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Studies on the hydrolysis of urea for production of ammonia and modeling for flow characterization in presence of stirring in a batch reactor using computational fluid dynamics

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Abstract−Ammonia is a highly volatile noxious material with adverse physiological effects, which becomes intolerable even at very low concentrations and presents substantial environmental and operating hazards and risk. But ammonia has long been known to be useful in the treatment of flue gases from the fossil fuel combustion process, such as in industrial furnaces, incinerators and coal-fired electric power generating plants. The present study is concerned with the methods and means to safely produce relatively small amount (i.e., up to 50 kg/hour) of ammonia. Current study involves experimental investigation for hydrolysis of urea for production of ammonia in a batch reactor at different temperature ranging from 110 °C to 180 °C against different initial feed concentration (10, 20, and 30 wt%) with different stirring speed ranging from 400 rpm to 1,400 rpm. Three-dimensional geometry and meshing of reactor is created in Gambit, a preprocessor of the commercial software, Fluent, for hydrodynamic study.

Key words: Flue Gas Conditioning, Ammonia, Urea, Hydrolysis of Urea, Batch Reactor, Computational Fluid Dynamics

INTRODUCTION

Ammonia, a colorless gas with a pungent, suffocating odor, is corrosive and exposure will result in a chemical-type burn. Since ammonia is extremely hygroscopic, it readily migrates to moist areas of the body such as eyes, nose, throat, and moist skin areas. Exposure to liquid ammonia will also result in frostbite since its temperature at atmospheric pressure is 2.2 °C. Specifically, upon sudden release to the atmosphere, as might occur in a train wreck or a traffic accident, the ammonia forms a cloud, an aerosol fog of liquid ammonia droplets. Unlike gaseous ammonia, which, though toxic, is lighter than air and quickly dissipates to harmless concentrations, the cloud can persist. The cloud is typically heavier than air and tends to drift along the ground or the surface of a body of water. The cloud moves with the wind and can sweep over a total area, i.e., a "footprint," much larger than the area covered by the cloud at any one moment. Contact with the cloud is instantly incapacitating, and a single breath can be fatal [1]. The Occupational Safety and Health Administration (OSHA) issues permissible exposure limits for ammonia of 50 ppm, or 35 mg/m^3, time-weighted average, and 35 ppm, or 27 mg/m^3, short-term exposure [2]. Ammonia as a highly hazardous chemical under the Process Safety Management Standard [3].

Many industrial plants require the supply of large quantities of ammonia; important users among these are industrial furnaces, incinerators and the electric power generation industry [4-15]. Examples include selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR) for nitrogen oxides abatement, for conditioning of the flue gas by which an improved collection and removal of particulate matter (fly ash) is obtained and also for alleviation of the "blue plume" problems when burning high sulfur content oil in a boiler [9].

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 [16-19]. 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 reacts 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 it that the Haber-Bosch and electrochemical distribution processes require large amounts of hydrogen, which adds significantly to the risk of operating an ammonia gener-

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ation facility. The requirement of ammonia for flue gas conditioning is a very small quantity compared to the ammonia synthesis from the above process. Thus, the Haber-Bosch process is not economically feasible for above-said purpose [18]. Moreover, the attainment of such a large pressure and temperature is not feasible for such a small quantity. Hydrolysis of urea is an alternate option for the synthesis of ammonia [12-22].

The method of urea to ammonia conversion is by hydrolysis, where urea is ideal candidate ammonia substituted. Urea is a non-toxic chemical compound and, for purposes of small requirements, i.e., up to 50 kg/hour, presents essentially no danger to the environment, animals, plants life and human beings [20-22]. 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 about hydrolysis of urea for production of ammonia for feedstock in different application areas flue gas conditioning and NO_x reduction, etc., is very little detailed and patented [21-30]. Therefore, we decided to study more thoroughly the phenomenon of urea hydrolysis for production of ammonia in different application areas that require safe use of relatively small quantities of ammonia. Computational fluid dynamics (CFD) provides a method for prediction of how reactor features affect the hydrodynamics and thus optimize reactor design and performance. Modeling of a complex flow field inside the reactor is done through the computational fluid dynamics literature review study. Complex flow field inside the reactor and hydrodynamic study is done with the help of commercial Fluent software.

EXPERIMENTAL SETUP AND TECHNIQUE

Fig. 1 shows a schematic diagram of a urea thermal hydrolyser setup. The experimental setup mainly consists of a high pressure (100 kg/cm^2) reactor, heat exchanger, condenser, pump, feed tank, control panel and product storage tank. The reactor has a capacity of 2 l volume and is made of stainless steel-316. A pump was used to feed the urea solution to the reactor at controlled flow rate against a positive differential head between pump suction and discharge. The shell and tube type condenser was used to exchange heat between products (NH_3, CO_2, H_2O vapor) and cooling water. The sys-

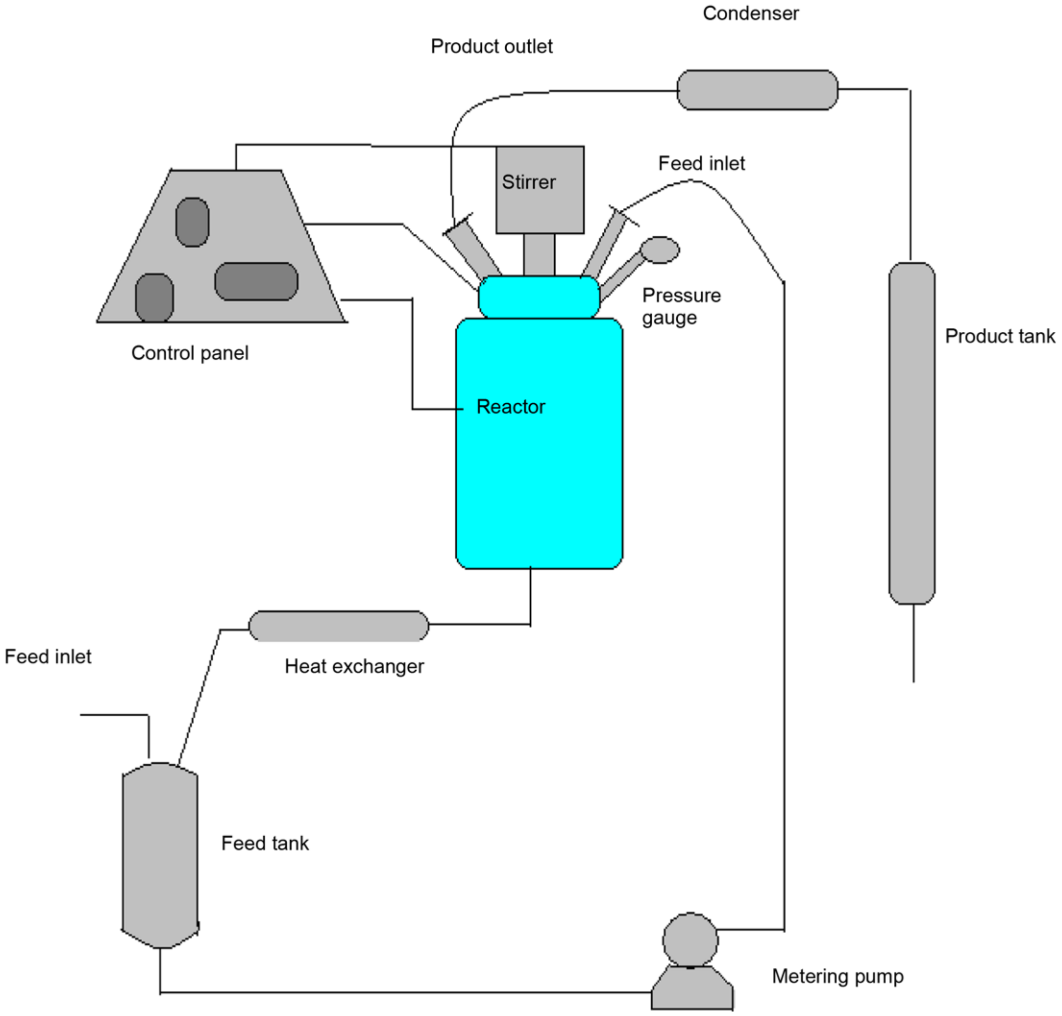

Fig. 1. Schematic diagram of the hydrolysis of urea reactor experimental setup.

tem has also a heat exchanger to cool the un-reacted urea for recycle to the reactor where tap water at room temperature without any pressure is used for cooling. Apart from the above it also have two storage vessels, one for urea solution another for product storage. The whole setup was built in stainless steel to prevent corrosion. The reactor contains two openings; one is for feeding urea solution and another for withdrawing the product to condense the gaseous product from the reactor where tap water is used for the purpose of condensation. To measure the temperature and pressure of the reactor, a thermocouple and pressure gauge were attached to the reactor through the control panel. A cooling coil was placed inside the reactor to cool the reactor when required, same tap water also used here as a coolant.

IFFCO make urea sample, which was used to conduct the experiment, was collected from the market. First, urea solutions of different concentration (10, 20, and 30 wt%) were prepared. In each case the volume of water was taken as 500 ml. Then the solution of particular concentration was fed into the feed tank. A metering pump was used to feed the urea solution to the reactor at high pressure at controlled flow rate against a positive differential between pump suction and discharge. The experiments were conducted without a stirrer. Heat was supplied by an electrical coil outside of reactor wall at a controlled rate by means of a control panel. The decomposition of urea takes place slowly starting around at 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 becomes condensed where tap water at room temperature without any pressure was circulated through the condenser. Then the product was stored in the product storage tank and was collected in a beaker with boric acid solution as it is an absorbing material for ammonia solution. Boric acid solution is prepared by dissolving 4 gm 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 became absorbed with boric acid, three samples each of 10 ml volume were for titration. Three drops of methyl orange indicator were 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 conversion was found.

The hydrolysis of urea to ammonia is endothermic and proceeds rapidly above approximately 120 °C. The basic chemistry employed in the process is the reverse of that employed in industrial production of urea from ammonia and carbon dioxide and employs two reaction steps [17,31]:

$$\underset{urea}{NH_2CONH_2} + \underset{water}{H_2O} \xrightarrow{-Heat} \underset{ammonium\ carbamate}{NH_2COONH_4},\ \Delta H_1 = -15.5\ \text{KJ/mole} \quad (1)$$

The ammonium carbamate decomposed then to yield carbon dioxide and ammonia gases:

$$\underset{ammonium\ carbamate}{NH_2COONH_4} \xrightarrow{+Heat} \underset{ammonia}{2NH_3} + \underset{carbon\ dioxide}{CO_2},\ \Delta H_2 = +177\ \text{KJ/mole} \quad (2)$$

The first reaction in which urea hydrolyzes to form ammonium carbamate is mildly exothermic, while the second, 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 withdrawn. Excess water promotes the hydrolysis reaction; the overall reaction for which is as follows:

$$xH_2O+NH_2CONH_2 \rightarrow 2NH_3+CO_2+(x-1)H_2O \quad (3)$$

The kinetic equation for hydrolysis of urea as given as:

$$r_A=(2.89\times10^7\ \exp(-8856.79/T))C_A \text{ and } \Delta H_{overall}=+161.5\ \text{KJ/mole} \quad (4)$$

The completion of the reaction is favored by high temperature, stirring speed and high reaction pressure. The overall reaction is endothermic and the first reaction, i.e., urea to ammonium carbamate reaction, is a slow reaction and the second reaction is very fast and goes towards completion [29-33].

The experiments were conducted for hydrolysis of urea for production of ammonia in a batch reactor at different temperature ranging from 110 °C to 180 °C against different initial feed concentration (10, 20, and 30 wt%) with different stirring speed ranging from 400 rpm to 1,400 rpm.

RESULTS AND DISCUSSION

1. Three-dimensional Geometry and Modeling of Reactor Using Gambit and Fluent

CFD is a computational technology that enables us to study the dynamics of things that flow. Using CFD, we can build a computational model that represents a system or device that we want to study. Then was applied the fluid flow physics and chemistry to this virtual prototype, and the software output a prediction of the fluid dynamics and related physical phenomena. Therefore, CFD is a sophisticated computationally-based design and analysis technique. CFD software gives us the power to simulate flows of gases and liquids, heat and mass transfer, moving bodies, multiphase physics, chemical reaction, fluid-structure interaction and acoustics through computer modeling [34-38].

Gambit, which is the main preprocessor of Fluent, is used to create geometry and meshing. With the available dimensions of the reactor a three-dimensional geometry is created. For meshing, tetrahe-

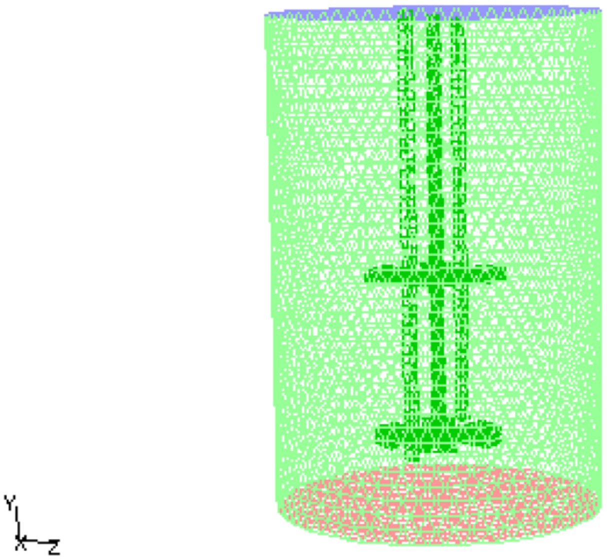

Fig. 2. Three-dimensional geometry of reactor with meshing created in Gambit (front view).

dral meshes are used for the reactor. As the whole study is based on the reaction in the reactor, the following is a Gambit diagram of a 3-D reactor, which has an impeller with two sets of blades on it as shown in Fig. 2. Using Fluent the created geometry by Gambit can be read and simulation is done. For analysis of the results the contour plots and vector plots are analyzed. Residual plot is observed continuously during simulation as accuracy and convergence are very important during simulation. Current study involves two things: one is to create three-dimensional geometry in Gambit along with the meshing, and second is to know the general procedure to simulate this reactor. Analysis of the result is also important to know the flow field and pressure distribution.

Convergence and accuracy are important during the simulation solution process. This can be seen by the residual plots in Fig. 3. A general convergence criterion is 10^{-4} and more than that is desirable. If not, then we have to change the solution parameters and sometimes the solution method also. Currently, modified *k*-epsilon method and water as the fluid medium is used for the hydrodynamic study of the reactor. Here, only one phase is considered for the study.

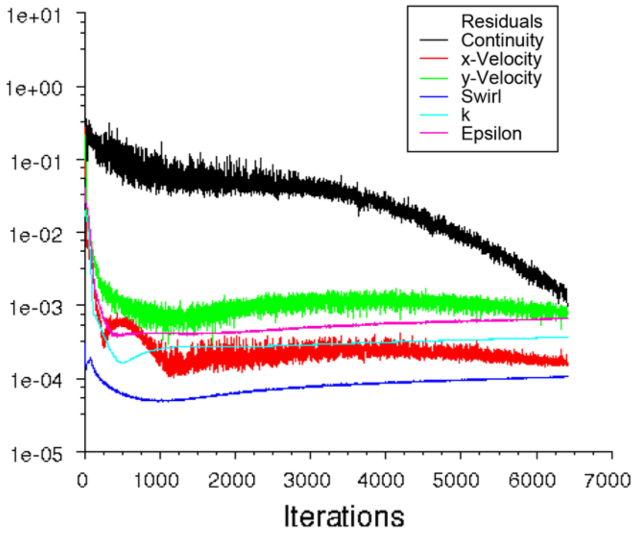

Fig. 3. Residuals plot for *k*-epsilon solver method.

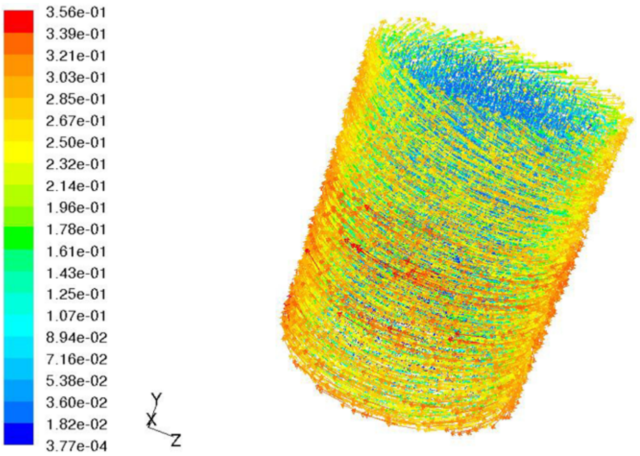

Fig. 4. Plot of velocity vector colored by velocity magnitude (m/s) (front view).

Results of residual plot for *k*-epsilon solver method are shown in Fig. 3. It shows the residual plots with desirable convergence criteria for the most of the solution parameters present in the reactor to achieve better efficiency. It is observed that the x, y and z velocity component reaches a stable value after 6500 iterations.

Fig. 4 shows the velocity magnitude plot indicated by the velocity vectors, and turbulent flow is observed inside our batch reactor. This turbulence only ensures the proper mixing and the uniformity of temperature and reactants throughout the reactor. This distribution of the absolute pressure and contour of turbulence kinetic energy can also be seen from Figs. 5 and 6. Colors indicated in this figure have the same significance as that of Fig. 4.

2. Effect of Stirring Speed on Conversion

It has been observed that the conversion increased steeply at first, by increased stirring speed. Slowly the rate of increase decreased till a stage came, when the conversion no longer increased with in-

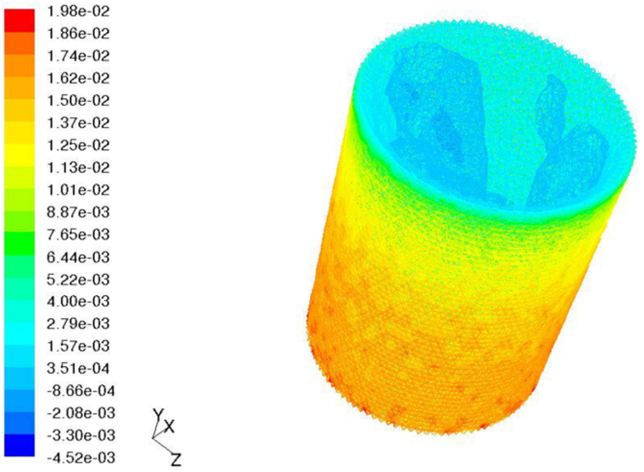

Fig. 5. Iso-surface profile of absolute pressure (Pascal) along the reactor (front view).

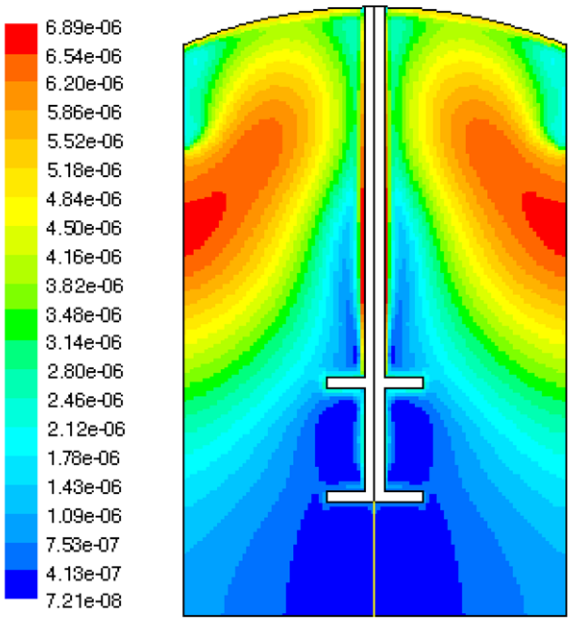

Fig. 6. 2D contour of turbulence kinetic energy for the reactor.

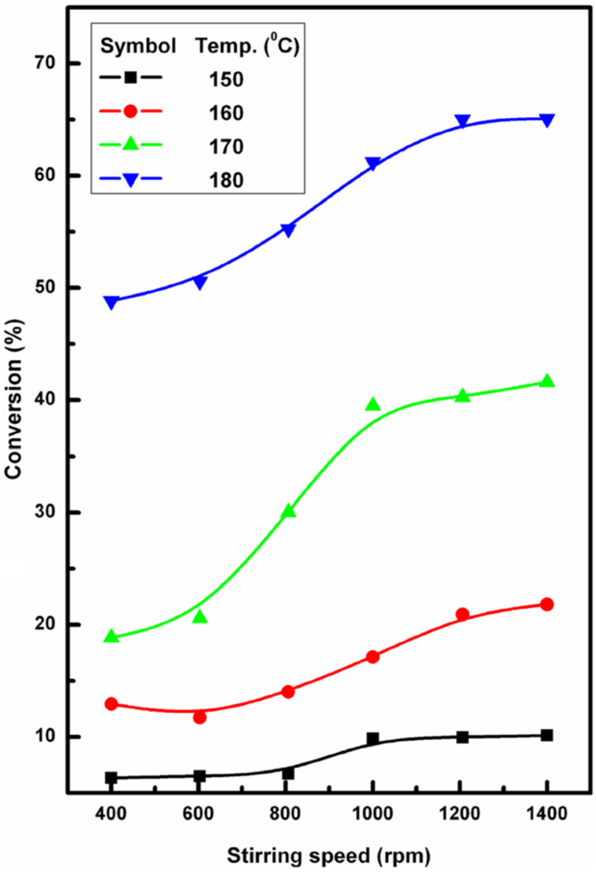

Fig. 7. Effect of stirring speed on conversion at different temperatures.

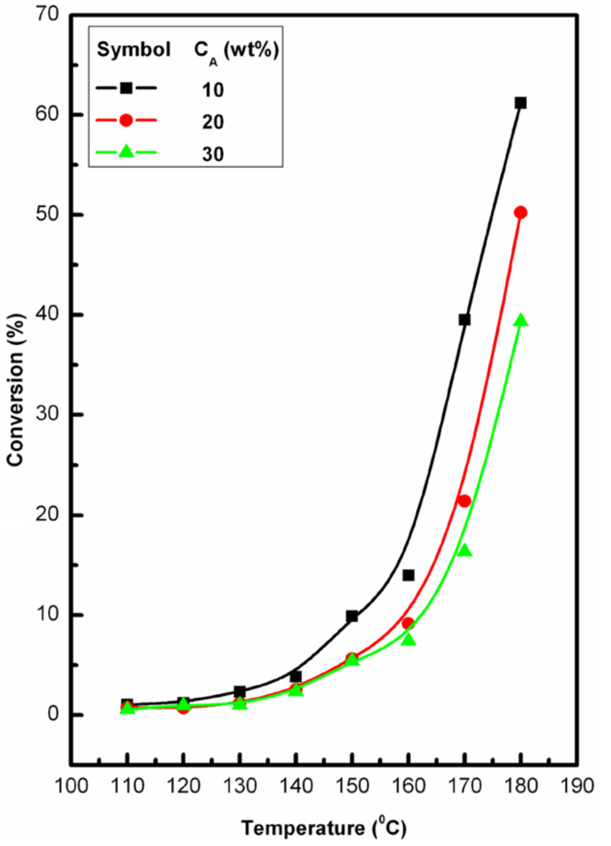

Fig. 8. Effect of temperature on conversion at different concentrations.

creased stirring speed. This means that the optimum point of conversion at that temperature was reached and no further conversion was possible by increasing the stirring speed. From Fig. 7 it is clear that, if temperature and initial concentration are kept constant at 150 °C and 10 wt% of urea, respectively, with the increase of stirring speed from 400 rpm to 1,400 rpm the conversion increased from 6.35% to 10.12%, respectively. Similarly, at constant temperature and initial concentration of 160 °C and 10%, respectively, the conversion increased from 12.93% to 21.81%; at constant temperature and initial concentration of 170 °C and 10%, respectively, the conversion increased from 18.86% to 41.57%, and at constant temperature and initial concentration of 180 °C and 10%, respectively, the conversion increased from 48.84% to 65.07% with the increase in stirring speed from 400 rpm to 1,400 rpm. The reason is that as stirring speed increased, the rate of mass transfer increased, which in turn favors the formation of ammonia and carbon dioxide and thereby decreases the unreacted urea in the reactor.

3. Effect of Temperature on Conversion

Experimental results indicate that the temperature of reaction for production of ammonia from urea is the most important parameter. It can be seen from the Fig. 8 that the conversion is a function of temperature, increasingb exponentially with increase in temperature. For 10 wt% of urea solution the conversion increased from 1.03% to 61.2% when temperature increased from 110 °C to 180 °C in 10 °C intervals. Similarly, a trend was observed for 20, and 30% feed solution and the conversions are 50.24% and 39.35%, respectively at 180 °C. It was observed that initially conversion was slower at lower temperature and it became rapid at around 130 °C. At this temperature the production of ammonia was higher than that at lower temperature. This may be due to the fact that as the overall reaction carried out in the reactor is endothermic, the release of ammonia and carbon dioxide requires heat and quickly stops when the supply of heat is withdrawn.

4. Effect of Initial Concentration on Conversion

The conversion was slightly affected by the initial concentration of urea that was fed to the reactor. It can be seen from Fig. 9 that by an increase in initial concentration of urea the conversion decreased marginally. The temperature varied from 150 °C to 180 °C for each initial feed concentration solution. Keeping temperature constant at 180 °C, the conversion decreased from 61.2% to 39.87% when concentration of initial feed solution varied from 10 to 30 wt% of urea. Similarly, for 170 °C, 160 °C, and 150 °C the equilibrium conversion decreased from 39.49% to 16.35%, 14% to 7.42%, and 9.87% to 5.44%, respectively, when the initial concentration of urea increased from 10% to 30% by wt of urea. Higher wt% of urea possesses less reaction pressure comparison to the lower wt% urea solution. Hence, during the decomposition the solution, having less urea content, will give more ammonia, carbon dioxide and water vapor as product from the reactor.

CONCLUSIONS

It can be concluded that the initial reaction rate is slower and it

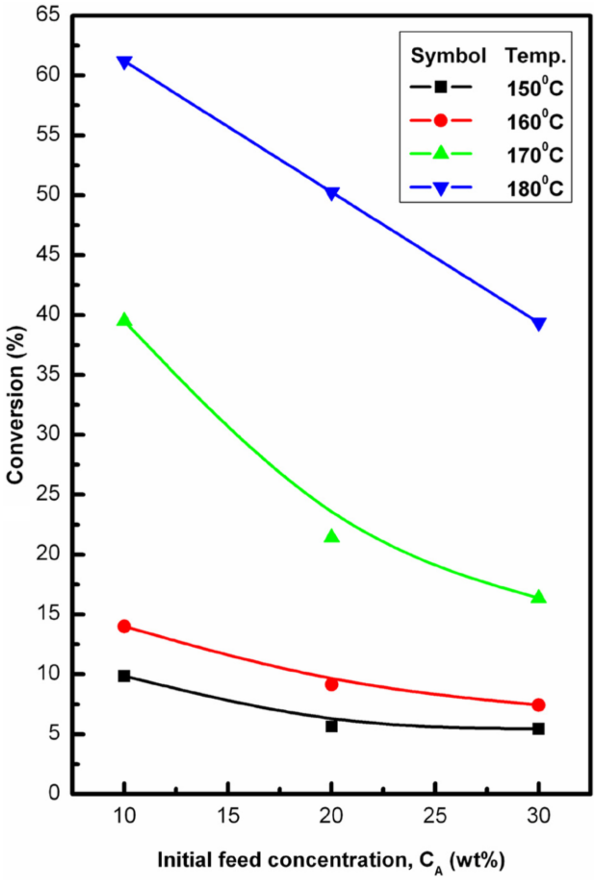

Fig. 9. Effect of initial feed concentration on conversion at different temperatures.

becomes rapid at around 130 °C. At this temperature the production of ammonia is higher than that at lower temperatures. Furthermore, the stirring speed shows a positive effect on the conversion increasing steeply at first, with increased in stirring speed. Hydrodynamics of reactor study was done with Fluent software. Flow pattern and pressure distribution were studied inside the reactor, which is the same as that of the theoretical study, and similar work is in progress for increasing the conversion of urea hydrolysis. The initial result implies that the hydrolysis of urea for manufacturing ammonia is a suitable technique for safe utilization in a coal fired thermal power plant.

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