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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, and the urea hydrolysis to ammonia using low-grade steam as heat source is gradually used for feedstock preparation in NOx reduction. In this paper, the urea hydrolysis to ammonia in a continuous tank reactor was mechanistically modeled, and a pilot plant was established to simulate the transfer process in the industrial reactor in order to obtain the scale-up rules of the process. The results of pilot test indicated that the reaction-diffusion criterion number was 0.036 when the operating temperature was 150 °C. The urea hydrolysis was a slow reaction in liquid and the ammonia production rate of reactor was dominated by kinetics. At last, the industrialized test was conducted and the ammonia production rates agreed well with the model predicted data, and the ammonia consumption of flue gas denitration in the selective catalytic reduction was satisfied. This study would provide a reference to the design and development of urea hydrolysis for gas denitration.

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1. Introduction

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 in the 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 NH_3–CO_2–H_2O–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

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Nomenclature

x_i	mole fraction of liquid phase component i, %
y_i, y_j	mole fraction of vapor phase component, %
P	operation pressure, MPa
p_i^S	saturated vapor pressure, MPa
T	operation temperature, K
T_l^S	saturation temperature of water in operation pressure, K
H_i	Henry's constant,$10^5 \cdot$Pa kg mol^{-1}
x_{ur}^0	feed concentration of urea solution,%
M_{ur}	molar mass of urea, g mol^{-1}
M_l	molar mass of water, g mol^{-1}
a,b	constants of PR state equation
a_{ij}	constant of PR state equation for mixture gas
b_i	PR constants of component i
V_g	volume of mixture gas, m^3
Δh_v	enthalpy rise of steam, kJ mol^{-1}
Δh_f	heat of chemical reaction, kJ mol^{-1}
Δh_l	enthalpy rise of residual steam, kJ mol^{-1}
Δh_{ur}	enthalpy rise of urea solution, kJ mol^{-1}
K	total coefficient of heat transfer, W m^{-2} K^{-1}
d_w	pipe thickness, m
d_i	internal diameter of tube, m
d_o	external diameter of tube, m
r_{ur}	reaction rate of urea solution, mol L^{-1} s^{-1}
c_{ur}	mole ratio of urea solution, mol L^{-1}
k	reaction rate constant, s^{-1}
n	reaction order
t	time, s
r_{NH3}	reaction rate of ammonia, mol L^{-1} s^{-1}
c_{NH3}	mole ratio of ammonia, mol L^{-1}
z	film thickness, m
M	Hatta number
$D_{NH3,\,l}$	diffusion coefficient of ammonia in the liquid, m^2 s^{-1}
$k_{NH3,\,l}$	mass transfer coefficient of ammonia in the liquid, m s^{-1}
$D_{CO2,\,l}$	diffusion coefficient of carbon dioxide in the liquid, m^2 s^{-1}
$k_{CO2,\,l}$	mass transfer coefficient of carbon dioxide in the liquid, m s^{-1}
c_{CO2}	mole ratio of carbon dioxide, mol L^{-1}
K_P	chemical equilibrium constant

Greek symbols

φ_i	fugacity coefficient of vapor phase component i
φ^S	fugacity coefficient of saturated water
γ_i	activity coefficient of component i in the liquid phase
α_o	heat transfer coefficient out the pipe, W m^{-2} K^{-1}
α_i	heat transfer coefficient in the pipe, W m^{-2} K^{-1}
λ_w	thermal conductivity of pipe, W m^{-1} K^{-1}
μ_l	viscosity of water, Pa s

Subscripts

I, j	component(NH_3,CO_2,H_2O)
l	water
v	steam
g	product gas
w	pipe

Superscripts

S	saturation state
C	Combinatorial
R	Residual
DH	Debye-Huckel

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 kinetic model which included the 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:

$$NH_2CONH_2+H_2O \leftrightarrow 2NH_3\uparrow+CO_2\uparrow \quad (1)$$

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):

$$y_l\phi_l P = x_l\gamma_l\phi_l^S P_l^S \exp\left[\left(P-P_l^S\right)V_l^S/(RT)\right] \quad (2)$$

where x_l (%) is the mole ratio of water in the liquid and y_l (%) is the mole ratio of water in the gas. φ_l is the fugacity coefficient of water in the gas and φ_l^S is the fugacity coefficient of saturated vapor. P denotes the reaction pressure, MPa. P_l^S is the saturated pressure of water, MPa. R denotes the gas constant, J$\cdot$mol$^{-1}\cdot$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):

$$y_j\phi_j P = x_j\gamma_j H_j \exp\left[\left(P-P_l^S\right)V_j^S/(RT)\right] \quad (3)$$

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. φ_j is the fugacity coefficient of gas components and γ_j is the activity coefficient of ammonia and carbon dioxide in the liquid. H_j

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