



## Kinetic studies on hydrolysis of urea in a semi-batch reactor at atmospheric pressure for safe use of ammonia in a power plant for flue gas conditioning

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### ABSTRACT

With growing industrialization in power sector, air is being polluted with a host of substances—most conspicuously with suspended particulate matter emanating from coal-fired thermal power plants. Flue gas conditioning, especially in such power plants, requires in situ generation of ammonia. In the present paper, experiments for kinetic study of hydrolysis of urea have been conducted using a borosil glass reactor, first without stirring followed by with stirring. The study reveals that conversion increases exponentially with an increase in temperature and feed concentration. Furthermore, the effect of stirring speed, temperature and concentration on conversion has been studied. Using collision theory, temperature dependency of forward rate constant has been developed from which activation energy of the reaction and the frequency factors have been calculated. It has been observed that the forward rate constant increases with an increase in temperature. The activation energy and frequency factor with stirring has been found to be 59.85 kJ/mol and  $3.9 \times 10^6 \text{ min}^{-1}$  respectively with correlation coefficient and standard deviation being 0.98% and  $\pm 0.1\%$  in that order.

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### 1. Introduction

Suspended particulate matter constitutes one of the major air pollutants and causes many respiratory diseases including the dreaded silicosis. Vehicular traffic, coal-fired thermal power stations and cement industry are the major culprits which contribute maximum suspended particulate matter in the ambient air. The flue gas from a coal-fired thermal power station contains fine particles of ash with sizes varying from 80  $\mu\text{m}$  to less than 5  $\mu\text{m}$ . Electrostatic precipitators are used to knock down the ash particles from the hot flue gas through a high voltage charge creating a transverse motion of the particles and getting attached to the collecting electrode [1]. Electrostatic precipitators are designed to maintain suspended particulate matter concentration within permissible limits specified by the State Pollution Control Boards, which are normally less than 115  $\text{mg}/\text{nm}^3$ ; in majority of the states in India. However, in many power stations, the concentration of the suspended particulate matter exceeds the specified limits.

Ammonia has long been known to be useful in the treatment of flue/tail/stack gases from industrial furnaces, incinerators and the electric power generation industry and also for conditioning of the flue gas by which an improved collection and removal of particulate matter (fly ash) is obtained [2]. In the earlier days, aqueous or anhydrous ammonia was supplied as feedstock for selective catalytic reduction and selective non-catalytic reduction. Unfortunately, anhydrous ammonia as well as aqueous ammonia in strengths above 20%, present significant danger to human health and are classified by Occupational Safety and Health Administration as hazardous chemicals. Their transportation, storage and handling triggers serious safety and environmental regulatory requirements for risk management plans, accident prevention programs, emergency response plans and release analysis. Aqueous ammonia solutions with low concentration present lower health and safety risks, but their usage results in a substantial increase in operating costs of selective catalytic reduction and selective non-catalytic reduction systems [3–5].

Many industrial plants require the supply of large quantities of ammonia, which must be frequently transported through and stored in populated areas. But 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

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## Nomenclature

### Notation

$A$	frequency factor, $\text{min}^{-1}$
$C_A$	concentration of urea, wt%
$E$	activation energy, $\text{kJ/mol}$
$\Delta H$	change in enthalpy, $\text{kcal/mol}$
$K$	forward rate constant, $\text{min}^{-1}$
$N$	stirring speed, rpm
$n$	order of the forward reaction, dimension less
$R$	ideal law gas constant, $\text{kJ}/(\text{kg mol K})$
$r_A$	rate of reaction of urea
$RI$	refractive index, dimension less
$T$	temperature, $^{\circ}\text{C}$
$t$	time, min

### Subscripts

1	reaction in Eq. (1)
2	reaction in Eq. (2)
over	overall reaction in Eq. (3)
A	urea

plans, accident prevention programs, emergency response plans and release analysis. An alternative approach to ammonia supply suggested in the late eighties includes using urea feedstock to generate ammonia on site. Urea is an environmentally safe material used primarily as fertilizer. It has zero pestilential impact and can be safely transported, stored and handled at the plant site without special precautions. It has been determined that using urea thermal hydrolysis is the preferred process for converting urea/water solution into a gaseous mixture containing ammonia, carbon dioxide and water vapor [6]. Therefore, in situ generation of ammonia is essential for flue gas conditioning, especially in coal-fired thermal power plants.

Literature survey reveals that only few works have been reported in the journal for urea hydrolysis. Most of the urea hydrolysis is patent protected and nothing much about the detailed

process is available in the literature. Brooks et al. [7] studied the processes for quantitative conversion of urea to ammonia from molten urea and a separate supply of water in the form of steam into a reactor. Jacob and Stiermann [8] reported production of ammonia from urea pellets in an ammonia reactor, urea pellets evaporator and a hydrolytic catalytic converter. The urea is converted into a gas mixture containing ammonia and isocyanic acid by means of a urea evaporation device. Macarthur et al. [9] studied the method of controlling the amount of soluble and/or insoluble contaminants in a liquid phase reaction mixture containing urea in a reaction vessel for ammonia production. Spencer and Peters [10] studied the process to provide a pressurized gas stream useful for removing nitrogen oxides from a combustion gas stream by hydrolyzing urea in an aqueous solution in a closed reactor. Glesmann et al. [11] reported the process and apparatus for on-site production of ammonia from aqueous urea for conditioning of combustion flue gases. The hydrolyser is divided into a plurality of stages by baffles to enhance hydrolysis and stripping. Cooper and Spencer [12] studied the method of production of gaseous ammonia from aqueous urea or mixture of urea containing biuret, or ammonium carbamate. Wojchowski [13] studied the method for decomposition of urea and urea polymerization by products into ammonia by direct blending with steam or hot air at a temperature of about  $149^{\circ}\text{C}$ . Hofmann and Rusch [14] studied the process for converting urea into ammonia with introducing energy into the reaction chamber by irradiating with microwaves. Lagana [15] studied the hydrolysis of aqueous urea feed in a heated and pressurized reactor vessel, and that uses steam to strip the ammonia and carbon dioxide product gases.

However all the work cited above is patented. None of the authors has disclosed the kinetic data for hydrolysis of urea. In these work kinetic studies on hydrolysis of urea to produce a gaseous mixture of ammonia, carbon dioxide and water vapour has been studied in a semi-batch reactor (glass reactor) at atmospheric pressure, without using any catalyst. Complete information about the rate constants and activation energy of the involved reactions is provided.

The basic chemistry employed in the process is the reverse of that employed in industrial production of urea from ammonia and

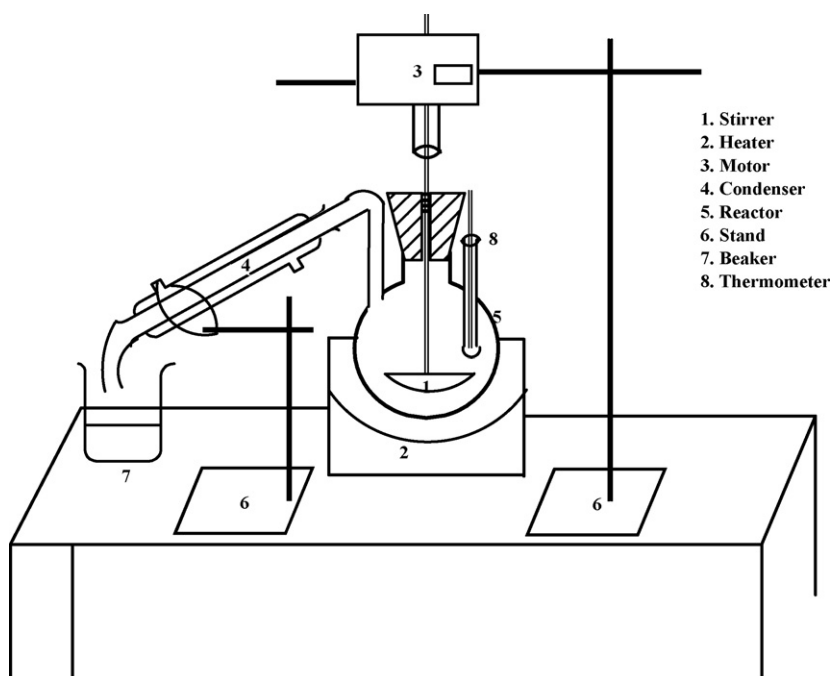
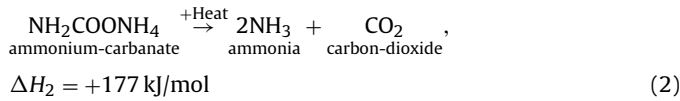
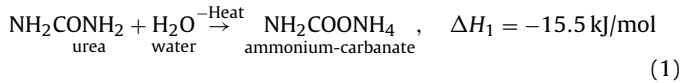
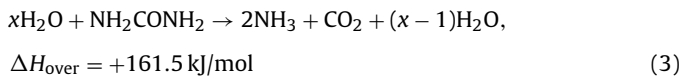


Fig. 1. Schematic diagram of experimental set up for urea hydrolysis (glass reactor).

carbon dioxide and employs two reaction steps as follows [16–18]:



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:



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.

## 2. Experimental set up and technique

The schematic diagram of the experimental set up is shown in Fig. 1. The experimental set up consists of a borosil glass reactor of

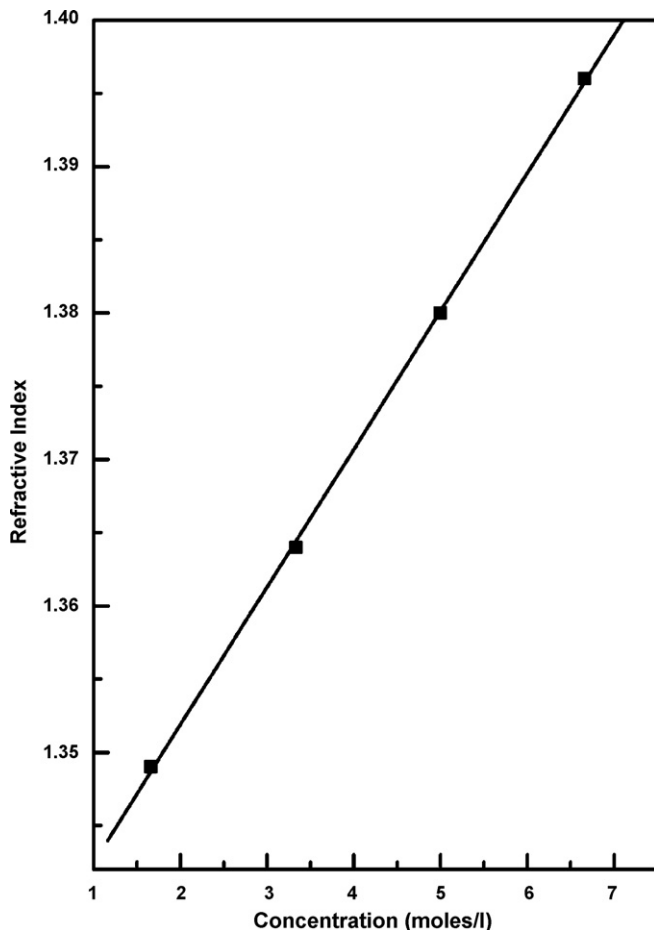


Fig. 2. Calibration plot for urea solution.

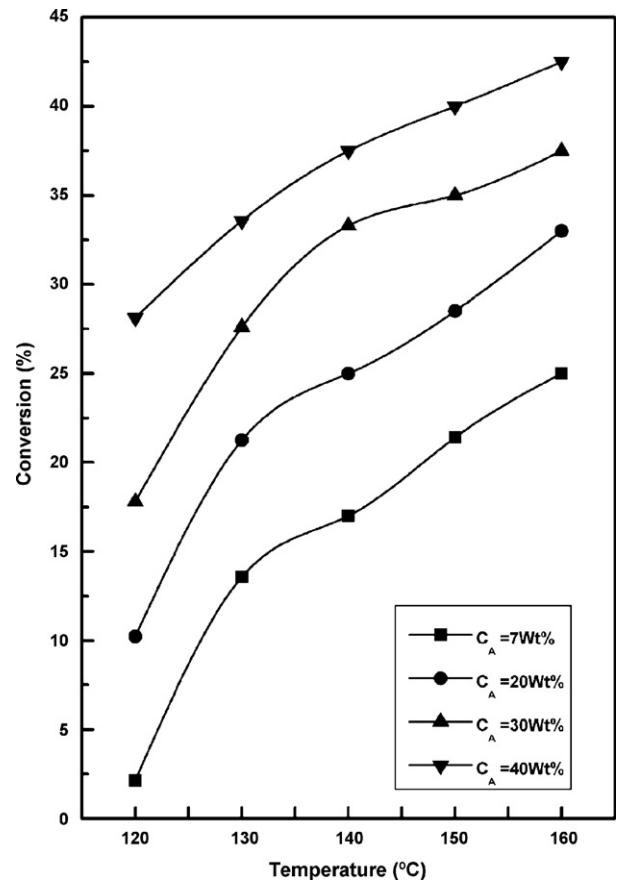


Fig. 3. Effect of temperature on conversion at different urea feed solution.

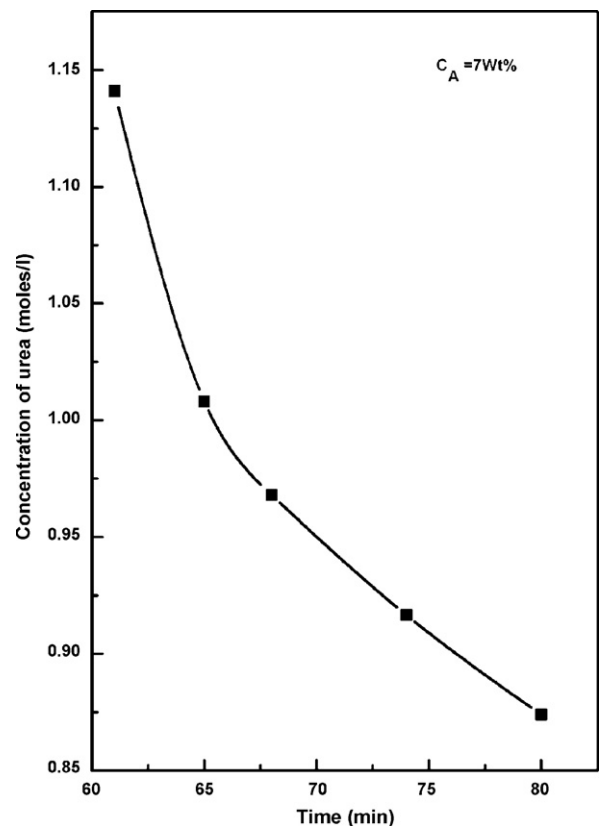


Fig. 4. Effect of time on concentration for 7 wt% feed solution.

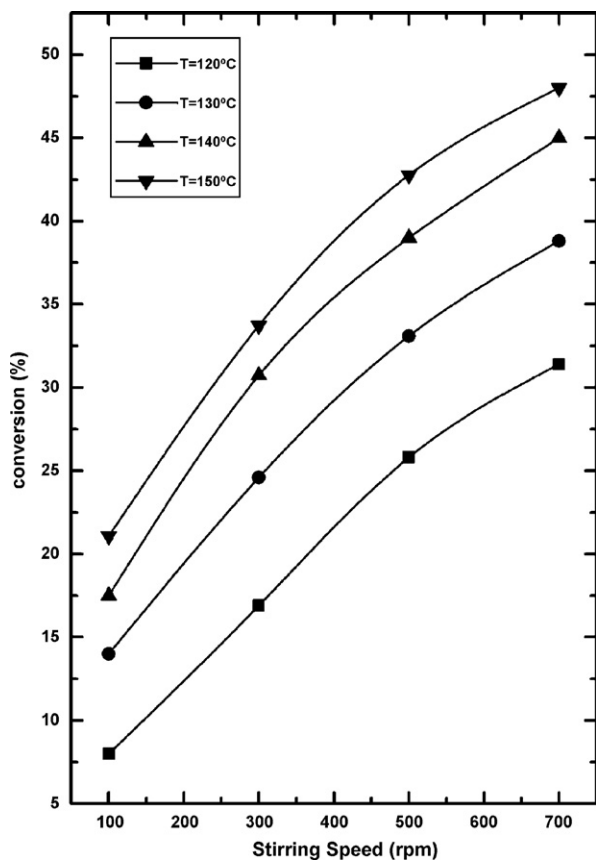


Fig. 5. Effect of stirring speed on conversion at 10 wt% urea feed solution.

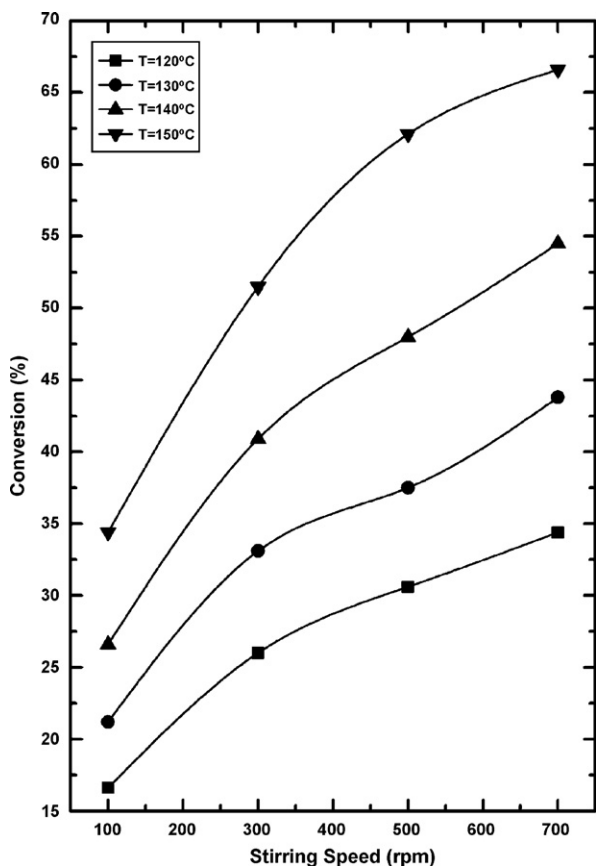


Fig. 6. Effect of stirring speed on conversion at 40 wt% urea feed solution.

capacity 1000 cc. The reactor comprises three openings. One is for inserting 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 (RQ – 120 M both with stirring shaft and horizontal retort rod) is mounted on the vertical retort rod at the square elbow and tightened by a black key knob. Glass is a vital element of composition for the stirrer shaft and for the stirrer, usually Teflon is recommended. A significant amount of space is occupied by or set aside for the reactor and it is in congruence with the electric heater of capacity 1000 kW and the heater is connected to 220 V A.C. supply. The outlet of the reactor is attached to a condenser to condense the gaseous product from the reactor where tap water comes in handy for the purpose of condensation.

First urea solution of different concentration (7 wt%, 20 wt%, 30 wt%, and 40 wt%) was prepared. In each case, the volume of the solution was taken as 500 ml. Then reactor is laden with a solution of the particular concentration. First the experiments are performed 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 the phenomenon of the evaporation of water comes into the picture. Then the decomposition of urea takes place slowly at around 120 °C. As the reaction proceeds, 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 gets condensed where cold water was circulated and the product was collected in a beaker. The time required to reach 120 °C was noted.

Then the content of the reactor was taken out and its volume was measured after it gets cold. An additional amount of water was

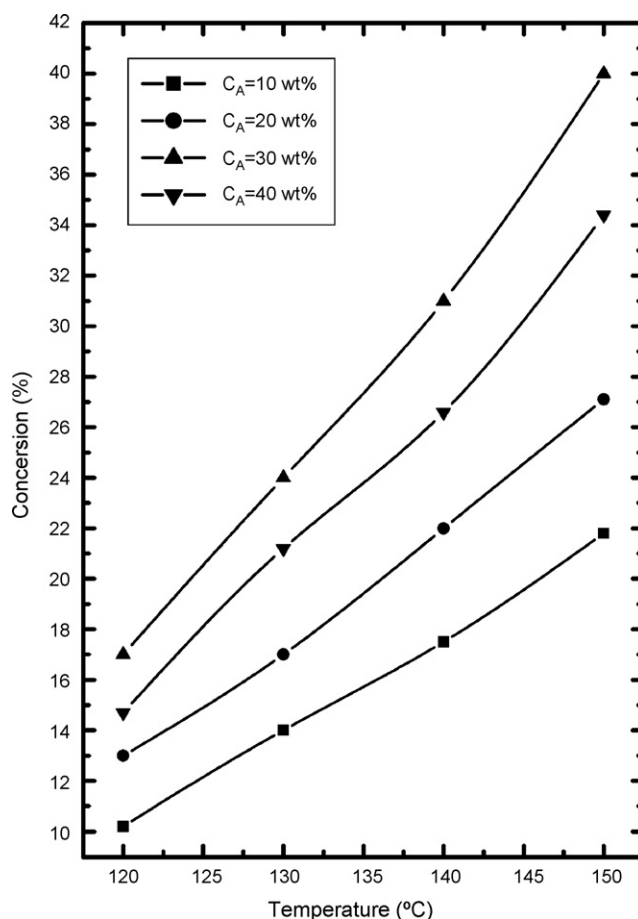


Fig. 7. Effect of temperature on conversion at a stirring speed of 100 rpm.

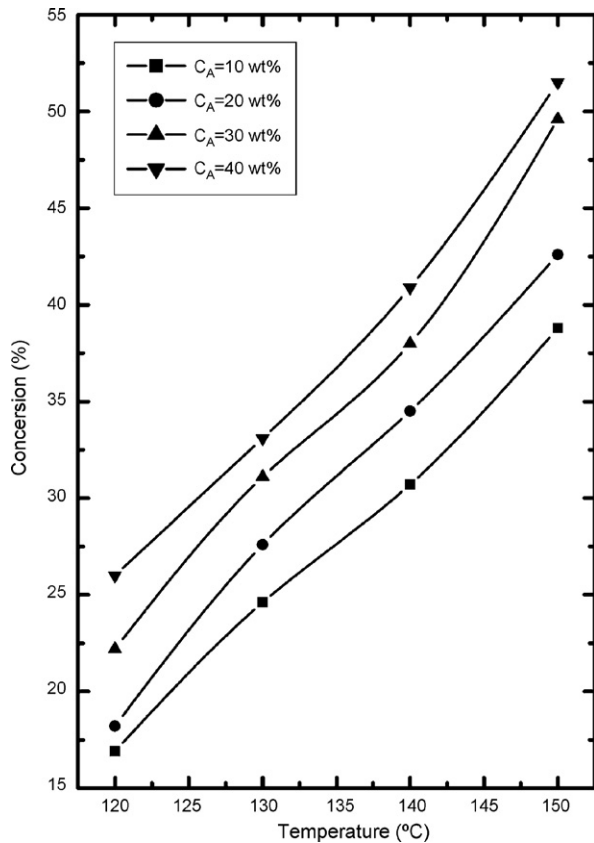


Fig. 8. Effect of temperature on conversion at a stirring speed of 300 rpm.

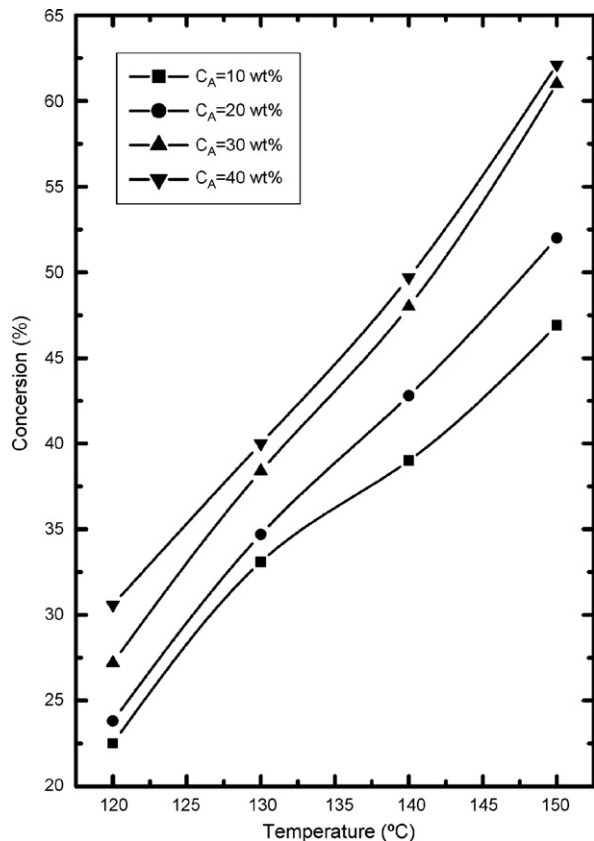


Fig. 9. Effect of temperature on conversion at a stirring speed of 500 rpm.

added to the reactor content to make the volume equal to the initial volume of the solution and its refractive index was determined by refractometer. The concentration of the reactor content was determined from the calibration chart obtained previously. Same procedure was repeated for other concentration (20 wt%, 30 wt% and 40 wt%) and temperatures (120 °C, 130 °C, 140 °C, 150 °C and 160 °C). Then by comparing the initial concentration and final concentration, the conversion was found out. Finally the rate of the reaction was found out from the slope of the time Vs concentration data. A graph was plotted between  $\ln(C_A)$  and  $\ln(r_A)$ . The slope and the intercept renders the value of order of the reaction and rate constant respectively. Similarly, experiments were conducted with different stirring speeds of 100 rpm, 300 rpm, 500 rpm and 700 rpm and the above-mentioned procedure is repeated for the determination of conversion.

### 3. Results and discussion

#### 3.1. Without stirring

Experiments have been extensively carried out for hydrolysis of urea at atmospheric pressure in a semi-batch reactor at different temperature and concentration and kinetic studies have been done both for with and without stirring. Distilled water is used for the calibration of refractometer. Refractive index of distilled water is 1.333. Hence taking distilled water as standard the refractive index of urea solution of different concentration has been measured. The calibration plot of urea solution is shown in Fig. 2. A calibration plot was obtained by measuring the refractive index of known concentration of urea solution. It is observed that with increase in concentration the refractive index increases. The unreacted urea solution from the reactor was analyzed by refractometer

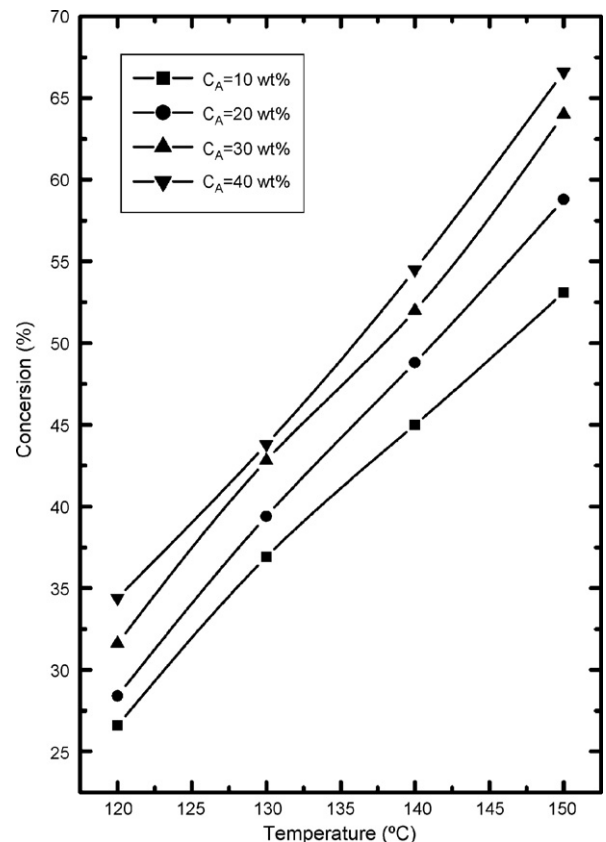


Fig. 10. Effect of temperature on conversion at a stirring speed of 700 rpm.

and its refractive index was measured. Then from the calibration plot the concentration of unreacted urea solution was measured.

### 3.1.1. Effect of temperature on conversion

It can be seen from Fig. 3 that the conversion is function of temperature for the case of without stirring. It increases exponentially with an increase in temperature owing to overall reaction of hydrolysis of urea to form ammonia and carbon dioxide is endothermic in nature. For 7 wt% urea solution the conversion increases from 2% to 25% when temperature increases from 120 °C to 160 °C in 10 °C interval. Similarly for 20 wt%, 30 wt% and 40 wt% feed solution the conversion are 32%, 38% and 42% respectively at 160 °C. It can be seen from Fig. 4 that with increases in initial concentration of urea the conversion increases. For each initial concentration the temperature was varied from 120 °C to 160 °C. Keeping temperature constant at 120 °C as the concentration increases from 7 wt% to 40 wt%, the conversion increases from 2% to 28%. This is due to the fact that more wt% urea has less access water then less wt% urea.

### 3.1.2. Effect of reaction time on concentration

From the concentration time data a kinetic study has been done. It is observed that the concentration decreases with time. For 7 wt% initial concentrations, the concentration decreases from 1.14 mol/l to 0.875 mol/l when time increases from 60 min to 80 min. This trend is shown by Fig. 4. More time requirement indicates that less wt% solution is less energy conserving. The effect of the rate on concentration at a fixed temperature has been observed and it is found that the order of the forward reaction is less than one. Further it is noticed that with increase in temperature from 120 °C to 150 °C the forward rate constant increases.

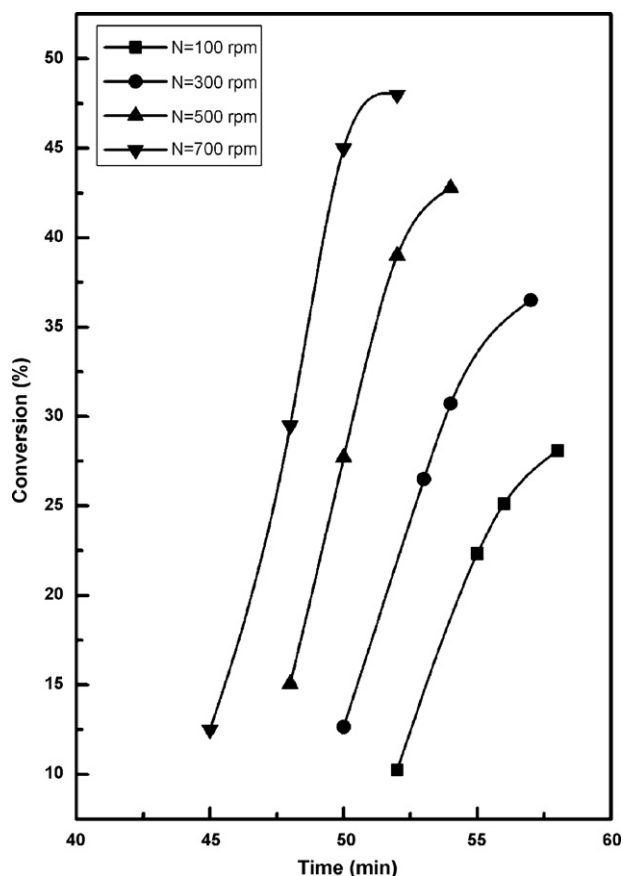


Fig. 11. Effect of time on conversion for 10 wt% urea feed solution.

### 3.2. With stirring

Experiments have been conducted by putting a stirring device inside the reactor for the hydrolysis reaction of urea and kinetic studies have been performed. The experiments were conducted at different concentration (10 wt%, 20 wt%, 30 wt% and 40 wt%), stirring speeds (100 rpm, 300 rpm, 500 rpm and 700 rpm) and temperatures (120 °C, 130 °C, 140 °C, 150 °C). After measuring the concentration of unreacted urea solution, the conversion was calculated by comparing with the initial concentration. Then from the concentration and time data the kinetic studies have been done.

#### 3.2.1. Effect of stirring speed on conversion

It has been observed that the conversion increases with increase in stirring speed. Further the conversion is more in case of higher initial concentration and at higher stirring speed. From Fig. 5 it is clear that, if temperature and initial concentration kept constant at 120 °C and 10% respectively, with the increase of stirring speed from 100 rpm to 700 rpm the conversion increases from 5% to 33% respectively. Similarly at constant temperature and initial concentration of 150 °C and 10% respectively, the conversion increases from 30% to 49% with the increase in stirring speed from 100 rpm to 700 rpm. The reason is due to the fact that as stirring speed increases, the rate of mass transfer increases which in turn increases the formation of ammonia and carbon dioxide, thereby decreases the unreacted urea in the reactor. Similarly 40% initial concentration a maximum conversion 66% is obtained at 150 °C. This is clearly evident from Fig. 6.

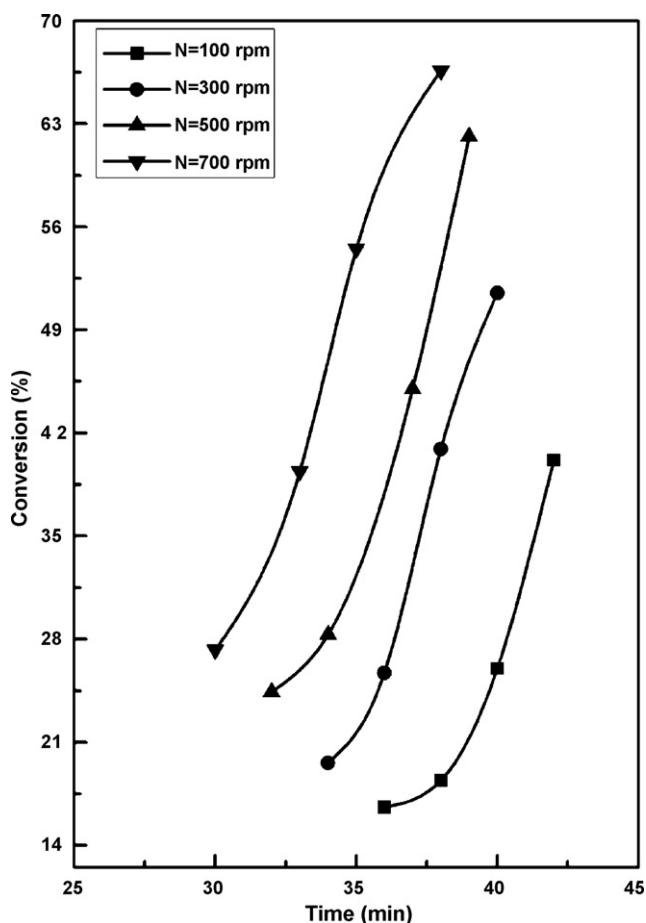


Fig. 12. Effect of time on conversion for 40 wt% urea feed solution.



### 3.2.2. Effect of temperature on conversion

Figs. 7–10 illustrate the effect of temperature on conversion at different stirring speeds. In Fig. 7, the stirring speed is kept constant at 100 rpm and the temperature is varied from 120 °C to 150 °C for a 10 °C interval. It is observed that at 40 wt% initial concentration, the conversion increases from 16% to 40% with an increase in temperature from 120 °C to 150 °C when stirring speed is 100 rpm because the forward reaction is endothermic in nature. The effect of temperature on conversion at different concentrations and at 700 rpm can be seen from Fig. 10. Here the stirring speed is kept constant and the temperature is varied from 120 °C to 150 °C for a 10 °C interval. For 10 wt%, the conversion increases exponentially from 26% to 53% when temperature increases from 120 °C to 150 °C for a 10 °C interval. The corresponding range of variation of conversion is 34% to 66% for the same range of temperature variation and at same stirring speed of 700 rpm. Further, if temperature remains constant at 120 °C, with an increase in stirring speed from 100 rpm to 700 rpm, the conversion increases from 10% to 20% at 10 wt% initial concentration. Similarly for other initial concentrations, the conversion increases with an increase in stirring speed even though the temperature remains constant. This is due to the fact that stirring enhances the rate of heat transfer. Hence, even though the temperature remains constant for higher initial concentrations, the conversion increases without providing any extra heat. Similarly, Figs. 8 and 9 illustrate the above facts for 300 rpm and 500 rpm respectively.

### 3.2.3. Effect of reaction time on conversion

Effect of reaction time on conversion plot shows how the conversion varies with time. As time increases the conversion increases. However the time required is less for higher initial concentration to reach a specified temperature, but for lower initial concentration it is the reverse. Figs. 11 and 12 show this trend. The obvious reason for less time requirement for higher initial concentration is less access water. Once water gets evaporated immediately, decomposition of ammonium carbamate takes place to form ammonia and carbon dioxide. Further with increase in stirring speed at a fixed initial concentration time required to reach a particular concentration is less.

For 10 wt% initial concentration the time required to reach 120 °C is 52 min and the corresponding conversion is 10%. This happens at 100 rpm. For 700 rpm the time required is 45 min when all other variables remain same and the corresponding conversion is 12%. This trend is shown by Fig. 11. Further as time increases the conversion increases as shown by Fig. 11 which is for 10 wt%. If we go on increasing the initial concentration from 10 wt% to 40 wt% the time required also decreases from 52 min to 36 min at a stirring speed of 100 rpm. This reduction of time is energy saving. In other words more wt% urea leads to more energy saving. From Fig. 12 it is clear that with increase in time the conversion increases. For 40 wt% urea solution the conversion increases from 27% to 66.6% as time increases from 30 min to 38 min at a stirring speed of 700 rpm.

### 3.2.4. Effect of reaction time on concentration

Figs. 13 and 14 depict the effect of time on concentration. With passage of time, more and more products i.e. a mixture of ammonia

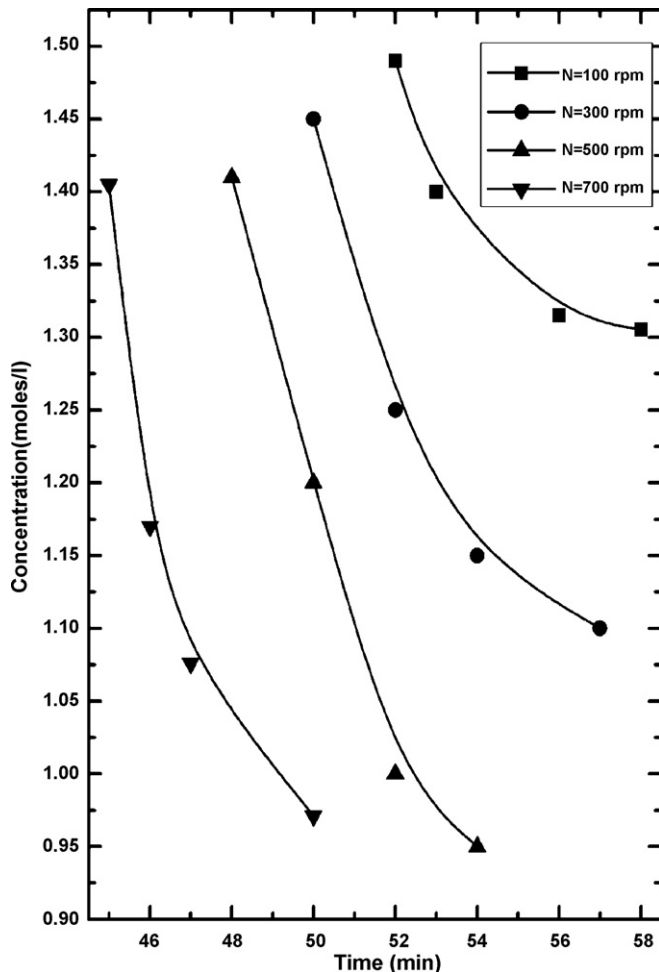


Fig. 13. Effect of time on concentration for 10 wt% urea feed solution.

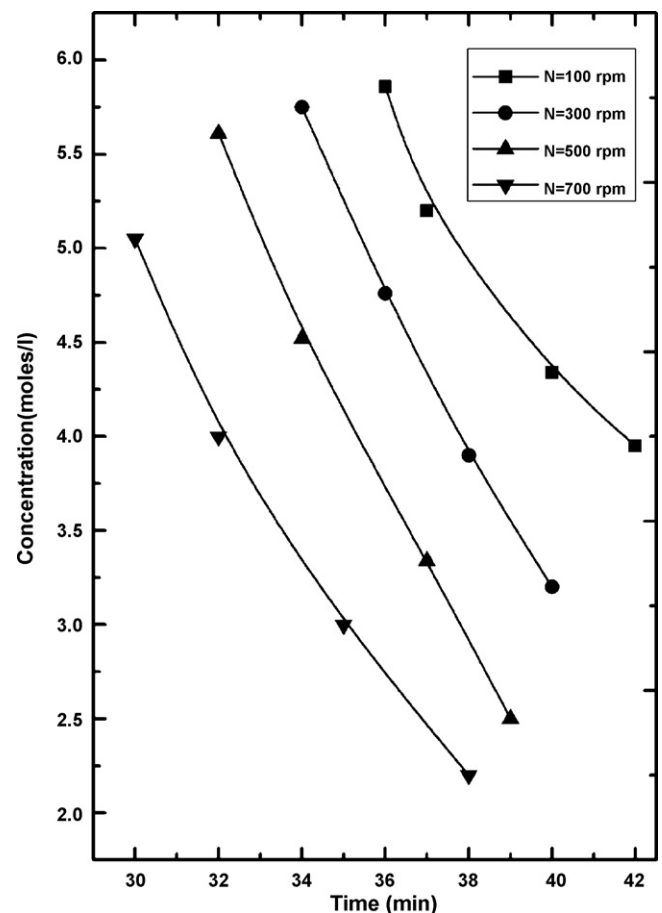


Fig. 14. Effect of time on concentration for 40 wt% urea feed solution.

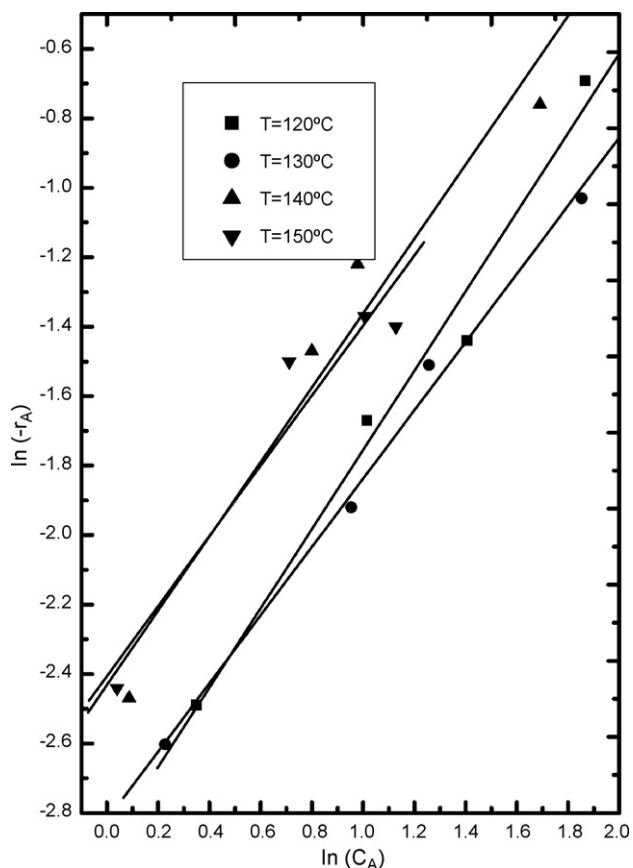


Fig. 15. Effect of concentration on reaction rate at different temperature.

carbon dioxide and water vapors are formed and hence less unreacted urea is left in the reactor. Further it has been observed that with increase in initial concentration the time required is less which leads to energy saving. In other words, higher wt% urea solution requires less time to achieve a particular temperature limit. From the above-mentioned figures, it is clear that the time required for 40 wt% solution to reach at 120 °C is much less than that of 10 wt% solution. Hence with increase in time, the concentration decreases exponentially. Fig. 13 indicates the concentration decreases from 1.5 mol/l to 1.3 mol/l as time increases from 52 min to 57 min for 10 wt% initial concentration and at a stirring speed of 100 rpm. The similar trend can be noticed from Fig. 14 but at different initial concentration 40 wt%. From the concentration versus time data the forward rate constant was determined.

The effect of rate on concentration at a fixed temperature is shown in Fig. 15. As the time increased, the concentration decreased, and it was highest in the case of higher temperature. From Fig. 8, it is observed that the slope of the plot is approximately equal to 1. This indicates that the forward reaction is first-order. Moreover, the intercepts of Fig. 15 give the values of forward rate constant, which is a function of temperature. It can be seen from the figure that, as the temperature was increased from 120 °C to 150 °C, the forward rate constant increased from 0.055 min<sup>-1</sup> to 0.099 min<sup>-1</sup>. Table 1 lists the values of the rate constant with temperature. From the above results, it was concluded that the order of the forward reaction is close to 1 and that the rate constant increases with increasing temperature. Therefore, the temperature dependency of the forward rate constant was explained by Arrhenius theory. The rate equation can be written as:

$$-r_A = kC_A \quad (4)$$

Table 1  
Kinetic data for urea hydrolysis at atmospheric pressure.

Temperature (°C)	$k$ (min <sup>-1</sup> )	$n$	$n$ (average)	$R^2$
120	0.0553	0.97		0.98
130	0.0602	0.98	1	0.99
140	0.088	0.97		0.95
150	0.090	0.98		0.94

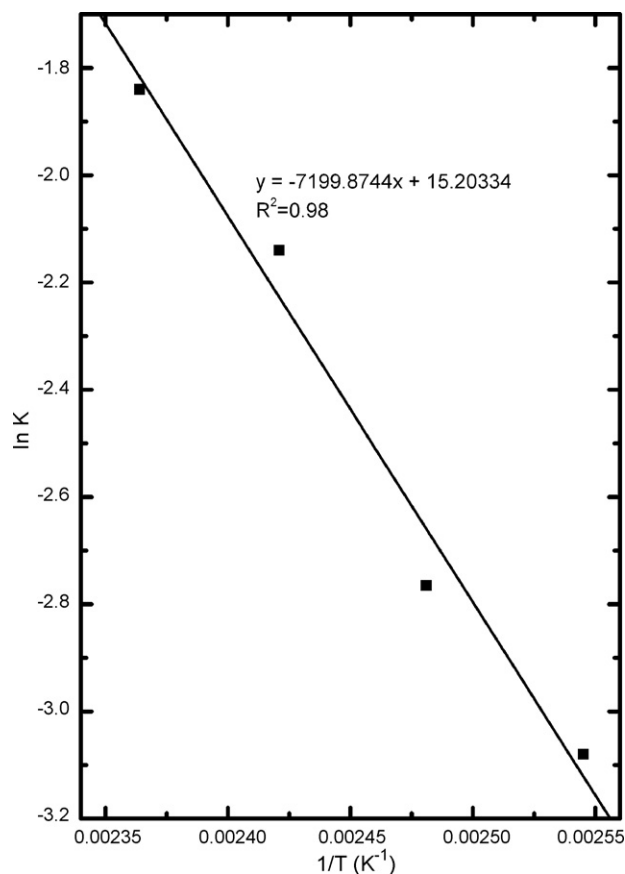


Fig. 16. Effect of temperature on rate constants.

where  $r_A$  is the rate of the reaction,  $k$  is the forward rate constant, and  $C_A$  is the concentration of reactant. According to Arrhenius theory, the temperature dependency of the forward rate constant can be written as:

$$k = Ae^{-E/RT} \quad (5)$$

where  $A$  is the frequency factor and  $E$  is the activation energy. From Fig. 16, the activation energy and frequency factor were determined to be 59.85 kJ/mol and  $3.9 \times 10^6$  min<sup>-1</sup> respectively. The  $R^2$  value and standard deviation were found to be 0.98% and  $\pm 0.1\%$  in that order.

#### 4. Conclusions

Hydrolysis of urea for manufacturing ammonia is a suitable technique for flue gas conditioning in coal-fired thermal power plants. Number of experiments was carried out in a semi-batch reactor without stirring and with stirring at atmospheric pressure taking different concentration of urea solution from 7 wt% to 40 wt% and kinetic study has been made. It has been observed that the conversion increases exponentially with increases in temperature.



Also the conversion increases with increase in feed concentration and stirring speed. A maximum conversion of 66.6% is obtainable at 150 °C with 40 wt% urea feed concentration and at a stirring speed of 700 rpm. The fractional order of reaction indicates that the conversion varies with the feed concentration. The temperature dependency of forward rate constant indicates that the forward rate constant increases with increases in temperature. The activation energy and frequency factor were found to 59.85 kJ/mol and  $3.9 \times 10^6 \text{ min}^{-1}$  be respectively.

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### References

- [1] I. Sengupta, Regulation of suspended particulate matter (SPM) in Indian coal-based thermal power plants: a static approach, *Energy Econ.* 29 (2007) 479–502.
- [2] E.B. Dismukes, Conditioning of fly ash with ammonia, *J. Air Pollut. Control Assess.* 25 (2) (1975) 152–615.
- [3] R. Salib, R. Keeth, Optimization of ammonia source for SCR applications, presented at the 2003 Mega Symposium, 2003.
- [4] H.W. Spencer, J. Peters, J. Fisher, U<sub>2</sub>A™ urea-to-ammonia “State of the technology”, presented at the 2001 Mega Symposium, 2001.
- [5] S. Bhattacharya, H.J. Peters, J. Fisher, H.W. Spencer, Urea-to-ammonia (U<sub>2</sub>A™) systems: operation and process chemistry, presented at the 2003 Mega Symposium, 2003.
- [6] M.R. Rahimpur, A non-ideal rate-based model for industrial urea thermal hydrolyser, *Chem. Eng. Process.* 43 (2004) 1299–1307.
- [7] B. Brooks, W.A. Jessup, B.W. Macarthur, W.B. Sheats, Process and apparatus for quantitatively converting urea to ammonia on demand, US Patent, No. US7,008,603B2, 2006.
- [8] E. Jacob, E. Stiermann, Device and method for producing ammonia from solid urea, US Patent, Application No. 2006/0045835A1, 2006.
- [9] B.W. Macarthur, W.A. Jessup, B. Brooks, Method for removing contaminants in urea hydrolysis reactor, European Patent, No. EP1,322,553B1, 2005.
- [10] H.W. Spencer, H.J. Peters, Method for controlling the production of ammonia from urea for NO<sub>x</sub> scrubbing, US Patent, No. US6,436,359B1, 2002.
- [11] R.T. Glesmann, J.J. Titus, JR., H.G. Walker, Process and apparatus for conditioning of combustion flue gases with ammonia from hydrolyzed urea, US Patent, Application No. 2003/0118494A1, 2003.
- [12] H.B.H. Cooper, H.W. Spencer, Methods for the production of ammonia from urea and/or biuret, and uses for NO<sub>x</sub> and/or particulate matter removal, US Patent, No. US 6,730,280 B2, 2004.
- [13] D.L. Wojichowski, Methods of converting urea to ammonia for SCR, SNCR and flue gas conditioning, US Patent, Application No. 2003/0211024A1, 2003.
- [14] L. Hofmann, K. Rusch, Process for converting urea into ammonia, US Patent, No. US6,471,927B2, 2002.
- [15] V. Lagana, S.N. S.p.A., Process for ammonia production through urea hydrolysis, US Patent, No. US5,985,224, 1999.
- [16] B. Claudel, E. Brousse, G. Shehadeh, Novel thermodynamic and kinetic investigation of ammonium carbamate decomposition into urea, *Thermochim. Acta* 102 (1986) 357–371.
- [17] A.M. Isla, A.H. Irazoqui, M.C. Genoud, Simulation of a urea synthesis reactor. Part 1. Thermodynamic framework, *Ind. Eng. Chem. Res.* 32 (1993) 2662–2670.
- [18] D.G. Jones, Method for converting urea to ammonia, US Patent, No. US5,827,490, 1998.