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Thermal Hydrolysis of Urea for On-site Generation of Ammonia and Carbon Dioxide

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Abstract

Thermal hydrolysis of urea into ammonia and carbon dioxide gases via ammonium carbamate is an accepted method for recovery of ammonia and carbon dioxide from dilute urea solutions in the urea production process as well as for removal of urea from the process wastewater. On-site generation of ammonia from urea by hydrolysis by the utilities to control NO_x emission has proven to be a safe and reliable alternative to either anhydrous or aqueous ammonia, which is subject to strict OSHA and EPA regulations for transport, storage and handling.

An experimental investigation was undertaken to study the thermal hydrolysis of urea for on-site generation of ammonia and carbon dioxide for local small users. Aqueous solutions of urea (1-5% w/w) were hydrolyzed in an electrically heated hydrolyzer set-up at pressures ranging from atmospheric to 5 kg/cm^{2}g with conversion of 1.18 to 44% of the urea fed to ammonia and carbon dioxide. The extent of hydrolysis was determined by measuring the urea concentration of the solution at the end of each experiment by colorimetric P-Dimethyl-aminobenzaldehyde method that is used by the local ammonia-urea industry. The hydrolysis was pressure dependent, and it was the lowest at atmospheric pressure. The conversions in terms of percent urea hydrolyzed were higher with lower urea concentrations. It was also observed that the p^{H}s of the hydrolyzed solutions were more than those of original urea solutions. And the unit for on-site hydrolysis of urea to obtain ammonia and carbon dioxide would not be one-step simple process in reality.

Keywords: *Urea, Hydrolysis*

1. Introduction

The thermal hydrolysis reaction of urea is the reverse reaction that takes place during the production of urea from ammonia and carbon dioxide via ammonium carbamate. In this reverse reaction urea is hydrolyzed with steam and converted back to ammonia and carbon dioxide via ammonium carbamate. This can lead to easy availability of ammonia and carbon dioxide for certain industrial applications on small scale when a safe and relatively reliable alternative to either anhydrous or aqueous ammonia is desired.

Thermal hydrolysis of urea leading to conversion of ammonia and carbon dioxide gases via ammonium carbamate is a proven method for recovery of ammonia and carbon dioxide from dilute urea solutions in the process as well as removal from the wastewater. This now forms an integral part of the urea plant design. Commercially operated process water treatment systems based on chemical hydrolysis and steam stripping include: Stamicarbon System, UTI (United Technologies, Inc.) Hydrolyzer Stripper and Snamprogetti System. These processes operate at elevated pressures in the range 5-37 bar [1].

On-site generation of ammonia from urea by hydrolysis to control NO_x emission by the utilities in the USA has proven to be sound alternative to anhydrous ammonia or aqueous ammonia, which is subject to strict regulations imposed by EPA, OSHA and additional restrictions by local authorities. This has led to reduction in operating costs and done away with risks associated with the transportation and storage requirement [2,3].

Available commercial process for urea based ammonia generation for power plants include (Spencer III et al, 2001; Spencer et al, 2000; Bhattacharya et al, 2003 and Hamilton, 2000): Ammonia-On-Demand (AOD^{TM}) offered by the Environmental Elements Corporation (EEC), Urea to Ammonia (U2A^{TM})

offered by Hamon Research-Cottrell & Wahlco. Inc., Safe De Nox^{TM} System offered by Chemithon

Corporation. It is reported that the higher initial investment cost of some system such as AOD^{TM} will

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*Corresponding Author: tonmoybutex23@gmail.com be paid back in less than one year due to the lower operating, maintenance and compliance costs. The third generation AOD^{TM} unit having 1,814 kg/hr module is available [4].

Urea containing 56% ammonia equivalent by weight provides a practical and economic source for on-site ammonia with minimum governmental oversights. The two-step reactions requiring net external supply of heat are:

$NH_2CONH_2 + xH_2O \rightarrow NH_4COONH_2 + (x\text{-}1)\ H_2O$,
$\Delta H = -31.4$kJ/g.mole of urea at 25^oC and 101.3 kPa

$NH_4COONH_2 + (x\text{-}1)\ H_2O \rightarrow 2NH_3 + CO_2\ (x\text{-}1)\ H_2O$,
$\Delta H = 159$ kJ/g.mole of solid carbamate at 25^oC and 101.3 kPa

This paper presents an experimental investigation studying the thermal hydrolysis of urea for on-site generation of ammonia and carbon dioxide for local small users for on-site production of ammonium bicarbonate and carbonate, aqueous ammonia or anhydrous ammonia.

The hydrolysis products are useful for the reduction of nitrogen oxides in combustion effluents without the generation of substantial amounts of nitrous oxide. The development of urea-to-ammonia technologies is in response to the greatly increased requirements for utilities to control NOx emissions and their implementation of SCR projects that require ammonia as the reducing agent. Anhydrous ammonia is regarded as a hazardous and toxic chemical and is subject to stringent regulations imposed by the EPA as well as OSHA. Aqueous ammonia, although less concentrated, poses similar risks, and is also becoming increasingly regulated or subject to restrictions by local authorities. The use of aqueous ammonia as an alternative to anhydrous, significantly increases operating costs for chemical and energy, and increases transport and storage requirements. These disadvantages are exacerbated as more dilute aqueous solutions are considered.

The urea to ammonia and other on demand urea to ammonia system uses urea as the feedstock chemical and thereby entirely avoids risks associated with the transportation and storage of ammonia. The process transforms urea solution to an ammonia gas mixture on demand to meet the dynamic requirements of the NOx control system and other systems using ammonia [5].

2. Experimental Study

The thermal hydrolysis of urea was carried out in a vertical cylindrical hydrolyzer having ID 0.0762m and length 0.3048m; the material of construction was SS 316L. The hydrolyzer was heated electrically with a heating coil wound around the vessel. The heating was controlled with a controller that used a sensor to measure the temperature of the fluid inside the hydrolyzer. It was provided with a safety valve and pressure gauge. The working volume used was 900 ml against the vessel volume of 1390 ml. The details can be found elsewhere [6].

This set-up was used to carry out hydrolysis over the pressure range 2-5kg/cm^{2}g while hydrolysis at atmospheric pressure was carried out in a glass beaker using the same volume of urea solution, i.e. 900 ml. For the experiments under pressure, heating was stopped as soon as the desired pressure inside the hydrolyzer was indicated by the pressure gauge. The temperatures of urea solution inside the hydrolyzer were noted also. The whole system was cooled and the hydroyzed urea solution was drained out when temperature had reached the room temperature by venting the gases from the hydrolyzer first. Extent of hydrolysis was measured from the concentrations of urea in the initial solution charged into the hydrolyzer and drained out solution from the hydroyzer at the end of experiment. The urea concentrations in the solutions were determined by using Colorimetric P-Dimethylaminobenzaldehyde Method with Shimadzu Recording Spectrophotometer: UV 2201, UV VIS [7]. The pHs of urea solution were measured with a pH meter (Denver Instrument Model 215).

The urea used for the experiments was reagent grade of MERCK, Germany with urea content min. 99.5% and biuret 0.1% maximum. The fertilizer grade urea produced locally was not used because of biuret content in excess of 1% and presence of formaldehyde and urea additives.

3. Results and Discussions

Aqueous urea solutions with urea concentration in the range 1 to 5% by weight were used in this study. For each concentration of urea, hydrolyses were carried out at pressures ranging from atmospheric to 5 kg/cm^{2}g and temperatures 96-156^oC.

Table 1 provides some data for final temperature and time for hydrolysis at different pressures for all the urea concentrations used.

The criterion for continuing hydrolysis was the point of indicating the desired pressure by the pressure gauge installed on the hydrolyzer top as well as the corresponding boiling temperature of water at desired pressure determined experimentally prior to hydrolysis experiments [6].

Table 1: Data for Final Temperature and Time for Hydrolysis at Different Pressures

Pressure, atm. or kg/cm^{2}g	Urea concentration, wt %	Time, min	Final Temperature, ºC	Average Time, min	Average Temperature, ºC
Atm	1-5	30-36	98.4-98.9	32.6	98.6
2	1-5	33-41	133.0-134.0	36.2	133.4
3	1-5	36-49	144.0-145.0	41.4	144.4
4	1-5	40-48	152.0-155.0	43.4	152.8
5	1-5	39-56	156.0-160.0	45.8	157.8

Table 2 and Fig.1 show the extent of hydrolysis of urea for all the urea concentrations at pressures from atmospheric to 5 kg/cm^{2}g.

Fig. 2 shows the typical variation of pH of initial urea solution and hydrolyzed solution for 5% by wt. urea in initial solution with hydrolysis pressure.

The different times required for the set hydrolysis pressure for different urea concentrations as shown in Table 1 were due to rate of heat being absorbed

Table 2: Data on Hydrolysis of Urea at Different Pressures

Sl. No.	Urea Concentration, Wt %	Pressure, atm or kg/cm^{2}g	Urea hydrolyzed, %
1.	1	atm	2.64
2.	1	2	8.43
3.	1	3	23.65
4.	1	4	31.92
5.	1	5	44.72
6.	2	atm	1.18
7.	2	2	13.78
8.	2	3	19.88
9.	2	4	26.08
10.	2	5	33.48
11.	3	atm	2.29
12.	3	2	8.30
13.	3	3	17.30
14.	3	4	27.69
15.	3	5	30.46
16.	4	atm	3.26
17.	4	2	9.58
18.	4	3	12.90
19.	4	4	20.78
20.	4	5	30.27
21	5	atm	3.42
22.	5	2	8.15
23	5	3	11.69
24.	5	4	17.12
25.	5	5	20.18

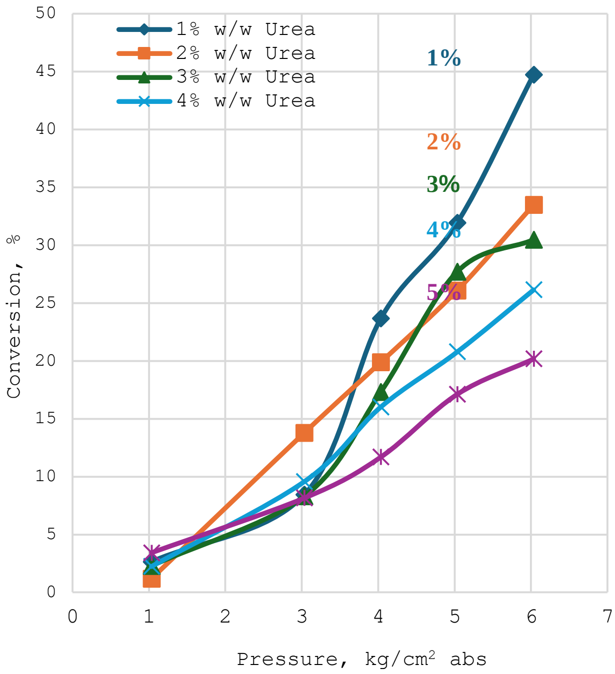

Figure 1: Conversion, % of Urea hydrolyzed vs Pressure with Concentration as parameter

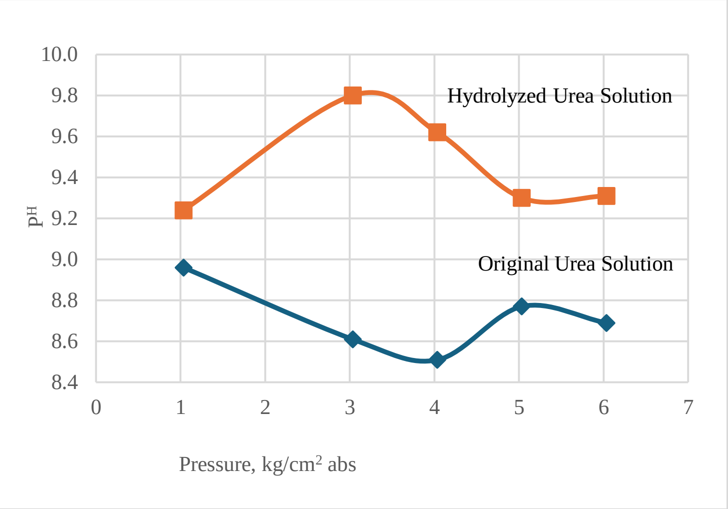

Figure 2: Typical Variation of P^H of Initial Urea Solution and Hydrolyzed Urea Solutions against Hydrolysis Pressure for 5% by wt Urea in Initial Solution.

The different times required for the set hydrolysis pressure for different urea concentrations as shown in Table 1 were due to rate of heat being absorbed by the urea solutions. If the solutions would had been stirred continuously during the experiment, such variations could have been minimized. However, this limitation does not seriously undermine the investigation to appreciate the measure of hydrolysis and its dependence on pressure, in other words corresponding temperature. Because the reactions for synthesis of urea from ammonia and carbon dioxide as well as breakdown of urea into ammonia and carbon dioxide require certain residence time in the reactor or decomposer in the real production process.

The study shows that the extent of hydrolysis is lowest at atmospheric pressure while it increases with elevation of pressures for all concentrations. Dilute solutions at increased pressure show greater breakdown of urea, Fig.1 and Table 2. This makes on-site generation of ammonia and carbon dioxide by hydrolyzing urea not so technologically easy and energy efficient. Moreover, subsequent separation of ammonia from the mixture of gases containing ammonia, carbon dioxide and water vapor would the desired final product. If the end products are ammonium carbonate/ biocarbonate or are to be used in the production of soda ash on small scale, this has a commercial potential.

4. Conclusions

Extent of thermal hydrolysis of urea into ammonia, carbon dioxide and water vapor is pressure dependent, in other words, temperature also.

On-site generation of ammonia and carbon dioxide by hydrolyzing aqueous urea solutions thermally for small users has a commercial potential in a developing country like Bangladesh as it's a safe alternative to transporting, storing, and transferring toxic anhydrous and aqueous ammonia provided the technical issues involving separation steps are incorporated in the total process.

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