CHAPTER III
EXPERIMENTALS

3.1 Development of Analytical Techniques for MEA Oxidative Degradation

3.1.1 Equipment and Chemicals

The oxidative degradation experiments were conducted using MEA concentration of 5 kmol/m^3. The degradation was fixed at 328 and 393 K representative of absorption-regeneration conditions in a typical flue gas treating process. O_2 pressure of 250 kPa was used in order to perform accelerated oxidative degradation experiments. This is a precursor for this current work (beyond the scope of the present study), which will determine the products and mechanism of the actual condition for O_2 in a typical CO_2 capture plant. For CO_2-loaded experiments, a loading of 0.55 mol CO_2/mol MEA was employed. The oxidative degradation reactions were carried out using a 600-ml stainless steel batch reactor (model 5523, Parr Instrument Co., Moline, IL). The removable reactor head assembly consisted of a magnetic drive connected to a stainless steel (T316) stirring shaft and 2 adjustable 4-rectangular blade impellers (diameter of about 1.5 inches) of which one was positioned almost at the bottom of the vessel while the other was about 2.5 inches above the bottom one. The positions of these impellers were held constant throughout the experiments. In addition, the reactor also had a 0-300 psi Bourdon-type pressure gauge, gas inlet, gas release and liquid sampling valves, a preset safety rupture disc, a J-type thermocouple, a dip tube for gas introduction and sample removal, and a cooling coil for maintaining the process at a constant temperature irrespective of the temperature rise caused by the exothermic nature of the reaction of MEA and O_2, and preventing any temperature overshoot during the experiment that may be caused by furnace heating. The cooling system was regulated by a solenoid valve. The heat was supplied to the reactor by a furnace in which the reactor vessel was inserted and regulated by a temperature controller (Model 4836, Parr Instrument Co., Moline, IL) whereas the temperature of the reaction mixture was measured by a J-type thermocouple. The temperature accuracy of the controller

was within ± 0.1 %. Research grade O_2 and CO_2 were supplied from Praxair (Regina, Saskatchewan, Canada). Concentrated MEA (reagent grade with > 99% purity) was purchased from Fisher Scientific, Neopean, Ontario, Canada. MEA was diluted to the desired concentration using deionized distilled water. Its exact concentration was established by volumetric tritration with a standard solution of 1 kmol/m^3 hydrochloric acid (HCl) also from Fisher Scientific, to the endpoint of methyl orange indicator.

3.1.2 Typical Experimental Run

3.1.2.1 MEA-H_2O-O_2 Degradation System

MEA solution of 450 mL with 5.1 kmol/m^3 was loaded into the reactor, and the reactor head assembly was placed on top and tightly sealed to obtain a leak-free environment. The solution was stirred at 500 rpm while heating to 328 or 393 K. A few minutes was allowed for the solution to stabilize at the desired temperature. At this point, some vapor pressure due to water was observed as the pressure inside the reactor, and then 250 kPa of O_2 was additionally introduced by opening the O_2 cylinder set at a predetermined value through the gas inlet valve. O_2 was sparged into the solution through the dip tube to enhance the contact area with the solution. By using an equation developed by a group of Rooney and Daniels (1998), the initial 250 kPa of O_2 pressure was equivalent to 2.45 mol/m^3 of dissolved O_2 concentration in the MEA solution. This was the amount of O_2 initially dissolved in the MEA solution causing a drop of O_2 pressure of approximately 5 kPa, inside the reactor. As a result, extra 5 kPa O_2 pressure was added to compensate for that dissolved in the solution in order to maintain a constant pressure. Based on the ideal gas law, the 5kPa of O_2 pressure was approximately equal to 1.50 mol/m^3 O_2 concentration. The amounts of O_2 initially added and later compensated were therefore very close. The total pressure of the O_2 alone experiments was a combination of the water vapor pressure and 250 kPa O_2 pressure (i.e. 250 kPa at 328 K and 450 kPa at 393 K). Approximately, 2.5-mL samples were withdrawn into 5-mL sampling bottles, from the reactor through the liquid sampling valve at predetermined intervals of time. Extra O_2 was quickly introduced into the reactor to

compensate for the pressure loss during the sampling process. Cold water was run over the vials containing the samples to quickly cool down and quench the degradation reaction. These samples were kept in a refrigerator at 277 K for less than a week to allow sufficient time for GC-MS, HPLC-RID, and CE-DAD analyses. Our experiments showed that under these conditions further degradation of the samples was avoided. Oxidative degradation of MEA is an exothermic process. Therefore, a cooling water system was used to ensure and maintain the degradation process under isothermal conditions.

3.1.2.2 MEA-H_2O-O_2-CO_2 Degradation System

Just as in the case of the MEA-H_2O-O_2 system, 400 ml of 5.03 kmol/m^3 MEA solution was transferred into the reactor and the head assembly was placed to tightly seal the reactor. Prior to heating up, a predetermined value of 250 kPa CO_2 was introduced through the gas inlet valve, into the solution by opening the CO_2 cylinder for 12 hours, after which 4 ml of the solution was removed from the reactor through the liquid sampling valve to check for the CO_2 loading by titration against standard solution of 1 kmol/m^3 HCl, whereby CO_2 was liberated and measured for its quantity by displacement of NaCl/$NaHCO_3$/methyl orange mixture. The loading was calculated on a basis of the number of moles of CO_2 per one mole of MEA. The mixture in the reactor was heated to 328 or 393 K and CO_2 loading was once again determined. The total pressure of the reactor at this point was the sum of the pressures of water vapor and non-dissolved CO_2. Then, O_2 of 250 kPa set at the O_2 cylinder was additionally introduced into the solution through the gas inlet valve. The rest of the procedures were then conducted following those of MEA-H_2O-O_2 experiments. As in the case of the O_2 alone degradation experiments, the total pressure of O_2-CO_2 experiment was the sum of the water vapor pressure, 250 kPa O_2 and CO_2 vapor pressure (i.e. 1070 kPa at 393 K). The overall schematic of the oxidative degradation experiments and analysis and a sketch of the internals of the reactor are shown in Figure 3.1 and 3.2, respectively.

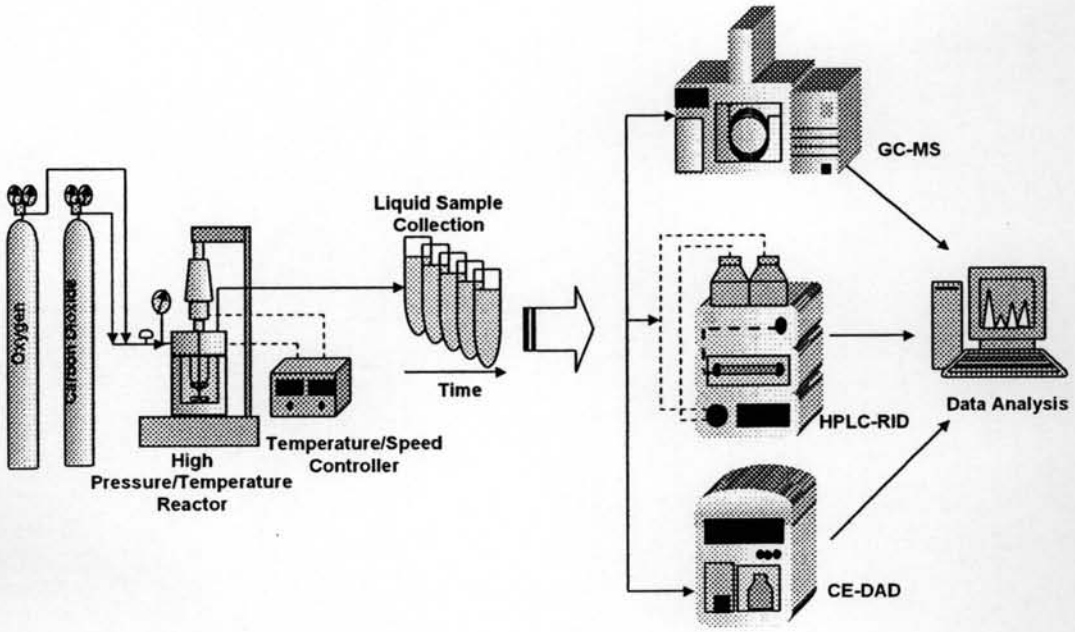


Figure 3.1 Schematic of MEA oxidative degradation experiments: Experimental set-up and analysis.

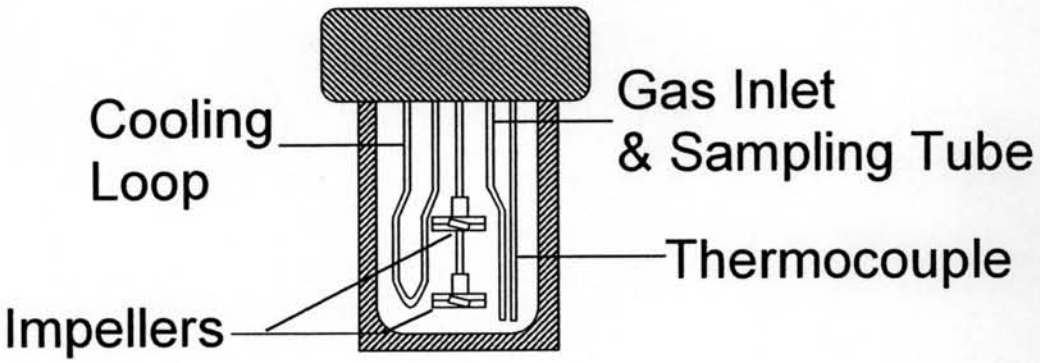


Figure 3.2 A sketch of the internals of the reactor.

3.1.3 Analysis of Degradation Products

3.1.3.1 Gas Chromatography/Mass Spectrometric Technique (GC-MS)

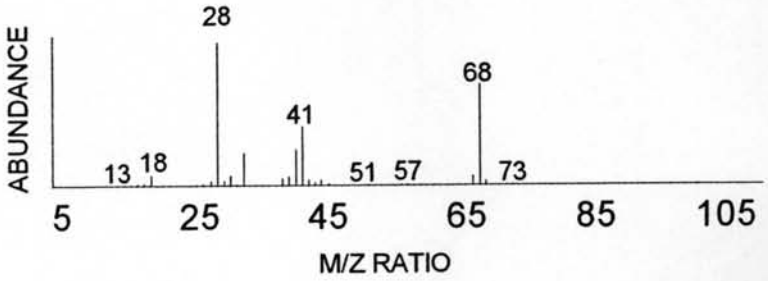
The GC-MS (model 6890/5073) was supplied by Hewlett-Packard Canada Ltd., Montreal, Quebec, Canada. Chromatographic capillary columns of different stationary phases and polarities were used as variables for comparison of the separation of MEA and its degradation products. These columns were HP-Innowax (high polar), HP-35MS (intermediate polar), and HP-5MS (non-polar) having crosslinked polyethylene glycol, crosslinked 5 and 35% phenyl methyl siloxane, respectively as stationary phases. All columns had the same dimension of 0.25 μm thickness × 0.25 mm id × 30 m length and supplied by Hewlett-Packard Canada Ltd., Montreal, Quebec, Canada. The introduction of sample was done using an autosampler/ autoinjector (model 7683, Hewlett-Packard Canada Ltd., Montreal, Quebec, Canada). The reproducibility of the autoinjector volume was 0.3% relative standard deviation (RSD) in terms of area percent of the peaks. Identical GC-MS operating conditions were applied to all columns. The criteria for GC-MS condition set-up began at the injector inlet in which its temperature had to be high enough to

completely evaporate the liquid sample. The initial temperature of the oven was selected at 373 K to ensure no condensation after the evaporated sample left the injection chamber. The ramp rate was 280 K/min lower than that of a previous condition (Supap et al., 2001) to improve separation of the products. The final temperature was set at 513 K which was high enough to provide for complete elution. It was also set to about 283 K lower than the limit temperature of the column used in this work, thus, preventing the column from being damaged. For a typical run, 1 μl sample was injected at the GC inlet set at 523 K using a split injection mode with a split ratio of 30:1. The GC oven was initially set at 373 K and ramped to 513 K at a rate of 280 K/min. The temperature was kept at 513 K for as long as 45 minutes to ensure a complete elution of all degradation products. Ultra high purity (UHP) grade Helium was used as the carrier gas, and this was regulated at a constant flow rate of 1 ml/min. The GC-MS interface, MS quad, MS source, and EM voltage were kept at 523K, 423K, 503 K and 1858, respectively. MS scan mode was used having a mass range from 10 to 300. The products were identified by matching their mass spectra with a commercial mass spectra of the National Institute of Standards and Technology (NIST) database (1998 version). Each sample was diluted using deionized distilled water in the ratio of 1:5 prior to the analysis to avoid column overload and improve separation of the components. The samples were analyzed twice to check for the reproducibility. MEA measurement was done in terms of concentration calibrated with standard MEA, peak area and area percent whereas those of products were based on peak area and its corresponding area percent only, and thus, represented relative concentrations. This methodology was also applied to the analyses that were used in the HPLC and CE techniques.

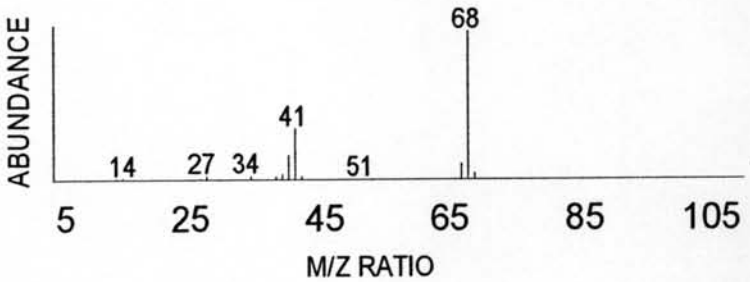
A matching technique which compared the mass spectra of the GC separated components with the NIST database was used for the initial product identification. Verification of some of the species was subsequently performed by comparing both the mass spectra and the GC retention time of commercially available pure standards with those of the initially identified components. In addition to MEA, some of the standards used included imidazole, formic acid, N-(2-hydroxyethyl) acetamide, 1-(2-hydroxyethyl)-2-imidazolidinone, and 18-crown-6.

Figure 3.3 (a)-(c) respectively illustrate mass spectra of imidazole in MEA-H_2O-O_2 degraded sample, imidazole in the NIST database, and imidazole of pure standard. The mass spectrum pattern of the sample was found to be in excellent agreement with those of the NIST database and the pure standard, therefore, the existence of imidazole was confirmed. Figure 3.4(a)-(c), 3.5(a)-(c), and 3.6(a)-(c) are respectively shown for the case of formic acid, N-(2-hydroxyethyl) acetamide, and 1-(2-hydroxyethyl)-2-imidazolidinone. Figure 3.7(a)-(c) indicates an existence of 18-crown-6, although, its sample mass spectrum gave a low-quality match to those of the NIST database and the standard verification. Although not perfectly matched, Figure 3.7(a) of this sample contains major peaks similar to those of the NIST and standard shown in Figure 3.7(b) and (c), respectively. This results from co-elution of 18-crown-6 and other components (not known) from the GC resulting in a mixed mass pattern.

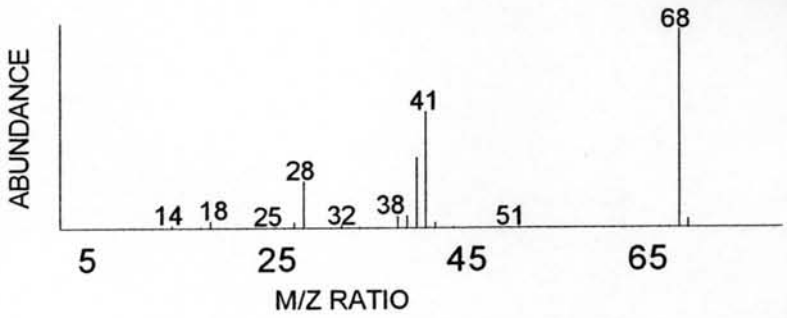
Standard injection was also used to verify that the GC-MS operating conditions did not cause further degradation, thus, products seen were actually a result of MEA oxidative degradation. Chromatograms of standard 4 kmol/m^3 MEA and 1 kmol/m^3 imidazole are given as examples in Figure 3.8 and 3.9 to confirm that their presence was not a result of thermal degradation by the GC-MS conditions. These figures show that only the water (used as a solvent in this study) peak and those of these compounds were present confirming that the GC-MS conditions were innocuous to the samples.



(a) In degraded MEA sample

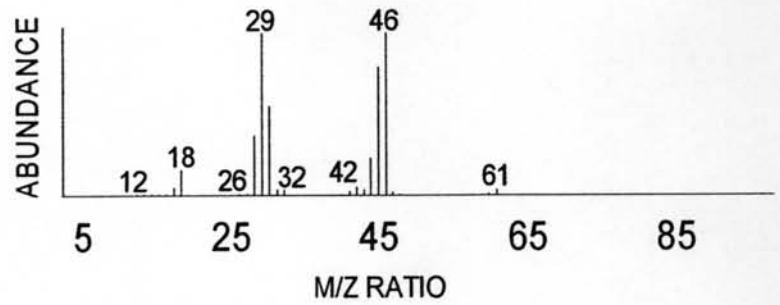


(b) NIST database

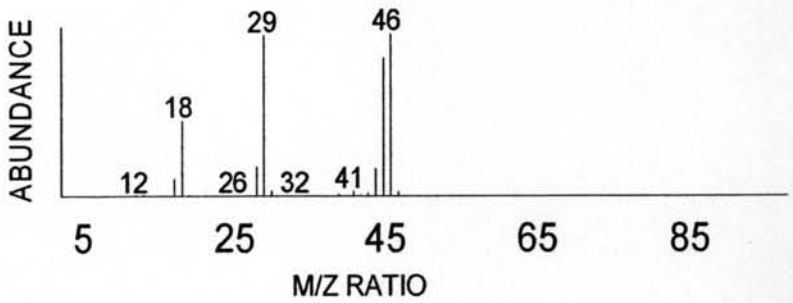


(c) Standard imidazole

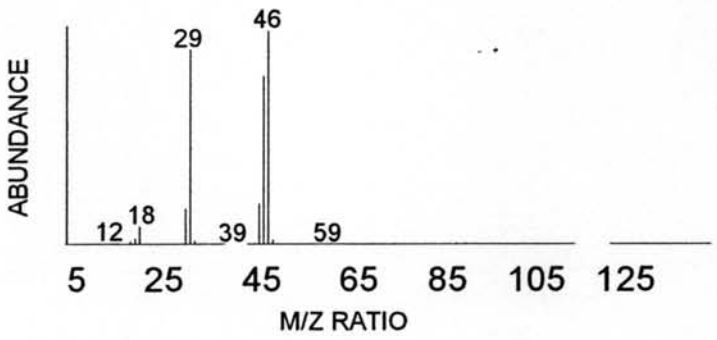
Figure 3.3 Mass spectra of imidazole: (a) In degraded MEA sample; (b) NIST database; (c) Standard imidazole.



(a) In degraded MEA sample

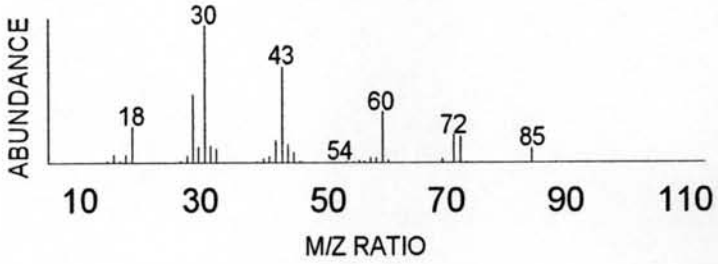


(b) NIST database

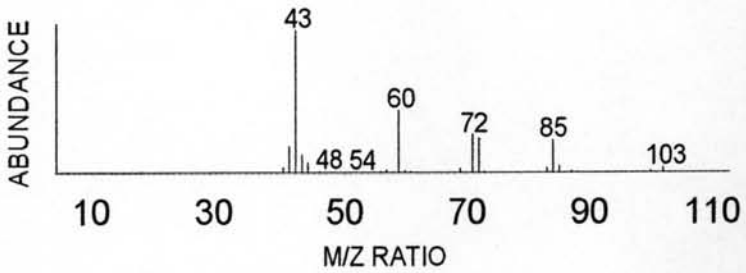


(c) Standard formic acid

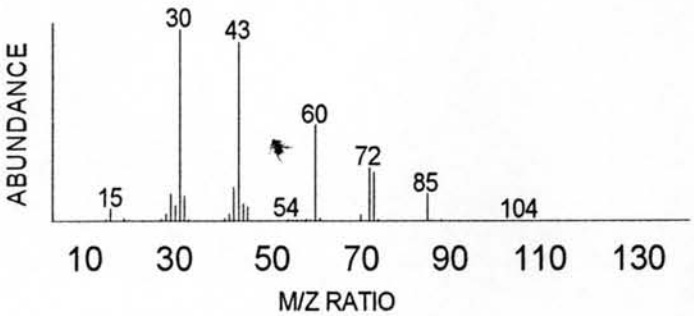
Figure 3.4 Mass spectra of formic acid: (a) In degraded MEA sample; (b) NIST database; (c) Standard formic acid.



(a) In degraded MEA sample

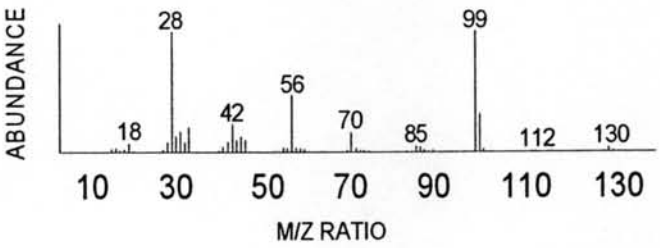


(b) NIST database

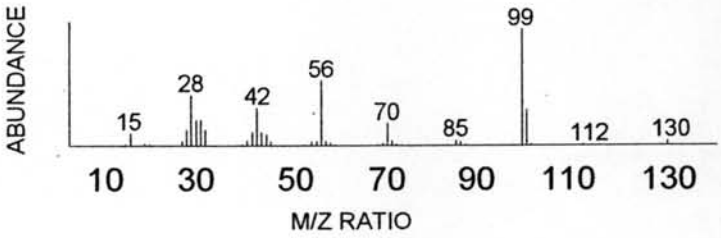


(c) Standard N-(2-hydroxyethyl) acetamide

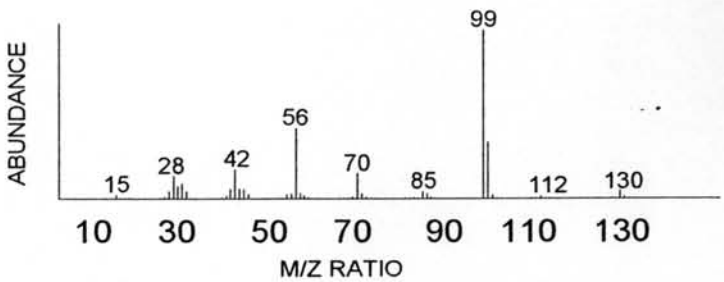
Figure 3.5 Mass spectra of N-(2-hydroxyethyl) acetamide: (a) In degraded MEA sample; (b) NIST database; (c) Standard N-(2-hydroxyethyl) acetamide.



(a) In MEA degraded sample

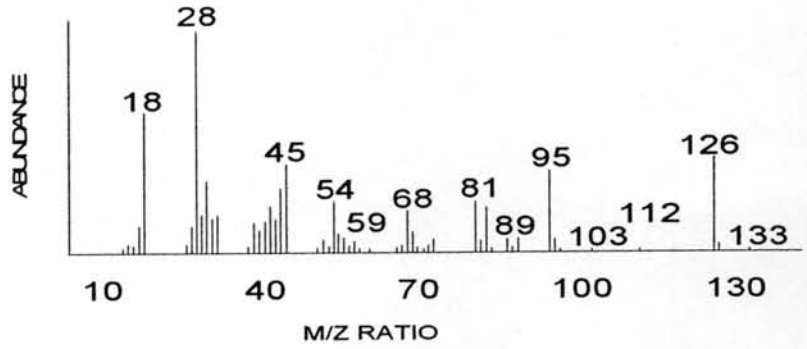


(b) NIST database

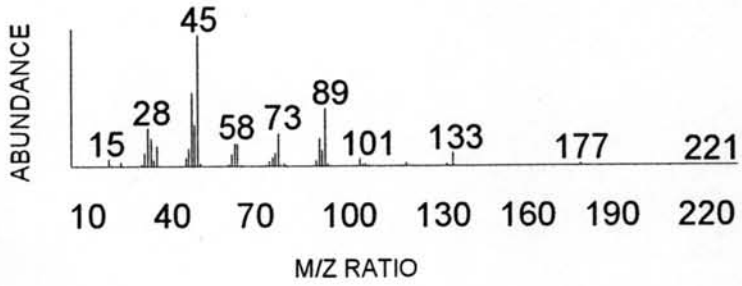


(c) Standard 1-(2-hydroxyethyl)- imidazolidinone

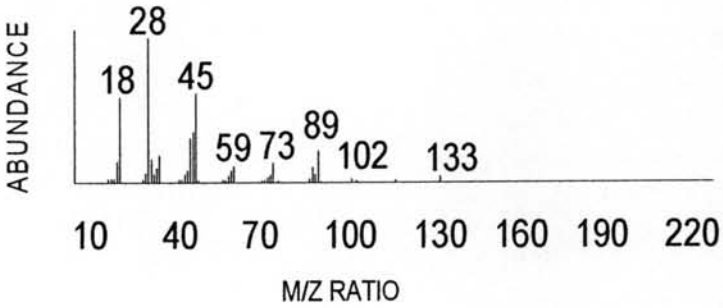
Figure 3.6 Mass spectra of 1-(2-hydroxyethyl)-2-imidazolidinone: (a) In degraded MEA sample; (b) NIST database; (c) Standard 1-(2-hydroxyethyl)-Imidazolidinone.



(a) In degraded MEA sample



(b) NIST database



(c) Standard 18-crown-6

Figure 3.7 Mass spectra of 18-crown-6: (a) In degraded MEA sample; (b) NIST database; (c) Standard 18-crown-6.

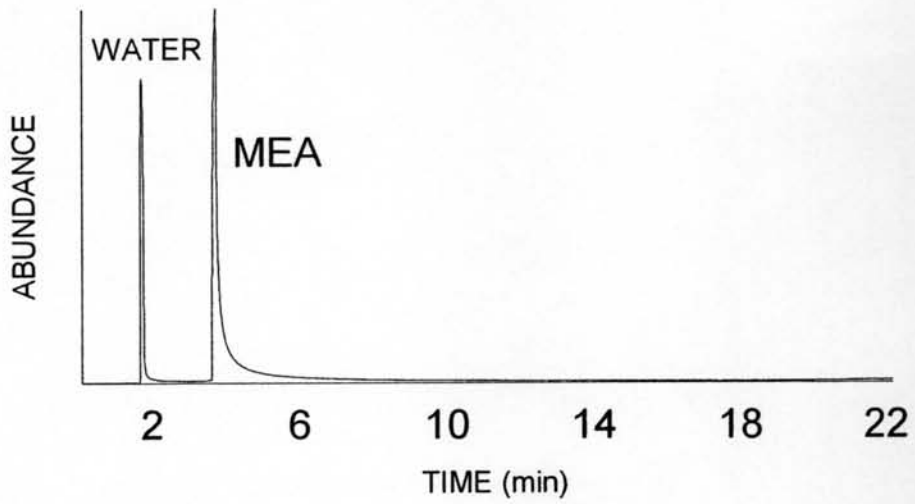


Figure 3.8 Chromatogram of standard 4 kmol/m^3 MEA.

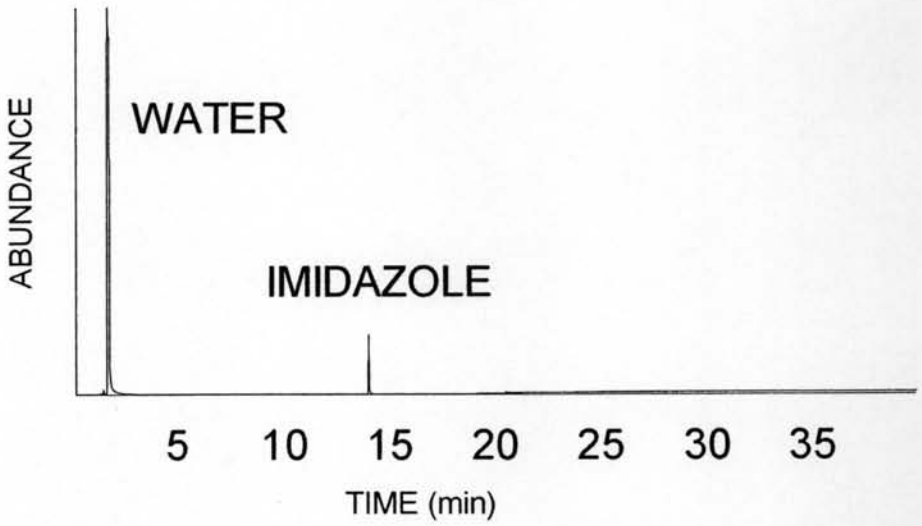


Figure 3.9 Chromatogram of standard 1 kmol/m^3 imidazole.

3.1.3.2 High Performance Liquid Chromatographic Technique (HPLC)

The HPLC used for analysis of the liquid samples was equipped with a refractive index detector (RID) and an on-line degasser (model 1100/G1315B/G1322A, Agilent Technologies Canada, Mississauga, Ontario, Canada). Two types of columns, Nucleosil 100-5 SA containing a strong cationic exchanger of sulphonic acid (Macherey-Nagel, Germany) of 250 mm length × 4.6 mm id and Shodex YK-421 packed with a weak carboxyl coated silica exchanger (Showa Denko, Japan) of 125 mm length × 4.6 mm id were selected. Two types of mobile phases were used. One was 0.05 kmol/m^3 potassium dihydrogen phosphate solution (KH_2PO_4) adjusted to a pH of 2.6 by adding 85% w/w phosphoric acid (H_3PO_4) in order to obtain a substantial modification based on the work of Kaminski et.al (2022) in order to suit our present system. This is based on the fact that their work was developed for wastewater and amines used in desulphurization processes, whereas this work's application is specifically for the CO_2 capture process in terms of the analysis of MEA and MEA oxidative degradation products. The other mobile phase had a combination of 0.005 kmol/m^3 L-tartaric acid ($C_4H_6O_6$), 0.001 kmol/m^3 2, 6-pyridinecarboxylic acid ($C_7H_5NO_4$), and 0.024 kmol/m^3 boric acid (H_3BO_3). Detection was aimed at MEA and the degradation products having the ability to acquire positive charges under acidic conditions. An autosampler (model G1313A, Agilent Technologies Canada, Mississauga, Ontario, Canada) was used for sample introduction. For a typical analysis, as much as 8 µl of sample was injected in order to ensure visualization of low concentrated products. The columns were kept at 303 K. All analyses were done using a simple isocratic approach in which 100% of a single mobile phase flowing at a rate of 1 ml/min was used throughout the analysis. The RID optical unit temperature was set at 303 K and operated under a positive mode. Prior to the analysis, samples were diluted to 1: 40 with nanopure water, followed by filtration using 0.20 µm nylon membrane filter. All mobile phases were degassed in an ultrasonic bath for at least 3 hours and filtered through 0.20 µm nylon membrane filter prior to use. All chemicals for mobile phases were reagent grade and

purchased from Sigma-Aldrich, Canada, except L-tartaric acid which was purchased from Fisher Scientific, Canada.

3.1.3.3 Capillary Electrophoresis Technique (CE)

CE equipped with diode array detector (DAD) (CE; model HP 3D CE, Hewlett-Packard Canada Ltd., Montreal, Quebec, Canada) was employed for detection of MEA and its basic and acidic degradation products. Selection of electrolyte solutions and CE conditions for MEA (Pereira and Tavares, 2004), basic and acidic products (Altria et al., 1995; Altria, Bryant, Hadgett, 1997) was based on suggestion in the literature. However, those were modified to suit the analysis of the present study. A mixture of 0.015 kmol/m^3 imidazole ($C_3H_4N_2$), 0.01 kmol/m^3 hydroxyisobutyric acid ($C_4H_8O_3$), and 0.01 kmol/m^3 18-crown-6 ($C_{12}H_{24}O_6$) was used for MEA detection. 0.025 kmol/m^3 KH_2PO_4 which was adjusted to a pH of 2.6 using 85% w/w of H_3PO_4 was used for separation of basic degradation products while 0.015 kmol/m^3 sodium tetraborate decahydrate ($Na_2B_4O_7.10H_2O$) was used for separation of acidic degradation products. For all CE analysis, a bare-fused silica capillary column with a dimension of 75 μm id × 805 mm length (720 mm effective length, Agilent Technologies Canada, Mississauga, Ontario, Canada) was used. The capillaries were each flushed before an analysis with 1 kmol/m^3 of NaOH solution and deionized water for 30 min, followed by flushing with the electrolyte for 45 min. In between runs, the capillaries were flushed with the electrolyte for 5 min and replenished after 4 runs. The capillaries were kept constant at 302 and 303 K throughout the analysis for MEA and basic-acidic degradation products, respectively. Sample injections were carried out using a hydrodynamic mode by applying 50 mbar pressure to the sample vial for 5 seconds. A voltage of +18 kV was applied after injection throughout the run. The DAD signal was set to a wavelength of 400 nm (reference at 214 nm) for indirect detection of MEA whereas a wavelength of 200 nm was used for direct measurement of basic and acidic MEA degradation products. To ensure a complete detection of all compounds, analysis times of 20, 35 and 45 min for MEA, basic and acidic degradation products were used, respectively. Samples of 1 : 4000 and 1 : 500 dilutions were used for MEA, and basic-acidic products analysis. Nylon membrane filters of 0.20 μm were used to filter samples

before analysis. The electrolyte solutions were degassed for at least 3 h and also filtered through 0.20 μm nylon membrane prior to use. All chemicals for CE experiments were reagent grade and purchased from Sigma-Aldrich, Neoprene, Canada, except for NaOH, which was obtained from Hewlett-Packard Canada Ltd., Montreal, Quebec, Canada.

3.2 Degradation Kinetics

3.2.1 Equipment and Chemicals

The degradation reactor and temperature-speed controller used for kinetics experiments were similar to those described in section 3.1.1. The degradation conditions used for kinetic experiments in this study are summarized in Table 3.1. These represent well-defined laboratory conditions. However, it has been attempted to use operating conditions that are close to what obtains in real life. The case of O_2 concentration greater than 6% was used for comparison only. The only parameter that was not fully reflective of real life situation either in the absorber or stripper was the pressure which was higher in order to obtain results within reasonable time frames. These conditions represent one of the very few attempts to use operating parameters that are very close to real life situations.

The kinetic experiments used research grade of 6-100% O_2, 100% CO_2 and mixtures of 6% O_2 (N_2 balance) containing SO_2 concentration in a range of 6 – 196 ppm were all supplied from Praxair (Regina, Saskatchewan, Canada). Concentrated MEA was purchased from Fisher Scientific, Nepean, Ontario. Its preparation to the desired concentration was also similar as previously described in section 3.1.1

Table 3.1 Degradation conditions for kinetic experiments

Parameter	Range
MEA concentration	3 - 7 kmol/m^3
O_2 in feed gas	6 - 100 %
SO_2 concentration in feed gas	0 - 196 ppm
CO_2 loading	0 - 0.55 mol CO_2/mole MEA
Temperature	328 - 393 K

3.2.2 Typical Experimental Run

Typical procedures for both CO_2-loaded and non-CO_2 loaded runs were similar to those given in section 3.1.2. The only exception was that, in addition to 100%O_2 feed gas, the kinetic runs also used 6% O_2 containing varied concentration of SO_2 between 0 – 196 ppm.

Since, MEA was the only compound needed to quantitatively analyze in the kinetic experiments. Therefore, HPLC-RID technique developed earlier in section 3.1.3.2 using the arrangement of nucleosil 100-5SA column with KH_2PO_4 mobile phase solution of 0.05 kmol/m^3 adjusted to pH 2.6 by H_3PO_4 solution was only adopted to assist in determination or MEA concentration.

3.2.3 Determination of MEA Concentration in Degraded Samples

A calibration curve of MEA was used to determine MEA concentration in all degraded samples using MEA concentrations raging from 2 – 8 kmol/m^3. Each calibration point was repeated three times to ensure reproducibility. MEA peak areas in all degraded samples obtained from the same HPLC technique were calculated and the exact MEA concentrations extracted from the calibration curve. The accuracy of the HPLC method was found to be 0.5%. MEA concentration time data were plotted to determine their corresponding degradation rate for further kinetic analysis. The rate analysis is discussed in more details in Chapter 5. Concentration-time data and corresponding rates of all degradation runs is summarized in appendix A.

3.3 Degradation Prevention Techniques using Degradation Inhibitors

3.3.1 Equipment and Chemicals

Inhibitor UR-A was evaluated using the same set of experimental set-up as respectively discussed for analytical techniques and degradation kinetic experiments in section 3.2 and 3.3. Also from Praxair, gases containing 100% O_2, 6% O_2 (N_2 balance), and mixture of 6% O_2/6 – 196 ppm SO_2 (N_2 balance) were used. 100% CO_2 used for study of inhibition effect was also obtained from Praxair. Solution analysis for MEA concentration was only required. Therefore, HPLC-RID technique previously developed in section 3.1.3.2 (Nucleosil 100-5SA column-mobile phase 0.05 kmol/m^3 KH_2PO_4 at pH 2.6) was only used. HPLC procedure is similar to what described also in section 3.1.3.2.

3.3.2 Experimental Procedures

Runs for non-CO_2 loaded with/without inhibitor UR-A and CO_2 loaded experiments were carried out as discussed in the previous sections. The HPLC technique with MEA standard calibration given in section 3.2.3 was subsequently used to determine MEA concentration of all the samples. MEA concentration-time data were subsequently converted to degradation rate-time plots using a similar approach given in Chapter 5.