CHAPTER III

EXPERIMENT

This chapter details the experimental methods used to measure the oxidative degradation of monoethanolamine used throughout this project. Description of the experimental runs conducted, the analytical equipment, reactor, chemicals, and solution preparation methods are presented in detail.

3.1 Equipment and Chemicals

The reactor used was a stainless steel high pressure batch reactor (model 5523, Parr Instrument Co., Moline, IL) with 2.5 inches inside diameter and 8 inches inside depth and an internal volume of 600 ml. The removable reactor head assembly consisted of a magnetically-coupled stirrer drive connected to an internal stainless steel (Type 316) stirrer shaft attached with 2 adjustable 4-rectangular turbine-type impellers (diameter about 1.5 inches) which one was positioned almost at the bottom of the reactor 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 vessel rated for a maximum working pressure of 3000 psi and also had a 0-300 psi Bourdon-type pressure gauge which shows the pressure within the vessel at all time. The maximum operating temperature is dependent upon the seal selected, in this study using PTFE gasket for up to 350°C. The reactor is equipped with gas inlet and outlet valves, a liquid sampling valve, a preset safety rupture disc, a J-type internal thermocouple, a dip tube for gas introduction and withdrawing liquid samples, and an internal cooling coil for maintaining the process at a constant temperature irrespective of the temperature rise caused by the exothermic reactions and preventing any temperature overshoot during the experimental running that may be caused by furnace heating. The cooling system was regulated by a solenoid valve. A 1/17 hp speed motor is incorporated directly into the magnetic stirrer drive in order to deliver sufficient torque to drive the

magnetic coupling and provides stirring speeds adjustable from 0 to 1500 rpm. The speed of the stirrer was controlled by a speed controller (Model 4836 programmable controller with tachometer display module, Parr Instrument Co., Moline, IL). The heater was supplied to the reactor by a furnace in which the reactor vessel was inserted and regulated by a temperature controller (Model 4836 programmable controller with tachometer display module, Parr Instrument Co., Moline, IL). The temperature of the reaction mixture was measured by a J-type internal thermocouple. The temperature accuracy of the controller was within ± 0.1 %.

Concentrated MEA solution (research grade, 99%+ purity) was used to prepare aqueous MEA solutions with the desired concentration by diluting with deionized water. Standard hydrochloric acid of 1 kmol/m^3 (HCl) with methyl orange indicator was used to determine the exact MEA concentration by volumetric titration techniques. Inhibitor UR-A, UR-B, UR-C, UR-D, UR-A blended with UR-B, and UR-A blended with UR-C were used as obtained and introduced into the solvent by dissolving a predetermined weight into the MEA solutions with known concentrations. All chemicals were purchased from Fisher Scientific (Nepean, Ontario, Canada).

Research grade gases containing 100% O_2, 100% CO_2, 6% O_2 (N_2 balance) and mixture of 6% O_2 (N_2 balance) containing SO_2 concentration in the range of 6 – 196 ppm were all supplied from Praxair (Regina, Saskatchewan, Canada).

Solution analysis for MEA concentration was carried out with a Nucleosil 100-5SA column (Macherey-Nagel, Germany) using a high performance liquid chromatograph (HPLC) equipped with a refractive index detector (RID), an on-line degasser, and an autosampler was used for sample introduction to the HPLC (model 1100/G1315B/G1322A/G1313A, Agilent Technologies Canada, Mississauga, Ontario, Canada). For the HPLC, mobile phase was 0.05 kmol/m^3 potassium dihydrogen phosphate (KH_2PO_4) added with 85% w/w phosphoric acid (H_3PO_4) to adjust the HPLC mobile phase solution to a pH of 2.6-2.8. All chemicals for mobile phases were reagent grade and purchased from Sigma-Aldrich, Canada.

3.2 Experimental Procedures

About 450 mL of 5 kmol/m^3 of MEA solution without or with inhibitor UR-A, UR-B, UR-C, UR-D, UR-A blended with UR-B and UR-A blended with UR-C were loaded into the reactor vessel each for each experimental run. The reactor head assembly was placed on top and tightly sealed with split O-ring snaps together with latches to provide a secure and positive closure. After insertion of the reactor into the furnace, connections to the magnetic stirrer drive motor, the cooling system, and the temperature-speed controller were made. Simultaneously, the MEA solution was stirred at the speed of 500 rpm while heating to 120°C. A few hours were allowed to stabilize the solution temperature after it had reached the set-point. At this point, the pressure gauge showed water vapor pressure of MEA solution inside the reactor vessel. The MEA solution was then pressurized with an additional predetermined 250 kPa of a desired feed gas composition from the appropriate gas cylinder. In this study, 100% O_2, 6% O_2 (N_2 balance), the mixtures of 6% O_2 (N_2 balance) containing SO_2 concentration of 6 ppm, and the mixtures of 6% O_2 (N_2 balance) containing SO_2 concentration of 196 ppm were introduced by opening the O_2 cylinder or O_2-SO_2 cylinder through the gas inlet valve. The total pressure of the reactor was the sum of the water vapor pressure and 250 kPa feed gas pressure. In order to maintain the system with constant temperature, the solenoid valve regulated the cooling system was available at this point to remove heat from the initial reaction of MEA and the feed gas. It was also required in case of temperature overshoots. Sampling process was done at predetermined intervals of times by closing the inlet feed gas valve and then opening the liquid sampling valve. The MEA solution mixture sample (approximately 2.5 mL) was withdrawn into a 5 mL sampling bottle and then was quickly cooled down around 1 minute by running cold water over the sampling bottle to prevent degradation reaction of the sample. Extra feed gas pressure (in this study O_2 and O_2-SO_2) was quickly introduced into the reactor vessel in order to compensate the pressure loss during the sampling process and keep the system pressure constant throughout the experiment. All of samples were kept in a refrigerator at 9°C for less than a week to allow sufficient time for analysis of collected samples via HPLC-RID technique.

3.2.1 Typical Experimental Run

The present study investigated the performance of inhibitor UR-A, UR-B, UR-C and UR-D as potential degradation inhibitors for the systems of MEA-O_2, MEA-O_2-SO_2, and MEA-O_2-CO_2-SO_2. The extreme degradation conditions represent the regeneration region normally found in a typical flue gas treating process. The MEA concentration used was in the range of 5 – 7 kmol/m^3. MEA solution was spiked with inhibitor UR-A, UR-B, UR-C, and UR-D having a concentration between 0 – 0.3 kmol/m^3, 0 – 0.3 kmol/m^3, and 0 – 0.1 kmol/m^3, and 0 – 1 kmol/m^3, respectively. The simulated flue gas used was composed of 6 – 100% O_2, N_2, and 0 -196 ppm SO_2. The degradation temperature was fixed at 120°C. O_2 or mixture of O_2 and SO_2 pressure of 250 kPa was used in order to accelerate the oxidative degradation experiments. For CO_2-loaded experiments, a loading of 0.33 mol CO_2/mol MEA was employed. All experiments were carried out to show the most severe effect of the oxidative degradation.

3.2.1.1 Degradation System without Inhibitor

3.2.1.1.1 Non-CO_2 Loaded Degradation System in MEA-H_2O-O_2 and MEA-H_2O-O_2-SO_2 degradation systems

The degradation reaction was conducted using 5 and 7 kmol/m^3 MEA concentration, degradation temperatures of 120°C, as well as only O_2 or mixture of O_2 and SO_2 pressures of 250 kPa. Approximately 450 mL of aqueous MEA was loaded into the reactor and the reactor head assembly was placed on top and tightly sealed with split O-ring snaps together with latches to provide a secure and positive closure. The solution was stirred at the rate of 500 rpm while heating to 120°C and simultaneously cooling the stirrer system. A cooling water system was used to maintain and ensure that the degradation process under isothermal conditions since the oxidative degradation of MEA is an exothermic process. A few hours were allowed for the solution to stabilize at the desired temperature, the pressure. At this point, as indicated on the reactor pressure gauge, some vapor pressure due to water was observed as the pressure inside the reactor, and then 250 kPa of only O_2 or mixture of O_2 and SO_2 was additionally fed into the reactor in order to obtain a final desired reactor pressure by opening the O_2 cylinder

or mixture of O_2 and SO_2 cylinder and regulated to the desired reactor pressure. O_2 or mixture of O_2 and SO_2 was sparged into the solution through the dip tube to enhance the contact area with the solution. The total pressure of the O_2 alone or mixture of O_2 and SO_2 experiments was a combination of the water vapor pressure and 250 kPa O_2 pressure or mixture of O_2 and SO_2 (i.e. 450 kPa at 120°C). The gas inlet and O_2 alone cylinder or mixture of O_2 and SO_2 cylinder were left open and the first sample, about 2.5 mL, was taken immediately into 5-mL sampling bottle. Due to the solubility of O_2 or O_2-SO_2 in MEA solution there was pressure depletion inside the reactor. The reactor was quickly boosted with extra O_2 or O_2-SO_2 to compensate the pressure loss during the sampling process and to maintain at the desired pressure. This was, also, repeated each time a sample was collected. About 2.5 mL of other samples were collected at predetermined intervals. The reaction in each sample taken was quenched by running cold water over the sample vials for about one minute to quickly cool down samples and quench the degradation reaction. In order to avoid further degradation of the samples, therefore, all of the samples were kept in a refrigerator at 9°C for less than a week to allow sufficient time for HPLC-RID analyses.

3.2.1.1.2 CO_2 Loaded Degradation System in MEA-H_2O-O_2-SO_2-CO_2 degradation system

The degradation reaction was conducted using 5 kmol/m^3 MEA concentrations. Prior to loading aqueous MEA into the reactor, CO_2 was introduced into the solution by opening the CO_2 cylinder for 14-17 minutes aqueous MEA in a beaker, after which 2 ml of the solution was removed from the beaker to check for the CO_2 loading by titration against standard solution of 1 kmol/m^3 HCl, whereas 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. At the desired CO_2 loading approximately 450 mL of the mixture MEA was loaded into the reactor. The reactor head assembly was placed on top and tightly sealed with split O-ring snaps together with latches to provide a secure and positive closure. The solution was stirred at the rate of 500 rpm while heating up the mixture to 120°C and simultaneously cooling the stirrer system. A cooling water system was used to

maintain and ensure that the degradation process under isothermal conditions since the oxidative degradation of MEA is an exothermic process. A few hours were allowed for the solution to stabilize at the desired temperature and CO_2 loading was determined again. At this point, as indicated on the reactor pressure gauge, the total pressure in the reactor 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 or mixture of O_2 and SO_2 of 250 kPa also set at the O_2-SO_2 cylinder was additionally introduced into the solution through the gas inlet valve. The rest of the procedures were then conducted following those of non-CO_2 loaded experiments.

3.2.1.2 Degradation system with Inhibitor UR-A, UR-B, UR-C and UR-D

3.2.1.2.1 Non-CO_2 Loaded Degradation System in MEA-H_2O-O_2 and MEA-H_2O-O_2-SO_2 Degradation Systems

A known concentration of inhibitor UR-A, UR-B, UR-C or UR-D was introduced into the 5 kmol/m^3 MEA solution by dissolving a predetermined weight. About 450 mL of MEA solution was transferred into the reactor and the reactor head assembly was placed on top and tightly sealed the reactor to prevent leakage. The solution was stirred at 500 rpm while heating to 120°C and simultaneously cooling the stirrer system. A cooling water system was used to maintain and ensure that the degradation process under isothermal conditions since oxidative degradation of MEA is an exothermic process. Gases containing 6% O_2 (N_2 balance), and mixture of 6% O_2/6 – 196 ppm SO_2 (N_2 balance) were used in this study. A few hours was allowed for the solution to stabilize at the desired temperature and pressure. At this point, as indicated on the reactor pressure gauge, some vapor pressure due to water was observed as the pressure inside the reactor, and then 250 kPa of gas mixture was additionally fed into the reactor in order to obtain a final desired reactor pressure by opening the O_2 or O_2-SO_2 cylinder and regulated to the desired reactor pressure. O_2 or O_2-SO_2 was sparged into the solution through the dip tube to enhance the contact area with the solution. The total pressure of the O_2 alone or mixture of O_2-SO_2 experiments was a combination of the water vapor pressure and 250 kPa O_2 alone or mixture of O_2-SO_2 pressures (i.e. 450 kPa at 120°C). The gas inlet and O_2 alone or O_2-SO_2 cylinder were left open and the first

sample, about 2.5 mL, was taken immediately into 5-mL sampling bottle. Due to the solubility of O_2 alone or O_2-SO_2 in MEA solution there was pressure depletion inside the reactor. The reactor was quickly boosted with extra O_2 alone or mixture of O_2-SO_2 in order to compensate the pressure loss during the sampling process and to maintain at the desired pressure. This was, also, repeated each time a sample was collected. About 2.5 mL of other samples were collected at predetermined intervals. The reaction in each sample taken was quenched by running cold water over the sample vials for about one minute to quickly cool down samples and quench the degradation reaction. In order to avoid further degradation of the samples, therefore, all of the samples were kept in a refrigerator at 9°C for less than a week to allow sufficient time for HPLC-RID analyses.

3.2.1.2.2 CO_2 Loaded Degradation System in MEA-H_2O-O_2-SO_2-CO_2 Degradation Systems

The degradation reaction was conducted using 5 kmol/m^3 MEA concentrations. Prior to loading aqueous MEA into the reactor, CO_2 was introduced into the solution by opening the CO_2 cylinder for 14-17 minutes aqueous MEA in a beaker, after which 2 ml of the solution was removed from the beaker to check for the CO_2 loading by titration against standard solution of 1 kmol/m^3 HCl, whereas 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. At the desired CO_2 loading with known concentrations of inhibitor UR-A, UR-B, and UR-C was introduced into the mixture MEA solution by dissolving a predetermined weight. Approximately 450 mL of the mixture was loaded into the reactor. The reactor head assembly was placed on top and tightly sealed with split O-ring snaps together with latches to provide a secure and positive closure. The solution was stirred at the rate of 500 rpm while heating up the mixture to 120°C and simultaneously cooling the stirrer system. A cooling water system was used to maintain and ensure that the degradation process under isothermal conditions since the oxidative degradation of MEA is an exothermic process. A few hours were allowed for the solution to stabilize at the desired temperature and CO_2 loading was determined again. At this point, as indicated on the reactor pressure gauge, the total pressure in the reactor was

the sum of the pressures of water vapor and non-dissolved CO_2. Then, the mixture of O_2 and SO_2 of 250 kPa also set at the O_2-SO_2 cylinder was additionally introduced into the solution through the gas inlet valve. The rest of the procedures were then conducted following those of non-CO_2 loaded experiments.

3.2.1.3 Degradation System with Blended Inhibitors: UR-A with UR-B and UR-A with UR-C in MEA-H_2O-O_2-SO_2 Degradation Systems

The best concentrations of each inhibitor in minimizing the degradation rate of MEA which are 0.05 kmol/m^3 of UR-A, 0.01 kmol/m^3 of UR-B, and 0.0025 kmol/m^3 of UR-C were used. The performances of blended inhibitors of UR-A with UR-B, or UR-A with UR-C were tested in the degradation systems of MEA-H_2O-O_2-SO_2. Blended inhibitors were introduced into the 5 kmol/m^3 MEA solution by dissolving a predetermined weight. About 450 mL of MEA solution was transferred into the reactor and the reactor head assembly was placed on top and tightly sealed the reactor to prevent leakage. The solution was stirred at 500 rpm while heating to 120°C and simultaneously cooling the stirrer system. A cooling water system was used to maintain and ensure that the degradation process under isothermal conditions since oxidative degradation of MEA is an exothermic process. Gases containing 6% O_2 (N_2 balance), and mixture of 6% O_2/6 – 196 ppm SO_2 (N_2 balance) were used in this study. A few hours was allowed for the solution to stabilize at the desired temperature and pressure. At this point, as indicated on the reactor pressure gauge, some vapor pressure due to water was observed as the pressure inside the reactor, and then 250 kPa of gas mixture was additionally fed into the reactor in order to obtain a final desired reactor pressure by opening the O_2 or O_2-SO_2 cylinder and regulated to the desired reactor pressure. O_2 or O_2-SO_2 was sparged into the solution through the dip tube to enhance the contact area with the solution. The total pressure of the O_2 alone or mixture of O_2-SO_2 experiments was a combination of the water vapor pressure and 250 kPa O_2 alone or mixture of O_2-SO_2 pressures (i.e. 450 kPa at 120°C). The gas inlet and O_2 alone or O_2-SO_2 cylinder were left open and the first sample, about 2.5 mL, was taken immediately into 5-mL sampling bottle. Due to the solubility of O_2 alone or O_2-SO_2 in MEA solution there was pressure depletion inside the reactor. The reactor was quickly boosted with extra O_2 alone or mixture of O_2-SO_2 in order to compensate the pressure loss during the

sampling process and to maintain at the desired pressure. This was, also, repeated each time a sample was collected. About 2.5 mL of other samples were collected at predetermined intervals. The reaction in each sample taken was quenched by running cold water over the sample vials for about one minute to quickly cool down samples and quench the degradation reaction. In order to avoid further degradation of the samples, therefore, all of the samples were kept in a refrigerator at 9°C for less than a week to allow sufficient time for HPLC-RID analyses. The overall schematic of the degradation experiments and analysis is shown in Figure 3.1.

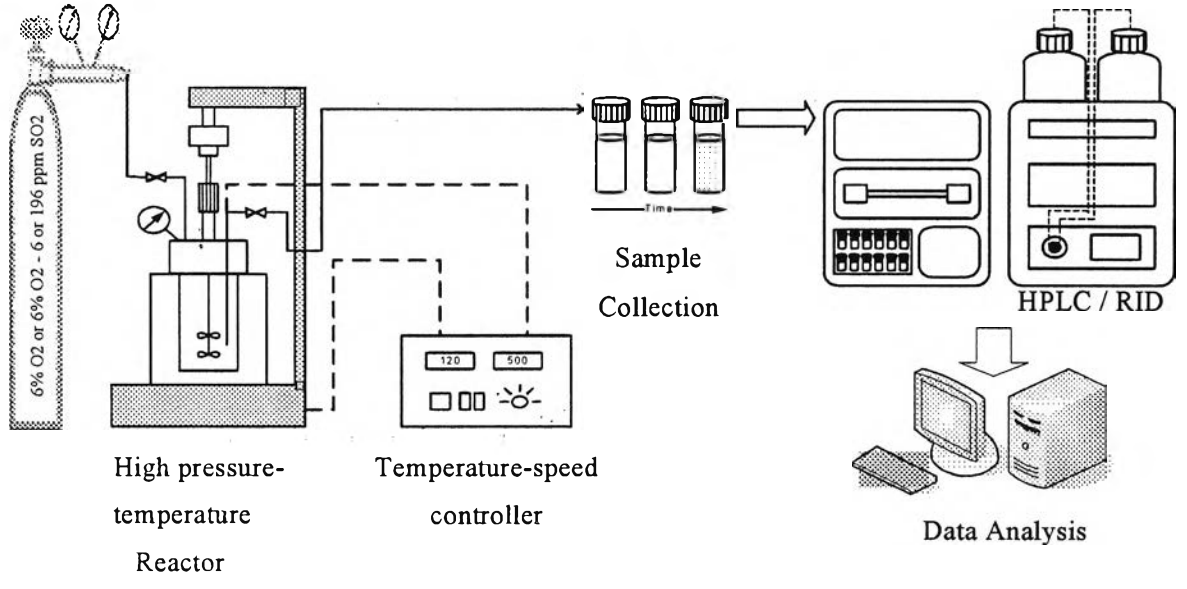

Figure 3.1 Schematic of inhibitors for MEA oxidative degradation experiments: Experimental set-up and analysis

3.3 Analysis of Degradation Products using a High Performance Liquid Chromatographic Technique (HPLC)

3.3.1 Preparation of HPLC Mobile Phase

As stated earlier, a liquid mobile phase is utilized to separate the components of a mixture deposited on a stationary phase. The HPLC mobile phase used 0.05 kmol/m^3 of potassium dihydrogen phosphate (KH_2PO_4), which was prepared with nanopure water. Added 85% w/w phosphoric acid (H_3PO_4) to the HPLC mobile phase solution in order to adjust the mobile phase solution to pH 2.6, followed by degassed the HPLC mobile phase in an ultrasonic bath for 270 minutes to remove bubble and dissolved O_2 that might cause interference during the sample analysis. The mobile phase was subsequently filtered using a 0.20 μm nylon membrane filter to remove any small particle to prevent them from plugging the HPLC column.

3.3.2 Preparation of Collected Samples

The collected samples were diluted with nanopure water to 1: 40 times of their original concentration, followed by filtration using 0.20 μm nylon membrane filter and a syringe before being analyzed by the HPLC.

3.3.3 HPLC Operating Conditions

Liquid samples analysis for MEA concentration was carried out with a Nucleosil 100-5SA column containing a strong cationic exchanger of sulphonic acid (Macherey-Nagel, Germany) of 250 mm length × 4.6 mm id. A HPLC used for analysis equipped with a refractive index detector (RID), an on-line degasser (model 1100/G1315B/G1322A/G1313A, Agilent Technologies Canada, Mississauga, Ontario, Canada)., and an autosampler (model G1313A, Agilent Technologies Canada, Mississauga, Ontario, Canada) was used for sample introduction. According to the work of Kaminski *et al.*, (2002) developed mobile phases 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 was developed by Supap *et al.*, (2006)

Detection was aimed at MEA and the degradation products having the ability to acquire positive charges under acidic conditions. An autosampler was used for sample introduction. Sample injection of 8 μl was done automatically by the automatic liquid sampler in order to ensure visualization of low concentrated products. The column was controlled isothermically at 30°C to maintain the column proper condition for analysis samples. 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 refractive index detector (RID) was used to detect MEA peak and the optical unit temperature was set at 30°C and operated under a positive mode.

3.4 Degadation Analysis

3.4.1 Determination of MEA Concentration

A calibration curve of MEA was first made to determine actual concentration of MEA in all collected samples using MEA concentrations ranging from 2 – 7.7 kmol/m^3. All the samples were analyzed quantitatively via HPLC/RID to determine the MEA concentration. MEA peak areas were obtained from the HPLC technique developed by Supap *et al.*, (2006). Each calibration point was repeated three times to ensure reproducibility. A plot of MEA concentration against the average areas of MEA peak from the HPLC was made to obtain a calibration curve (Appendix C, Figure C1), and the equation of the line were derived using Microsoft Excel 2003. The equation of the calibration line was then used to obtain the actual concentration of MEA.

Each data point from collected samples was repeated three times to ensure reproducibility. The actual MEA concentrations were calculated by inputting the MEA peak areas into the equation of the calibration line. At this point, the MEA concentration was plotted against the degradation time as shown in Appendix C, Figure C2, and the equation of the MEA concentration-time line was derived using Microsoft Excel 2003. The equation of the MEA concentration-time line was then used to calculate the degradation rate.

The degradation rate was determined by differentiating the equation of the MEA concentration-time line. The MEA degradation rate-time curves were then plotted as shown in Appendix C, Figure C3. The overall schematic of the degradation analysis is shown in Appendix C, Figure C4. The concentration-time data and the corresponding degradation rates of all experiments are summarized in appendix B. In addition, throughout this study, the efficiency of degradation inhibitors was calculated using Equation (3.1).

$$\text{The percentage of degradation inhibition} = \frac{\left|Rate_{w/o} - Rate_{w}\right|}{Rate_{w/o}} \times 100 \qquad (3.1)$$

where $Rate_{w/o}$ and $Rate_{w}$ are the degradation rate of MEA without and with inhibitors ($kmol/m^3.h$)