Ammonia Formation in Diethylenetriamine-Methyldiethanolamine (DETA-MDEA) System in the Presence of O\textsubscript{2} during Amine-based Capture of CO\textsubscript{2} from Combustion Flue Gases

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Abstract

Ammonia (NH\textsubscript{3}) is a major volatile degradation product formed from oxidative degradation of diethylenetriamine (DETA), methyldiethanolamine (MDEA), and their blend. Three molar DETA and MDEA were used in their single amine systems while mixture of the two amines using 1.5 M each was also tested. The reaction was operated at 0.65 CO\textsubscript{2} loading, 6 % mole O\textsubscript{2}, and 393 K. The results indicated that DETA generated NH\textsubscript{3} from the oxidative degradation in liquid and gas phases the most, followed by 1.5 M DETA/1.5 M MDEA blend and single MDEA.
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Keywords: NH\textsubscript{3} formation; DETA; MDEA; CO\textsubscript{2} capture; Emissions; Degradation

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1. Introduction

Global warming worsened by the emission of carbon dioxide (CO₂) from human activities, especially combustion of fossil fuels (e.g. coal, natural gas, and oil) for energy and transportation [1] is a very serious issue that affects directly on environment and human. In order to cope with this problem, CO₂ capture process must be used to control the concentration of this greenhouse gas before being discharged into the atmosphere. Chemical absorption using aqueous amine solution is the most effective technique which has been used for decades for removing CO₂ from many industrial sources. This technique is also suitable to reduce CO₂ emission from post-combustion power plants.

Amine development for the capture of CO₂ has been particularly focused on blended amine solution due to its effectiveness in increasing high CO₂ loading capacity and decreasing amine degradation, corrosion rate, energy consumption during regeneration, and also the overall operational cost. MDEA, one of the most popular tertiary amine used extensively, has many advantages, such as low energy consumption, low corrosion, high degradation resistance, and good absorption capacity [2]. However, its reaction with CO₂ is slow, thus blending with primary and secondary amines, such as monoethanolamine (MEA) and piperazine (PZ), is essential to increase the CO₂ capture reactivity. Diamines, specifically diethylenetriamine (DETA) can also be blended with MDEA to enhance the solvent kinetics and absorption ability as confirmed already in our previous study [3]. Fig. 1 shows the chemical structure of DETA and MDEA.

Though, MDEA can potentially benefit from DETA’s high absorption capacity and fast kinetics. The presence of O₂ in flue gases combined with high temperature usage during the amine regeneration can induce a severe degradation of this amine solvent which will also lead to the emission of potentially toxic substances with the process off-gas. Ammonia (NH₃) known as a major volatile amine degradation product can also be quickly formed in the liquid phase as a result of the oxidative degradation and subsequently emitted with the off-gas to the atmosphere via the top of the absorber column. Its uncontrollable emission affects human health and can be poisonous if inhaled in great quantities and irritating to the eye, nose, and throat in lesser amounts. Pollution of air and environment is also a concern from the amine based capture process emissions of NH₃. Nevertheless, we still lack the information related to degradation and NH₃ emissions of DETA and MDEA which is not readily searchable in the literature. Also, the quantitative data of NH₃ emission rates measured from actual experiments is rarely reported, even though it would provide practical data to later help CO₂ plant operators handle with NH₃ emissions in real application [4].

This study determined NH₃ concentrations formed in liquid, gas, and total phases from oxidative degradation of DETA, MDEA, and blended DETA/MDEA solutions, to clearly understand characteristics of DETA and MDEA on NH₃ formation under CO₂ capture conditions. At 0.65 CO₂ loading, 6 %mole O₂, and 393 K, both single amines (i.e. DETA and MDEA) and their blend (i.e. molar ratios of DETA/MDEA at 1.5/1.5) were used to study the effect of single and blended amine on NH₃ formation.

![Chemical structures of DETA and MDEA.](image)

2. Experiments

2.1. Chemicals and equipment

Amines used to study NH₃ formation were diethylenetriamine (DETA) and methyl diethanolamine (MDEA), all obtained from Sigma-Aldrich. Carbon dioxide (CO₂, 99.99 %), oxygen (O₂, 99.99 %), and nitrogen (N₂, 99.99 %) were purchased from Praxair, Thailand. Ammonium hydroxide (NH₄OH, 30 % w/v) obtained from Sigma-Aldrich, and ammonium chloride (NH₄Cl, 100 % purity) from Univar, were used to prepare standard solutions to determine NH₃ concentrations in liquid and gas phases, respectively.
Experimental set up used in this study is shown in Fig. 2. Three gas cylinders consisting of CO\textsubscript{2}, O\textsubscript{2} and N\textsubscript{2} were used for introducing a desired CO\textsubscript{2} loading into the amine solution, initiating the oxidative degradation reaction, and balancing the total reaction pressure of 43 psi, respectively. Parr reactor (Parr Instrument Co. model 4576A) with the vessel volume of 0.25 L and the reactor controller model 4848 (623-773 K operational range) were used to carry out the reaction. Isothermal degradation run could be maintained by cooling water regulated by the solenoid valve throughout the experiment. Liquid samples were withdrawn through the tube immersed in the amine solution. Gas sampling was done via another tube situated above the amine solution. N\textsubscript{2} flush as also used to help collect gas phase NH\textsubscript{3} into the impingers containing HCl trapping solution. An ice bath was used to control the temperature of the impingers at 274 K. Both single amines of DETA and MDEA, and blended amine (DETA/MDEA) with equal molar ratios of 1.5/1.5 were prepared with the total concentration of 3.0 M by diluting predetermined weight of concentrated amine with deionized water. Standard HCl solutions of 1.0 M with methyl orange indicator was used to determine the exact concentration of amine solutions.

2.2. Experimental procedure

The amine solution with the volume of 0.22 L was transferred into the reactor vessel. The vessel was inserted in the furnace to control the desired temperature at 393 ± 1 K. The removable reactor head was carefully assembled and tightened to prevent leakage during the degradation process. 20 psi of CO\textsubscript{2} was fed into the amine solution while being stirred at rate of 300 rpm. At regular intervals, CO\textsubscript{2} loading in the liquid phase was determined by using Chittick apparatus with HCl titration and CO\textsubscript{2} displacement solution. Once the desired CO\textsubscript{2} loading was attained, CO\textsubscript{2} valve was closed and the solution was heated to the desired temperature. When the required temperature was achieved, 6 % mole O\textsubscript{2} (N\textsubscript{2} balance) was fed into the solution until the total pressure at 43 psi was reached. To maintain the total pressure during degradation run, any decrease in the total pressure due to dissolution of O\textsubscript{2} or pressure lost during sampling was immediately compensated by boosting up the total pressure to 43 psi from the O\textsubscript{2} cylinder.

At 24 intervals for the period of 10 days, 3.0 mL of amine in the reactor was sampled and sent for analysis of NH\textsubscript{3} concentration with HPLC technique given in details later in this section. For gas samples, on day 10 of reaction, the reactor headspace was flushed out to the impingers by N\textsubscript{2} gas. NH\textsubscript{3} in gas phase was then trapped in 0.8 M of HCl solution and ready for HPLC analysis.

For analysis of NH\textsubscript{3} concentration in liquid and gas phases, high performance liquid chromatograph (HPLC) was used. HPLC (model 200 LC/S/N291N5060508 from Perkin Elmer) was equipped with a refractive index detector (RID). Nucleosil 100-5 SA analytical column (stronger acidic cation exchanger column with sulfonic acid modified silica) with a dimension of 250 mm × 4.6 mm in length and internal diameter (i.d) was used to separate ammonium (NH\textsubscript{4}+) in all samples. The injection volume of sample introduced was 10 µL. The HPLC operations were controlled...
under these following conditions: column temperature 303 K, flow rate of 0.8 mL/min, RID positive mode, and isocratic mode of 100 % mobile phase made up of 0.05 M mobile phase solution at pH 2.6 (adjusted by 85 % w/w H3PO4). Mobile phase and samples were all filtered by using 0.45 µm nylon membrane filter to get rid of any solid particles. The mobile phase was also degassed for an hour to remove dissolved O2 that might cause interference during analysis. All liquid samples were diluted 1 to 15 dilution ratio using deionized water before injection. Quantitative analysis of NH4+ in amine solution and HCl trapping solution were done using calibration curve of NH4+ in the amine or HCl standard solutions.

3. Results and Discussion

3.1. NH3 concentration in single and blended amine solution.

Fig. 3a and 3b show the concentrations of NH3 generated in liquid phase at 24 hours interval for 10 days and gas phase at the end of 10 days, respectively. DETA solution produced NH3 concentrations the most among the 3 amines in both liquid and gas phases. At day 10, the liquid phase contained as high as 8,060 ppm NH3 while 9.83 × 10^4 ppmV was found in the gas phase. These were higher than that of MDEA solution found at 533 ppm and 1.80 × 10^4 ppmV in liquid and gas phases, respectively. According to the structure shown in Figure 1, DETA contains two primary and one secondary amino groups compared to only one tertiary amino group in MDEA. Based on chemical reactivity of amines, primary and secondary amino groups are more reactive, thus vulnerable to oxidative reaction than their tertiary amino counterpart found in MDEA structure. These highly reactive groups present in DETA could react and then degrade easily by O2 to produce more amount of NH3 than MDEA. Hartono et al [5] also reported that DETA degradation was subjected to a high rate of oxidation, which an increase of reaction and degradation rate would be observed if the number of amine functionalities in the molecules was increased. For the blended amine solution of 1.5 M DETA/1.5 M MDEA, NH3 concentrations in the liquid phase (4,495 ppm) and gas phase (5.82 × 10^4 ppmV) were found in between those in the DETA and MDEA. The results show that adding of MDEA into DETA to obtain blended (DETA/MDEA) amine solution helped to reduce the NH3 formation in liquid phase which also led to a decrease of the NH3 emissions in the gas phase. This information could be useful when formulating the optimum ratio of DETA and MDEA blend to CO2 most effectively while minimizing NH3 formation and emissions in liquid and gas phases.

The total NH3 concentration in liquid and gas phases at the finished of 10 days was determined and reported in molar unit. The combined NH3 concentrations for 3.0 M DETA, 1.5 M DETA/1.5 M MDEA, and 3.0 M MDEA were 0.48, 0.27, and 0.03 M, respectively, as shown in Fig. 3c. Due to lower reactivity of MDEA, it hardly degraded, so generated the least NH3 in both liquid and gas phases, and total phase.

4. Conclusion

The study of single amine (DETA and MDEA) and blended amine solution (1.5 M DETA/1.5 M MDEA) at 3.0 M total amine concentration, 0.65 CO2 loading, 6 %mole O2, and 393 K indicated that among the amines used in this study, DETA easily degraded to generate the highest amount of NH3. MDEA had the highest resistance to oxidative degradation generating the least NH3 concentrations in all phases.
Fig. 3. NH$_3$ concentrations in (a) liquid phase; (b) gas phase; (c) total phase from the effect of single (DETA and MDEA) and blended DETA/MDEA amine solutions containing 3.0 M amine solution, CO$_2$ loading 0.65 mole CO$_2$/mole amine, 6 %mole O$_2$, and 393 K.

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