

Equilibrium studies on hydrolysis of urea in a semi-batch reactor for production of ammonia to reduce hazardous pollutants from flue gases

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ARTICLE INFO

Article history:

Received 20 April 2008
Received in revised form 24 June 2008
Accepted 15 August 2008
Available online 27 August 2008

Keywords:

Ammonia
Urea
Hydrolysis
Air pollutant
Flue gas conditioning

ABSTRACT

The increasing environmental awareness and the mandate of the pollution control agencies in various part of country for lowering emission of air pollutants such as CO₂, NO_x, SO₂ and fly ash emissions, has increased the urgency for reviewing options and alternatives to accomplish the above objective. The addition of ammonia into the flue gas stream as a conditioning agent is found to be used in recent years for the reduction of air pollutants. Flue gas conditioning requires in situ generation of ammonia as the transportation and storage of anhydrous ammonia is hazardous in nature. The equilibrium study on hydrolysis of urea was done in a semi-batch glass reactor to investigate the effect of reaction temperature, initial feed concentration and stirring speed on ammonia production. Few experiments were carried out in a semi-batch reactor at atmospheric pressure by using different concentration of urea solution from 10 to 40 wt% of urea to water and equilibrium study has been done. The study reveals that conversion increases exponentially with an increase in temperature but the conversion decreases with increase in the inlet feed concentration of urea solution. Furthermore, the effect of stirring speed on conversion has also been studied and it found that conversion increases with increase in stirring speed.

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1. Introduction

Environmental problems span a continuously growing range of pollutants hazards and ecosystem degradation over ever wider areas. Problems with energy supply and use are related not only to global warming, but also to such environmental concerns as air pollution, acid precipitation, ozone depletion, forest destruction, and emission of radioactive substances. Increasing concerns over protecting the environment have led to regulations limiting the amount of suspended particulates matters (SPM), oxides of nitrogen (NO_x), oxides of carbon (CO₂) and oxides of sulfur (SO₂), which can be emitted from combustion sources. To meet future emission standards, significant reductions in SPM, NO_x, CO₂ and SO₂ emissions are required.

The control technology used to collect the majority of this SPM is the electrostatic precipitator (ESP). However, the efficiency of the ESPs in India is adversely affected due to the low sulfur content and the abrasive nature of high ash domestic coal [1]. Existing

precipitators were designed to provide a particular efficiency of collection for the coals in use or proposed at the time of design. From environmental legislation, state and federal requirements demand high efficiency removal of fly ash, even in older units. Additionally, many power companies have chosen to switch to low sulfur coal as a means of meeting environmental restrictions on sulfur dioxide emissions. Uncertain fuel supplies have often forced the burning of lower quality fuels. In many cases, these problems have resulted in the deterioration of precipitator efficiency with the result that particulate emissions exceed the limits. Considerable field experience indicates that fly ash in flue gas conditioning can materially improve the performance of these precipitators at relatively low cost. More complex organic mixtures have also been proposed for gas conditioning, but NH₃ and SO₃ are still the most popular agents used. The injection of NH₃ has improved the resistivity of fly ash from coal-fired boilers with low flue gas temperatures [2]. Ammonia also increases cohesiveness of the particles, allowing their agglomeration [3] and the number of particles re-entrained during electrode rapping is also reduced [4].

One of the important methods for removing nitrogen oxides derived from the burning of fossil fuels embodies their conversion to inert nitrogen gas by reaction with amine-type reluctant materials, by processes such as selective catalytic reduction (SCR) or

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selective non-catalytic reduction (SNCR) [5]. Two main redundant materials have achieved commercial acceptance for this purpose, namely, ammonia and urea [6,7]. Ammonia is superior to urea as such for SNCR in several important aspects for this application and is required for SCR applications [8,9].

Oxide of sulfur removal from flue gas by NH_3 gas injection is a dry flue gas desulfurization (FGD) technique that has been studied by several researchers [10]. The aqueous ammonia process can simultaneously remove CO_x , SO_2 , NO_x , plus HCl and HF that may exist in the flue gas [6,11]. Also ammonia at the low concentrations found useful for bag-house gas conditioning has been found to be capable of reducing SeO_2 to the element, and it also has the potential of reducing As_4O_6 to the element [12].

Ammonia is used as a feedstock for uses such as described above, is often delivered in the form of anhydrous ammonia. Unfortunately, ammonia presents significant danger to human health as a hazardous chemical. Its transportation, storage and handling triggers serious safety and environmental regulatory requirements for risk management plans, accident prevention programs, emergency response plans and release analysis [13].

There are several chemical processes that are used to manufacture ammonia. The three most prevalent methods include the Haber–Bosch process, indirect electrochemical dissociation, and urea decomposition. The Haber–Bosch process reacts gaseous hydrogen and nitrogen over a metal catalyst at high temperatures (e.g., at 475°C) and pressures (e.g., at 20 MPa). This process is a proven large-scale industrial process; however, it uses harsh conditions and has not been proven technically or economically effective below the ton/hour range. The electrochemical dissociation process has been proposed by some in the semiconductor industry as an alternative to the Haber–Bosch process for the generation of ammonia. This process also react hydrogen and nitrogen. However, it is an indirect synthesis via a molten alkali-metal halide electrolyte with nitrogen introduced at the cathode and hydrogen introduced at the anode. The electrochemical dissociation process also operates at elevated temperatures (e.g., at 400°C) but at ambient pressure. While utilizing less harsh operating conditions or parameters than the Haber–Bosch process, the electrochemical dissociation process has not been proven above pilot scale production rates and has a high risk of alkali metal contamination. Another concern with adopting these two processes for generating ammonia is that the Haber–Bosch and electrochemical distribution processes require large amounts of hydrogen, which adds significantly to the risk of operating an ammonia generation facility. Another process for generating ammonia is through the hydrolysis of urea.

The method of urea to ammonia conversion by hydrolysis process, where urea is ideal candidate ammonia substituted. Urea is a non-toxic chemical compound and, for purposes of small requirement, i.e. up to 50 kg/h, presents essentially no danger to the environment, animals, plants life and human beings. It is solid under ambient temperatures and pressures. Consequently, urea can be safely and inexpensively shipped in bulk and stored for long periods of time until it is converted into ammonia. It will not leak, explode, be a source of toxic fumes, require pressurization, increase insurance premiums, require extensive safety programs, or be a concern to the plant, community and individuals who may be aware of the transportation and/or storage dangers of ammonia.

The published information in literature about hydrolysis of urea for production of ammonia is very little detailed and patented [14]. However, there is no information available in the literature regarding the equilibrium study of urea hydrolysis for production of ammonia. Therefore, we decided to study more thoroughly the phenomenon of urea hydrolysis for productions of ammonia in different application areas require safe use of relatively small quantities of ammonia.

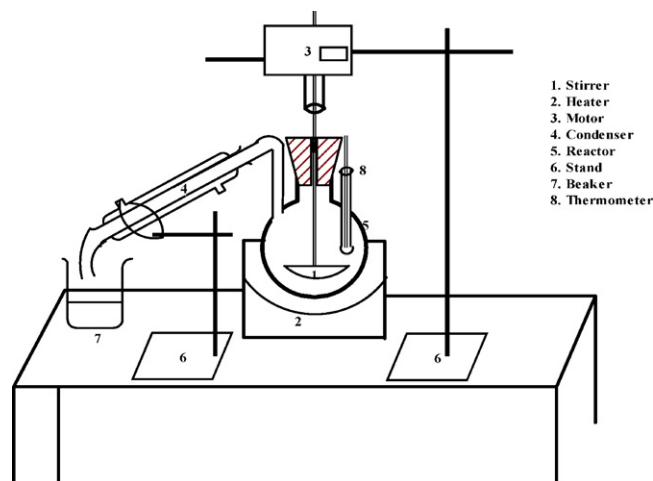


Fig. 1. Schematic of experimental set-up for urea hydrolysis.

2. Materials and methods

2.1. Characterization of urea

Urea and biuret was detected and quantified using HPLC (high performance liquid chromatography). The HPLC equipment consisted on a PerkinElmer chromatograph series 200 UV/VIS LC detector (PerkinElmer, USA) equipped with an isocratic pump series 200 and a rheodyne injector with a $20\ \mu\text{l}$ loop, with variable-wavelength ultra violet/visible detector was used. The equipment was controlled by Total chrom software that controlled the solvent gradient, data acquisition and data processing. The column was a reversed-phase agilent column. Separation in a C-18 column ($250\ \text{mm} \times 4.6\ \text{mm}$ dia.), $5\ \mu\text{m}$ pore size and a UV detector set at a wavelength of 199 nm. The mobile phase used here 0.1 M phosphate buffer pH 6.7 at flow rate 1 ml/min, the column temperature was $25 \pm 1^\circ\text{C}$. HPLC provides the following feature, these are high resolving power, speedy separation, continuous monitoring of the column effluent, accurate quantitative measurement, repetitive and reproducible analysis using the same column and automation of the analytical procedure and data handling.

2.2. Reagents

All the chemicals used in the study were from Merck (India) Ltd. and Qualigens Glaxo (India) Ltd. analytical grade.

3. Experimental set-up and technique

The experimental set-up as shown in Fig. 1 has been used for the studies of hydrolysis of urea for production of ammonia in laboratory. The experimental set-up consists of a borosil glass reactor of capacity $1000\ \text{cm}^3$. The reactor contains three openings. One is for putting a thermometer to measure the temperature of the reactor content. Second is for feeding and withdrawing urea solution. In the third opening, a stirrer cum motor assembly is mounted on the vertical retort rod at the square elbow and tightened by a black key knob. The stirrer shaft and the stirrer are made up of glass and Teflon, respectively. The reactor is placed on an electric heater of capacity 1000 kW and the heater is connected to 220 V AC supply. The outlet gaseous products (ammonia, carbon dioxide and water) from the reactor are attached to a condenser to condense the water product from the reactor, where tap water is used for the purpose of condensation.

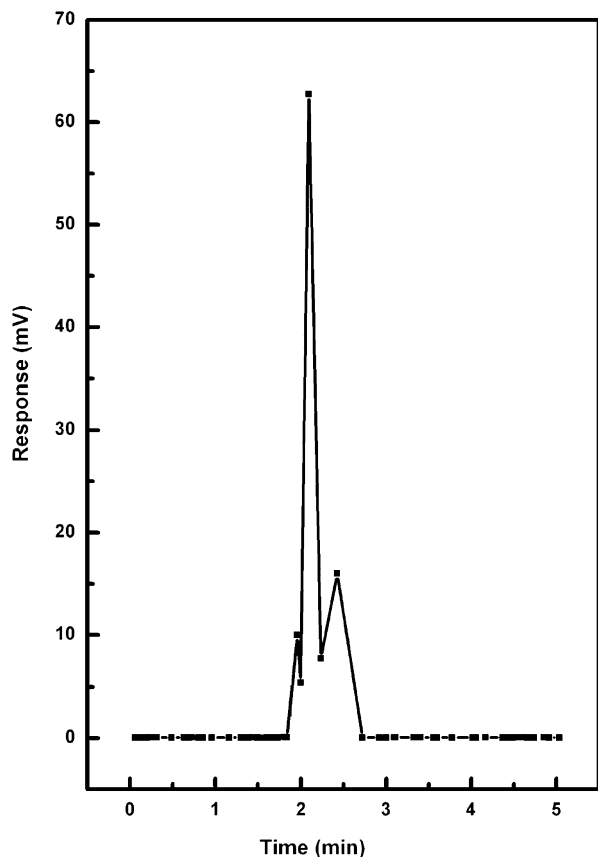


Fig. 2. HPLC analysis of standard urea.

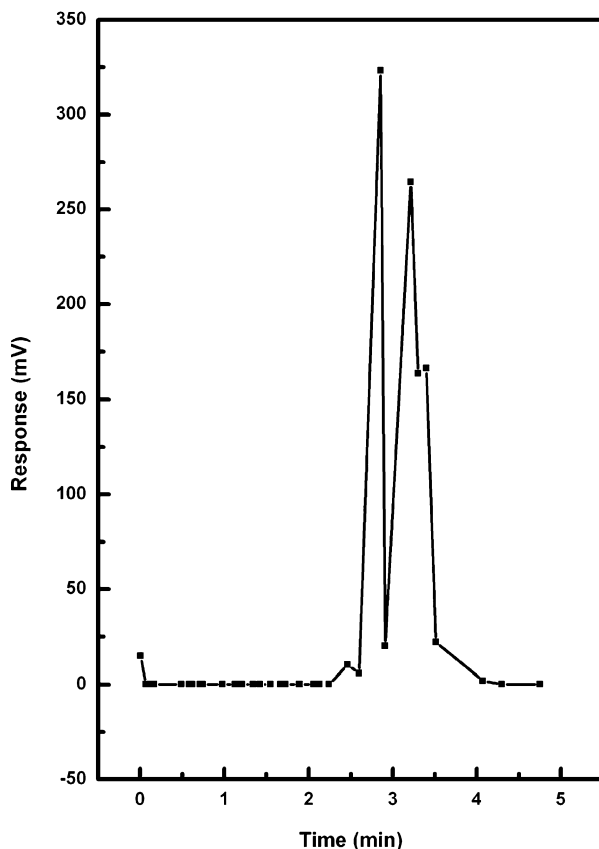


Fig. 3. HPLC analysis of standard biuret.

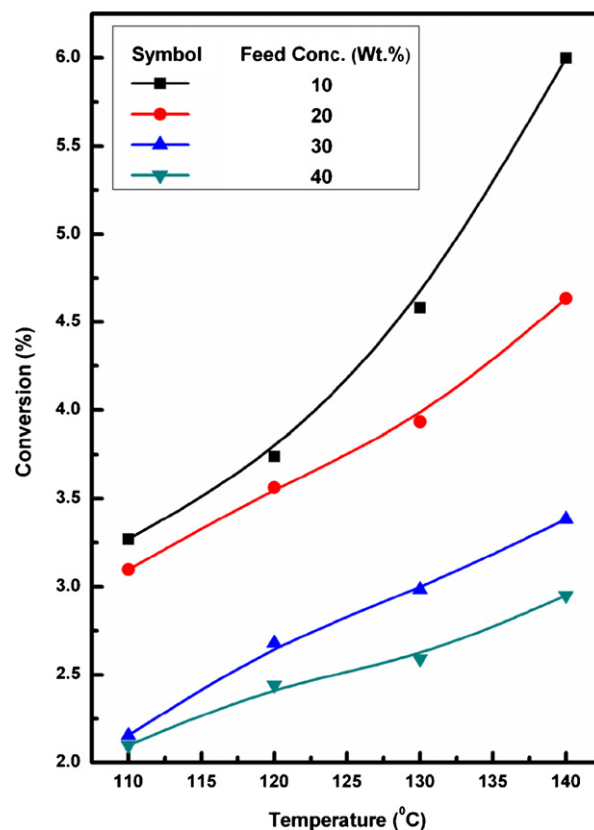


Fig. 4. Effect of temperature on conversion at different initial feed concentrations.

First urea solution of different concentration (10, 20, 30, and 40 wt% urea to water) was prepared. In each case the volume of the solution was taken as 500 ml. Then the solution of particular concentration was fed into the reactor. First the experiments were conducted without stirrer and motor assembly. Heat was supplied from the bottom of the reactor at a controlled rate by means of electricity. As the temperature increases initially, evaporation of water will take place and the decomposition of urea takes place slowly at around 110 °C. As the reaction starts, the product which is a gaseous mixture of ammonia, carbon dioxide and water vapor goes through the condenser. In the condenser the gaseous product mixture get condensed where cold water was circulated and the product was collected in a beaker with boric acid solution as it is an absorbing material for ammonia solution. Boric acid solution was prepared by dissolving 4 g of boric acid in 100 ml of warm distilled water. Then the absorbing ammonia solution was taken out and its volume was measured. After it gets absorbed with boric acid, three samples each of 10 ml volume has taken for titration. Three drops of methyl orange indicator was mixed in each sample. Then it was titrated with hydrochloric acid. Boric acid is so weak that it does not interfere with acidimetric titration. Then by comparing the initial concentration and final concentration the equilibrium conversion

Table 1
Impurity data for different grade of urea

Name of samples	Urea (%)	Biuret (%)	Other impurities (%)
IFFCO, New Delhi	91.21	2.05	6.74
Nagarjuna, Kakinada	94.32	2.89	2.79
Shaktiman, Sultanpur	91.74	2.26	6.0
IFFCO, Imported	96.34	2.38	1.28
Kribhco, UP	93.73	2.28	3.99
TATA	97.44	1.25	1.31

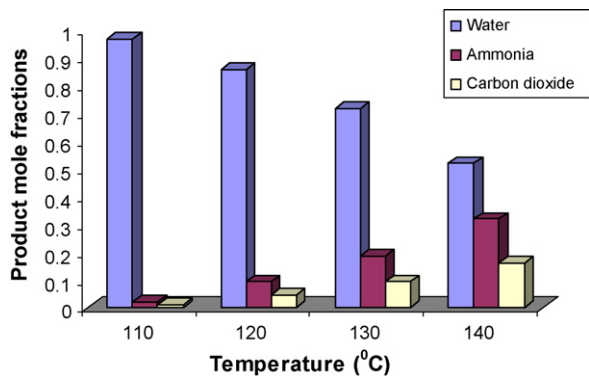


Fig. 5. Temperature evolution of reactor products for initial feed concentration of 40 wt% urea to water and steering speed 600 rpm.

was found out. Same procedure was repeated for other concentration (20, 30 and 40 wt% urea to water) and temperature (110, 120, 130 and 140 °C). Then by comparing the initial concentration and final concentration the conversion was found out. Similarly, experiments were conducted with different stirring speed of 200, 400, 600 and 800 rpm.

4. Results and discussions

4.1. Physical and chemical characterization of the urea samples

Various sources of urea have been collected from near local market at Kharagpur, India, e.g. Tata, IFFCO, Nagarjuna, Khribco and were characterized to know the purity before conduct the experiment. Urea samples have been characterized by HPLC to find out

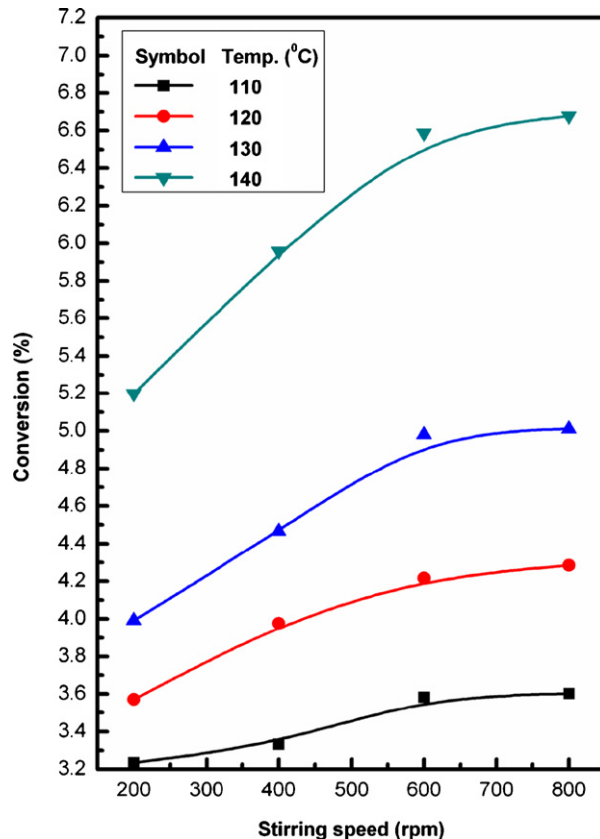


Fig. 7. Effect of stirring speed on conversion at different temperature and initial feed concentration of 10 wt% urea to water.

the impurity. The urea samples compare to find out the purity with standard urea and biuret as shown in Figs. 2 and 3, respectively. It has been observed that Tata urea shows highest percentage of purity, i.e. 94% having biuret content of 1.25% while IFFCO urea contains 2.05% biuret and its purity is 91.21. Table 1 shows the impurity data of different grade of urea samples. All the experiment conducted by using Tata urea as it possesses highest purity.

4.2. Reaction pathway

The basic chemistry employed in the hydrolysis of urea, is a reverse of that employed in the industrial production of urea from ammonia and carbon dioxide and employs two reaction steps, as follows [15,16]:



The reaction in Eq. (1) where urea hydrolysis to form ammonium carbamate is mildly exothermic, while Eq. (2), in which ammonia and carbon dioxide are produced is strongly endothermic, with the result that the reaction to release ammonia and carbon dioxide requires heat and quickly stops when the supply of heat is withdraw. Excess water promotes the hydrolysis reaction, the overall reaction for which is as follows:



4.3. Effect of temperature on conversion

It can be seen from Fig. 4 that the conversion is function of temperature for the case of without stirring. It increases exponentially

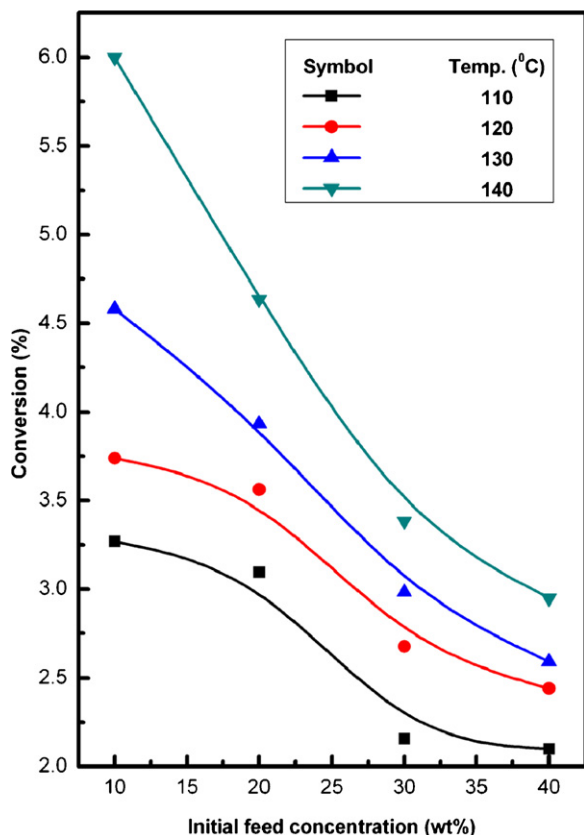


Fig. 6. Effect of initial feed concentrations on conversion at different temperature.

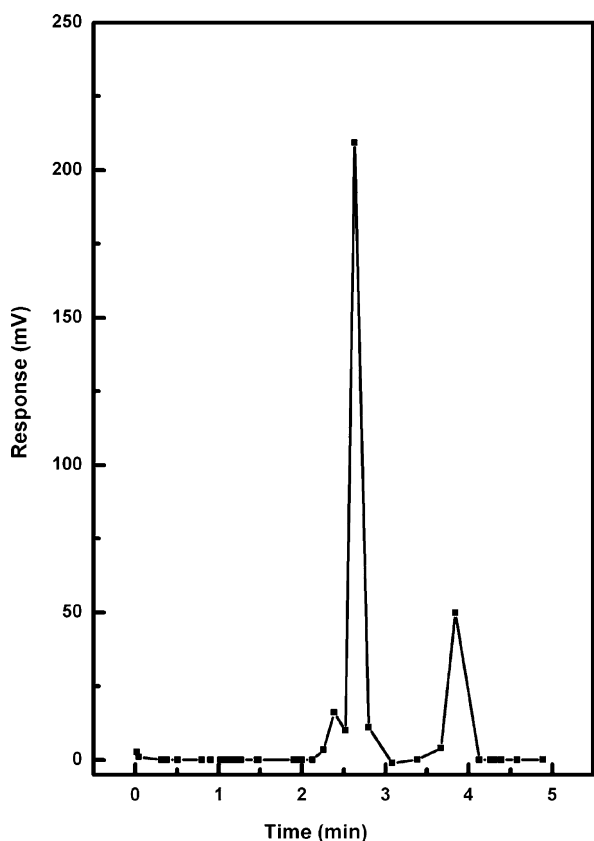


Fig. 8. HPLC analysis of the urea feed solution.

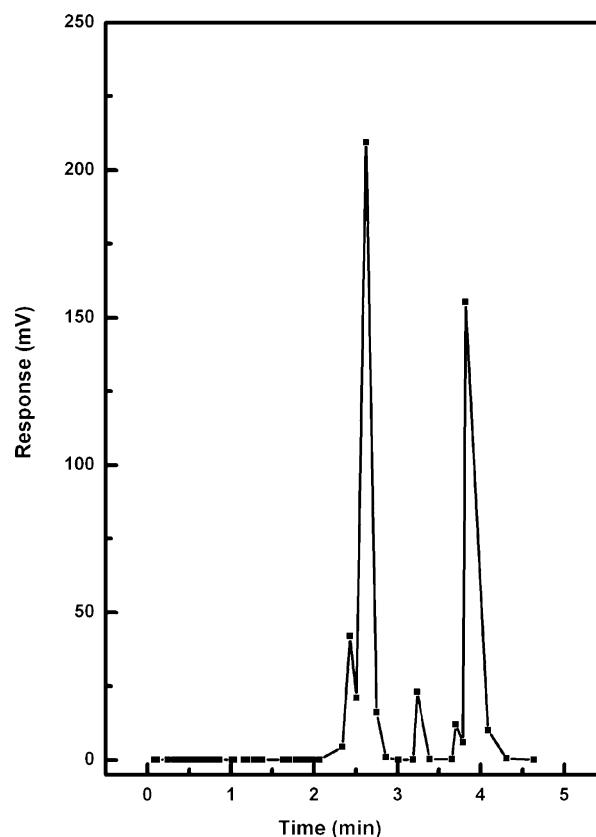


Fig. 9. HPLC analysis of the precipitated solids from the reactor solution.

with an increase in temperature owing to overall reaction of hydrolysis of urea to form ammonia and carbon dioxide is endothermic in nature. For 10 wt% urea to water solution the conversion increases from 3.27% to 5.99% when temperature increases from 110 to 140 °C in 10 °C interval. Similarly for 20 wt%, conversion increases from 3.09% to 4.63%; for 30 wt%, conversion increases from 2.15% to 3.38% and for 40 wt%, conversion increases from 2.1% to 2.94% at temperature 110–140 °C for respective inlet feed solution of urea.

The product composition (moles of product/total moles of products) obtained from the reactor with 40 wt% of urea to water feed inlet solution at different temperatures with constant steering speed of 600 rpm is shown in Fig. 5. It can be seen from the figure that the production of ammonia and carbon dioxide increases markedly as the temperature increased and the production of excess water decreased.

4.4. Effect of initial concentration on conversion

It can be seen from Fig. 6 that with increases in initial concentration of urea solution the conversion decreases. For each initial concentration the temperature was varied from 110 to 140 °C. Keeping temperature constant at 110 °C the conversion decreases from 3.27% to 2.1% when concentration varies from 10 to 40 wt% of urea to water. Similarly for 120, 130 and 140 °C the equilibrium conversion decreases from 3.74% to 2.44%, 4.582% to 2.59% and 5.99% to 2.94%, respectively, when the initial feed concentration of urea increases from 10 to 40 wt% of urea to water. This is due to the fact that more wt% urea has less excess water than less wt% urea, so less chance to achieve hydrolysis reaction, as it favors for higher concentrate water to urea present in the less wt% have higher conversion.

4.5. Effect of stirring speed on conversion

It has been observed that the conversion increases steeply at first, with increased in stirring speed. Slowly, the rate of increase decreases till a stage comes, when the conversion no longer increases with increased stirring speed. This means that the optimum point of conversion at that temperature has been reached and no further conversion is possible by increased the stirring speed. From Fig. 7 it is clear that, if temperature and initial concentration kept constant at 110 °C and 10%, respectively, with the increase of stirring speed from 200 to 800 rpm the conversion increases from 3.23% to 3.6%, respectively. Similarly, at constant temperature and initial concentration of 120 °C and 10%, respectively, the conversion increases from 3.57% to 4.28%; at constant temperature and initial concentration of 130 °C and 10%, respectively, the conversion increases from 3.99% to 5.01% and at constant temperature and initial concentration of 140 °C and 10%, respectively, the conversion increases from 5.19% to 6.67% with the increases in stirring speed from 200 to 800 rpm. The reason is due to the fact that as stirring speed increases the rate of mass transfer increases which in turns increases the formation of ammonia and carbon dioxide, thereby decreases the unreacted urea in the reactor.

4.6. Characterization of the reactor liquor samples

The detailed analysis of reactor liquid sample have taken at 140 °C and with inlet feed concentration of 10 wt% of urea to water having stirring speed of 600 rpm. The reactor liquid typically contains 3–4% urea, 0–5% higher urea derivatives and 1–2% ammonia. At temperature above 120 °C, any ammonium carbamate in the liquid formed immediately decomposes to ammonia and carbon dioxide and hence very small concentrations (1–2%) of ammonium carba-

mate will be present in the reactor liquor and the rest is water. The HPLC analysis of the feed urea sample and reactor liquor sample are shown in Figs. 8 and 9, respectively. The chromatograph shows the presence of urea and biuret in the inlet feed solution of urea. The HPLC analysis of reactor liquor samples shows the presence of urea, biuret and other new products also observed. The presence of urea in reactor liquor decreases compare to inlet feed urea solution, but the biuret percentage increases, it may be due to the formation of higher urea derivatives as new peaks also observed.

5. Conclusion

Hydrolysis of urea for manufacturing ammonia is a suitable technique for flue gas conditioning in the reduction of hazardous pollutants from process and energy industries. Urea samples of different grades were collected from the market and characterization was performed by HPLC. It has been observed that Tata urea shows highest purity, i.e. 97.4% as compared to other urea samples. Few experiments were carried out in a semi-batch reactor at atmospheric pressure by using different concentration of urea solution from 10 to 40 wt% of urea to water and equilibrium study has been done. The conversion is function of temperature for the case of without stirring, for 10 wt% of urea to water inlet feed solution the conversion increases from 3.27% to 5.99% when temperature increases from 110 to 140 °C in 10 °C interval. But with increases in initial feed concentration of urea solution the conversion decreases. Also the effect of stirring speed was conducted varying stirring speed from 200 to 800 rpm to observe the mass transfer effect. It has been observed that the conversion increase steeply at first, with increased in stirring speed. From equilibrium study it is concluded that with increase in the temperature and stirring speed the equilibrium conversion increases and a maximum conversion of 6.67% is possible with 10% concentration of inlet feed solution of urea, stirring speed 800 rpm and at 140 °C temperature, similar work in progress for investigating to increase of the conversion hydrolysis of urea. The initial results imply that the hydrolysis of urea for manufacturing ammonia is a suitable technique for safe utilization in coal fired thermal power plant.

Acknowledgements

The authors would like to gratefully acknowledge the financial support to the National Thermal Power Corporation (NTPC), New Delhi, India, has extended towards them for this work.

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