wetted SGL. It can be seen from Figure 110 that some degradation product concentrations were reduced as the carbon dosage increased, reflecting that they were adsorbed by the carbon, and the adsorption was improved compared to the dry SGL case. Also, solvent concentration loss was minimized compared to water wetted SGL. 3-picoline completely disappeared from treated sample after the dosage of 0.17 gm carbon/gm solvent. Ammonia was not adsorbed at the same rate as with dry and water wetted SGL, while N-(2-hydroxyethyl) ethanol was gradually adsorbed as carbon dosage increased. It seems only ethylamine and 2-methylamino ethanol would not adsorb or have very low tendency to be adsorbed on SGL wetted with MEA/MDEA solvent.

Figure 111 shows the carbon loading for removal of 3-Picoline in SGL in its three forms; dry, wetted with water and wetted with blend amine. The later one gives the best results. Slightly different observations were made in the case of the removal of N-(2-hydroxyethyl) ethanol with SGL wetted with blended amine versus the dry or water wetted carbons. Blended amine wetted SGL had superior results in reducing the impurity concentration at a much higher magnitude than the other two carbons and with comparable carbon dosage, as shown in Figure 112.

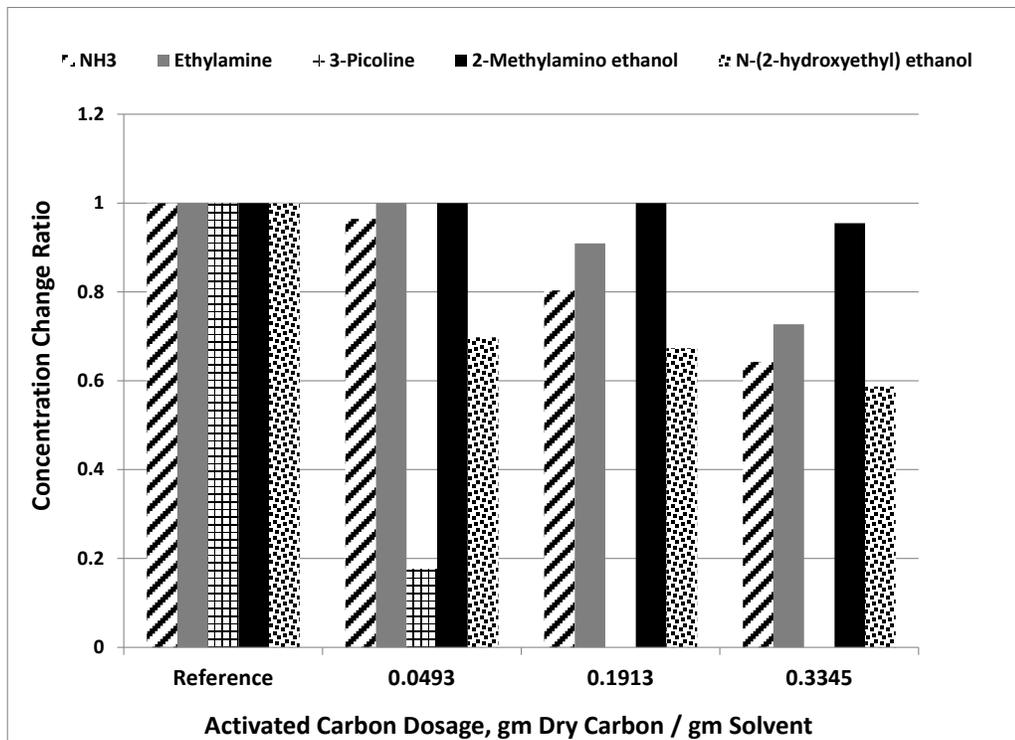


Figure 108 Isotherm of dry SGL for contaminants in MEA/MDEA

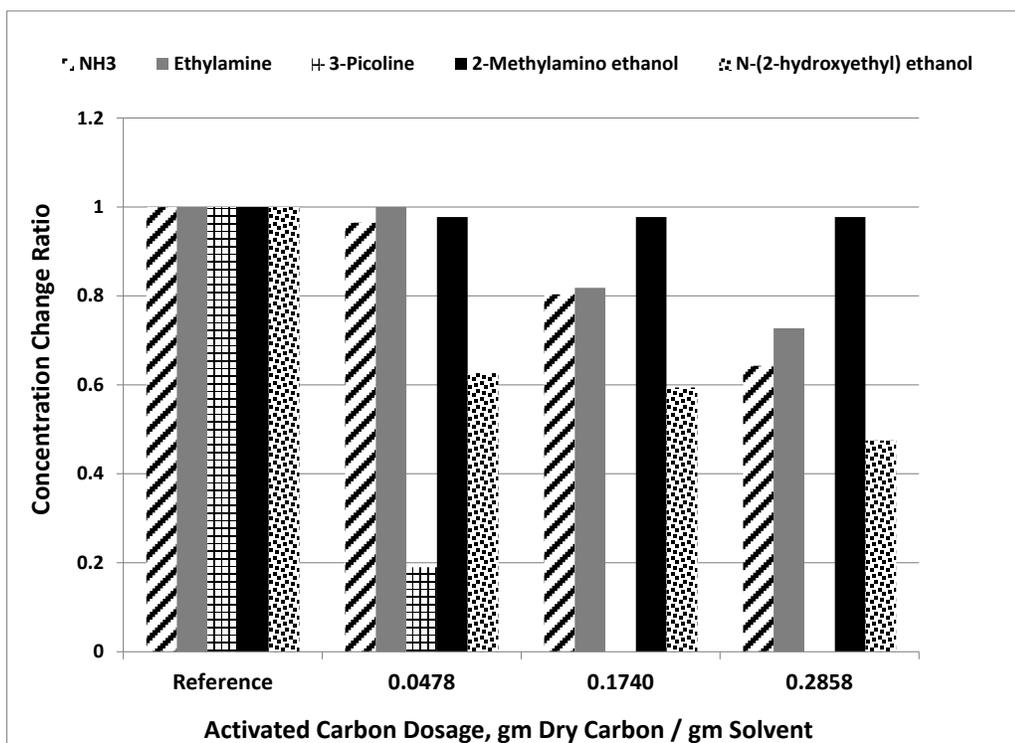


Figure 109 Isotherm of water wetted SGL for contaminants in MEA/MDEA

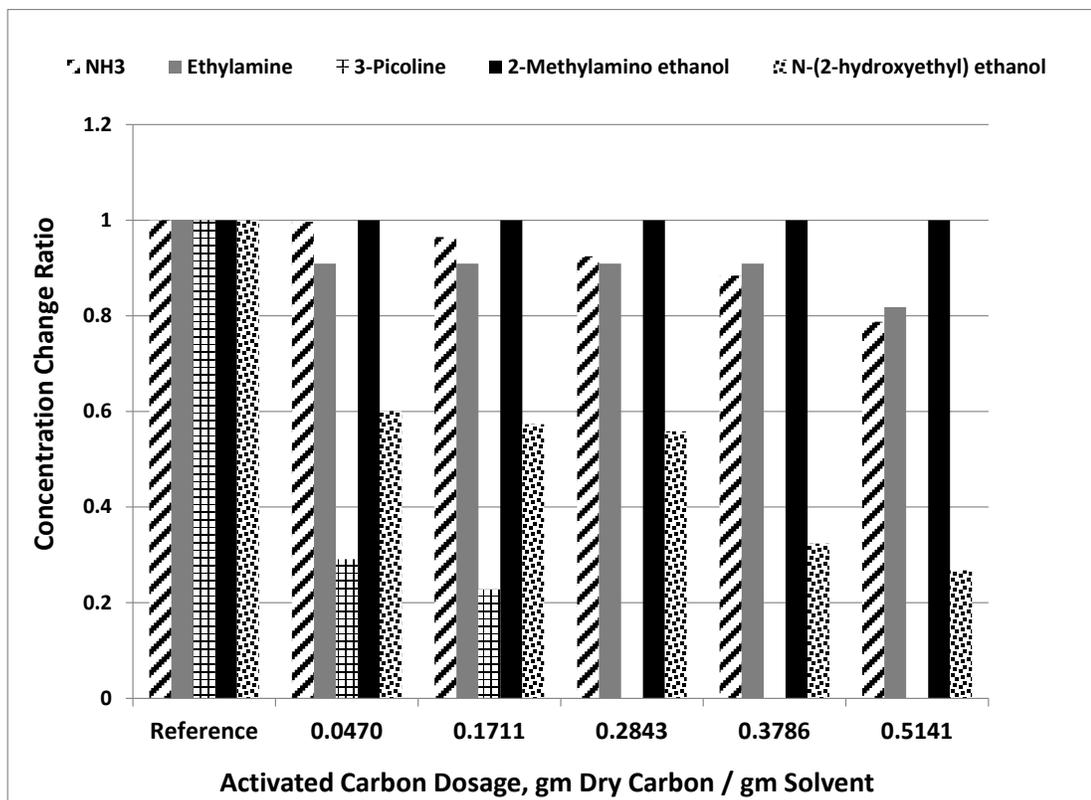


Figure 110 Isotherm of amines wetted SGL for contaminants in MEA/MDEA

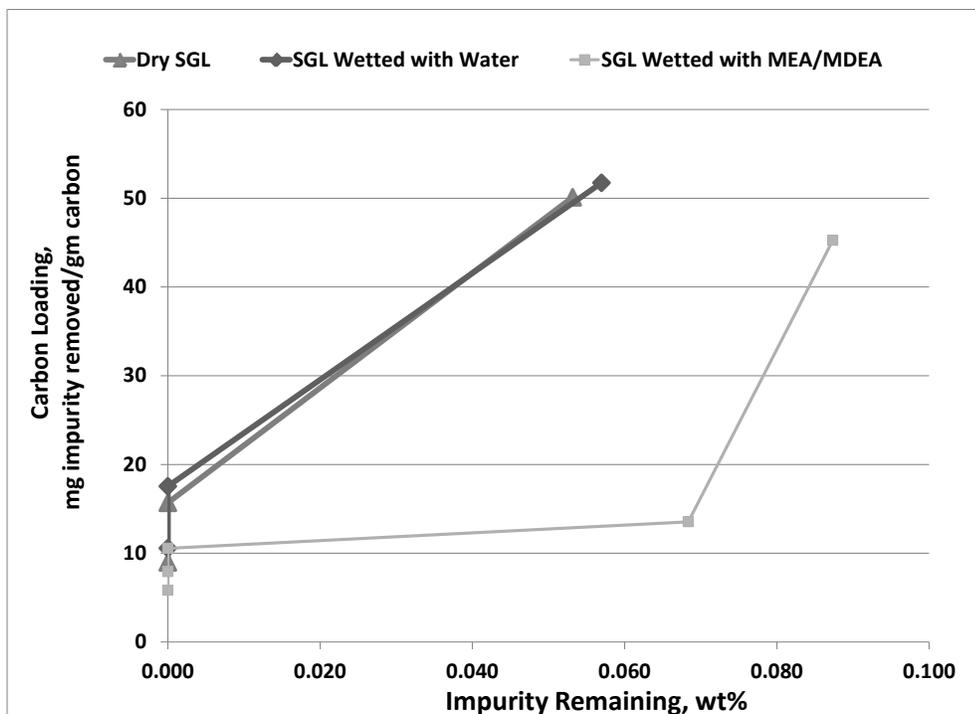


Figure 111 Isotherm SGL loading for 3-Picoline vs. 3-Picoline remaining in MEA/MDEA

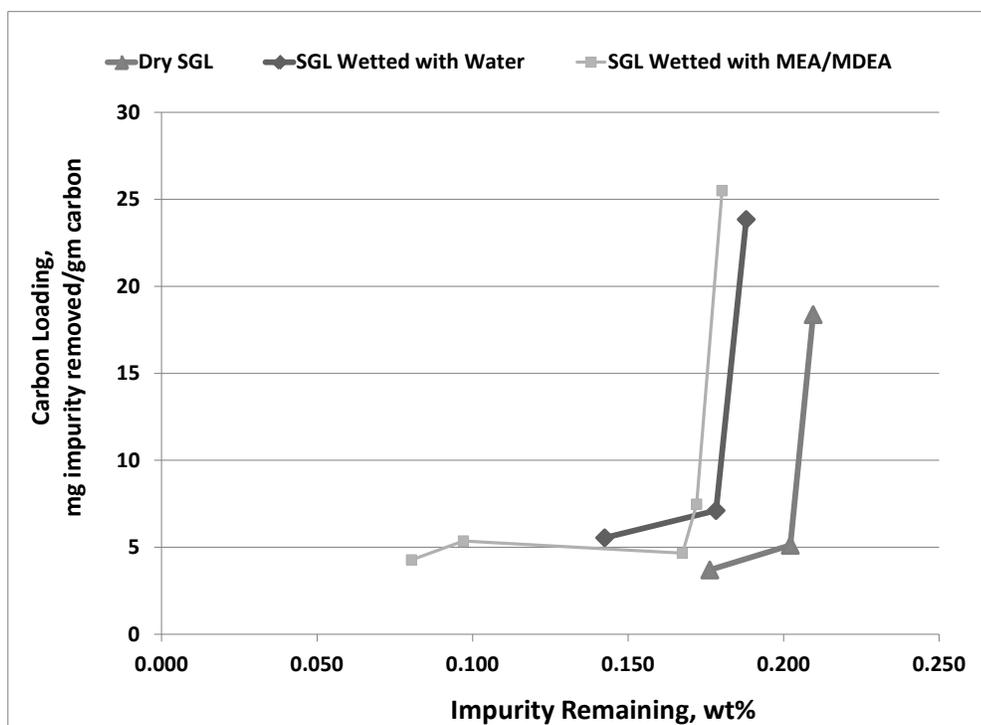


Figure 112 Isotherm SGL loading for N-(2-hydroxyethyl) ethanol vs. N-(2-hydroxyethyl) ethanol remaining in MEA/MDEA

10.3.2.2 M-1657 activated carbon treatment

Figure 113 illustrates a comparison of the adsorption of 3-Picoline over M-1657 carbon in its three forms: dry, wetted with water, and wetted with blended amine. From the graph, it can be seen that the carbon loading that is required to remove 3-Picoline is minimized when the activated carbon is wetted by water and then when it is wetted with blended amine followed by dry carbon. The dry carbon would not achieve the maximize removal of 3-Picoline. Removal of N-(2-hydroxyethyl) ethanol in M-1657 is illustrated in Figure 114. The three forms of carbon could lead to the reduction of the concentration of this degradation product; however, the M-1657 wetted with amine provided the ultimate reduction in concentration from 0.3 wt% to around 0.025 wt% at loading of around 15 mg N-(2-hydroxyethyl) ethanol/gm carbon at lower loading. The removal of the degradation product at the lower loading worsened but still gave a low concentration of 0.1 wt%, which is a reduction by 66% of the original contamination.

10.3.2.3 M-1731 activated carbon treatment

Figure 115 gives the adsorption of 3-Picoline, which could be treated by the three carbon forms; however, the cases in which M-1731 was wetted with water and amine provided superior results for removal of this degradation product. Removal of N-(2-hydroxyethyl) ethanol by M-1731 is given in Figure 116. It can see that the carbon wetted with blended amine could reduce the degradation products to low levels and at lower carbon loading.

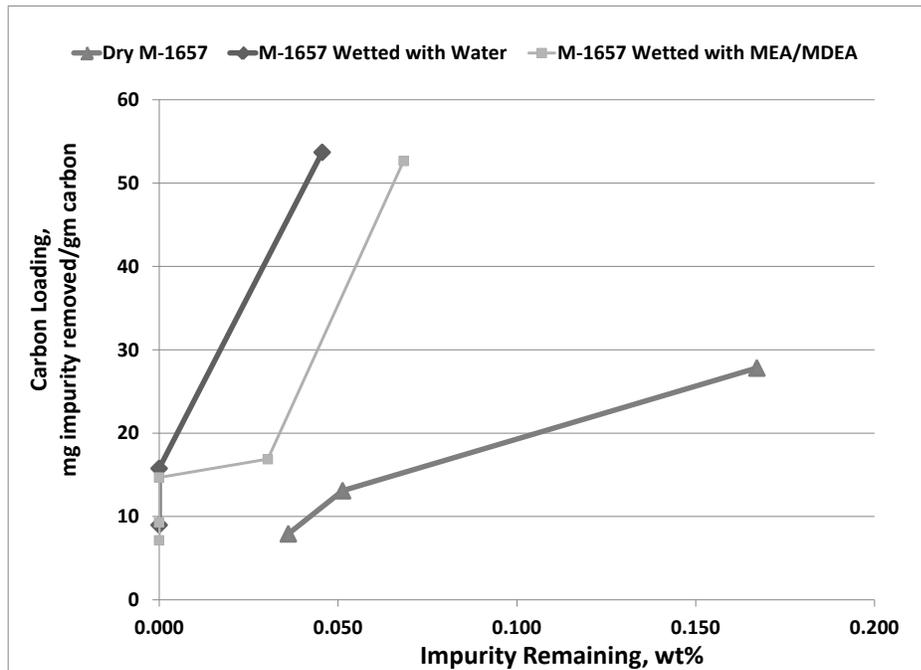


Figure 113 Isotherm M-1657 loading for 3-Picoline vs. 3-Picoline remaining in MEA/MDEA

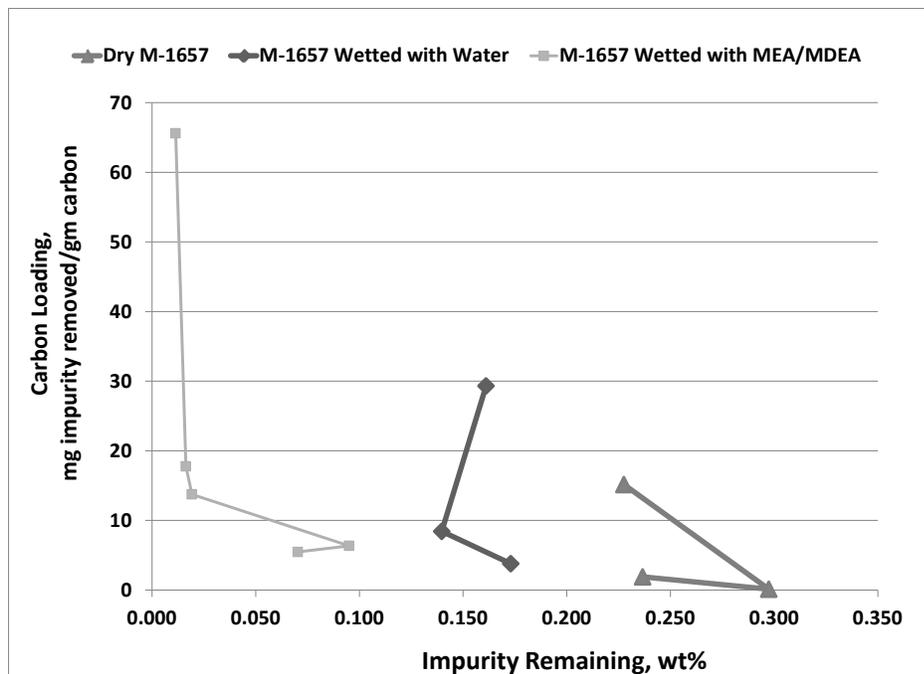


Figure 114 Isotherm M-1657 loading for N-(2-hydroxyethyl) ethanol vs. N-(2-hydroxyethyl) ethanol remaining in MEA/MDEA

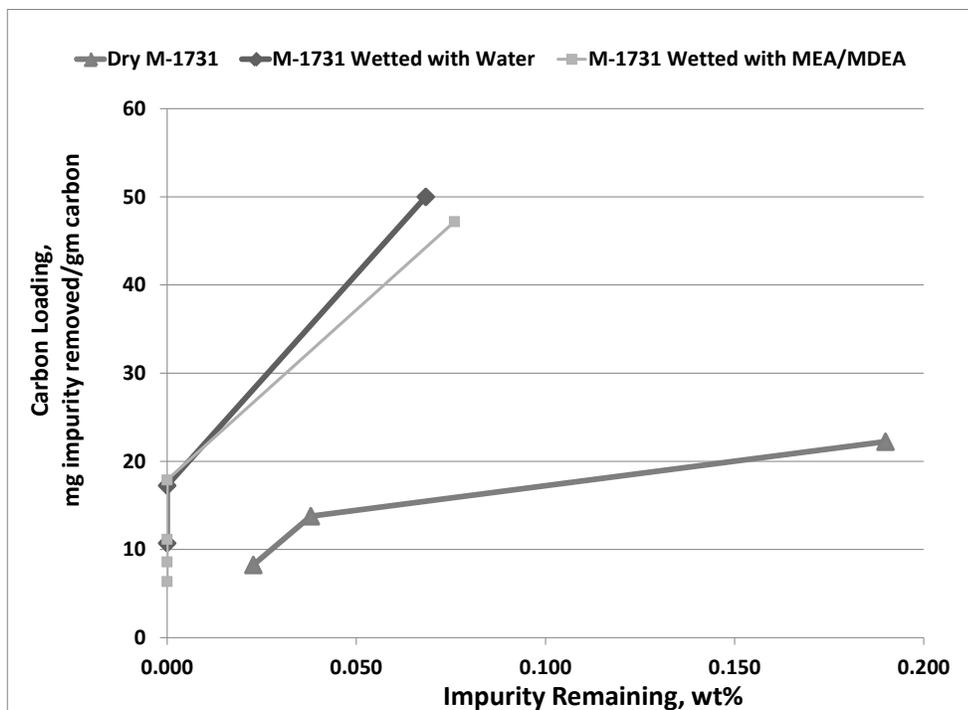


Figure 115 Isotherm M-1731 loading for 3-Picoline vs. 3-Picoline remaining in MEA/MDEA

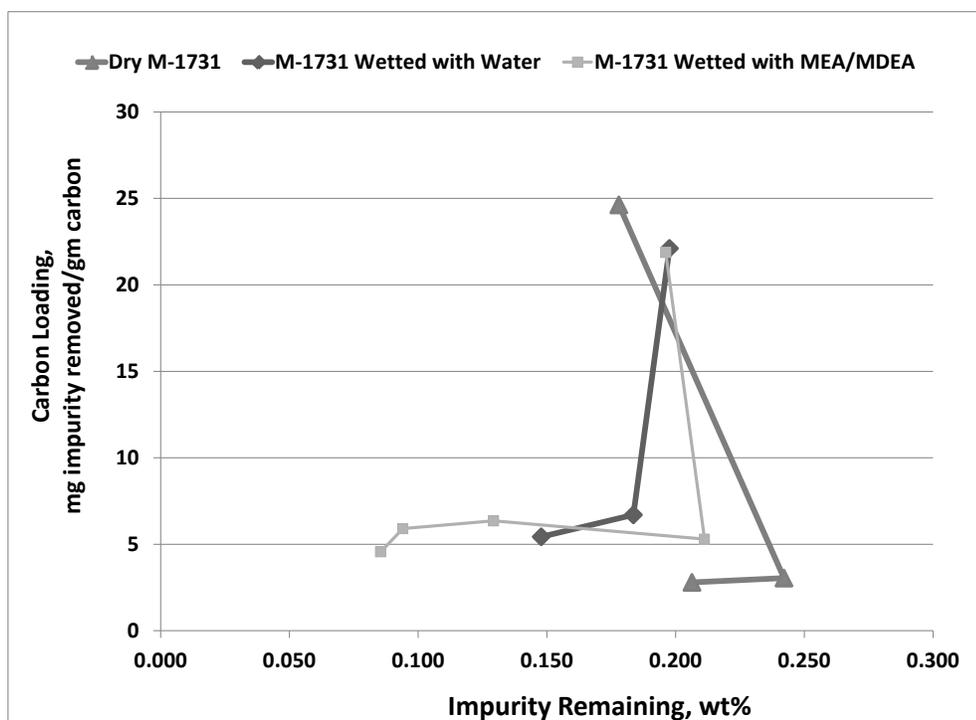


Figure 116 Isotherm M-1731 loading for N-(2-hydroxyethyl) ethanol vs. N-(2-hydroxyethyl) ethanol remaining in MEA/MDEA

10.3.3 Isothermal adsorption to treat distillate of MEA/MDEA-4-1.0%-70mmHg

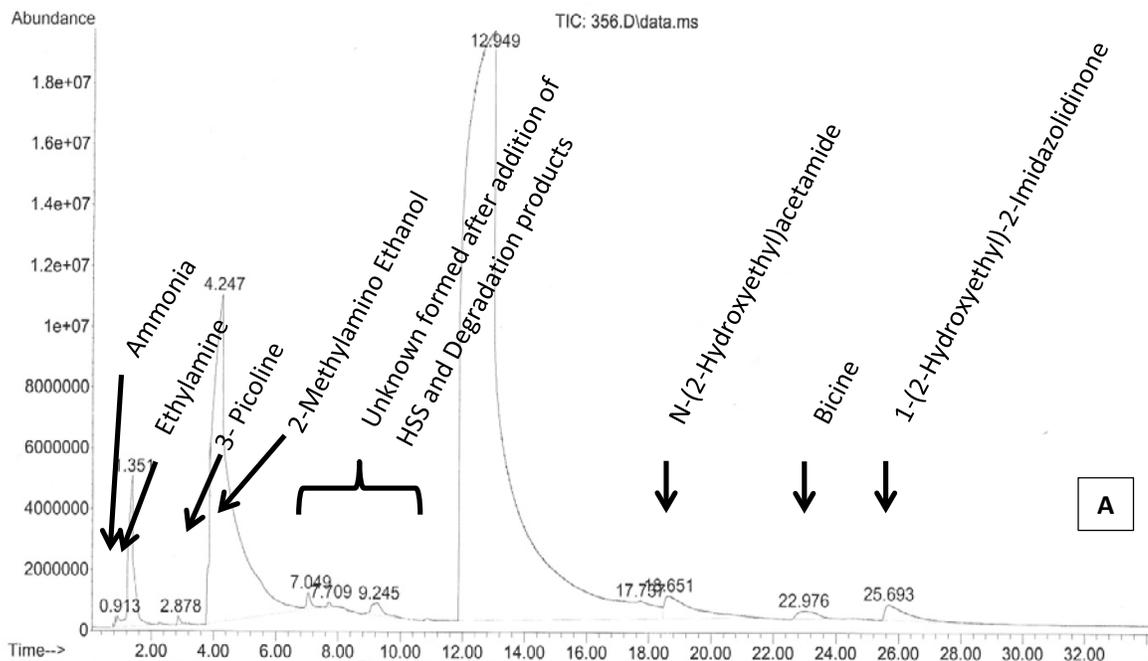
Contaminated distillate obtained from MEA/MDEA-4-1.0%-70mmHg was treated with activated carbon. From the GC-MS chromatograph, the concentration distribution of the contaminants or light degradation products is given in Table 67. The GC chromatograph for the degraded solvent and distillate is given in Figure 117. The degradation content in the original solvent, excluding HSS, was about 0.5 wt%, and there are 7 degradation products. After thermal distillation, all HSS and some degradation products were removed, appearing in the residue, while some contaminated the distillate. The total degradation content contaminating the distillate was 0.2845 wt%. Five of the 7 degradation products contaminated the distillate, and their concentrations are given in Table 67.

The contaminated distillate was treated with two activated carbons, SGL and M-1731, wetted with blended amine prior the experiment. The selection of these two carbons was based on the previous screening results of isotherm adsorption with artificially contaminated distillate. The treated distillates with the two activated carbons are shown in Figures 119 and 120. It is obvious that most of the degradation products would be removed, except the ethylamine and 2-methylaminoethanol. As an example, the GC chromatograph of treated distillate at low carbon dosage of 0.04 gm solvent / gm carbon is given in Figure 118, and it shows that all degradation products that contaminate the distillate have disappeared, except the ethylamine and 2-methylamino ethanol, which were not removed.

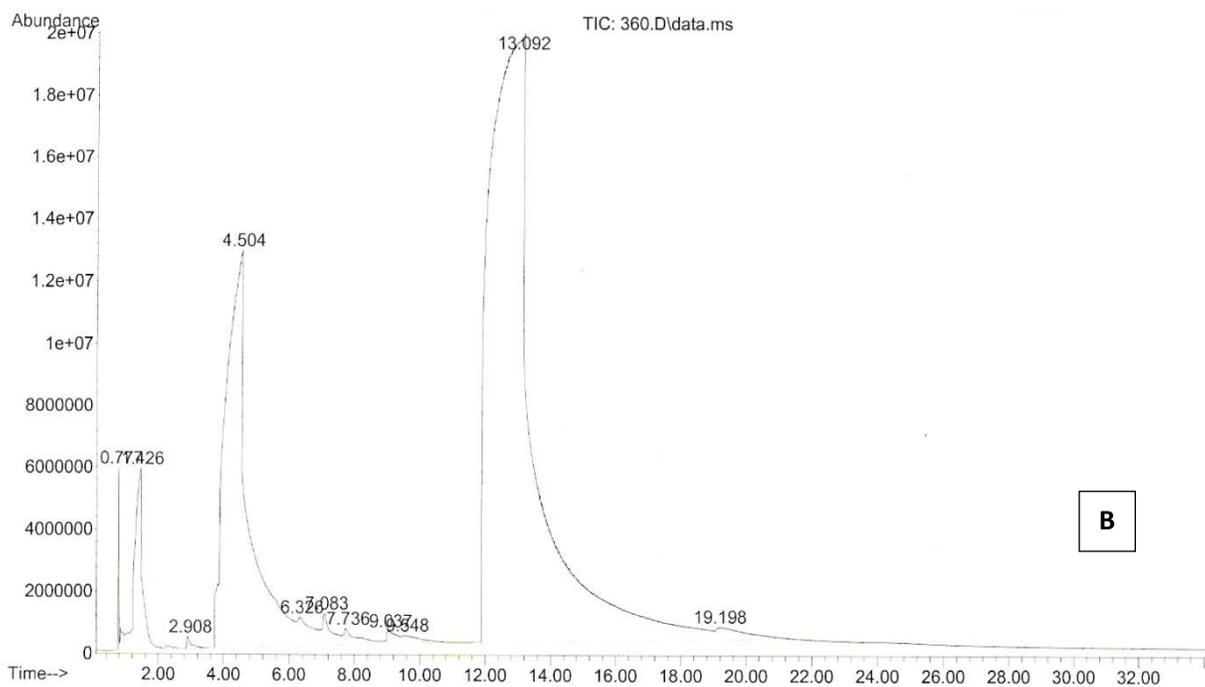
Table 67 Degradation products distribution in distillate MEA/MDEA-4-1.0%-

70mmHg

| | Concentration, wt% | |
|--|---------------------------|--------------------------------|
| | Degraded Solvent | Contaminated Distillate |
| NH₃ | 0.0000 | 0.0000 |
| Ethylamine | 0.0833 | 0.0792 |
| 3-Picoline | 0.0833 | 0.0764 |
| 2-Methylamino Ethanol | 0.0833 | 0.0833 |
| N-(2-Hydroxyethyl) acetamide | 0.0833 | 0.0456 |
| Bicine | 0.0833 | 0.0000 |
| 1-(2-Hydroxyethyl)- 2-Imidazolidinone | 0.0833 | 0.0000 |
| Total Degradation Products | 0.5000 | 0.2845 |



A



B

Figure 117 GC chromatograph of degraded solvent (A) and contaminated distillate (B) of MEA/MDEA-4-1.0%-70mmHg

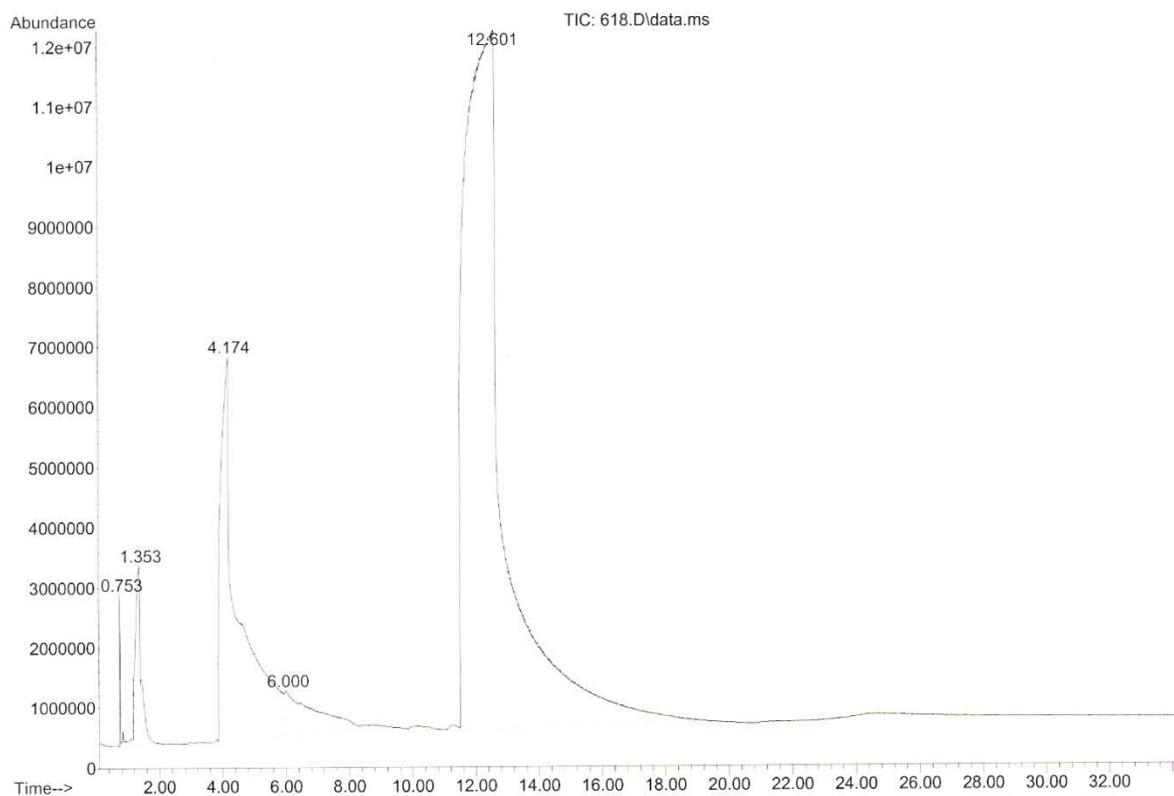


Figure 118 Treated distillate at low SGL carbon dosage 0.04 gm Solvent / gm

Carbon (MEA/MDEA-4-1.0%-70mmHg)

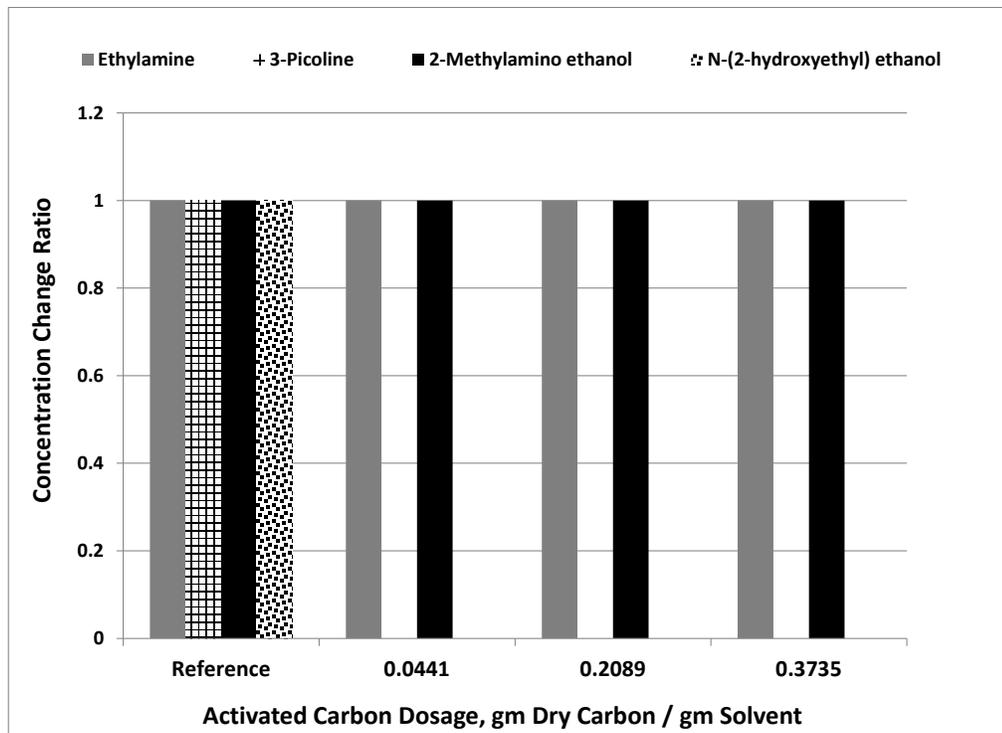


Figure 119 Isotherm of amine wetted SGL for contaminants for contaminated distillate of MEA/MDEA-4-1.0%-70mmHg

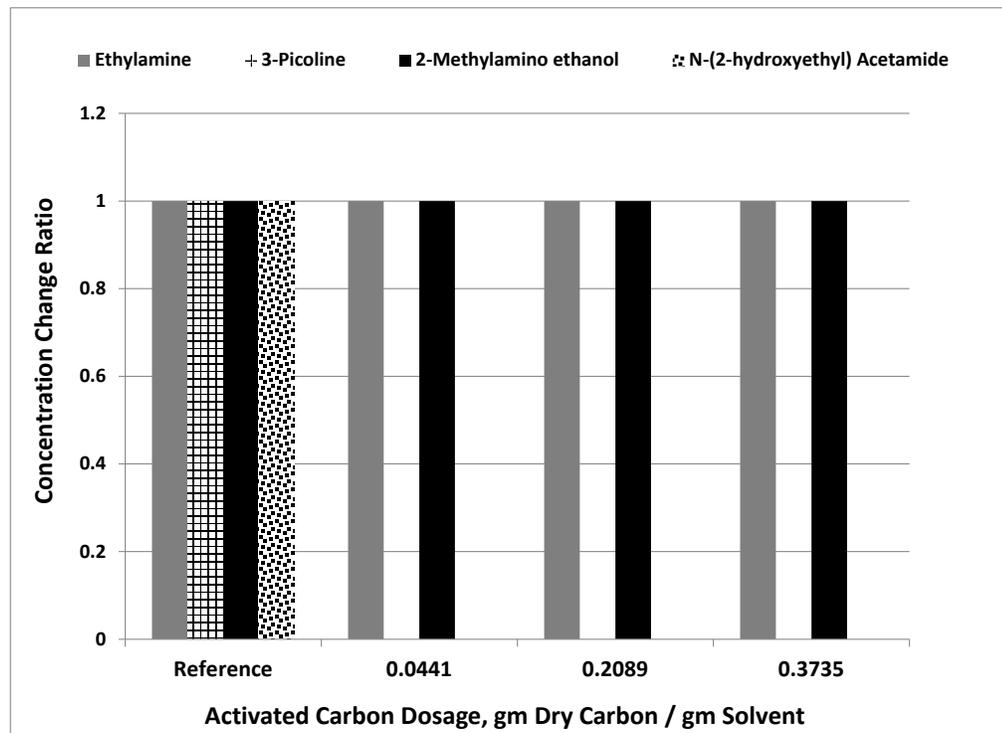


Figure 120 Isotherm of amine wetted M-1731 for contaminants for contaminated distillate of MEA/MDEA-4-1.0%-70mmHg

10.3.4 Dynamic adsorption for MEA/MDEA solvent

A degraded MEA/MDEA solvent was prepared for the dynamic adsorption “open-loop” tests. The solvent was not loaded with CO₂ to allow better determination of the ammonia and ethylamine chromatograph peaks. Amine solvent concentration and concentrations of the selected degradation products are given in Table 68. It should be mentioned that some other minor degradation products were formed after the addition of degradation products, but they were not considered in this test. Two types of activated carbon have been tested: SGL and M-1731. Both carbons were wetted with clean and unloaded MEA/MDEA for two days or more in sealed beakers. The experiment was carried to test the effectiveness of treating degraded solvent with two activated carbons in parallel.

The schematic diagram of the activated carbon dynamic test is given in Figure 121. It consists of feed and washing tanks, a liquid pump, a flow meter, two activated carbon columns, waste tanks, and sampling ports. The experimental procedures were as follows:

- 1- At the start-up, the wetted activated carbon was loaded into the column. The column of activated carbon was compressed manually to remove air pockets and to fill the column with carbon. Glass fibers were used at the top and bottom of the activated carbon column to prevent small particles from exiting the column and to hold the bed of carbon. Column 1 was filled with wetted SGL while Column 2 was filled with M-1731,
- 2- The set-up was washed with clean and unloaded solvent from the pre-washing solvent tank (T-01) to flush the lines and equipment. Then, the wash solvent was drained to the waste tanks.

- 3- The run was initiated by allowing the degraded solvent to flow from the degraded solvent tank (T-02) to the liquid pump (P-01), through the flow meter (F-01), and then to the carbon columns (C-01 and C-02), in parallel. The time was measured from the beginning of the run, and from time to time, samples were taken for GC-MS analysis and to measure the refractive index.
- 4- The flow rate was equivalent for both columns. The total flow rate per measure from the flow meter (F-01), which was calibrated for the solvent, was 2.0 gph.
- 5- After the whole degraded solvent was treated with carbon, the run was completed, and the lines and equipment were flushed with water in preparation dissembling the set-up for further cleaning and drying.

Table 68 Amines and degradation products used for dynamic adsorption test

| Chemical | Concentration, wt% |
|-----------------------------|-------------------------------|
| MEA | 15.27 |
| MDEA | 29.73 |
| Degradation Products | |
| Ammonia | 0.30 |
| Ethylamine | 0.30 |
| 3-Picoline | 0.30 |
| 2-(Methylamino)ethanol | 0.30 |
| N-(2-Hydroxyethyl)acetamide | 0.33 |

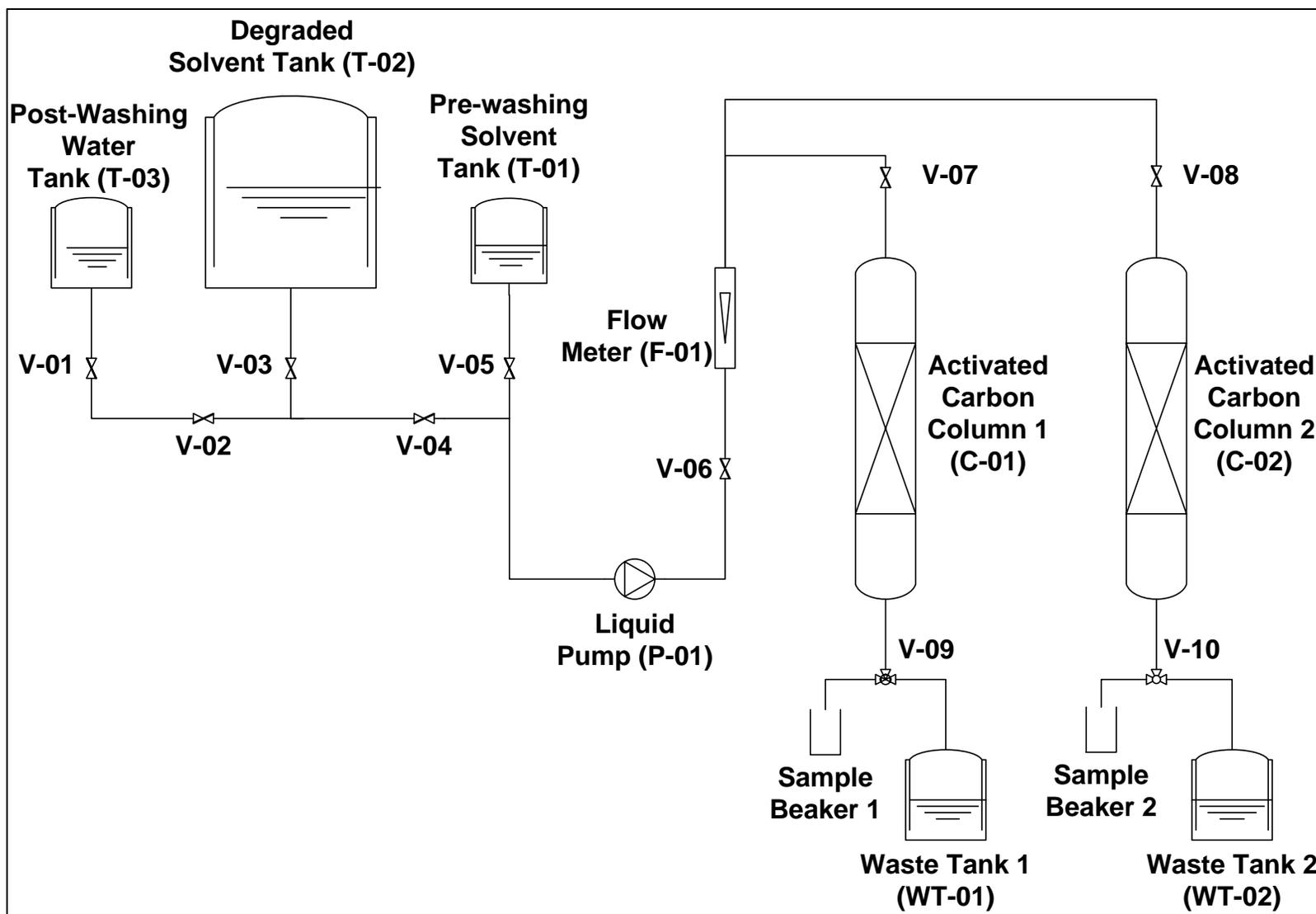


Figure 121 Schematic diagram of open-loop activated carbon dynamic adsorption test – MEA/MDEA solvent

The samples obtained from the experiment were analysed with GC-MS. The variation of the amine solvent concentration is illustrated in Figures 122 and 123 for SGL and M-1731, respectively. It can be seen that the overall solvent concentration and ratio of MEA to MDEA are generally constant, although there is variation in MEA and MDEA concentrations. For instance, MEA concentration was slightly smaller than the feed MEA concentration, while the MDEA was a little bit higher than the feed concentration. This could suggest that a small amount of MEA was being adsorbed on the carbon to take the place of MDEA. This variation is more noticeable for SGL than M-1731 carbon.

The breakthrough curves of the degradation products are presented in Figures 124 and 125. Some degradation products show different removal efficiency by adsorption over the test period than others. For instance, 3-Picoline, ammonia, and N-(2-Hydroxyethyl)acetamide were removed by adsorption, but they did not reach the breakthrough concentration, which means the adsorption column still had some capacity for further adsorption of degradation products. Though, some of the degradation products' concentrations dropped inside the feed, they did not change or had only slightly change over a 5.5 hour run, such as in the case of 2-Methylamino ethanol and ethylamine. The curves indicate that both carbons had a very similar performance; although, SGL provided relatively higher adsorption capacity than M-1731.

The refractive indices were measured for the samples collected, and the results are illustrated in Figures 126 and 127. The refractive indices indicate that the solvent was much cleaner over time compared with the degraded and clean solvent refractive index values for both carbons.

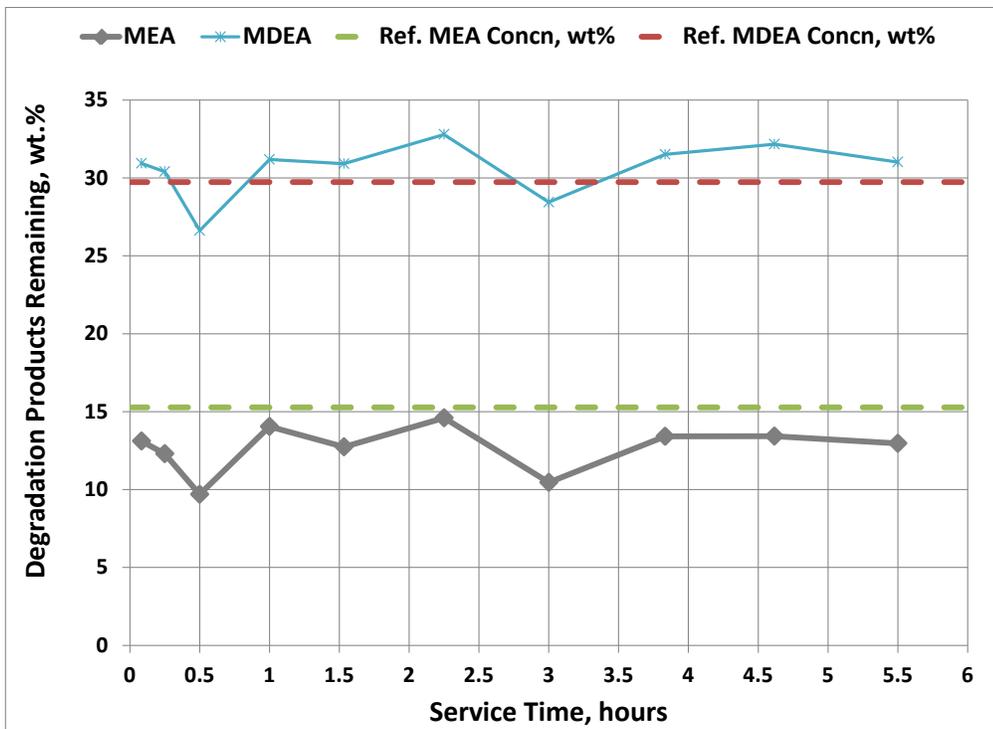


Figure 122 Dynamic adsorption curves of amine wetted SGL with MEA/MDEA

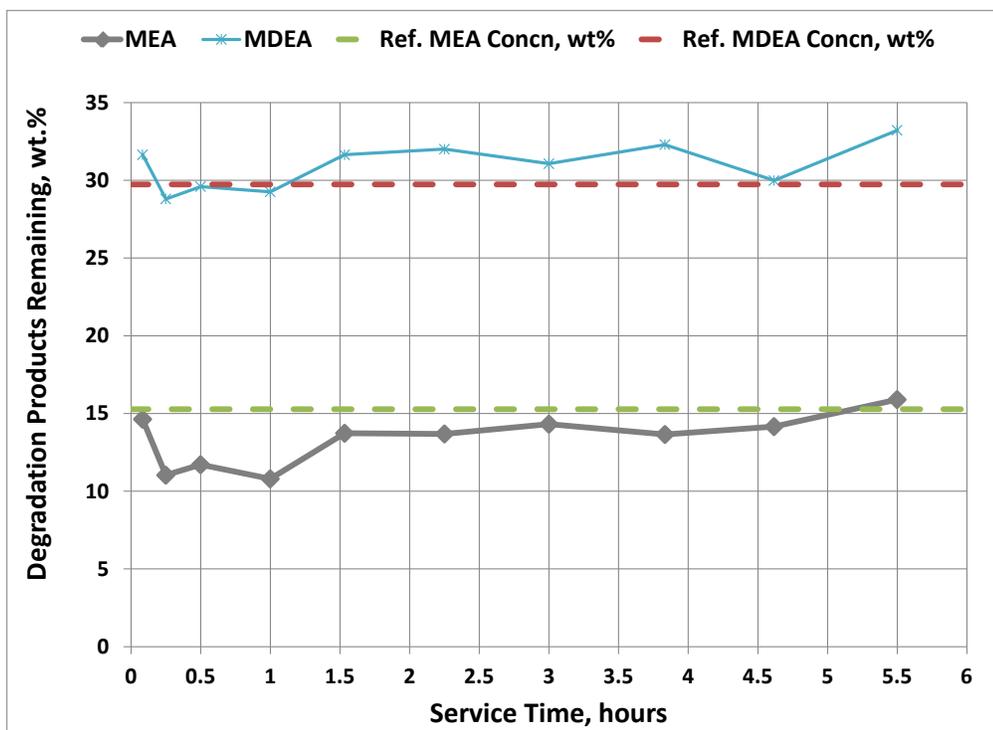


Figure 123 Dynamic adsorption curves of amine wetted M-1731 with MEA/MDEA

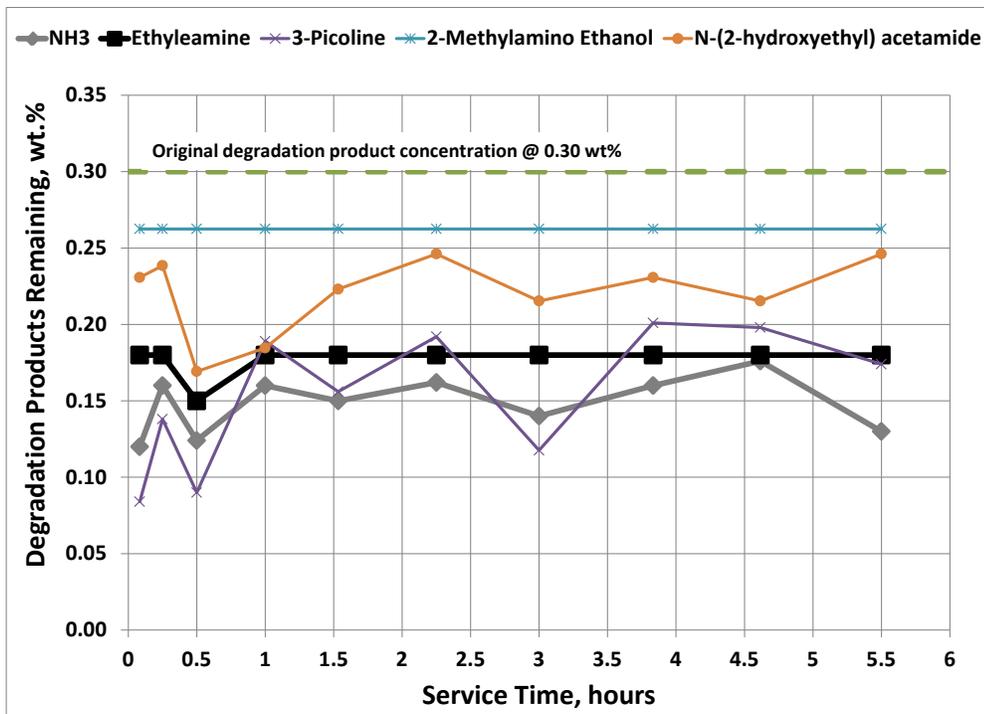


Figure 124 SGL dynamic adsorption curves: degradation product concentrations vs. time in MEA/MDEA

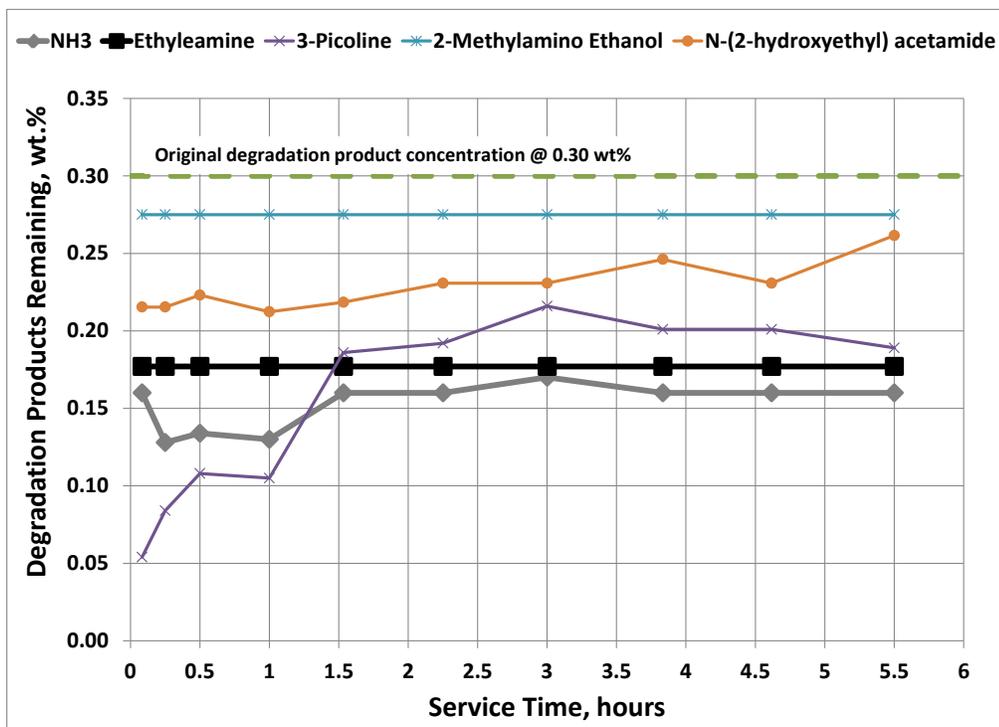


Figure 125 M-1731 dynamic adsorption curves: degradation product concentrations vs. time in MEA/MDEA

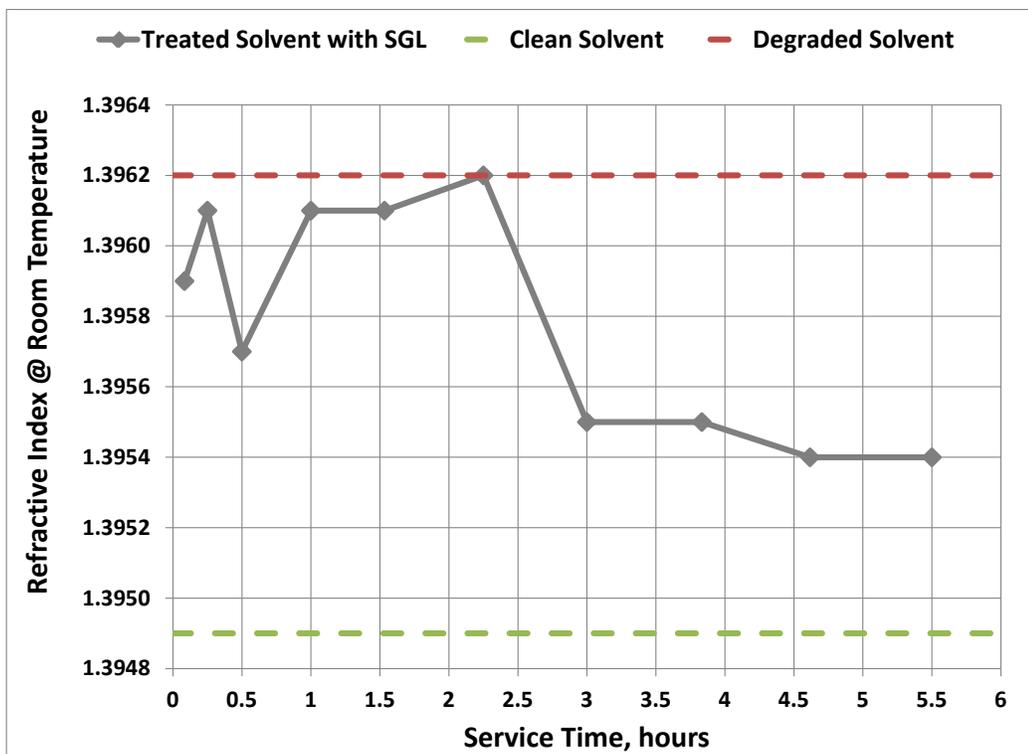


Figure 126 Refractive index measurement of treated MEA/MDEA solvent for SGL

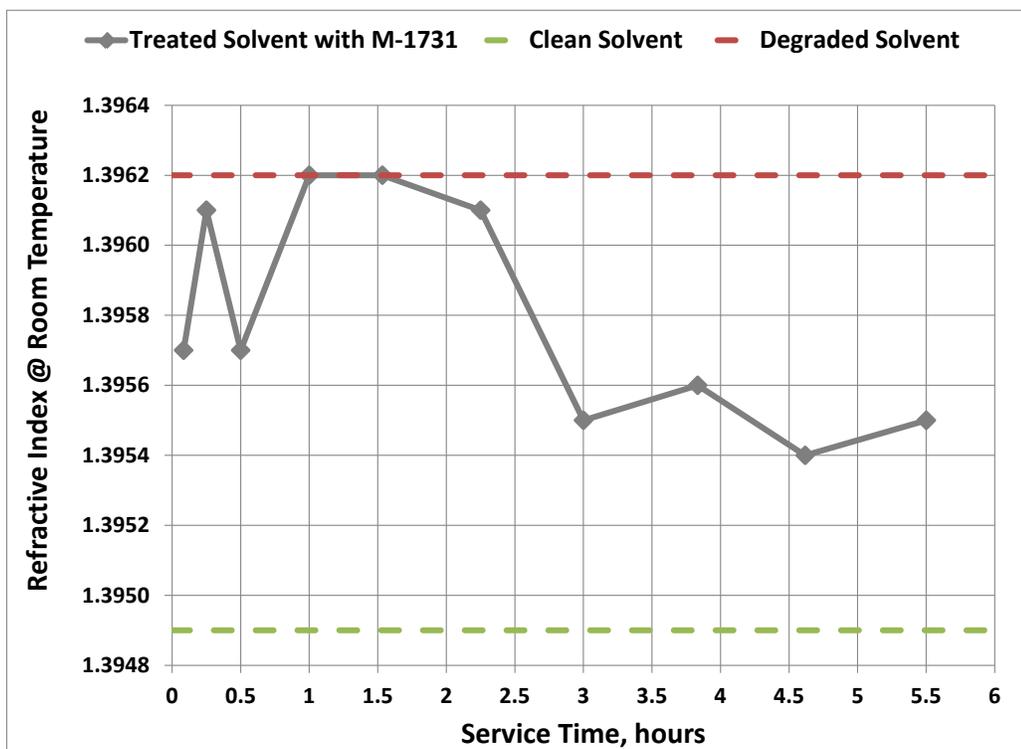


Figure 127 Refractive index measurement of treated MEA/MDEA solvent for M-1731

10.4 Concluding Remarks

- 1- Activated carbon was proposed to remove the contamination of degradation products from the solvent recovered from thermal purification.
- 2- Three types of activated carbons were studied in this research: SGL, M-1657, and M-1371. Three forms of activated carbon were considered: dry as received, water wetted carbon, and amine(s) wetted carbon.
- 3- MEA distillates were found to be contaminated with two degradation products, ammonia and ethylamine. Investigation of the treatment of the distillates with carbon was carried out in two major steps: isotherm adsorption and dynamic adsorption.
 - 3.1 Isotherm adsorption experiments for treating the contaminated MEA were carried out to check the adsorption capacity of carbon and its ability in removing the contamination. Ammonia and ethylamine had low or no adsorption tendency in the activated carbon studied.
 - 3.2 Dynamic adsorption with closed-loop or open-loop operation showed that ammonia and ethylamine have low or no adsorption tendency in the activated carbon under study.
- 4- MEA/MDEA distillates were found to be contaminated with five degradation products, ammonia, ethylamine, 3-picoline, 2-methylamino ethanol, and N-(2-hydroxyethyl) ethanol. Investigation of the treatment of these distillates with carbon was carried out in two major steps: isotherm adsorption and dynamic adsorption.
 - 4.1 Isotherm adsorption experiments for treating the contaminated MEA were carried out to check the adsorption capacity of carbon and its ability in removing the contamination expected in MEA/MDEA distillates.

- 4.1.1 Investigation of treating artificially contaminated distillates or distillates obtained from two thermal purification tests showed many degradation products could be removed. For instance, 3-picoline was completely removed, even at low carbon dosage, while N-(2-hydroxyethyl)ethanol was reduced by 50% or more. However, ammonia and ethylamine had low adsorption or no adsorption tendency, while 2-methylaminoethanol is not removed.
- 4.1.2 Superior adsorption behaviour was observed in removing the degradation products with activated carbon wetted with amine(s) solvent compared to the water wetted carbon and then the dry carbon. This suggests that wetting the carbon with amine would help immigrate the degradation products from the contaminated bulk of the solvent to the adsorption sites on the activated carbon.
- 4.2 Dynamic adsorption with open-loop operation showed that 3-picoline and N-(2-hydroxyethyl) ethanol could be removed, and the carbon used had a larger capacity, even after 5 hours of processing the contaminated distillate; the full capacity of the carbons studies for adsorbing these two degradation products was not reached. However, ammonia, ethylamine, and 2-methylamino ethanol had low or no adsorption in the activated carbons under study.

Chapter 11: Evaluation of Purification and Treating Industrial Samples

11.1 Chapter introduction

To demonstrate the concept of purifying amine solvent by thermal purification followed by activated carbon treatment, three industrial samples of lean amine solvents that were used to capturing CO₂ from different sources were purified using this approach. Each sample was thermally purified to remove the amine from its heavy degradation products, and then the recovered solvent, which could be contaminated with light degradation products, was treated with two activated carbons. SGL and M-1731 activated carbons were selected because they have larger adsorption capacity over M-1657. The carbons were wetted with relevant amine solvent prior to the each test. The objectives of this chapter are:

- To evaluate the solvent quality in term of the degradation products level.
- To recover the solvent under vacuum thermal reclamation.
- To treat the recovered solvent with activated carbon, if it is contaminated.

11.2 Evaluation of industrial samples from Plant A

Plant A is a CO₂ capture plant from which lean amine and reclaimer waste samples were obtained. This plant is integrated into a natural gas combined cycle power plant in which the CO₂ is captured to meet food grade specification. This capture plant utilizes MEA solvent at a concentration of 16 wt%. More information on the samples is given in Table 69.

11.2.1 Thermal reclamation of plant A lean amine

Prior to the reclamation test, the lean amine sample was analysed with GC-MS to examine the extent of degradation products in the lean amine (Figure 128). The sample was also analysed by titration to determine the solvent concentration, CO₂ loading, and HSS content in the lean amine, and the results are given in Table 69. HSS concentrations indicate how much of the MEA solvent reacted with organic acid anions that should be liberated by the addition of caustic soda. NaOH addition will form non-volatile sodium salts with these acid anions, which will not be able to evaporate during the thermal reclamation. It is expected that lean amine has a low level of non-volatile content, 0.53 wt%, including the organic acids that form HSS. Another point from Table 1 is the slight reduction in the CO₂ loading from 0.175 in lean amine to 0.106 in the collected distillate. This has been experienced in all reclamation tests in our study in which typically 50% of loaded acid gas is lost, likely in the venting of the vacuum pump. The solvent recovery was found to be 96.28%, which is quite satisfactory. Although the amount of residue is very small compared to the solvent charged to the distillation flask. The residue contains high levels of amine and degradation products, as well as neutralized HSS.

The GC-MS analysis for lean amine and distillate shows the presence of light degradation products, as shown in Figure 128, though their concentration is very small. Due to the absence of standard chemicals to compare to the peak and its retention time, it is very difficult to identify the chemicals that appeared at the retention time of 0.962 and 1.888 min. However, GC-MS suggests that the first peak is possibly 2-Methoxyisopropylamine (CAS: 37143-54-7) and the second peak might be pyrazine (CAS: 290-37-9).

Table 69 Summary of Reclamation of Plant A Lean Amine

| | Loaded lean amine | Reclaimer Waste | Distillate amine | Residue |
|--|--------------------------|------------------------|-------------------------|----------------|
| Solvent Concentration, wt% | 15.88 | 55.23 | 14.54 | 57.17 |
| CO₂ Loading, mol/mol | 0.175 | - | 0.106 | - |
| HSS, wt% as MEA | 1.10 | - | - | - |
| Solvent Recovery, % | - | - | 96.28 | - |
| Total Non-volatile Content, wt% | 0.53 | - | - | 42.80 |

Table 70 Summary of reclamation of Plant B lean amine

| | Loaded lean amine | Reclaimer Waste | Distillate amine | Residue |
|--|--------------------------|------------------------|-------------------------|----------------|
| Solvent Concentration, wt% | 20.77 | 62.68 | 17.59 | 61.20 |
| CO₂ Loading, mol/mol | 0.121 | - | 0.135 | - |
| HSS, wt% as MEA | 2.20 | - | - | - |
| Solvent Recovery, % | - | - | 95.10 | - |
| Total Non-volatile Content, wt% | 2.33 | - | - | 38.80 |

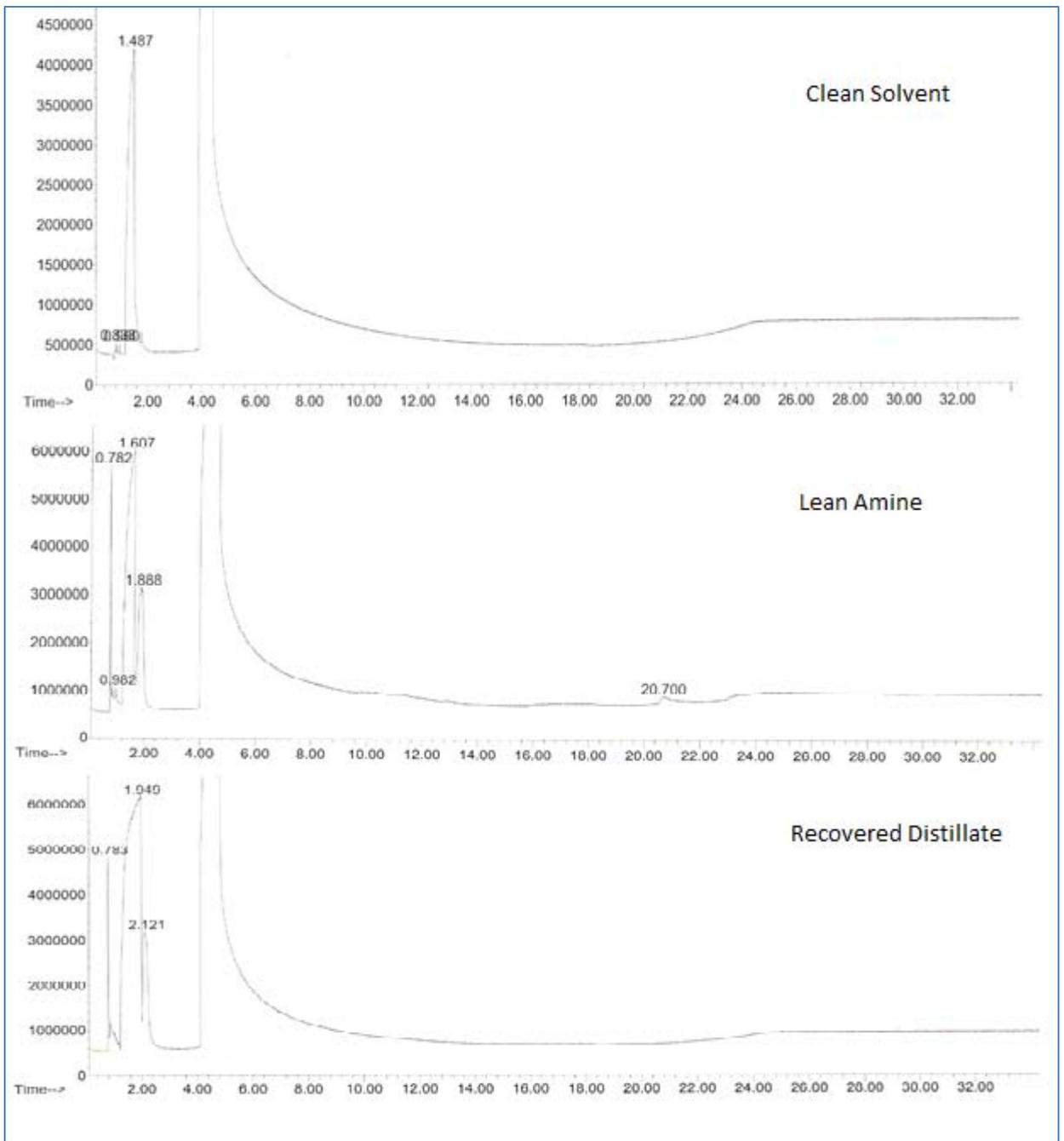


Figure 128 Presence of light degradation products in Plant A lean amine and distillate

11.2.2 Activated carbon treatment of recovered distillate of Plant A

Two types of activated carbon were used to treat the distillate collected from the thermal reclamation test to see how much of the light degradation products (peak 1 at 0.962 min. and peak 2 at 1.888 min. shown in Figure 128) could be removed. The types of activated carbon selected for isotherm tests were SGL and M-1731. The isotherm test would enable evaluation of the activated carbon efficiency in removing contaminated chemicals and obtaining the optimum dosage of activated carbon. Prior the test, the dry activated carbon was soaked in clean MEA solvent for more than 48 hours in a covered beaker that was gently shaken from time to time to remove trapped air.

The isothermal treatment was carried out after four 60 ml vials were charged with wetted activated carbon at dosages of 0.04 to 0.35 dry carbon gm/solvent gm. The vials were sealed and then placed in the shaker for 48 hours and were checked from time to time. After the test was completed, the contents of each vial were filtered with Whatman paper # 4, and then further filtered in a 0.2 um nylon filter and placed in GC vials to be analysed by GC-MS. Figure 129 gives a summary of the results on the percentage removal of these degradation products. Both activated carbons were found to remove chemical peaks 1 and 2 at different percentages; however, the removal was not considerably changed with increase of the activated carbon dosage. There is a minimum dosage between the removal efficiency and the amount of activated carbon needed. For instance, the optimum activated carbon (SGL and M-1731) needed for efficient removal of the chemicals of peaks 1 and 2 were low dosages between 0.05 to 0.20 gm/gm.

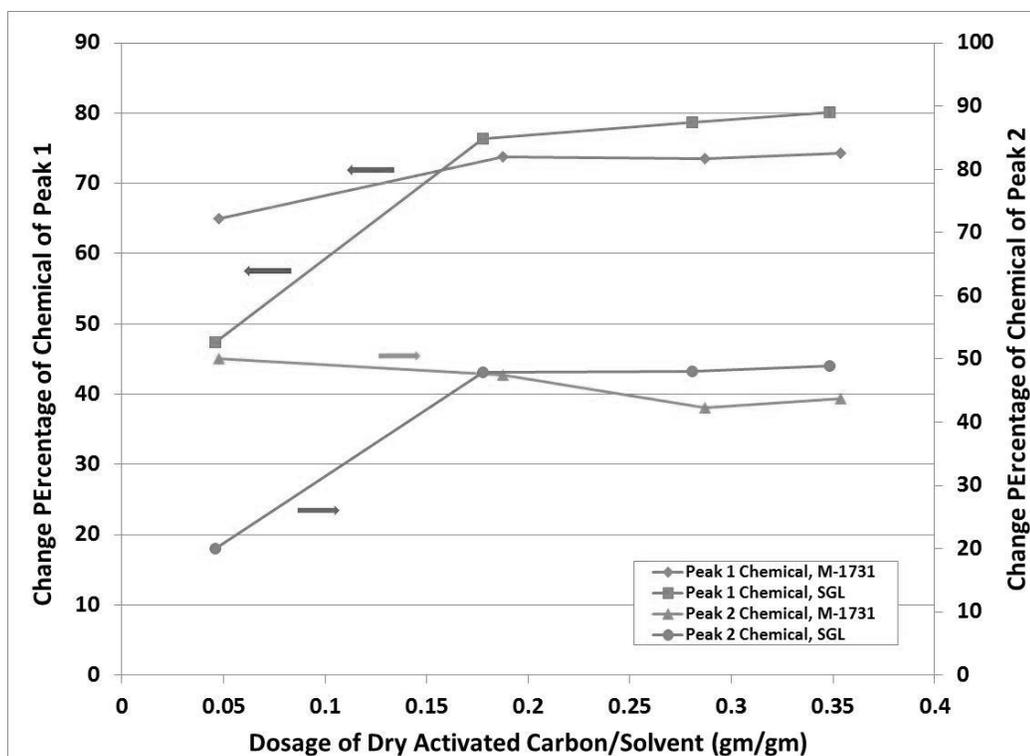


Figure 129 Isotherm treatment for Plant A distillate with SGL and M-1731 activated carbon

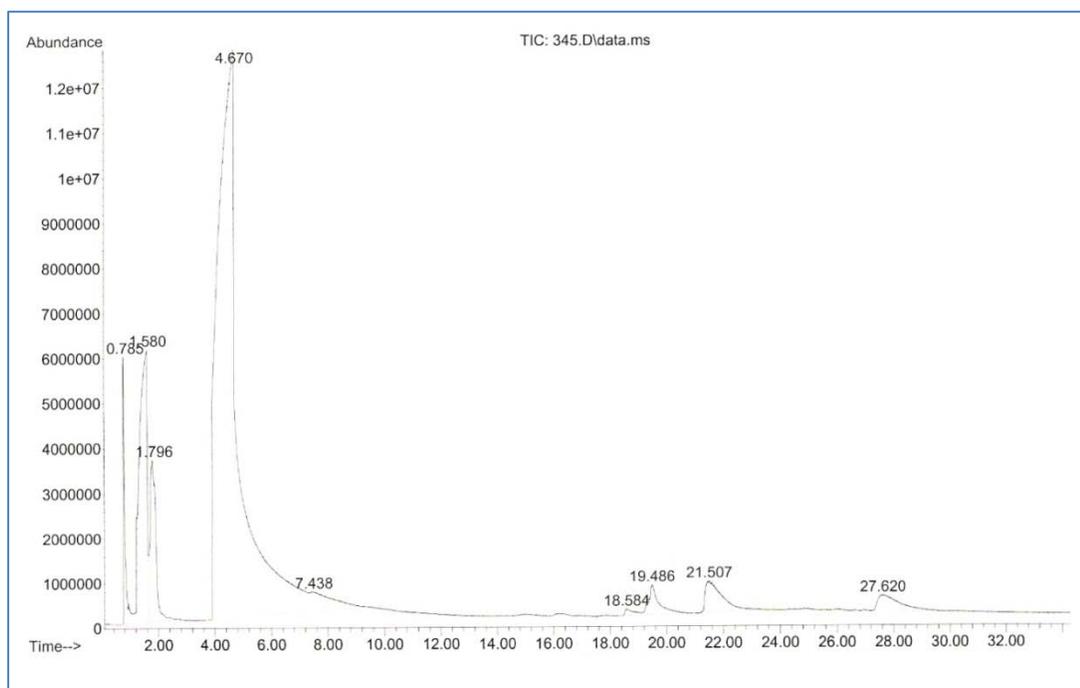


Figure 130 GC chromatograph of Plant B lean amine

11.3 Evaluation of industrial samples from Plant B

The second amine sample was obtained from Plant B, which was used to capture the CO₂ from the flue gas of a coal-fired power plant within a chemical complex. Two sample types were received: lean amine and reclaimer waste samples. The capture plant is designed to operate with MEA solvent at low concentrations (i.e., 20 wt%). Table 70 provides analysis results of these two samples. Table 70 shows the analysis of lean and reclaimer waste samples by titration to determine the solvent concentration, CO₂ loading, and heat stable salt content to suggest the amount of bound amine. As can be seen, the solvent concentration was 20.5 wt%, and it had a high level of HSS (2.20 wt% as MEA). Finally, the reclaimer waste had a high level of amine, 62.68 wt%, which is quite high compared to other studies and samples.

The lean amine sample was analysed with GC-MS as received. The reclaimer waste was diluted with water to prevent overloading of the GC column and reduce the impact of the presence of sodium salts on the GC-MS detector. From the visual inspection of the GC chromatographs, it could be seen that this lean amine (Plant B) is more contaminated than the Plant A samples evaluated previously. The reclaimer waste confirmed the presence of the chemicals found in the lean amine but at higher concentrations. Therefore, the GC chromatograph for the reclaimer waste is not given in this section. The GC-MS results for the lean amine are shown in Figure 130, and, as can be seen, there are 6 distinct degradation products peaks. However, it is not possible to positively identify these chemicals without standard reference peaks. GC-MS evaluation based on its software statistical analysis will be considered here. Table 71 gives the best matches of these degradation products according to GC-MS statically analysis.

Table 71 Predicted degradation products in lean amine of Plant B

| Degradation products | 1 | 2 | 3 | 4 | 5 | 6 |
|--|-----------|------------------|------------------------------|---------------------|------------|--------------------------|
| Retention time | 1.796 | 7.438 | 18.584 | 19.486 | 21.507 | 27.620 |
| Possible chemicals per GC-MS Evaluation | ? | Amino-2-propanol | N-(2-Hydroxyethyl)-Acetamide | 2-methyl-2-pentanol | Uracil | 4-Butyl-2-methylthiazole |
| Contamination of Recovered amine (Concentration level) | Yes (Low) | Yes (Low) | Yes (Low) | Yes (Low) | Yes (High) | Yes (Low) |

11.3.1 Thermal reclamation of Plant B lean amine

The lean amine sample was analysed by GC-MS to examine the extent of degradation products in the lean amine as shown in the previous section. The sample was also analysed by titration to determine the solvent concentration, CO₂ loading, and HSS content in the lean amine, and the summary of results is given in Table 70. Before the start of the test and the charge of the lean amine solvent in the distillation flask, the lean amine sample was mixed with calculated caustic soda prior the reclamation test to neutralize the heat stable salts, which were 2.20 wt% of MEA. The solvent recovery was 95.10%, which is quite satisfactory with lean amine containing so much degradation product and HSS, as much as 2.33 wt% and 2.20 wt% of MEA, respectively. Although the amount of residue is small compared to the solvent charged to the distillation flask, the residue contains high levels of amine, degradation products as well as neutralized HSS.

The GC-MS analysis for lean amine and distillate shows the presence of degradation products as illustrated in Figure 131. Due to the absence of standard chemicals to compare with the peaks and their retention times, it is very difficult to identify when these chemicals appeared. One light degradation product that appeared in the distillate at a retention time of 1.831 is unknown, but it could be pyrazine (CAS: 290-37-9), which was found in the GC results of Plant A distillate. In general, the recovered amine from the reclamation test was very clean when compared to the reclaimer vapour obtained from the plant, which was unexpected. This suggests the operation at deep vacuum could enhance solvent recovery and minimize solvent contamination, and, also, the presence of a fractionation column in the set-up prevents heavy and semi-heavy degradation products from contaminating of distillate. Contamination of the industrial samples might be due to the process configuration of simple reclamation (one stage evaporation), or there might be aggressive evaporation within the reclaimer, leading to carry over.

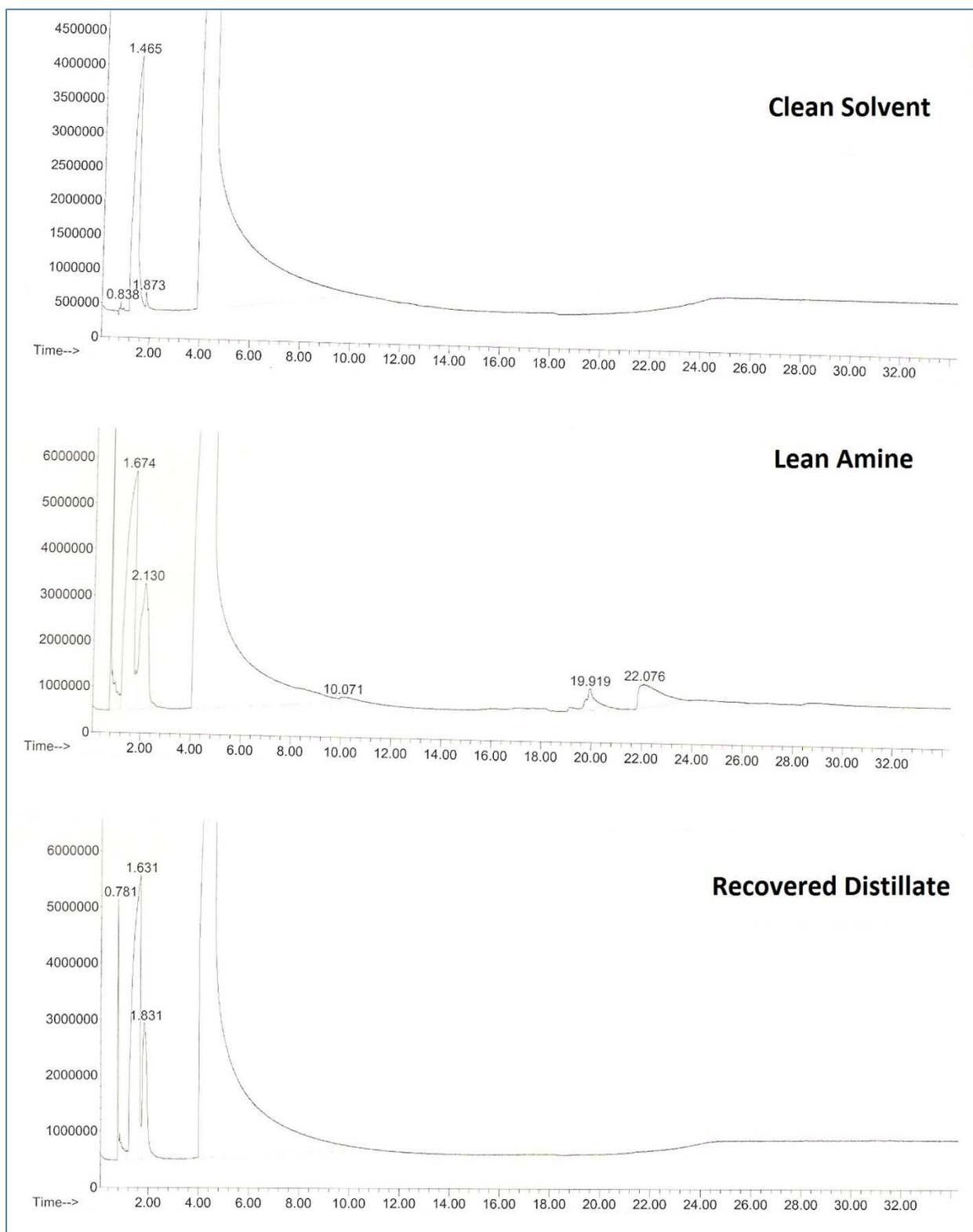


Figure 131 Presence of light degradation products in the Plant B lean amine and distillate

11.3.2 Activated carbon treatment of recovered distillate of Plant B

Two types of activated carbon were used to evaluate the treatment of distillate collected from the thermal reclamation experiments in order to see how much of the light degradation product (peak 1 at 1.888 min. shown in Figure 132) that contaminated the distillate could be removed. The types of activated carbon selected for isotherm tests were SGL and M-1731. The isotherm test demonstrated the activated carbon efficiency in removing contaminated chemicals and obtained the best dosage of activated carbon to achieve optimum removal. Prior to the test, the dry activated carbon was soaked in clean MEA solvent for more than 48 hours in a covered beaker that was gently shaken from time to time to remove the trapped air.

The isothermal treatment of activated carbon was carried out after four vials of 60ml were charged with wetted activated carbon at the dosage of 0.05 to 0.7 (dry carbon gm/solvent gm) and allowed to sit for a day. Then, a specific amount of solvent was added (10 gm). The vials were sealed and then placed in the shaker for 48 hours. After the shaking cycle was completed, the contents of each vial were filtered with Whatman filter paper #4, and a sample was taken for analysis with GC-MS. Figure 132 gives a summary of results on the percentage removal of the light degradation product. Both activated carbons were found to remove chemical peak 1 at a different percentage; however, the removal efficiency was low. The removal efficiency improved when the carbon dosage was increase, but even at a high dosage, the maximum removal was only 50% or less for both carbons. It is believed that the chemical that appeared in peak 1 could not easily be removed by activated carbon, even though it is thought to be similar to peak 1 that appeared in the distillate chromatograph of Plant A. The removal efficiency would only be about 10%-15% at a low and reasonable carbon dosage. The SGL carbon was slightly favoured over M-1731 for the removal of chemical of peak 1.

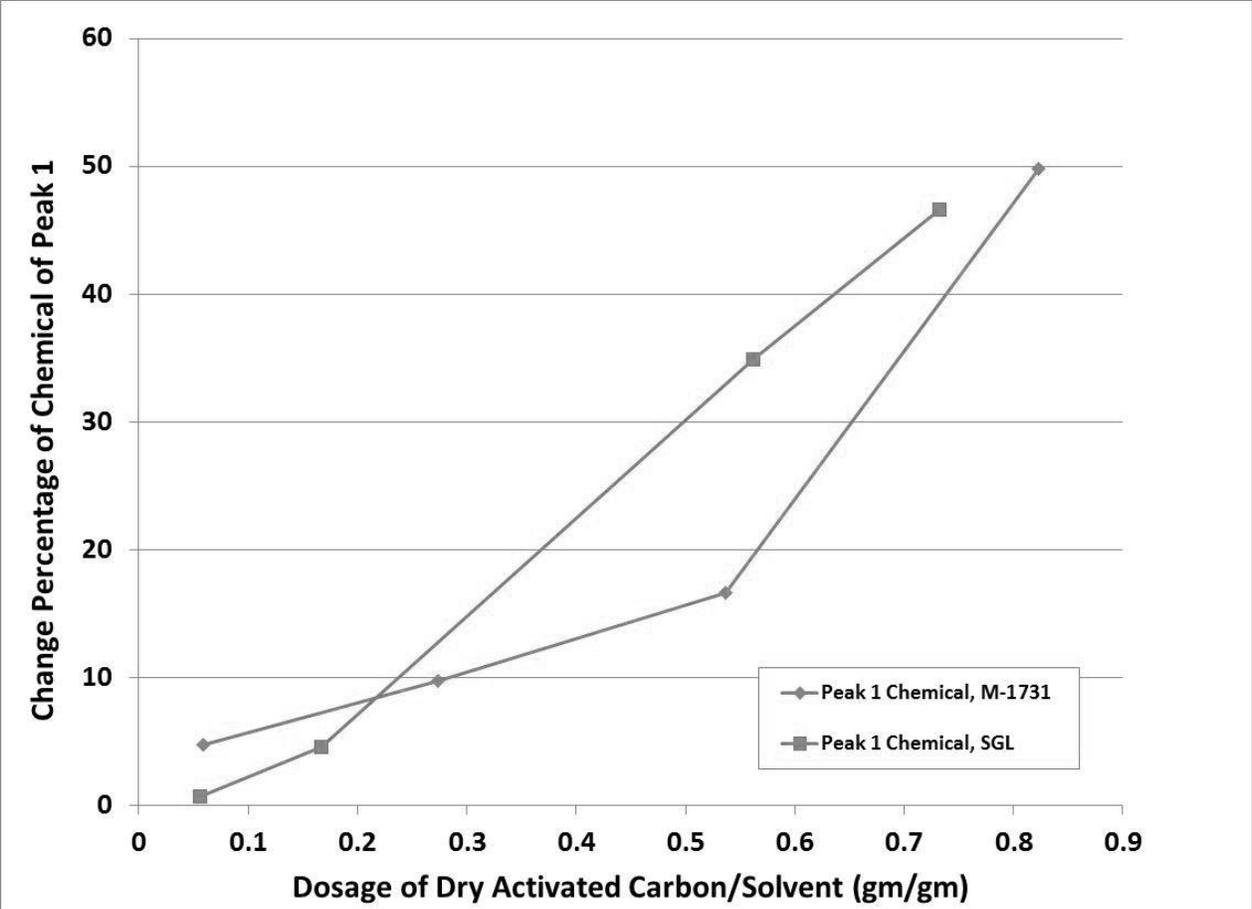


Figure 132 Isotherm treatment for Plant B distillate with SGL and M-1731 activated carbon

11.4 Evaluation of industrial samples from Plant C

The third sample, lean amine, was obtained from Plant C, which captures the H₂S from multiple gas streams within an oil refinery. This gas treatment plant is utilizing DGA solvent at a concentration of 50 wt%. All experimental work for this sample was carried out in the fume hood, although the level of H₂S loading was low. The sample received was analysed using GC-MS. It is also analysed to determine the solvent concentration, H₂S loading, and presence of HSSs. Figure 6 shows the chromatographs of lean amine that show high levels of degradation products. Actually, if the peaks for H₂S (0.786 min), water (1.609 min), and DGA (10.636 min.) are excluded, the chromatograph shows the presences of 11 degradation products. GC-MS could provide a statistical estimate of what chemicals these peaks might be, but this is not accurate without using the standard chemicals.

11.4.1 Thermal reclamation of Plant C lean amine

Summary of analysis is given in Table 72. Before the test was started, the lean amine sample was mixed with calculated caustic soda prior to the reclamation test to neutralize the heat stable salts. The solvent recovery was found to be 95.10%, which is satisfactory with a lean amine containing so much degradation product and HSSs. Although the amount of residue was very small compared to the solvent charge to the distillation flask, the residue contains high levels of amine and degradation products, as well as neutralized HSS. The GC-MS analysis for distillate shows the presence of 5 degradation products, as shown in Figure 133. Due to the absence of standard chemicals to compare to the peak and its retention time, it is difficult to identify when these chemicals appeared. However, GC-MS suggested the relevant chemicals to those peaks based on its statistical analysis, and Table 73 summaries them.

Table 72 Summary of reclamation of Plant C lean amine

| | Loaded lean amine | Distillate amine | Residue |
|--|--------------------------|-------------------------|----------------|
| Solvent Concentration, wt% | 50.58 | 50.18 | 56.20 |
| H₂S Loading, mol/mol | 0.054 | 0.030 | - |
| HSS, wt% as DGA | 0.742 | - | - |
| Solvent Recovery, % | - | 96.07 | - |
| Total Non-volatile Content, wt% | 1.47 | - | 43.80 |

Table 73 Degradation products found in distillate of Plant C

| Degradation Products | 1 | 2 | 3 | 4 | 5 |
|-------------------------------|------------|----------|-----------------------|---------------------------|------------|
| Retention Time, Minute | 3.949 | 13.820 | 14.820 | 16.523 | 24.571 |
| Chemical | Morpholine | Unknwon | n-methyldibutyl amine | n,n-di-n-propyl formamide | 12-Crown-4 |
| CAS | 110-91-8 | - | 3405-45-6 | 6282-00-4 | 294-93-9 |

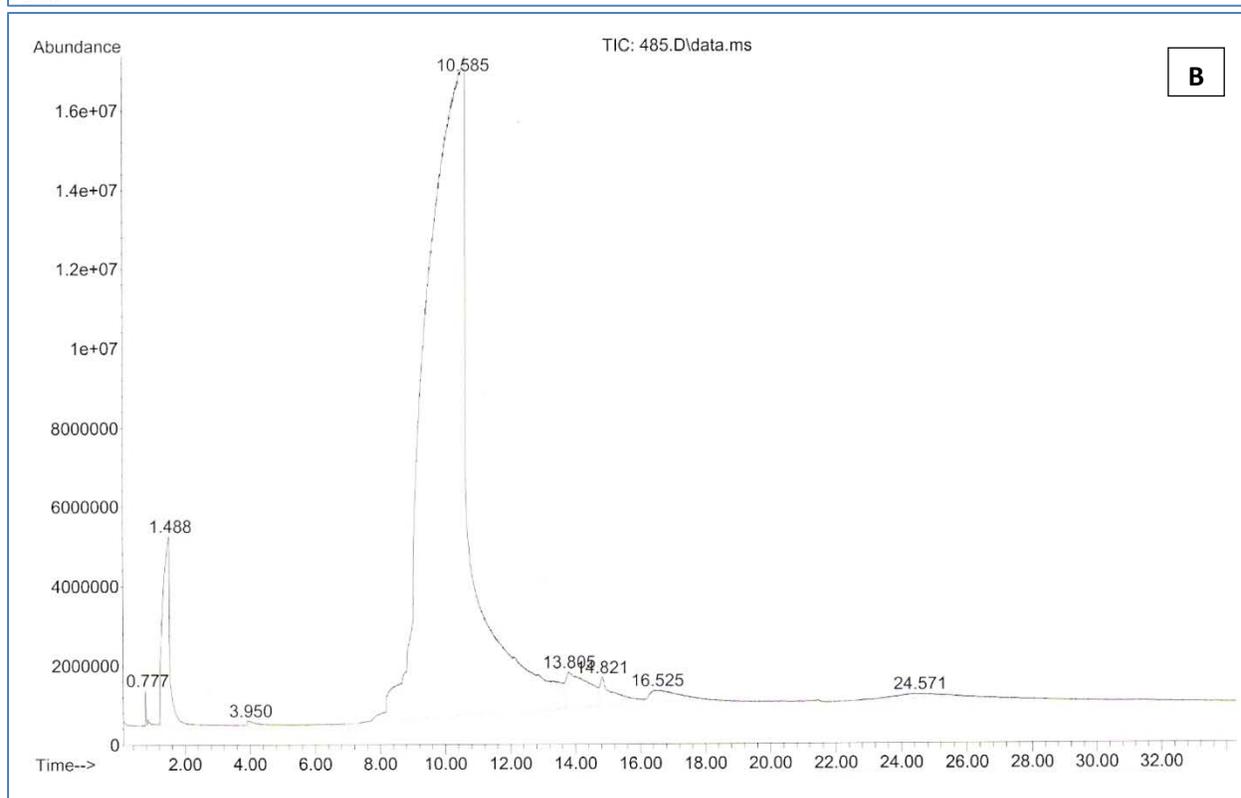
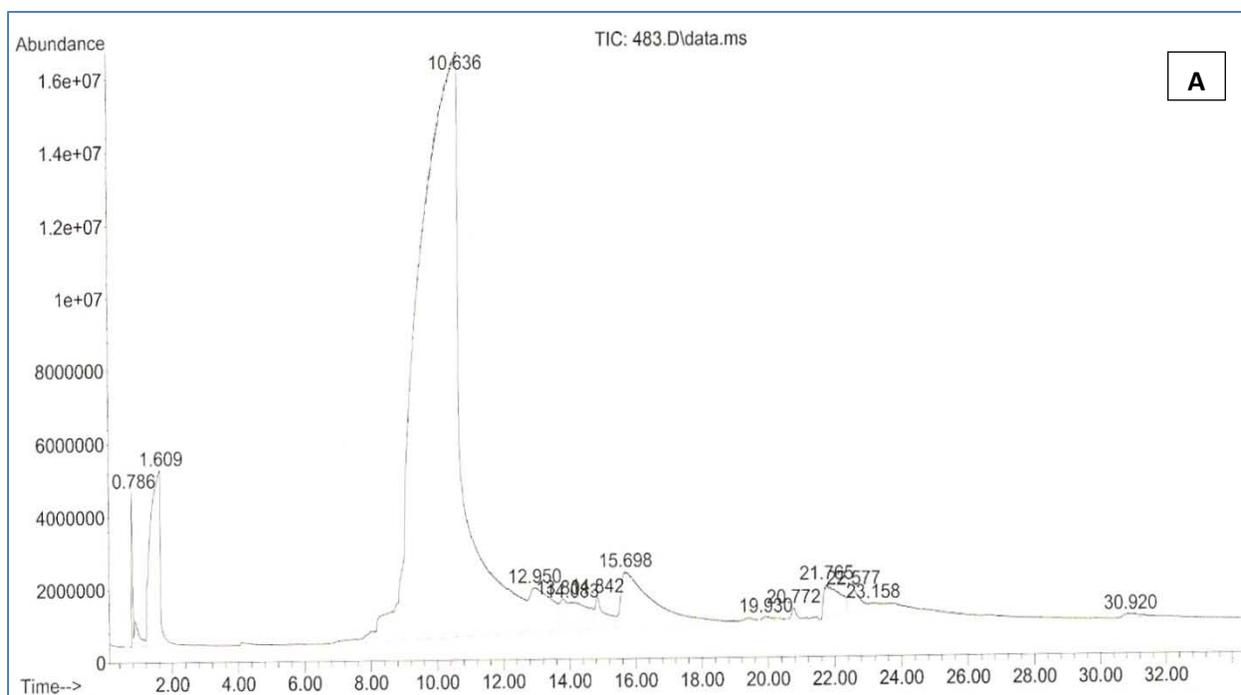


Figure 133 GC chromatograph of Plant C lean amine (A) and distillate (B)

11.4.2 Activated carbon treatment of recovered distillate of Plant C

SGL activated carbon was used to evaluate the treatment of distillate collected from the thermal reclamation experiment in order to see how much of the degradation product detected in the distillate could be removed. The isotherm test measured the activated carbon efficiency in removing contaminated chemicals and identified the best dosage of carbon to achieve optimum removal.

The isothermal treatment was carried out after four 60 ml vials were charged with wetted activated carbon at a dosage of 0.05 to 0.75 (dry carbon gm/solvent gm) and left to sit for one day. Then, a specific amount of solvent was added (20 gm). The vials were sealed and then placed in the shaker for 48 hour. Then, the contents of each vial were filtered with Whatman paper #4, and the filtrates were further filtered in a 0.2 um nylon filter and placed in GC vials to be analysed by GC-MS. Figure 134 gives a summary of the results in terms of the percentage removal of the degradation products. The SGL had high removal efficiency (50 to 100%) for the four degradation products at low dosage of carbon (0.05 – 0.25 gm/gm) except for one chemical, which could not be removed at the same efficiency.

11.5 Concluding Remarks

Treating three industrial lean amine samples (two MEA and one DGA) obtained from three facilities have been thermally purified and the recovered distillates are treated with isotherm activated carbons: SGL and M-1731. Most of degradation products and HSS are eliminated from the thermal reclamation step while the isotherm activated carbon treatments show considerable reduction in the contaminants in distillates by 50% to 100% depends on the nature and concentration of contaminants.

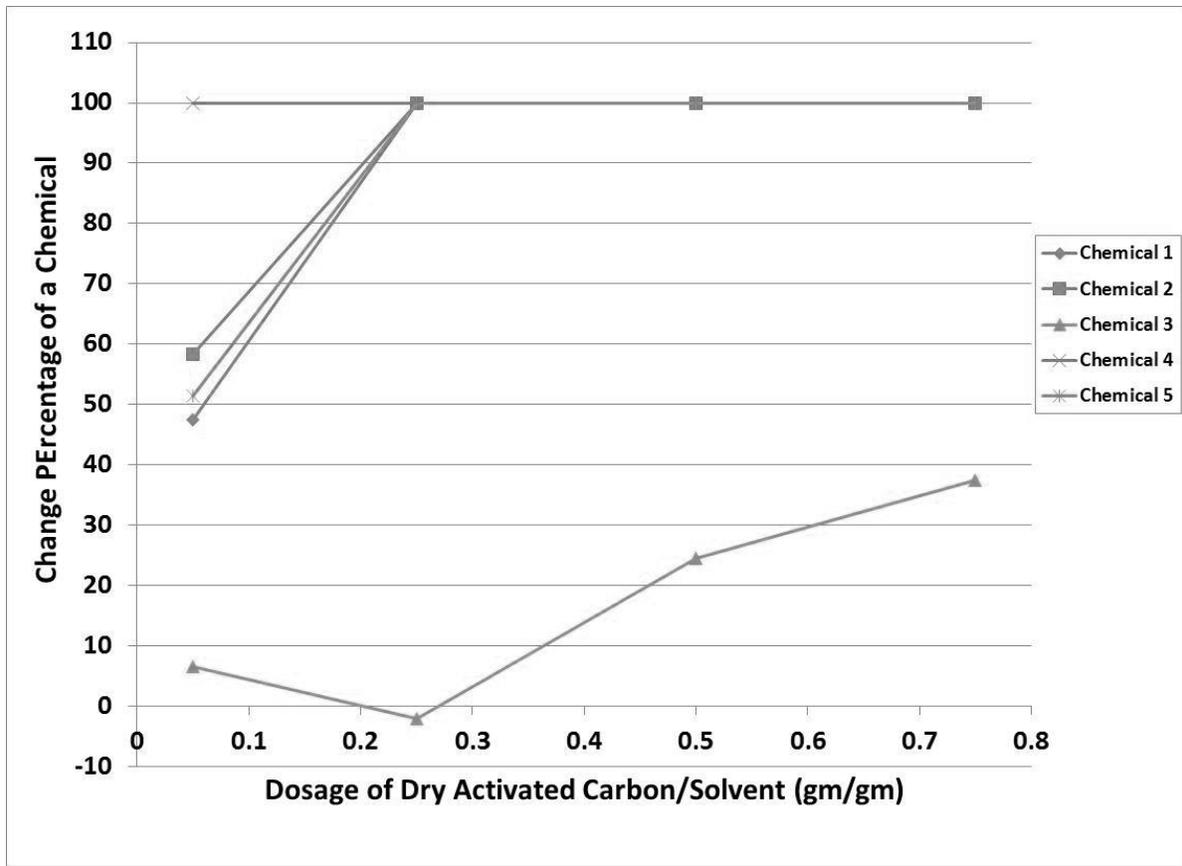


Figure 134 Isotherm treating for Plant C distillate with SGL activated carbon

Chapter 12: Simulation of CO₂ Capture Plant with/without HSS

12.1 Chapter introduction

Simulation is an excellent tool to assess the impact of HSS on a CO₂ capture plant. HSS has been reported to affect solvent absorption capacity and then the removal of CO₂ from the flue gas stream. ProTreat process simulation has been used to predict the performance of CO₂ capture plants when the solvent contains some HSS. ProTreat is a non-equilibrium process simulator developed by Optimized Gas Treating, Houston, TX. The non-equilibrium stage approach or, what could be called Mass transfer rate approach, for absorption/stripping process simulation is recommended for complex and non-ideal systems such as amine treatment plants (Sardar & Weiland 1984; Katti & Langfitt 1986; Pacheco & Rochelle 1998). Three HSSs were considered in this simulation: formic acid, acetic acid, and oxalic acid. The total concentration of HSS was varied from 0.5 to 7 wt%, but distribution of concentration for each HSS was kept the same. The CO₂ capture plant water balance was optimized so that the plant would not need external water make-up, and if water were required, it would be taken from either the purge of the reflux or from the direct cooling tower (DCC). Figure 135 shows the ProTreat model used for the simulation of MEA and MEA/MDEA solvents. ProTreat is based on the Deshmukh-Mather thermodynamic package. The flue gas composition for coal flue gas was (Hendriks, 1994) as given in Table 74. This flue gas was used for both solvents.

12.2 CO₂ capture plant with MEA solvent

MEA solvent at a concentration of 5M was studied in terms of its use for capturing CO₂ with/without HSS. It should be mentioned that in all cases the amount of MEA in the

solvent was kept controlled at 5M. An example of the material and energy balance for clean solvent is given in Appendix E. Table 75 gives the parameters set for the unit operations within the ProTreat model for the simulation of MEA solvent. Many of these settings are either typical for the amine process (i.e., pressure drop in the heat exchangers) or optimized (the column height). Table 76 summarizes the performance output of the simulation cases. Solvent capacity is the difference between rich and lean loading, and this gives the absorption capacity for a solvent under the given conditions. Figure 136 (A) shows that HSS could impact the CO₂ production but only under higher HSS content (i.e., > 2 wt%). A little bit of HSS could actually help the absorption process due to the shift of the reaction towards making the lean solvent leaner than the original. Also, even with some MEA solvent being bonded by HSS, MEA solvent still has a high capacity for absorption of CO₂.

Figure 136 (B) shows the cooling duty demand, which is reduced with the increase of HSS. This could be due to the effect of HSS on overall heat balance or specific heat capacity of the solvent. Furthermore, the waste water produced from the DCC and reflux purging increases with the increase of HSS content. It has been found that to bring the plant under water balance for the optimum make-up required, the waste water produced could be increased. Water produced from the reflux drum could have traces of amine, while the water produced from DCC could contain fly ash and traces of chemicals used for de-NO_x and de-SO_x. This water could be utilized for reclaimer operations, but during the time the reclaimer is not in service, it should be dumped to the wastewater treatment facility. The power consumption is quite constant over the change of HSS, with a slight increase due to change of solvent density and viscosity.

Table 74 Flue gas conditions used for simulation (Hendriks 1994)

| | |
|-------------------|-------|
| Temperature, °C | 50 |
| Pressure, kPa | 101.6 |
| Flow rate, kg/sec | 616 |
| Composition, mol% | |
| Water | 11.25 |
| CO ₂ | 13.30 |
| N ₂ | 71.63 |
| O ₂ | 3.81 |
| SO _x * | <<1 |
| NO _x * | <<1 |

*they will not be included in the simulation because their impact on solvent cannot be considered

Table 75 ProTreat simulation model parameters for MEA solvent cases

| | Setting parameters | Comments |
|--------------------------------------|---|--|
| Blower (B101) | Pressure outlet = 1.2 bar Efficiency = 60% | |
| DCC column (C101) | Packed tower; Packing = Pall rings 2" metal Packing height = 5 m Flooding = 65% | |
| DCC Pump (P-101) | Pressure increase = 0.9 bar Efficiency = 65 % | |
| DCC cooler (HE101) | Pressure drop = 0.3 bar Temperature outlet = 35°C | |
| Absorber (C102) | Packed tower; Packing = Pall rings 2" metal Packing height = 11.5 m Flooding = 65% | The height is optimized for 90% recovery. |
| Rich Pump (P102) Lean Pump (P103) | Pressure outlet = 5 bar Efficiency = 65% | |
| Lean/Rich Heat Exchanger (HE102) | Pressure drop (both sides) = 0.3 bar Rich temperature outlet = 110°C | |
| Stripper (C103) | Packed tower; Packing = Pall rings 2" metal Packing height = 10 m Flooding = 65% Reflux ratio = 80% Condensation temperature = 35°C Condenser pressure drop = 0.1 bar Reboiler pressure = 1.75 bar Reboiler duty = 540 MW | In ProTreat, the stripper consists of the column, condenser, and reboiler. |
| Washing section (C104) | Packed tower; Packing = Pall rings 2" metal Packing height = 5 m Flooding = 65% | |
| Wash Pump (P104)) | Pressure increase = 3 bar Efficiency = 65% | |
| Cooler (HE103) | Pressure drop = 0.3 bar Temperature outlet = 35°C | |

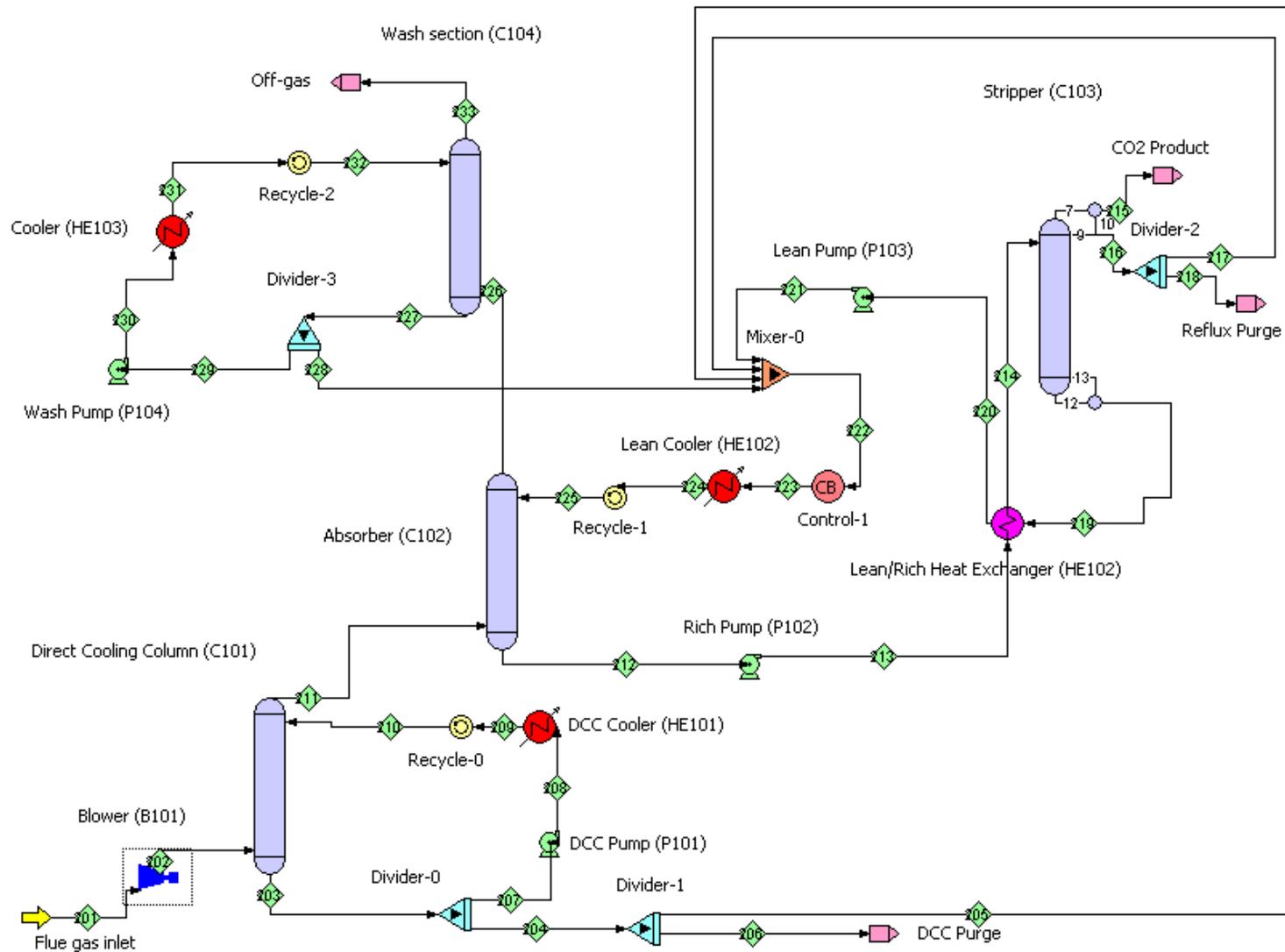


Figure 135 ProTreat process flow diagram for CO₂ capture plant with MEA solvent

Table 76 Predicted impact of HSS in MEA solvent on CO₂ capture plant

| Inputs | | | | | | | | |
|--|---------|---------|---------|---------|----------|---------|---------|---------|
| HSS, wt% | 0 | 0.5 | 1 | 2 | 3 | 4 | 5 | 7 |
| Solvent Flow Rate, m3/sec | 2.44 | 2.44 | 2.44 | 2.44 | 2.44 | 2.44 | 2.44 | 2.44 |
| Solvent Conc, wt% | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 |
| Energy consumption, MW | 540 | 540 | 540 | 540 | 540 | 540 | 540 | 540 |
| Performance variables | | | | | | | | |
| CO₂ production, kg/sec | 111.15 | 110.98 | 111.204 | 111.251 | 110.985 | 110.589 | 110.26 | 109.335 |
| CO₂ Recovery, % | 89.89 | 89.76 | 89.94% | 89.98% | 89.76% | 89.44% | 89.18% | 88.43% |
| Reduction in CO₂, % | 0% | 0.15% | -0.05% | -0.10% | 0.14% | 0.50% | 0.80% | 1.63% |
| Solvent Make-up, kg/sec | 0.03614 | 0.03966 | 0.04614 | 0.0538 | 0.062117 | 0.07265 | 0.07958 | 0.0964 |
| Total waste water, kg/sec | 13.767 | 14.198 | 14.928 | 15.957 | 16.954 | 18.156 | 18.90 | 20.81 |
| Total cooling consumption, MW | 599.35 | 587.72 | 573.89 | 548.66 | 523.41 | 498.42 | 472.76 | 420.47 |
| Total power consumption, MW | 18.99 | 18.99 | 19.00 | 19.00 | 19.01 | 19.02 | 19.03 | 19.04 |
| Solvent capacity, mol/mol | 0.205 | 0.204 | 0.203 | 0.201 | 0.198 | 0.196 | 0.194 | 0.19 |

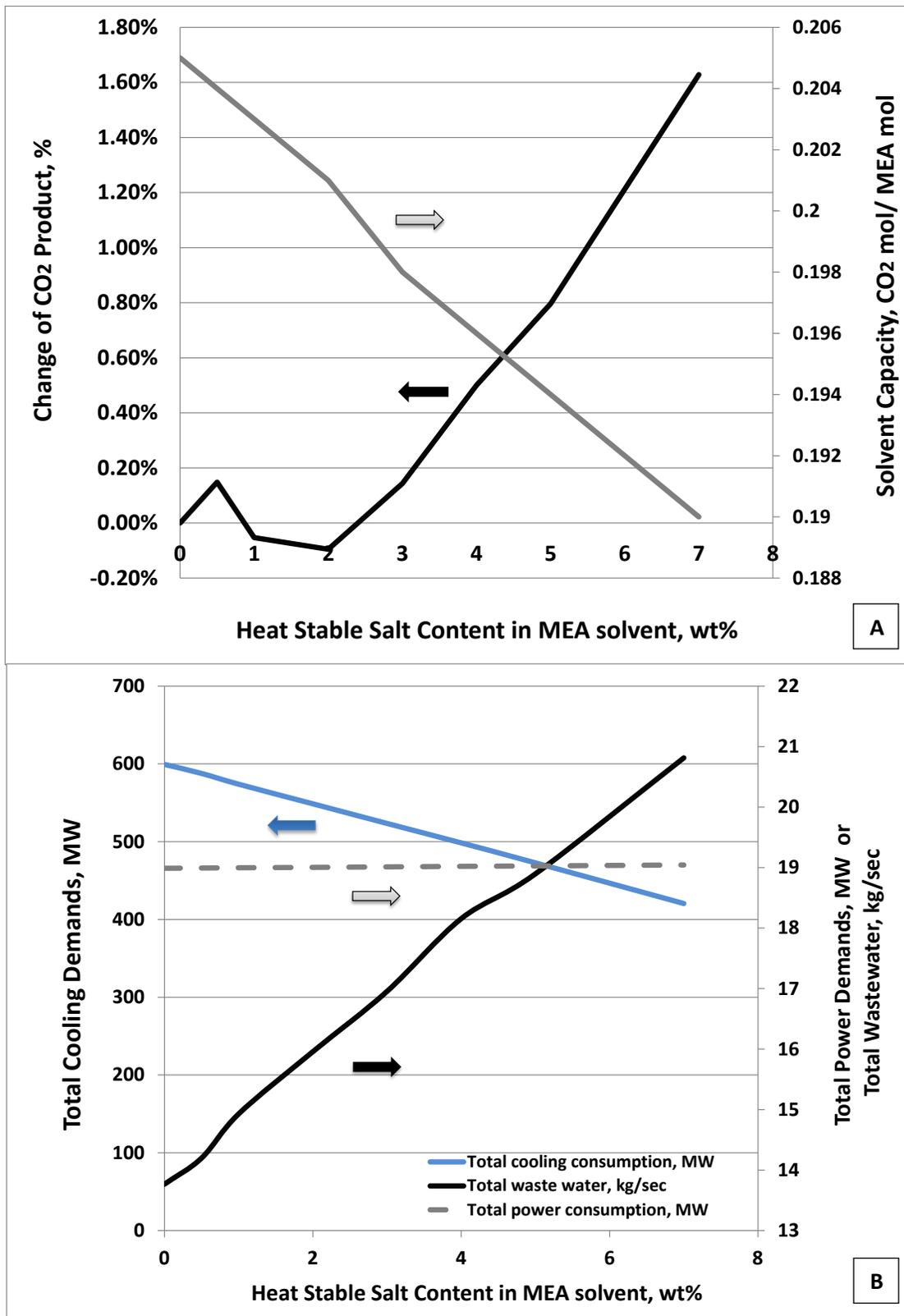


Figure 136 HSS impact on CO₂ production and solvent capacity (A) and utilities consumption and wastewater produced (B) in MEA case

12.3 CO₂ capture plant with MEA/MDEA solvent

MEA/MDEA solvent at a concentration of 5M was studied in terms of its use for capturing CO₂ with/without HSS. It should be mentioned that in all cases the concentration of MEA and MDEA in the solvent were kept controlled at 2.5M/2.5M. Table 77 gives the parameters set for the unit operations within the ProTreat model for the simulation, which is the same for the MEA solvent model in most parts. The absorber column height was optimized for 90% removal efficiency. Table 78 summarizes the performance output of the simulation cases. Figure 137 (A) shows that HSS could impact the CO₂ production very significantly. Even at HSS levels as low as 1 wt% in MEA/MDEA solvent, the CO₂ absorption could be reduced by 0.27%. MDEA solvent is known to be very sensitive to HSS compared to MEA, as reported by the ProTreat developers¹¹. For a variety of reasons, the impact of HSS is more dangerous to the CO₂ capture plant if HSS levels exceed the 2 to 3 wt%. Figure 137 (A) illustrates the solvent capacity reduction with the increase of HSS levels in the solvent.

Figure 137 (B) shows the cooling duty demand, which is reduced with the increase of HSS, and this could be due to the effect of HSS on solvent physical properties (i.e., heat capacity of solvent). Furthermore, the waste water produced from DCC and reflux purging increases with the increase of HSS content. However, water purged from a mixed amine plant is much lower than an MEA plant, and even water reflux, in most cases, is returned to the process completely to maintain water balance and make-up. The power consumption is quite constant over the change of HSS, with a slight increase due to the change of solvent density and viscosity.

¹¹ <http://www.ogtrt.com/>

Table 77 ProTreat simulation model parameters for MEA solvent cases

| | Setting parameters | Comments |
|--------------------------------------|---|---|
| Blower (B101) | Pressure outlet = 1.2 bar Efficiency = 60 % | |
| DCC column (C101) | Packed tower; Packing = Pall rings 2" metal Packing height = 5 m Flooding = 65% | |
| DCC Pump (P-101) | Pressure increase = 0.9 bar Efficiency = 65 % | |
| DCC cooler (HE101) | Pressure drop = 0.3 bar Temperature outlet = 35°C | |
| Absorber (C102) | Packed tower; Packing = Pall rings 2" metal Packing height = 30 m Flooding = 65% | The height is optimized for 90% recovery. |
| Rich Pump (P102) Lean Pump (P103) | Pressure outlet = 5 bar (rich)/8 bar (lean) Efficiency = 65 % | |
| Lean/Rich Heat Exchanger (HE102) | Pressure drop (both sides) = 0.3 bar Rich temperature outlet = 110°C | |
| Stripper (C103) | Packed tower; Packing = Pall rings 2" metal Packing height = 10 m Flooding = 65% Reflux ratio = 80% Condensation temperature = 35°C Condenser pressure drop = 0.1 bar Reboiler pressure = 1.75 bar Reboiler duty = 420 MW | In ProTreat, the stripper consists of the column, condenser and rebuilders. |
| Washing section (C104) | Packed tower; Packing = Pall rings 2" metal Packing height = 5 m Flooding = 65% | |
| Wash Pump (P104)) | Pressure increase = 3 bar Efficiency = 65 % | |
| Cooler (HE103) | Pressure drop = 0.3 bar Temperature outlet = 35°C | |

Table 78 Predicted impact of HSS in MEA/MDEA solvent on CO₂ capture plant

| Inputs | | | | | | | | |
|--|----------|----------|----------|----------|----------|----------|----------|----------|
| HSS, wt% | 0 | 0.5 | 1 | 2 | 3 | 4 | 5 | 7 |
| Solvent Flow Rate, m3/sec | 2.44 | 2.44 | 2.44 | 2.44 | 2.44 | 2.44 | 2.44 | 2.44 |
| Solvent Conc, wt% | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 |
| Energy consumption, MW | 540 | 540 | 540 | 540 | 540 | 540 | 540 | 540 |
| Performance variables | | | | | | | | |
| CO₂ production, kg/sec | 111.44 | 111.306 | 111.141 | 110.688 | 110.026 | 109.111 | 107.822 | 98.131 |
| CO₂ Recovery, % | 90.13% | 90.02% | 89.89% | 89.52% | 88.99% | 88.25% | 87.20% | 79.37% |
| Reduction in CO₂, % | 0% | 0.12% | 0.27% | 0.68% | 1.27% | 2.09% | 3.25% | 11.95% |
| MEA solvent Make-up, kg/sec | 2.40E-03 | 2.33E-03 | 2.27E-02 | 2.12E-03 | 1.95E-03 | 1.75E-03 | 1.51E-03 | 7.71E-04 |
| MDEA solvent Make-up, kg/sec | 7.26E-06 | 6.94E-06 | 6.66E-06 | 6.05E-06 | 5.43E-06 | 4.83E-06 | 4.27E-06 | 2.43E-06 |
| Total waste water, kg/sec | 0.903 | 1.305 | 1.667 | 2.362 | 3.153 | 4.011 | 4.946 | 9.61 |
| Total cooling consumption, MW | 439.43 | 430.49 | 421.12 | 402.09 | 382.69 | 362.89 | 343.28 | 312.32 |
| Total power consumption, MW | 19.66 | 19.66 | 19.67 | 19.68 | 19.69 | 19.70 | 19.71 | 19.73 |
| Solvent capacity, mol/mol | 0.241 | 0.240 | 0.241 | 0.240 | 0.238 | 0.236 | 0.233 | 0.213 |

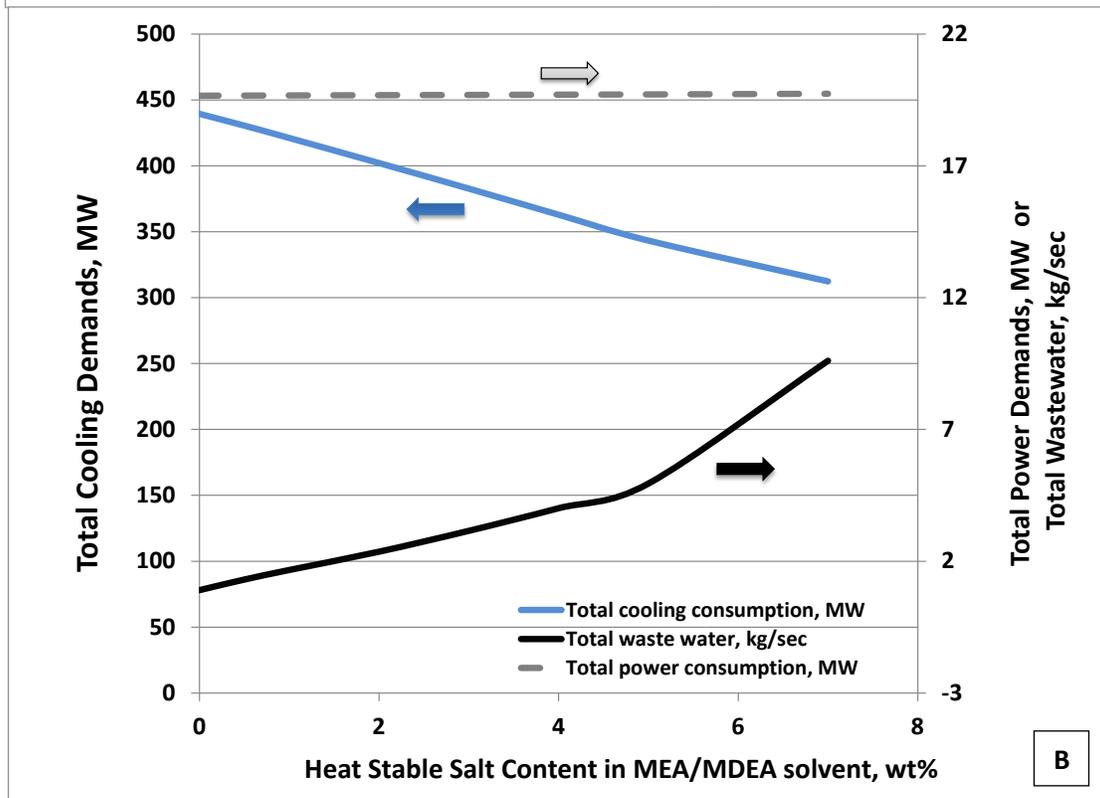
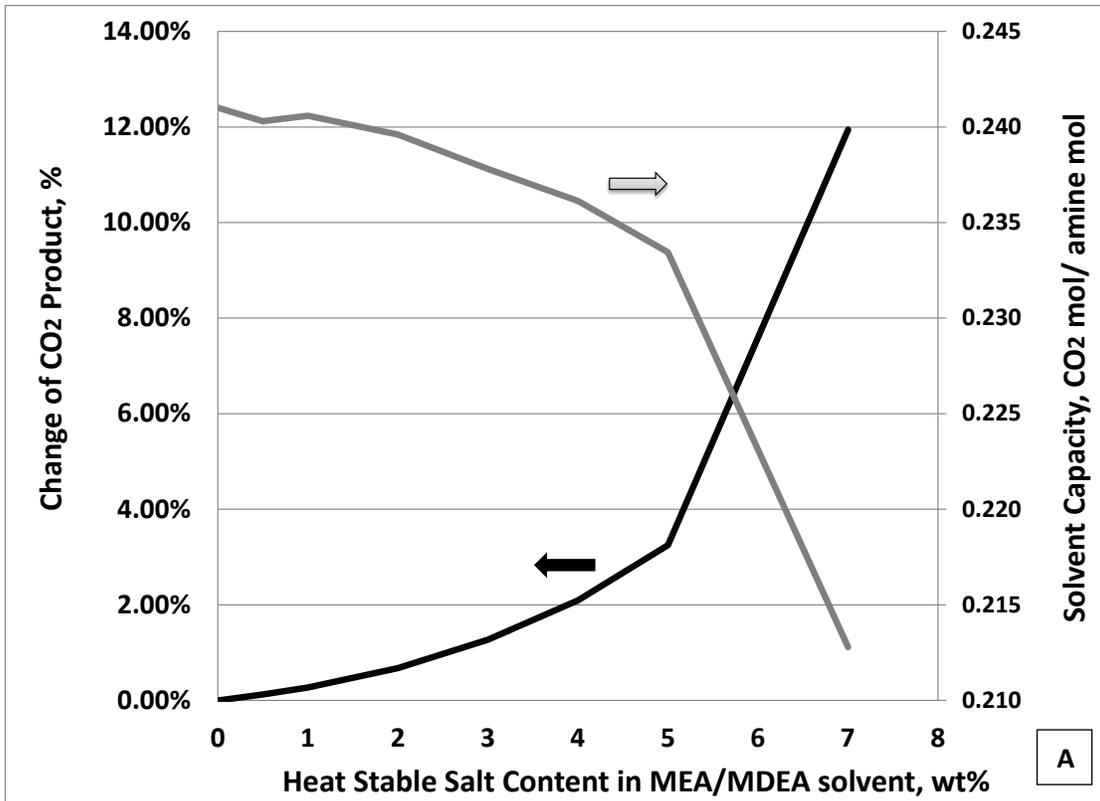


Figure 137 HSS impact on CO₂ production and solvent capacity (A) and utilities consumption and wastewater produced (B) in MEA/MDEA case

12.4 Concluding Remarks

Process simulation with ProTreat for CO₂ capture plant has been studied for clean and degraded (with HSS) 5M MEA and 5M MEA/MDEA solvents. The CO₂ production could be affected by the presence of HSS and this is more sensitive for MEA/MDEA than MEA. For instance at 3% HSS in solvent, the CO₂ reduction is 1.27% for MEA/MDEA case while it is 0.14% for MEA solvent. Other observations include the change of the utility consumption and the increase of wastewater produced from amine plant as the HSS concentration increases.

Chapter 13: Conclusions and Recommendation for Future Work

13.1 Conclusions

1. HSS presence and type impacts the solvent absorption capacity greatly. For instance, MEA/MDEA solvent is more sensitive than MEA solvent for the same concentration of HSS. The organic acids affect MEA and MDEA absorption by forming HSS: Formic acid > Malonic acid > Acetic acid > Glycolic acid.
2. Solvent recovery in vacuum was found to enhance solvent recovery, reduce solvent in the waste, reduce the demands for water and steam, and reduce the amount of waste water produced.
3. Clean MEA could be recovered at 260 mmHg while, if it is degraded, ≤ 210 mmHg is required to recover the solvent. The same results apply to MEA/MDEA solvent, except that the vacuum needs to be much deeper (i.e., 60-110 mmHg).
4. The high level of degradation products and HSSs in the solvent linearly reduce the solvent recovery and increase the waste quantity.
5. The recovered MEA solvent was found to be contaminated with two light degradation products out of five: ammonia and ethylamine. For recovered MEA/MDEA solvent, the contamination came from five degradation products out of eight considered, and they were ammonia, ethylamine, 3-Picoline, 2-Methylaminoethanol, and N-Acetyethanolamine.
6. Three types of activated carbons were studied in this research: SGL, M-1657 and M-1731. Three forms of activated carbon were considered: dry as received, water wetted carbon, and amine(s) wetted carbon. SGL and M-1731 are the most attractive in the amine wetted form.

7. MEA distillates were found to be contaminated with ammonia and ethylamine. Investigations on treating these distillates with carbon were carried out by isotherm adsorption and dynamic adsorption testing. However, it was found that these two degradation products could not be removed by activated carbon.
7. MEA/MDEA distillates were found to be contaminated with ammonia, ethylamine, 3-picoline, 2-methylamino ethanol, and N-Acetyethanolamine. Investigation of treating these distillates with carbon was carried out by isotherm adsorption and dynamic adsorption testing. It was found that 50 – 60% contamination reduction was observed due to removal of 3-Picoline and partial removal of N-Acetyethanolamine. The other three are unlikely to be removed by activated carbon. However, they have low impact on the solvent quality.
8. Three industrial lean amine samples (two MEA and one DGA) obtained from three facilities were thermally purified, and the recovered distillates were treated with isotherm activated carbons (SGL and M-1731). Most of degradation products and HSSs were eliminated via thermal reclamation, while the isotherm activated carbon treatments showed considerable reduction in the contaminants in distillates (by 50% to 100%, depending on the nature and concentration of the contaminants).
9. Process simulation for a CO₂ capture plant was studied for clean and degraded (with HSS) 5M MEA and 5M MEA/MDEA solvents. The CO₂ production was affected by the presence of HSS, and this is more sensitive with MEA/MDEA than MEA. Other observations include change of the utility consumption and increase of wastewater produced.

7. Hybrid amine reclaimer has been proposed in this research. It consists of two stages; thermal purification and adsorption treatment.

13.2 Recommendations for future work

1. It is recommended to search for alternative methods to remove ammonia, ethylamine, and 2-methylamino ethanol. Possibly, using some sort of additive that removes these chemicals or converts them back to useful amine or non-harmful chemicals for the amine system should be explored.
2. It is important to verify the results obtained in this study for the laboratory-scale hybrid purification process by scaling it up to pilot plant level and checking its feasibility in treating degraded solvent either for MEA or its blends and possibly other amine solvents used in CO₂ capture processes or even natural gas sweetening.
3. Thermodynamic and physical properties for amine solvent in conjunction with degradation products, HSSs, and CO₂ should be measured and studied. This could lead to a better understanding of the solvent behaviour, better predictions in simulation, and more accurate design for amine plants and reclaimer process.
4. Two process simulators (ProMax and ProTreat) have been tested to simulate the amine reclaimer. The predictions in the simulations were unsatisfactory. It is advisable to develop accurate VLE/solubility data for amine solvents.
5. Amine solvent thermal purification is more of a dynamic process than a steady state process. It is advisable to conduct dynamic and steady state simulations of the amine plant and reclaimer versus the field data.

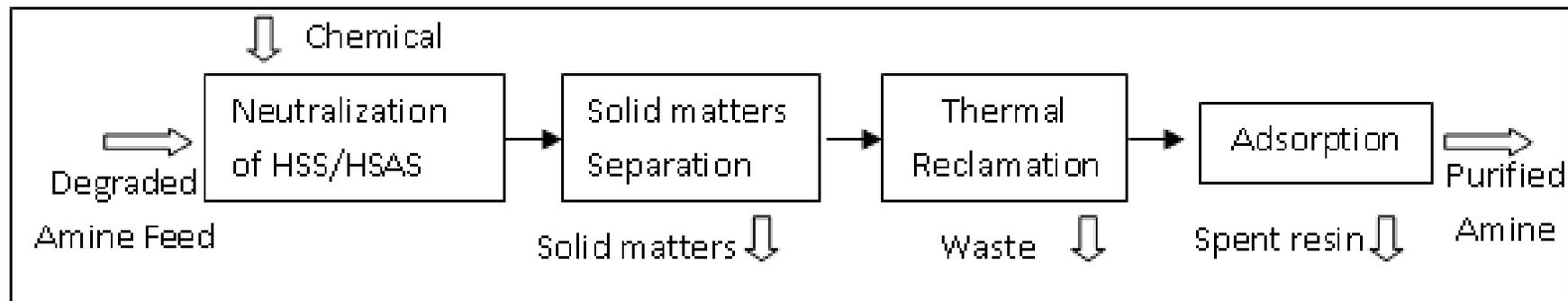


Figure 138 Hybrid Reclaimer proposed in this research

Reference

- Abdi, Majid Abedinzadegan, Mohammed M. Golker, and Axel Meisen (2001) "Improve Contaminant Control in Amine Systems." *Hydrocarbon Processing*, pp. 102 (October).
- Aboudheir, Ahmed, and Walid ElMoudir (2009) "Performance of Formulated Solvent in Handling of Enriched CO₂ Flue Gas Stream." *Energy Procedia*, Vol. 1, No. 1, pp. 195–204 (February).
- Abry, Raymond G., Todd S. Beasley, Stephen W. Carlson, and Stephen G. Kresoyak (1999) "Process for Recovering Processing Liquids." US Patent 5,993,608
- Anderson, Herbert M. (1959) "Diethanolamine Recovery by Steam Stripping." US Patent 2,892,775
- Anderson, Herbert M., Frederick C. Draemel, and Daniel J. Lyons. (1959) "Diethanolamine Reclamation." US Patent 2,914,469
- Armarego, W.L.F., and Christina Chai (2009) "Purification of Laboratory Chemicals" Sixth Edition, Butterworth-Heinemann.
- Aroonwilas, Adisorn, and Amornvadee Veawab (2004) "Characterization and Comparison of the CO₂ Absorption Performance into Single and Blended Alkanolamines in a Packed Column." *Industrial & Engineering Chemistry Research* 43 (9) (April 1): 2228–2237.
- Asperger, R. G., H. J. Liu, and J. W. Dean (1995) "Accurate, Reproducible Measurement of Reduced Corrosion in Gas Treating Amine Systems after Application of Judicious Neutralization Techniques." AICHE 1995 Spring National Meeting, Houston, TX. (March 21-23).
- Astarita, Giovanni (1983a) "Chapter 14: Process Selection." In *Gas Treating with Chemical Solvents*, 356–388. John Wiley & Sons, Inc.
- Astarita, Giovanni (1983b) "Chapter 15: Design and Scaleup." In *Gas Treating with Chemical Solvents*, 437–464. John Wiley & Sons, Inc.
- ASTM D3860-98 (2008) Determination of Adsorptive Capacity of Activated Carbon by Aqueous Phase Isotherm Technique. West Conshohocken, PA, USA: ASTM International.
- Bacon, T. R. (1987) "Amine Solution Quality Control Through Design, Operation and Correction." Gas Conditioning Conference, University of Oklahoma, Norman, OK.

- Ballard, Don (1966) "How to Operate an Amine Plant." *Hydrocarbon Processing*, 137-144 (April).
- Beasley, Todd, and Dwight A. Merritt (1992a) "Process for Reclaiming Waste Gas Treatment Chemical." US Patent 5,152,887
- Beasley, Todd, and Dwight A. Merritt (1992b) "Apparatus for Reclaiming Waste Gas Treating Chemical." US Patent 5,158,649
- Beasley, Todd, and Dwight A. Merritt (1995) "Process for Reclaiming And/or Concentrating Waste Aqueous Solutions of Gas Treating Chemicals." US Patent 5,389,208
- Bedell, S. A, C. M Worley, K. Darst, and K. Simmons (2010) "Thermal and oxidative disproportionation in amine degradation—O₂ stoichiometry and mechanistic implications." *International Journal of Greenhouse Gas Control* (April).
- Bedell, Stephen A., and Susan S. Kuan Tsai (1989a) "Process for the Recovery of Alkanolamine from Their Heat-Stable Salts Formed during Absorbent Thermal Regeneration Step of Gas Conditioning Processes." US Patent 4,808,284
- Bedell, Stephen A., and Susan S. Kuan Tsai (1989b) "Process for the Recovery of Alkanolamine from Their Heat-Stable Salts Formed Alkanolamine Absorbent Solutions." US Patent 4,814,051
- Berlie, Elmer M., James W. Estep, and Fred J. Ronicker (1965) "Preventing MEA Degradation." *Chemical Engineering Progress*, Vol. 61, No. 4, pp. 82–85 (April).
- Blachly, C. H., and H. Ravner (1964) *The Stabilization of Monoethanolamine Solutions for Submarine Carbon Dioxide Scrubbers*, Report # 6189, Unclassified. US Naval Research Laboratory, Washington D.C. (December 4).
- Blachly, C. H., H. Ravner, and C. R. Singleterry (1961) *Factors Affecting the Determination of Monoethanolamine Normality by Refractive Index Measurement*, Report # 5698: US Naval Research Laboratory, Washington D.C. (October 27).
- Blake, R. J. (1963) "Why Reclaim Monoethanolamine Solutions?" *Oil and Gas Journal*, pp 130–134 (September 9).
- Blake, R.J., and K.C. Rothert (1962) "Reclaiming Monoethanolamine Solutions." *Laurance Reid Gas Conditioning Conference*, , Norman, OK.
- Blanc, C.J., J. Elgue, and F. Lallemand (1981) "MDEA Process SElectivity Extracts H₂S", *Hydrocarbon Processing*, Vol. 60, No. 8, pp 111-116 (August)
- Brown, Craig J. (1987) "Fluid Treatment Process and Apparatus". US Patent 4,673,507.

- Brown, William H., and Thomas Poon (2004) *Introduction to Organic Chemistry*. 3rd ed. John Wiley & Sons, Inc.
- BS 2000-189/190 BRITISH STANDARD (BSi) (2004) "Methods of Test for Petroleum and Its Products — BS 2000-189/190: Crude Petroleum and Liquid or Solid Petroleum Products — Determination of Density or Relative Density — Capillary-stoppered Pyknometer and Graduated Bicapillary Pyknometer Methods". Energy Institute, London, UK.
- Burgers, Kenneth Leroy, Shrikar Chakravarti, and William Robert Williams (2007) "Reclaiming Amines in Carbon Dioxide Recovery." US Patent 0148068 A1
- Burns, David, and Al Gregory (1995a) "Waste Minimization and Compliance Benefits to be Gained from a Good Amine Management Program." 1995 NPRA Environmental Conference, San Francisco, California (October 15-17).
- Burns, David, and R. Alan Gregory (1995b) "The UCARSEP Process for On-line Removal of Non-Regenerable Salts from Amine Units." 1995 Laurence Reid Gas Conditioning Conference, University of Oklahoma, Norman, OK.
- Butwell, Kenneth F. (1968) "How to Maintain Effective MEA Solutions." *Hydrocarbon Processing*, Vol. 47, No. 4, pp 111-113 (April).
- Byszewski, Carolyn H. (2002) "Process for the Removal of Heat Stable Amine Salts." US Patent 0020625 A1.
- Chakma, A., and A. Meisen (1989) "Activated Carbon Adsorption of Diethanolamine, Methyl Diethanolamine and Their Degradation Products." *Carbon*, Vol. 27, No. 4, pp 573-584.
- Chakravarty, T., U.K. Phukan, and R.H. Weiland (1985) "Reaction of Acid Gases with Mixtures of Amines." *Chemical Engineering Progress*, pp 32-36 (April).
- Cheremisinoff, Paul N., and Fred Ellerbusch (1978) *Carbon Adsorption Handbook*, Chapter 2. Ann Arbor Science Publishers.
- Ciferno, Jared P., Timothy E. Fout, Andrew P. Jones, and James T. Murphy (2009) "Capturing Carbon from Existing Coal-Fired Power Plants." *Chemical Engineering Progress*, pp 33-41, (April).
- Clark, Robert M., and Benjamin W. Lykins Jr. (1989) *Granular Activated Carbon: Design, Operation and Cost*. 1st ed., pp 342, Lewis Publishers.
- Claud, Gabrielle, and Alain Blanc (1994) "Process for Eliminating the Diethanolamine Present in Triethanolamine and Preparation Process for Purified Triethanolamine." US Patent 5,292,958

- Coberly, Steven H., Thomas H. Laven, and Arthur I. Cummings (1998) "Amine Heat Stable Salt Removal from Type II Anion Exchange Resin." US Patent 5,788,864
- Corsi, Carlos, Roberto Betaneur, Pablo Trovarelli, and Carlos Frey (2002) "Considerations for Design - Operation of Reclaimer." Laurence Reid Gas Conditioning Conference, pp 273–828. Norman, Oklahoma.
- Critchfield, J., and G.T. Rochelle (1987) "CO₂ Absorption into Aqueous MDEA and MDEA/MEA Solutions." the AIChE National Meeting, Houston, TX (March 30).
- Cummings, Arthur L, Fred C Veatch, Alfred E Keller, Shade M Mecum, and Robert M Kammiller (1990) "An Analytical Method for Determining Bound and Free Alkanolamines in Heat Stable Salt Contaminated Solutions." AIChE 1990 summer national meeting symposium on gas processing, Ponca city, OK.
- Cummings, Arthur L., and Shade M. Mecum (1998) "Remove Heat Stable Salts for Better Amine Plant Performance." Hydrocarbon Processing, pp 63–67 (August).
- Cummings, Arthur L., and Shade M. Mecum (2000) "Increasing Profitability And Improving Environmental Performance by Maintaining Amine Solvent Purity." the 50th Annual Laurence Reid Gas Conditioning Conference, Norman, Oklahoma (Feb 27 to March 1).
- Cummings, Arthur L., Glen D. Smith, and Dennis K. Nelsen (2007) "Advances In Amine Reclaiming – Why There's No Excuse To Operate A Dirty Amine System." the Laurence reid gas conditioning conference, Norman, OK, pp 227-244.
- Cummings, Arthur L., David Street, and Gary Lawson (2003) "Contaminants and Their Effects on Operations – Yes! You Can Have Better Operating Amine and Glycol Systems!" The Brimstone Sulfur Conference, Banff, Alberta, (May).
- Cummings, Arthur L., Fred C. Veatch, Alfred E. Keller, James C. Thompson, and Regina A. Severson (1992) "Process for Monitoring and Controlling an Alkanolamine Reaction Process." US Patent 5,162,084.
- Cummings, Arthur L., Scott W. Waite, and Dennis K. Nelsen (2005) "Corrosion and Corrosion Enhancers in Amine Systems." The Brimstone Sulfur Conference, Banff, Alberta, (May).
- Dandekar, Sunil, and Jenny Shao (2011) "Continuous Removal of Contaminants from Amine Solutions." Petroleum Technology Quarterly (PTQ) Magazine, pp 81-87, (Q4)
- Davis, Jason, and Gary Rochelle (2009) "Thermal Degradation of Monoethanolamine at Stripper Conditions." Energy Procedia, Vol. 1, No. 1, pp 327–333. (February)

- Dawodu, Olukayode Fatai, and Axel Meisen (1996) "Degradation of Alkanolamine Blends by Carbon Dioxide." *The Canadian Journal of Chemical Engineering*, Vol. 74, No. 6, pp 960–966, (December).
- deMontigny, David (1998) "Carbon Dioxide Absorption Studies Using Ultra-highly Concentrated Monoethanolamine". Master of Applied Science Thesis, University of Regina.
- Dow (1962) *Gas Conditioning Fact Book*, Dow Chemical Company, Midland, Michigan.
- Duke, Mikel C., Bradley Ladewig, Simon Smart, Victor Rudolph, and João C. Diniz da Costa (2009) "Assessment of Post-combustion Carbon Capture Technologies for Power Generation." *Frontiers of Chemical Engineering in China*, Vol. 4, No. 2, pp 184–195 (September).
- Fabio, David G., Don Ballard, and John Parkins (1992) "The 3M Bag Filter: the Cost Cutting Problem Solver." *Laurance Reid Gas Conditioning Conference*, pp 118–126. Oklahoma.
- Faucher, Joseph A (1989) "Process for Inhibiting Mon and Diethanolamine Degradation." US 4,840,777
- Fuchs, Eberhard, Tom Witzel, and Klaus P. Stadler (1996) "Decontamination of Tertiary Amines from Primary and Secondary Amines." US Patent 5,481,037
- George, Joseph T. (2001) "Process for the Reclamation of Spent Alkanolamine Solution." US Patent 6,245,128 B1
- Goff, George S., and Gary T. Rochelle (2004) "Oxidative Degradation of Monoethanolamine in CO₂ Capture: O₂ Mass Transfer." the 7th Greenhouse Gas Control Technologies Conference (GHGT 7), Vancouver, BC, Canada, (September 5-9).
- Gregory, Richard Alan, and Martin Frank Cohen (1999) "Aqueous Alkanolamines Using an Electrodialysis Cell with An Ion Exchange Membrane." US Patent 5,910,611
- Van Grinsven, Petrus Franciscus Antonius, and Gijsbert Jan Van Heeringen (1999) "Process for the Purification of An Alkanolamine." WO Patent 21821
- Van Grinsven, Petrus Franciscus Antonius, and Gijsbert Jan Van Heeringen (2000) "Process for the Purification of An Alkanolamine." US 6,152,994
- Hankinson, R. W., and G. H. Thomson (1979) "Calculate Liquid Densities Accurately." *Hydrocarbon Processing*, pp 278-283 (September).
- Harston, J. D., and F. Ropital (2007) *Amine Unit Corrosion in Refineries* (EFC 46), Woodhead Publishig.

- Hatcher, Nathan A., Alfred E. Keller, Ralph H. Weiland, and M. S. Sivasubramanian (2006) "Are Your Simulation Amines Too Clean?" Laurence Reid Gas Conditioning Conference, Norman, Oklahoma (February).
- Hendriks, C. (1994) Carbon Dioxide Removal from Coal-Fired Power Plants. 1st ed., Springer.
- Hofmeyer, B.G., H.G. Scholten, and W.G. Lloyd. 1956. "Conamination and Corrosion in Monoethanolamine Gas Treating Solutions." A Symposium on Chemicals from Petroleum, Division of Petroleum Chemistry, American Chemical Society, Dallas, pp. 91–99, (April 8-13).
- Hollo, Janos, Eva Kurucz, and Attila Borodi (1971) The Application of Molecular Distillation. Budapest, Hungary: Akadémiai Kiadó.
- Huntsman (2005) Performance Products Diglycolamine® Agent Product Information. The Woodlands, Texas. www.huntsman.com/performance_products.
- Idem, Raphael O, Ito J Uyanga, Ahmed Aboudheir, and Paitoon Tontiwachwuthikul (2007) "Kinetic Study of SO₂ and O₂ Induced Degradation of Aqueous MEA." Chemindix 2007, Manama, Bahrain.
- Idem, Raphael, Paitoon Tontiwachwuthikul, Don Gelowitz, and Malcom Wilson (2010) "Latest Research on Fundamental Studies of CO₂ Capture Process Technologies at the International Test Centre for CO₂ Capture." The Greenhouse Gas Control Technologies 10 (GHGT-10) conference, Amsterdam, The Netherlands, (September 19-23).
- Idem, Raphael, Paitoon Tontiwachwuthikul, Chintana Saiwan, and Teeradet Supap (2009) "Method for Inhibition Amine Degradation During CO₂ Capture from a Gas Stream." WO Patent 065218 A1
- IDSWater, the Information Resource for the Water Industry (2011) "Eco-Tec AmiPur for CO₂ Recovery." http://www.idswater.com/water/us/carbon_recovery/933/products.html.
- Islam, M., and A. Chakma (1990). "Simulation of Activated Carbon Adsorbers Used in Gas Plants." Gas Separation & Purification, Vol. 4, No 2, pp 103–108 (June).
- Jameh, A.Atash (2010) "Amine Solution Recovery Package and Controlling Corrosion in Regeneration Tower." World Academy of Science, Engineering and Technology, Vol. 69, pp 107–110.
- Jefferson Chemicals (1963) "Monoethanolamine Reclaiming Part II Design Considerations." Hydrocarbon Processing and Refinery, Vol. 42, No 10, pp 225 (October).

- Jouravleva, Daria, and Peter Davy (2000) "Impact of Continuous Removal of Heat Stable Salts on Amine Plant Operation." 2000 Laurance reid gas conditioning conference, Norman, Oklahoma (Feb 27-March 1).
- Katti, Sanjeev S., and Bruce D. Langfitt (1986) "Development of a Simulator of Commercial Absorbers Used for Selective Chemical Absorption Based on a Mass Transfer Rate Approach." In The 65th Annual Convention Gas Processors. San Antonio, Texas, USA.
- Keller, Alfred E (1991) "Reactivation of Spent Alkanolamine." US Patent 5,045,291
- Keller, Alfred E., Robert M. Kammiller, Fred C. Veatch, Arthur L. Cummings, James C. Thompsen, and Shade M. Mecum (1992) "Heat-Stable Salt Removal from Amines by the HSSX Process Using Ion Exchange." Laurance Reid Gas Conditioning Conference, Norman, OK., pp 61–92 (March 2).
- Kindrick, R. C. (1950) A Prolonged Oxidation Test on Amine Solutions Resistant to Oxidation. Report No. T2.15-1-31, Unclassified Report issued for The US Navy Department. Louisville, Kentucky: The Girdler Corporation, Gas Processing Division, Process Development and Research Laboratories (May 25).
- Kindrick, R. C., Kenton Atwood, and M. R. Arnold (1950) The Relative Resistance to Oxidation of Commercially Available Amines. Report No. T2.15-1-30, Unclassified Report issued for The US Navy Department. Louisville, Kentucky: The Girdler Corporation, Gas Processing Division, Process Development and Research Laboratories (May 19).
- Kohl, Arthur L., and Richard B. Nielsen (1997) Gas Purification. 5th ed. Gulf Publishing Company, Houston, TX.
- Krell, Erich (1981) Handbook of Laboratory Distillation, With an Introduction to Pilot Plant Distillation, page 524. 2nd Revised ed. Elsevier Science Ltd.
- Lawal, Ayanduntan O, and Raphael O Idem (2005) "Effects of Operating Variables on the Product Distribution and Reaction Pathways in the Oxidative Degradation of CO₂-Loaded Aqueous MEA-MDEA Blends During CO₂ Absorption from Flue Gas Streams." Industrial & Engineering Chemistry Research, Vol. 44, No 4, pp 986–1003 (February).
- Lawal, Ayanduntan O, and Raphael O Idem (2006) "Kinetics of the Oxidative Degradation of CO₂ Loaded and Concentrated Aqueous MEA-MDEA Blends During CO₂ Absorption from Flue Gas Streams." Industrial & Engineering Chemistry Research, Vol. 45, No 8, pp 2601–2607 (April).
- Lawal, Olanike, Adeola Bello, and Raphael Idem (2005) "The Role of Methyl Diethanolamine (MDEA) in Preventing the Oxidative Degradation of CO₂ Loaded and Concentrated Aqueous Monoethanolamine (MEA/MDEA Blends

- During CO₂ Absorption from Flue Gases.” Industrial & Engineering Chemistry Research, Vol. 44, No 6, pp 1874–1896 (March).
- Lawson, Gary L., Arthur L. Cummings, and Shade Mecum (2003) “Amine Plant Corrosion Reduced By Removal of Bicine.” Gas Processors Association Annual Convention, San Antonio, Texas, USA (March 12).
- Lehman, John W. (2008) Student Lab Companion: Laboratory Techniques for Organic Chemistry. 2nd ed. Prentice Hall.
- Liu, H. J., J. W. Dean, and Sidney F. Bosen (1995) “Neutralization Technology to Reduce Corrosion from Heat Stable Amine Salts.” NACE International, Corrosion 95, Orlando, Florida (March 26-31).
- Lohwater, Robert K. (1967) “Advances in the Technology of Molecular Distillation.” Vacuum, Vol. 17, No 1, pp 1-3, (January).
- Maddox, Robert N., and John Morgan (1998) Gas Conditioning and Processing; Gas Treating and Sulfur Recovery. Vol. 4. Norman, Oklahoma: John M. Campbell and Company.
- Meisen, Axel, Majid Abedinzadegan, Raymond G. F. Abry, and Micheal G. Millard (1996) “Degraded Amine Solutions: Nature, Problems and Distillative Reclamation.” Laurance Reid Gas Conditioning Conference, Norman, Oklahoma, pp 168–189.
- Millard, M. G., and T. Beasley (1993) “Contamination Consequences and Purification of Gas Treating Chemicals Using. Vacuum Distillation.” Laurence Reid Gas Conditioning Conference Proceedings, University of Oklahoma, Norman, OK., pp 183–198.
- Morgan, Charles, and Terry Klare (1977) “Chloride Remvoal from DEA by Ion Exchange.” The Gas Conditioning Conference, Norman, Oklahoma, pp K–1 to K–8..
- MPR Services (2010) “Amine Headache # 1 Understanding Amine System Terminology.” <http://www.mprservices.com>.
- MPR Services (2011) “Carbon Capture Amine Reclamation (CCAR).” <http://www.mprservices.com/services/Pages/carbon-capture.aspx>.
- Neely, James W. (1982) Carbonaceous Adsorbents for the Treatment of Ground and Surface Waters, page 240. Marcel Dekker Inc.
- Norit Activated Carbon (2001) Measuring Adsorptive Capacity of Powered Activated Carbon, Report NA00-3 2000, www.Norit-americas.com.

- OPEC (2010) World Oil Outlook 2010. Organization of the Petroleum Exporting Countries, Vienna, Austria. www.opec.org.
- Pacheco, Manuel A., and Gary T. Rochelle (1998) "Rate-Based Modeling of Reactive Absorption of CO₂ and H₂S into Aqueous Methyldiethanolamine." *Ind. Eng. Chem. Res.*, Vol. 37, No 10, pp 4107–4117.
- Parisi, Paul, and Sid Bosen (2006a) "Amine Reclamation with Minimal Operational Impact Through Electrodialysis." Laurence Reid Gas Conditioning Conference, Norman, Oklahoma, pp 301.
- Parisi, Paul, and Sid Bosen (2006b) "Electrodialysis-Effective Amine Reclamation with Minimal Operational Impact." 85th GPA Annual Convention, Grapevine, TX (March).
- Pauley, C. R. (1991) "Face Abd Facts About Amine Foaming." *Chemical Engineering Progress*, pp 33-38, (July).
- Paulsen, Henry C., John B. Holtzelaw, and Thomas P. McNamara (1955) "Recovery of Diethanolamine and Salts." U.S. Patent 2,701,750
- Pearson, Herb, Sunil Dandekar, Jenny Shao, and Don Norton (2005) "Case Study of Effects of Bicine in CO₂ Only Amine Treater Service." Laurance Reid Gas Conditioning Conference, University of Oklahoma, Norman, OK (Feb. 27-March 2).
- Perry, Dunman (1966) "What You Should Know About Filters." *Hydrocarbon Processing*, pp 145-148, (April).
- Polderman, L.D., C.P. Dillon, and A.B. Steele (1955a) "Why MEA Solution Breaks Down in Gas Treating Service." *Oil and Gas Journal*, Vol. 54, No 2, pp 180–183.
- Polderman, L.D., C.P. Dillon, and A.B. Steele (1955b) "Degradation of Monoethanolamine in Natural Gas Treating Service." *Oil and Gas Journal*, Vol. 53, pp 180-183, (May 16).
- Razzaghi, Minoo, Stephen G. Kresnyak, Brain A. Keast, and Timothy W. Giles (2000) "Process for Recovering Processing Liquids." WO Patent 00/76624 A2
- Reddy, S., J. Scherffius, S. Freguia, and C. Roberts (2003) "Fluor's Econamine FG PlusSM Technology An Enhanced Amine-Based CO₂ Capture Process." the Second National Conference on Carbon Sequestration, Alexandria, VA (May 5-8).
- Reddy, Satish, Dennis Johnson, and John Gilmartin (2008) "Fluor's Econamine FG PlusSM Technology for CO₂ Capture at Coal-fired Power Plants." Power Plant Air Pollutant Control "Mega" Symposium, Baltimore, Maryland (August 25-28).

- Rooney, P.C., M.S. DuPart, and T.R. Bacon (1996) "Effect of Heat-stable Salts on Solution Corrosivity of MDEA-Based Alkanolamine Plants." Laurance Reid Gas Conditioning Conferenc. Univ. of Oklahoma, Norman, OK.
- Rooney, Peter C. (1999) "Amine Heat Stable Salt Neutralization Having Reduced Solids." US Patent 5,912,387
- Rooney, Peter C. (2002) "Process for Purifying Aqueous Tertiary Amine and Alkanolamine Solutions." US Patent 6,353,138 B1
- Roy, Veronique, Leo E. Hakka, and Jean I. Sarlis (1994) "Process for Converting Heat Stable Salts to Heat Regenerable Amine Salts." US Patent 5,292,407
- Sardar, Hisham, and Ralph H. Weiland (1984) "A Non- Equilibrium Stage Approach for the Design and Simulation of Gas Treating Units." AIChE Annual Meeting. San Francisco, California (Nov. 25).
- Sarlis, Nicholas John (2007) "Regeneration of Ion Exchange That are Used for Salt Removal from Acid Gas Capture Plants." WO Patent 2007/104134 A2
- Scheirman, W. L. 1973. "Filter DEA Treating Solution." Hydrocarbon Processing, pp65-66, (August).
- Setameteekul, Anothai (2006) "Statistical Factorial Design Analysis of Mass-Transfer in CO₂ Absorption Using MEA and MEA/MDEA". Master of Applied Science Thesis, University of Regina.
- Shao, J., G. Lu, and M. Ye (2002) "Removal of Heat Stable Salts - A Solution to Amine Plant Operational Problems." Chemical Engineering in Petroleum & Natural Gas Journal (December).
- Singh, Kshatra Pati (1970) "Method pf Stabilizing a Monoethanoamine Solution by Adding A Trialkanolamine." US Patent 3,535,260
- Sokolik, Joseph E., Alexander J. M. Kosseim, and Gilbert R. Awtood (1983) "Regenerable Process for Selective Removal of Sulfur Dioxide from Effluent Gases." US Patent 4,389,383
- Soria, John (1998) "Method for Minimizing Solvent Degradation and Corrosion in Amine Solvent Treatment Systems." US Patent 5,766,548
- StatoilHydro (2009) CarbonDioxide Capture, Transport and Storage (CCS). StatoilHydro. www.statoilhydro.com.
- Strazisar, Brian R., Richard R. Anderson, and Curt M. White (2003) "Degradation Pathways for Monoethanolamine in a CO₂ Capture Facility" Energy & Fuels, Vol. 17, No 4, pp 1034-1039 (July).

- Supap, Teera, Chintana Saiwan, Raphael Idem, and Paitoon Tontiwachwuthikul (2011) “Part 2: Solvent Management: Solvent Stability and Amine Degradation in CO₂ Capture Processes.” *Carbon Management*, Vol. 2, No. 5, pp 551-566 (October).
- Supap, Teeradet, Raphael Idem, and Tontiwachwuthikul Paitoon (2010) “Mechanism of Formation of Heat Stable Salts (HSSs) and Their Roles in Further Degradation of Monoethanolamine During CO₂ Capture from Flue Gas Streams.” *Greenhouse Gas Control Technologies (GHGT-10)*, Amsterdam, The Netherlands.
- Supap, Teeradet, Raphael Idem, Paitoon Tontiwachwuthikul, and Chintana Saiwan (2006) “Analysis of Monoethanolamine and Its Oxidative Degradation Products During CO₂ Absorption from Flue Gases: A Comparative Study of GC-MS, HPLC-RID, and CE-DAD Analytical Techniques and Possible Optimum Combinations.” *Industrial & Engineering Chemistry Research*, Vol. 45, No 8, pp 2437-2451 (April).
- Supap, Teeradet, Raphael Idem, Amornvadee Veawab, Adisorn Aroonwilas, Paitoon Tontiwachwuthikul, Amit Chakma, and Brian D Kybett (2001) “Kinetics of the Oxidative Degradation of Aqueous Monoethanolamine in a Flue Gas Treating Unit.” *Industrial & Engineering Chemistry Research*, Vol. 40, No 16, pp 3445–3450 (August).
- UOP LLC (A) (1981) *Monoethanolamine in Solutions by Color Indicator Titration*. UOP Method 825-81, West Conshohocken, PA, USA: ASTM International.
- UOP LLC (B) (1981) *Titration Determination of CO₂ in Ethanolamines*. UOP Method 829-82, West Conshohocken, PA, USA: ASTM International.
- Uyanga, Ito J., and Raphael O. Idem (2007) “Studies of SO₂- and O₂-Induced Degradation of Aqueous MEA During CO₂ Capture from Power Plant Flue Gas Streams.” *Industrial & Engineering Chemistry Research*, Vol. 46, No. 8, pp 2558–2566. (April 1).
- Verma, Narendra, and Anil Verma (2009) “Amine System Problems Arising from Heat Stable Salts and Solutions to Improve System Performance.” *Fuel Processing Technology*, Vol. 90, No. 4, pp 483–489 (April).
- Wilson, M., P. Tontiwachwuthikul, A. Chakma, R. Idem, A. Veawab, A. Aroonwilas, D. Gelowitz, J. Barrie, and C. Mariz (2004) “Test Results from a CO₂ Extraction Pilot Plant at Boundary Dam Coal-fired Power Station.” *Energy*, Vol. 29, No (9-10), pp 1259–1267 (July).
- Wonder, D. K., R. J. Blake, J. H. Frager, and J. V. Tierney (1959) “An Approach to Monoethanolamine Solution Control: Chemical Analysis and Its Interpretation.” *Lurance Reid Gas Conditioning Conference*, Norman, Oklahoma, pp 42–59.
- Yan, Tsoung Y. (1992a) “Reclamation of Alkanolamine Solutions.” US Patent 5,108,551

Yan, Tsoung Y. (1992b) "Regeneration of Used Alkanolamine Solutions." US Patent
5,137,702

Appendices

Appendix A: The Impact of Slip Ratio of Lean Amine on the Solvent Reclamation

An amine plant to treat gas stream has the following information;

- Circulation rate of the lean amine = 1,000 gpm
- Solvent inventory = 50,000 gal
- Reclaimer efficiency is the ability of reclaimer in removing of contaminants

The reclamation cycle could be calculated as following to remove the solvent degradation products. This method is a general method (could be used for any reclamation process) to explore the reclamation cycle days and link that with the efficiency of removal of the contaminations from the solvent.

Reclaimer Cycle

$$= \frac{\text{Solvent Inventory}}{\text{Slip Stream} \times \text{Reclaimer Efficiency}} \quad \text{--- Equation (A - 1)}$$

As can be seen form Table 1 and Figure 1, when the slip ratio is small, this means the reclamation cycle is long while if the slip ratio is big, then the reclamation cycle is short. Lower reclamation efficiency also increases the reclamation cycle.

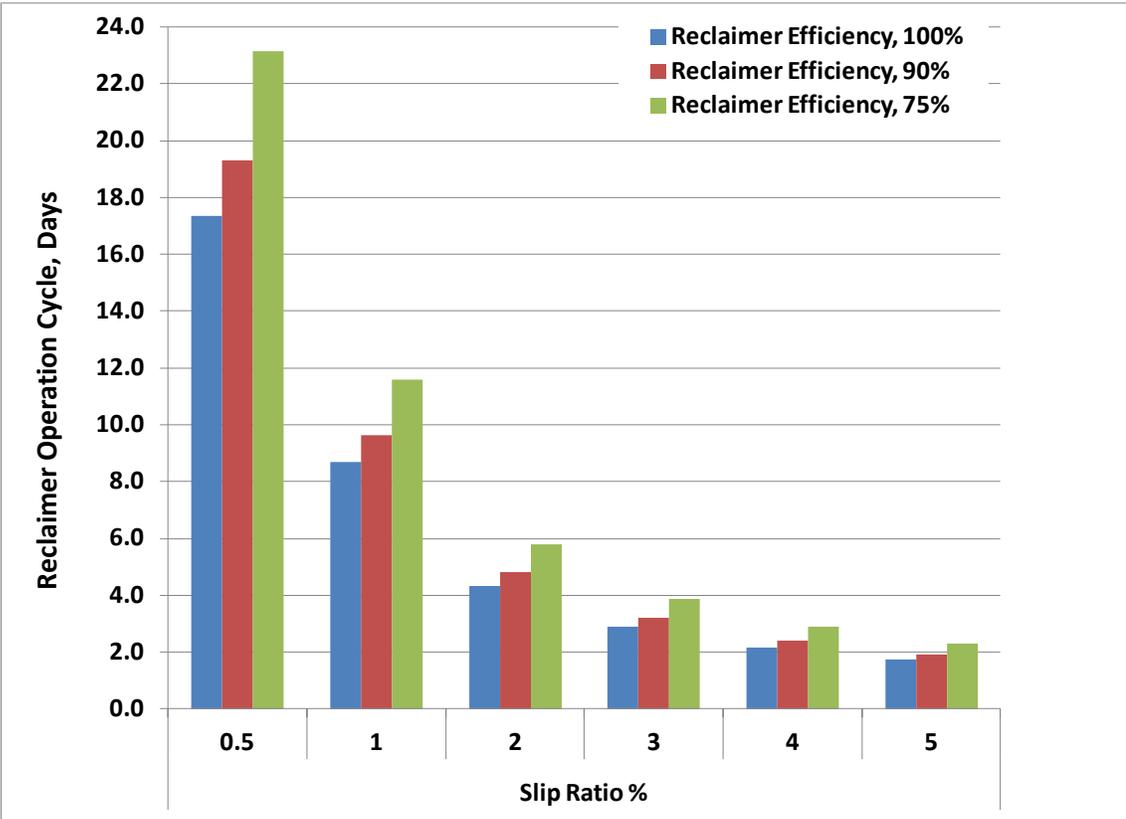


Figure 139 Reclaimer cycle vs. slip ratio lean feed to the reclaimer

Appendix B: Analysis Sample of acid gas loading, HSS and Solvent Concentration

| | | | | | |
|--|---------------|--------------|------------------------|----------------------------|----------------|
| H2S Loading | | | | Date: | 20.6.2011 |
| Sample: DGA sample from Plant C used in H2S absorption | | | | | |
| Solvent | DGA | Concn: | 50 | wt% | Sample 0.25 ml |
| Mwt | 105.14 | Sp.Gr.: | 1.0477 | (estimated from ProTreat™) | |
| 1- Pre-Conditioning Water (pH 11.40 - 11.60) | | | | | |
| Base Solution: | NaOH | Concn: | 0.1 | N | |
| pH of Water added prior titration | 7.50 and down | | | | |
| Ref. reading of base in Buret (V0) = | 4.02 | ml | | | |
| Reading of base in Buret (V1) = | 6.17 | ml | | | |
| | | pH = | | 11.41 | |
| 2- Titration for CO2 Loading (Endpoint 11.50) | | | | | |
| | | Desired pH = | | 11.5 | |
| Reading of base in Buret (V2) = | | ml | (i.e. pH before 11.50) | pH = | |
| Reading of base in Buret (V3) = | 6.85 | ml | (i.e. pH after 11.50) | pH = 11.51 | |
| for logical check | 6.844049 | ml | | | |
| Final base reading @ 11.50= | 6.8440 | ml | | | |
| 3- Calculations | | | | | |
| H2S Loading = | 0.269619 | eq/lit | | | |
| H2S Loading = | 0.054114 | mol/mol | | | |

HSS Determination

Date: 20.6.2011

Sample: DGA sample from Plant C used in H₂S absorption

| | | | | | | | |
|---------|--------|----------|--------|----------------------------|--------|------|----|
| Solvent | DGA | Concn: | 50 | wt% | Sample | 0.25 | ml |
| Mwt | 105.14 | Sp.Gr. : | 1.0477 | (estimated from ProTreat™) | | | |

1- Pre-Conditioning Water (pH 11.40 - 11.60)

| | | | | |
|--------------------------------------|------------------|--------|------|-------|
| Base Solution: | NaOH | Concn: | 0.1 | N |
| pH of Water added prior titration | 7.30 => 6.93down | | | |
| Ref. reading of base in Buret (V0) = | 2.2 | ml | | |
| Reading of base in Buret (V1) = | 3.8 | ml | pH = | 11.42 |

2- Titration for HSS determination (Endpoint 11.50)

Desired pH = 11.5

| | | | | | |
|---------------------------------|--------|----|------------------------|------|-------|
| Reading of base in Buret (V2) = | 3.95 | ml | (i.e. pH before 11.50) | pH = | 11.49 |
| Reading of base in Buret (V3) = | 4.02 | ml | (i.e. pH after 11.50) | pH = | 11.51 |
| for logical check | 3.985 | ml | | | |
| Final base reading @ 11.50= | 3.9850 | ml | | | |

3- Calculations

| | | |
|-------|----------|------------|
| HSS = | 0.074 | eq/lit |
| HSS = | 0.742613 | wt% as DGA |

| | | | | | | | |
|---|--------|-------------|--------|----------------------------|------------------|-----------|----|
| Solvent Conc | | | | Date: | | 20.6.2011 | |
| Sample: DGA sample from Plant C used in H2S absorption | | | | | | | |
| Solvent | DGA | Concn: | 50 | wt% | Sample | 0.25 | ml |
| Mwt | 105.14 | Sp.Gr. : | 1.0477 | (estimated from ProTreat™) | | | |
| 1- Titration for CO2 Loading (Endpoint 4.50) | | | | | Desired pH = 4.5 | | |
| Base Solution: | | HCl | | Concn: | | 1 N | |
| pH of Water added prior titration | | 7.04 down | | with amine | | 10.59 | |
| Ref. Reading of acid in Buret (V0) = | | 2 ml | | | | | |
| Reading of acid in Buret (V1) = | | ml | | (i.e. pH before 4.5) | | pH = | |
| Reading of acid in Buret (V2) = | | 3.3 ml | | (i.e. pH after 4.5) | | pH = 2.89 | |
| for logical check | | 5.138408 ml | | | | | |
| Final base reading @ 4.50= | | 1.3000 ml | | | | | |
| 2- Calculations | | | | | | | |
| Solvent concn = | | 52.18364 | | wt% | | | |

Appendix C: ProMax process simulator prediction for MEA-water VLE

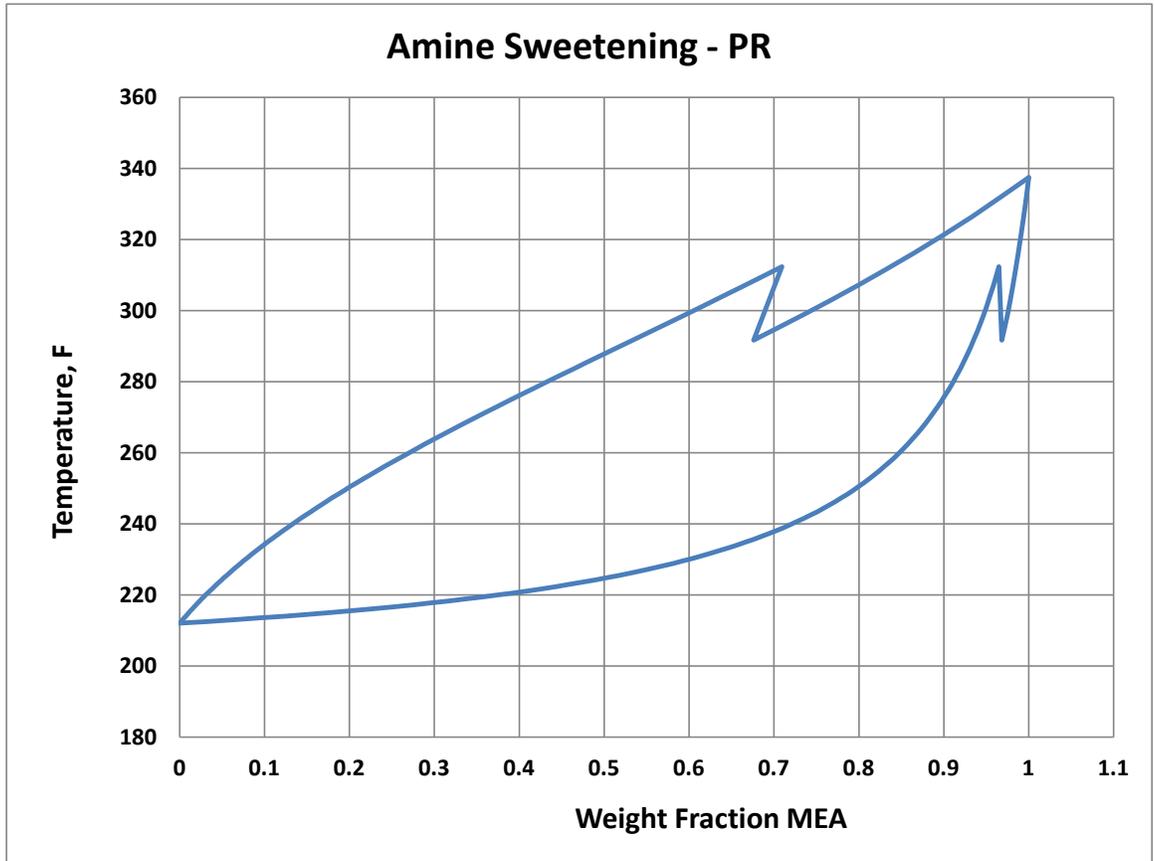


Figure 140 VLE of MEA-Water with best model proposed for amine system

Appendix D: Tables of laboratory equipments, tools and consumables
Table 79 Supporting equipments and devices

| # | Item | Manufacture company | Obtained from | Specification |
|----------|--------------------------------------|--|-------------------------------------|--|
| 1 | Distillate water evaporator, NOVA 4 | Jencons Scientific, Bridgeville, PA, USA | - | Distillate 4 liter/hr |
| 2 | pHydrion ultrafine pH Paper set | Micro Essential Lab., Brooklyn, NY, USA | Cole-Parmer, Montreal, QC, Canada | pH at 0.5 unit intervals (1 to 14) |
| 3 | Whatman Filter paper # 4 | Whatman Laboratory Division, Maidstone, Kent, UK | Science store, University of Regina | Qualitative, circles, 125mm |
| 4 | PC 510 pH / Conductivity meter | Oakton Instruments, Vernon Hills, IL, USA | Cole-Parmer, Montreal, QC, Canada | - Range (pH) - 2.00 to 16.00 pH - Range (Conductivity) 0.0 to 19.99 μ S, 0 to 199.9 μ S, 0 to 1999 μ S, 0 to 19.99 mS |
| 5 | Vortex-Genie 2T Shakers, SI-T236 | Scientific Industries, Bohemia, NY, USA | Cole-Parmer, Montreal, QC, Canada | Min/Max speed rpm 600/3200 |
| 6 | Thermo Scientific IEC CL2 centrifuge | Thermo Scientific, Asheville, NC, USA | Cole-Parmer, Montreal, QC, Canada | Speed range 0 to 3900 rpm |
| 7 | Fast release Pipette Pump, 2ml | Bel-Art Products, Pequannock, NJ, USA | Science store, University of Regina | Volume upto 2ml |
| 8 | Fast release Pipette | Bel-Art Products, Pequannock, NJ, USA | Science store, | Volume upto 10ml |

| | | | | |
|-----------|----------------------------------|--|-------------------------------------|---|
| | Pump, 10ml | | University of Regina | |
| 9 | Fast release Pipette Pump, 25ml | Bel-Art Products, Pequannock, NJ, USA | Science store, University of Regina | Volume upto 25ml |
| 10 | Timer Stopwatch, Touch Timer 480 | GoWalking MC, Oakville, ON, Canada | - | - |
| 11 | Balance Sartorius, CP224S | Sartorius, Goettingen, Germany | - | Max. weight 220 gm |
| 12 | Balance Mettler Toledo, PB602-S | Mettler-Toledo GmbH, Greifensee, Switzerland | - | Max. weight 610 gm |
| 13 | Balance Mettler Toledo, PB3002-S | Mettler-Toledo GmbH, Greifensee, Switzerland | - | Max. weight 3100 gm |
| 14 | Hotplate and Stirrer, Model 1103 | Techne Incorporated, Burlington, NJ, USA | Cole-Parmer, Montreal, QC, Canada | Temperature range (0-450°C) Stirrer speed (100-1200 rpm) |
| 15 | Bottle Gay-Lussac Adjusted 5ml | | Cole-Parmer, Montreal, QC, Canada | |
| 16 | Bottle Gay-Lussac Adjusted 2ml | | Cole-Parmer, Montreal, QC, Canada | |
| 17 | Tips 1000-5000 U1 | | Cole-Parmer, Montreal, QC, Canada | |
| 18 | Discovery Pipette 100-1000 ul | | Cole-Parmer, Montreal, QC, Canada | |
| 19 | Discovery | | Cole-Parmer, | |

| | | | | |
|----|---|--|--|-------------------------|
| | Pipette 1000-5000 ul | | Montreal, QC, Canada | |
| 20 | Digital Refractomet er Brix/RI | | Cole-Parmer, Montreal, QC, Canada | |
| 21 | Tips 200- 1300 ul Rack | | Cole-Parmer, Montreal, QC, Canada | |
| 22 | Tips 0-200 Ul | | Cole-Parmer, Montreal, QC, Canada | |
| 23 | Flaks Supprot, Neoprene | | Cole-Parmer, Montreal, QC, Canada | |
| 24 | Glass vials 20 ml | | Science store, University of Regina | 20 ml |
| 25 | Weight Boat Hexagonal Disposable | | Science store, University of Regina | Small size |
| 26 | Kimwipes, | | Science store, University of Regina | Large and small size |
| 27 | Clear glass vials, 40 ml | | Cole-Parmer, Montreal, QC, Canada | 40 ml |
| 28 | Parafilm Roll | | Science store, University of Regina | |
| 29 | Vinyl Tubing | | Science store, University of Regina | 1/4X1/16 |
| 30 | Clear Tubing | | Science store, | 3/16 ID, 1/16 OD |

| | | | | |
|-----------|--------------------------------|--------------------------------------|-------------------------------------|---------------|
| | | | University of Regina | |
| 31 | Tips 200-1000 U1 | | Cole-Parmer, Montreal, QC, Canada | |
| 32 | Tips 0.1-1 ml | | Cole-Parmer, Montreal, QC, Canada | |
| 33 | Burette Class-B | | Cole-Parmer, Montreal, QC, Canada | 10 ml |
| 34 | Burette Class-B | | Cole-Parmer, Montreal, QC, Canada | 25 ml |
| 35 | Beakers | | Cole-Parmer, Montreal, QC, Canada | 250 ml |
| 36 | UBS Link | Pasco Scientific, Roseville, CA, USA | | |
| 37 | High accuracy drop counter | Pasco Scientific, Roseville, CA, USA | | |
| 38 | pH Sensor | Pasco Scientific, Roseville, CA, USA | | |
| 39 | Pipettor Nichiryo LE 10-100 U1 | | Cole-Parmer, Montreal, QC, Canada | 10-100 ul |
| 40 | Centrifuge tubes 50ml | | Science store, University of Regina | 50ml |
| 41 | Paper filter # 5 | | Science store, University of Regina | 12.5 cm |
| 42 | Variable speed pump drive | | | Max. 200 psig |

| | | | | |
|-----------|------------------|-----------------------------|---|----------------|
| 43 | CO2 gas cylinder | Praxair, Regina, SK, Canada | - | Research grade |
| 44 | N2 gas cylinder | Praxair, Regina, SK, Canada | - | Research grade |

Table 80 GC and HPLC consumables

| # | Item | Manufacture company | Obtained from | Specification |
|----------|----------------------------|---|-------------------------------------|---------------------------|
| 1 | GC Syringe 10 uL | Agilent Technologies, Mississauga, ON. Canada | - | 10 UL, Accuracy $\pm 1\%$ |
| 2 | 25mm Syringe filter | Fisher Scientific, Ottawa, ON, Canada | Science store, University of Regina | 0.2 um, Nylon |
| 3 | Screw Cap green | Agilent Technologies, Mississauga, ON. Canada | - | - |
| 4 | 0.2 Um syringe filter | Cole-Parmer, Montreal, QC, Canada | - | 0.20 um, Nylon membrane |
| 5 | BD 3ml Syringe, REF 309585 | BD, Franklin Lakes, NJ, USA | Cole-Parmer, Montreal, QC, Canada | 3ml volume |
| 6 | Vail holder | - | Cole-Parmer, Montreal, QC, Canada | 25 vials |

Table 81 Adsorption set-up components

| # | Item | Manufacture company | Obtained from | Specification |
|---|---------------------------------|---------------------------------------|-----------------------------------|--|
| 1 | Floating ball flow meters | Cole-Parmer, Montreal, QC, Canada | Cole-Parmer, Montreal, QC, Canada | 2 to 20 GPH flow range |
| 2 | Pyrex plus laboratory glassware | Corning Pryex, Corning, NY, USA | Corning Pryex, Corning, NY, USA | Volume, 500 ml to 2 liters |
| 3 | Mini-Sieve Set | Bel-Art Products, Pequannock, NJ, USA | Cole-Parmer, Montreal, QC, Canada | screens (25, 35, 45, 60, 80, 120, 170, and 230 mesh) |
| 4 | Brush/Sieves No. 120 & Finer | | Cole-Parmer, Montreal, QC, Canada | |

Table 82 Distillation set-up components

| # | Item | Manufacture company | Obtained from | Specification |
|---|---------------------------------|---------------------|-----------------------------------|--------------------|
| 1 | Manual Vacuum valve (regulator) | | Cole-Parmer, Montreal, QC, Canada | 0 to 30" Hg |
| 2 | Vacuum pump feed filter | | Cole-Parmer, Montreal, QC, Canada | 31.8 cfm max. flow |
| 3 | Glass cold figure | | Cole- | Low temperature (- |

| | | | | |
|----|---|---|---|--|
| | | | Parmer, Montreal, QC, Canada | 198°C) |
| 4 | Vacuum grease | | Cole- Parmer, Montreal, QC, Canada | Max temperature (260°C) |
| 5 | Air Cadet Dry Diaphragm Vacuum Pump | Fisher Scientific Limited, Nepean ON, Canada | Cole- Parmer, Montreal, QC, Canada | Max Vac. 23" Hg (176 mmHg) |
| 6 | Diaphragm vacuum Pump | KNF, Trenton, NJ, USA | Cole- Parmer, Montreal, QC, Canada | Max. Vac. 29.5" Hg (10 mmHg) |
| 7 | Refrigerated Circulators, F12-MD | Julabo Labortechnik GmbH, Seelbach, Germany | - | Temperature range (- 20 to 200°C) |
| 8 | Power Controller for heating mantles, MC242 | Electrothermal Eng. Ltd, Essex, UK | - | Power from 0 to 9 |
| 9 | Standard heating mantles, U-1, O series | Glas-Col, Terre Haute, In, USA | - | 50 ml → Duty 60W 250 ml → Duty 180W 500 ml → Duty 270W |
| 10 | Distillation adaptor 75 Degree | SG & P, Freeport, Texas | - | |
| 11 | Distillation adaptor offset ACE thread | SG & P, Freeport, Texas | | |
| 12 | Distillation adaptor 75 degree angle ACE thread | SG & P, Freeport, Texas | | |
| 13 | Condenser 400 mm length | SG & P, Freeport, | | |

| | | | | |
|----|---|-------------------------------|--|--------------------------|
| | | Texas | | |
| 14 | Cold Finger | SG & P, Freeport, Texas | | |
| 15 | Distillation receiver with vacuum jacket | SG & P, Freeport, Texas | | |
| 16 | Adapter, flow control Teflon | SG & P, Freeport, Texas | | |
| 17 | Funnel, Addition graduated | SG & P, Freeport, Texas | | |
| 18 | Glass Adaptor 24/40 – 14/20 | - | Science store, University of Regina | |
| 19 | Flask 50 ml, 2 necks 14/20 | | Science store, University of Regina | |
| 20 | Rubber Tubing 1/4X5/8 | | Science store, University of Regina | |
| 21 | Thermometer glass | | Cole- Parmer, Montreal, QC, Canada | -1 to 200 ⁰ C |
| 20 | Thermometer Magnifier | | Cole- Parmer, Montreal, QC, Canada | |
| 21 | Keck Metal Standard Taper Clips | | Cole- Parmer, Montreal, QC, Canada | Size 14 |
| 22 | Keck Metal Standard Taper Clips | | Cole- Parmer, Montreal, | Size 19 |

| | | | | |
|-----------|---|--|-------------------------------------|----------------------|
| | | | QC, Canada | |
| 23 | Keck Metal Standard Taper Clips | | Cole-Parmer, Montreal, QC, Canada | Size 24 |
| 24 | Oakton Thermometer F/C water resistance | | Cole-Parmer, Montreal, QC, Canada | |
| 25 | Thermometer with Timer & probe | | Cole-Parmer, Montreal, QC, Canada | |
| 26 | 6 section Snyder Column | Lasalle Scientific Inc, Guelph, ON, Canada | | |
| 27 | Rubber Adapter (Fitment) | Lasalle Scientific Inc, Guelph, ON, Canada | | |
| 28 | Distillation column, Vigreux | | Science store, University of Regina | 450 mm column length |
| 29 | Flask Round bottom, 2-neck | | Science store, University of Regina | 250 – 500 ml |
| 30 | Flask Round bottom, 3-neck | | Science store, University of Regina | 250 – 500 ml |
| 31 | Flask Round bottom, 3-neck | | Science store, University of Regina | 50-100 ml |

Appendix E: Material and Energy Balance for MEA solvent with 0% HSS Case

Table 83 Summary of M&EB for MEA solvent with 0% HSS (Part 1)

| Stream | | 201 | 202 | 205 | 206 | 211 | 212 | 215 |
|----------------------|----------|----------|----------|-----|-----------|----------|-----------|----------|
| Water | kg/s | 42.81 | 42.81 | 0 | 9.966 | 32.822 | 1651.143 | 1.85 |
| Carbon Dioxide | kg/s | 123.642 | 123.642 | 0 | 1.16E-03 | 123.641 | 226.178 | 111.145 |
| MEA | kg/s | 0 | 0 | 0 | 4.40E-09 | 6.49E-15 | 754.925 | 7.62E-07 |
| Nitrogen | kg/s | 423.795 | 423.795 | 0 | 1.12E-04 | 423.795 | 1.09E-02 | 1.09E-02 |
| Oxygen | kg/s | 25.753 | 25.753 | 0 | 1.24E-05 | 25.753 | 1.21E-03 | 1.21E-03 |
| ** Total Flow | | 21.119 | 21.119 | 0 | 0.553 | 20.565 | 109.152 | 2.629 |
| Frac Vapor | | 1 | 1 | | 0 | 1 | 0 | 1 |
| Molec Wt | | 29.168 | 29.168 | | 18.016 | 29.469 | 24.115 | 42.992 |
| Temperature | Celsius | 50 | 74.568 | | 51.993 | 42.549 | 59.134 | 35 |
| Pressure | bar | 1.016 | 1.2 | | 1.17 | 1.154 | 1.1 | 1.452 |
| Mass Flow | kg/s | 616 | 616 | | 9.968 | 606.011 | 2632.257 | 113.008 |
| Volume Flow | cum/s | | | | 1.01E-02 | | 2.423 | |
| | cum/s | 557.603 | 508.09 | | | 467.053 | | 46.039 |
| Enthalpy | J/kmol | 7.55E+05 | 1.52E+06 | | -4.20E+07 | 5.22E+05 | -4.53E+07 | 3.15E+05 |
| Entropy | J/kmol-K | 12185.25 | 15346.98 | | -1.29E+05 | 9353.683 | -1.31E+05 | 660.745 |
| Heat Capacity | J/kmol-K | 31007.84 | 31181.39 | | 76903.24 | 30790.35 | 78122.62 | 37755.58 |
| Density | kg/cum | 1.105 | 1.212 | | 991.004 | 1.298 | 1086.322 | 2.455 |
| Viscosity | Pa-s | 1.75E-05 | 1.86E-05 | | 4.85E-04 | 1.76E-05 | 1.68E-03 | 1.53E-05 |
| Thermal Conductivity | W/m-K | 2.48E-02 | 2.66E-02 | | 0.631 | 2.43E-02 | 0.462 | 1.73E-02 |
| Cp/Cv | | 1.372 | 1.369 | | | 1.376 | | 1.297 |
| ZFactor | | 0.998 | 0.999 | | | 0.998 | | 0.993 |
| Surface Tension | N/m | | | | 6.74E-02 | | 4.86E-02 | |
| Vapor Pressure | Pa | | | | 1.14E+05 | | 98654.64 | |
| pH | | | | | 4.427 | | 8.465 | |
| MEA | Mol Frac | | | | 1.30E-10 | | 0.113 | |
| Water | Mol Frac | | | | 1 | | 0.84 | |
| Water | Mol Frac | 0.113 | 0.113 | | | 8.86E-02 | | 3.91E-02 |
| Carbon Dioxide | Loading | | | | 3.67E+05 | | 0.416 | |
| Carbon Dioxide | Mol Frac | | | | 4.78E-05 | | 4.71E-02 | |

Table 84 Summary of M&EB for MEA solvent with 0% HSS (Part 2)

| Stream | | 217 | 218 | 219 | 222 | 225 | 226 | 228 | 232 | 233 |
|----------------------|----------|-----------|-----------|-----------|-----------|-----------|----------|-----------|-----------|----------|
| Water | kg/s | 14.518 | 3.742 | 1631.356 | 1647.871 | 1647.356 | 29.256 | 1.997 | 90.886 | 27.255 |
| Carbon Dioxide | kg/s | 0.105 | 2.70E-02 | 114.616 | 114.772 | 114.772 | 12.127 | 5.11E-02 | 2.324 | 12.076 |
| MEA | kg/s | 0.115 | 2.97E-02 | 754.784 | 755.049 | 755.112 | 0.151 | 0.149 | 6.789 | 6.42E-03 |
| Nitrogen | kg/s | 4.80E-08 | 1.24E-08 | 0 | 2.30E-05 | 2.30E-05 | 423.784 | 2.30E-05 | 1.04E-03 | 423.784 |
| Oxygen | kg/s | 1.02E-08 | 2.62E-09 | 0 | 2.63E-06 | 2.63E-06 | 25.752 | 2.62E-06 | 1.19E-04 | 25.752 |
| ** Total Flow | | 0.81 | 0.209 | 105.516 | 106.441 | 106.413 | 17.835 | 0.114 | 5.209 | 17.72 |
| Frac Vapor | | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 1 |
| Molec Wt | | 18.192 | 18.192 | 23.7 | 23.653 | 23.655 | 27.534 | 19.198 | 19.198 | 27.588 |
| Temperature | Celsius | 35 | 35 | 118.277 | 69.524 | 35 | 40.741 | 45.078 | 35 | 42.545 |
| Pressure | bar | 1.452 | 1.452 | 1.75 | 4 | 3.7 | 1.076 | 1.05 | 3.75 | 1.03 |
| Mass Flow | kg/s | 14.738 | 3.799 | 2500.756 | 2517.691 | 2517.239 | 491.07 | 2.197 | 100 | 488.874 |
| Volume Flow | cum/s | 1.46E-02 | 3.75E-03 | 2.533 | 2.441 | 2.372 | | 2.15E-03 | 9.70E-02 | |
| | cum/s | | | | | | 432.073 | | | 450.99 |
| Enthalpy | J/kmol | -4.34E+07 | -4.34E+07 | -3.92E+07 | -4.36E+07 | -4.65E+07 | 4.54E+05 | -4.33E+07 | -4.41E+07 | 5.09E+05 |
| Entropy | J/kmol-K | -1.40E+05 | -1.40E+05 | -95128.1 | -1.23E+05 | -1.47E+05 | 7196.923 | -1.35E+05 | -1.42E+05 | 7790.06 |
| Heat Capacity | J/kmol-K | 76084.38 | 76084.38 | 90425 | 83820.73 | 83330.6 | 29747.04 | 76563.06 | 76540.6 | 29716.34 |
| Density | kg/cum | 1012.156 | 1012.156 | 987.172 | 1031.574 | 1061.23 | 1.137 | 1022.482 | 1030.706 | 1.084 |
| Viscosity | Pa-s | 7.54E-04 | 7.54E-04 | 5.62E-04 | 1.12E-03 | 2.42E-03 | 1.79E-05 | 7.56E-04 | 9.29E-04 | 1.80E-05 |
| Thermal Conductivity | W/m-K | 0.613 | 0.613 | 0.481 | 0.467 | 0.446 | 2.57E-02 | 0.588 | 0.577 | 2.58E-02 |
| Cp/Cv | | 0 | 0 | | | | 1.393 | | | 1.393 |
| ZFactor | | 0 | 0 | | | | 0.999 | | | 0.999 |
| Surface Tension | N/m | 6.82E-02 | 6.82E-02 | 4.04E-02 | 4.72E-02 | 5.17E-02 | | 6.32E-02 | 6.49E-02 | |
| Vapor Pressure | Pa | 1.45E+05 | 1.45E+05 | 1.75E+05 | 27224.72 | 5073.086 | | 1.05E+05 | 91986.24 | |
| pH | | 6.73 | 6.73 | 8.046 | 8.989 | 9.838 | | 8.599 | 8.836 | |
| MEA | Mol Frac | 2.33E-03 | 2.33E-03 | 0.117 | 0.116 | 0.116 | | 2.13E-02 | 2.13E-02 | |
| Water | Mol Frac | 0.995 | 0.995 | 0.858 | 0.859 | 0.859 | | 0.969 | 0.969 | |
| Water | Mol Frac | | | | | | 9.11E-02 | | | 8.54E-02 |
| Carbon Dioxide | Loading | 1.258 | 1.258 | 0.211 | 0.211 | 0.211 | | 0.475 | 0.475 | |
| Carbon Dioxide | Mol Frac | 2.93E-03 | 2.93E-03 | 2.47E-02 | 2.45E-02 | 2.45E-02 | | 1.01E-02 | 1.01E-02 | |