Experimental study on urea hydrolysis to ammonia for gas denitration in a continuous tank reactor

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ABSTRACT

In recent years, the risk of anhydrous and aqueous ammonia in transportation and storage has been a concern of power plants around the world [1], and the urea hydrolysis to ammonia is gradually used for feedstock preparation for gas denitration [2]. Compared with the traditional technology of urea thermal hydrolysis in the urea production plant [3], the mechanism and technological design of urea hydrolysis to ammonia are very different [4].

Another common method to convert urea into ammonia is pyrolysis, which requires high temperature (650 °C) for the decomposition of urea [5]. The pyrolysis method costs extra energy and expense to maintain the high temperature atmosphere, while the heat source in the hydrolysis technology is low grade steam in the power plant. Thus the urea hydrolysis is much cheaper and more convenient than urea pyrolysis to ammonia [6].

Several articles about hydrolysis of urea for production of ammonia are very detailed. Sahu et al. presented an equilibrium and kinetic study of urea hydrolysis in a batch reactor, and studied on the single and combined effects of operating parameters such as initial feed concentrations, temperature, time and stirring speed on the production of ammonia from urea [7,8]. Kenichi et al. updated values for some dissociation equilibrium constants and Henry's constants for urea hydrolysis system at temperature range of 100–205 °C [9]. Zheng et al. have carried out a theoretical analysis and built a simulation model of urea hydrolysis in power plant [10]. The published information in the literature about urea hydrolysis to ammonia was mainly conducted on a semi-batch or batch reactor. Sahu et al. have found the frequency factor and activation energy of urea hydrolysis to be 2.89 × 10^7 min^-1 and 73.6 kJ mol^-1 respectively in a semi-batch reactor [11,12]. Aoki et al. detected the parameters of urea thermal hydrolysis to be 3.753 × 10^7 min^-1 and 87.78 kJ mol^-1 in a batch reactor [13]. However, the hydrolysis reaction in the industrial continuous tank reactor is coupled with heat and mass transfer, and the process is different from which in the semi-batch or batch reactor.

The hydrolysis of urea is carried out in a system of NH₃–CO₂–H₂O–Urea mixtures which are non-ideal solutions. Raoult's law and Dalton's law were used to solve the equilibrium of solution when the concentrations of ammonia and carbon dioxide in the liquid solution were neglected [14]. Rahimpour has proposed a non-ideal rate-based model for thermal hydrolysis of urea based on extended UNIQUAC model, and the predicted data of the model were consistent with the plant data [15]. M. Bernardis et al. applied a modified UNIQUAC equation to calculate the non-ideality of liquid phase in the quaternary system, and simulated the operating data.
of hydrolysis equipment in different conditions [16].

Firstly in this work, the urea hydrolysis to ammonia in a continuous tank reactor was mechanistically modeled. The significance of the model was correcting the vapor and liquid non-ideality by fugacity coefficient and activity coefficient respectively. Then a pilot plant was established to simulate the transfer process in the industrial reactor, in order to obtain an apparent influence of transfer process. Finally, an industrial hydrolysis reactor of urea for production of ammonia was designed and the industrialized test was conducted.

2. Reaction mechanism and experimental setup

2.1. Reaction mechanism

The hydrolysis of urea to ammonia proceeds rapidly above a temperature of approximately 120 °C [17], the overall reaction is as follows:

\[ \text{NH}_2\text{CONH}_2 + \text{H}_2\text{O} \rightarrow 2\text{NH}_3 \uparrow + \text{CO}_2 \uparrow \quad (1) \]

In the continuous tank reactor, the urea solution is pumped into the bottom and the product gas is discharged from the top, as shown in Fig. 1. The pressure and gas-liquid interface keep unchanged. The steam heating by coil inside the reactor is provided at a controlled rate, without mixing with the urea solution. As the large holdup of liquid in the tank reactor, the mass and heat transfer is similar to the perfect mixing process, and the temperature and concentration are uniform distributed.

Ammonia is generated from urea by a hydrolysis reaction that yields a vapor phase mixture of ammonia, carbon dioxide, and water vapor, while the liquid phase is mixed of ammonia, carbon dioxide, water and urea. The vapor and liquid phase reach equilibrium at a certain temperature and pressure.

The phase equilibrium of solvents water can be described by the modified Lewis-Randall equation [18], as shown in Eq. (2):

\[ y_j \phi_j P = x_j \gamma_j \phi_j^1 \exp \left[ \left( P - P^\text{s} \right) \frac{V_j^f}{RT} \right] \quad (2) \]

where \( x_j \) (%) is the mole ratio of water in the liquid and \( y_j \) (%) is the mole ratio of water in the gas. \( \phi_j^1 \) is the fugacity coefficient of water in the gas, \( \gamma_j \) is the activity coefficient of saturated water. \( P \) denotes the reaction pressure, MPa. \( P^\text{s} \) is the saturated pressure of water, MPa. \( R \) denotes the gas constant, J mol\(^{-1}\) K\(^{-1}\). \( T \) is the reaction temperature, K.

Ammonia and carbon dioxide dissolved in the liquid are regarded as volatile solutes, and the phase equilibrium are described by the modified Henry equation [18], as shown in Eq. (3):

\[ y_j \phi_j P = x_j \gamma_j H_j \exp \left[ \left( P - P^\text{s} \right) \frac{V_j^f}{RT} \right] \quad (3) \]

where \( x_j \) (%) is the mole ratio of ammonia and carbon dioxide in the liquid, and \( y_j \) (%) is the mole ratio of ammonia and carbon dioxide in the gas. \( \phi_j \) is the fugacity coefficient of gas components and \( \gamma_j \) is the activity coefficient of ammonia and carbon dioxide in the liquid. \( H_j \)
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