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Simultaneous Removal of Urea, Ammonia, and Carbon Dioxide from Industrial Wastewater Using a Thermal Hydrolyzer–Separator Loop

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In this work, simultaneous removal of urea, ammonia, and carbon dioxide from industrial wastewater was studied via modeling and simulation of a hydrolyzer–separator loop. The extended electrolytic UNIQUAC equation has been used to describe the nonideality of the liquid phase and the perturbed-hard-sphere (PHS) equation of state has been applied to predict the vapor fugacity coefficients. This work also uses a multistage well-mixed model for the liquid and vapor flows with a nonideal rate-based model for urea thermal hydrolyzer. Our study incorporates the reaction rate of urea hydrolysis and takes into account the effects of solution nonideality and backmixing on the reactor performance. The rates of urea reaction are written in terms of activity of reactants. The model provides temperature and flow rate distributions of different components along the height of the hydrolysis reactor and the desorbers. The simulation results have been found to be in good agreement with the plant data indicating the validity of the model. The impact of different parameters on the performance of the wastewater treatment loop has been examined. The results of this work showed that an increase in the inlet temperature of the wastewater and steam flow rate and also decrease the reflux ratio would improve the urea and ammonia removal efficiency.

1. Introduction

Urea is commercially produced by reaction of ammonia and carbon dioxide at elevated temperature and pressure. In a urea production plant, water forms as a byproduct which is collected in various wastewater streams. For every ton of urea produced, 0.3 tons of water is formed. This water is usually discharged from the urea concentration and evaporation section of the plant.^{1,2}

Aqueous waste streams from urea plants contain about 2–9% by weight ammonia, 0.8–6% by weight carbon dioxide, and 0.3–1.5% by weight urea.³ To prevent environmental pollution, these solutes must be removed. These wastes, if improperly dealt with, can threaten both public health and the environment. Consequently, waste minimization has become a major concern of our society. The benefits of adopting a workable and practicable environmental management system include reduced environmental risks, higher process efficiency and lower process cost, higher costs can result from environmental penalties, a positive public image, and progress toward sustainable development.⁴

Urea is an environmentally safe material used primarily as fertilizer but is considered deleterious in natural waterways because it promotes algae growth and hydrolyses slowly. Ammonia is regarded as a hazardous, toxic, and volatile material. At high levels of ammonia, death of animals, birds, and fish and death or a low growth rate in plants can be observed. In humans, the greatest risk is from inhalation of ammonia vapor, with effects including irritation and corrosive damage to the skin, throat, lungs, and eyes.^{5–7} Therefore, treatment of urea plant wastewater has been suggested. The treated wastewater can be used for a variety of purposes depending on the required quality such as cooling water or boiling feedwater makeup. While in the past decade, due to stricter environmental legislation, 100 ppm of urea was con-

sidered acceptable for waste, today's requirements mostly call for a maximum concentration of 10 ppm.²

There are various methods for treating these urea-containing streams. Simultaneous thermal hydrolysis and stripping is an existing technique to achieve wastewaters with ammonia and urea levels below 1 ppm. Urea and water react to produce ammonia and carbon dioxide in a process called hydrolysis. The rate of hydrolysis or decomposition is mainly influenced by the temperature of the solution and the concentration of urea.⁸

On the industrial scale, the urea thermal hydrolysis reactors operate in cocurrent or countercurrent modes. Rahimpour and Azarpour presented various model for studying the urea thermal hydrolyzer in cocurrent mode.^{9–11} Also Barmaki et al. proposed a nonideal rate-based model for an industrial urea thermal hydrolyzer in countercurrent mode.¹² In conventional urea plants with cocurrent hydrolyzers, wastewater from the treatment section discharges to the sewage system because of the outlet treated liquid has no qualities to use in the utility unit or in other units, but in modern urea plants, hydrolysis reactors are in a countercurrent configuration. In this manner, the ammonia and urea content of the treated stream can be reduced to a level of 10 ppm or even less than 1 ppm, so this water can then be used as boiler feedwater or cooling water.

The wastewater treatment process of a urea plant is carried out in a system including $\text{NH}_3\text{--CO}_2\text{--H}_2\text{O}$ –urea mixtures which are nonideal solutions.¹³ Therefore, a supporting thermodynamic model for this system must be used to incorporate the effect of liquid nonideality on the treatment performance.

Until now, the published information in the literature about simultaneous urea, ammonia, and carbon dioxide removal from the industrial wastewater of urea plants is very little detailed and patented, especially in the hydrolyzer–separator loop.^{3,8} In this work, we decided to develop a simulation program for a wastewater treatment loop. In this loop, a countercurrent thermal hydrolyzer is used for urea decomposing and two desorbers are used for removal of ammonia and carbon dioxide. An extended UNIQUAC model and perturbed-hard-sphere (PHS) equation of state proposed by Nakamura et al. have been

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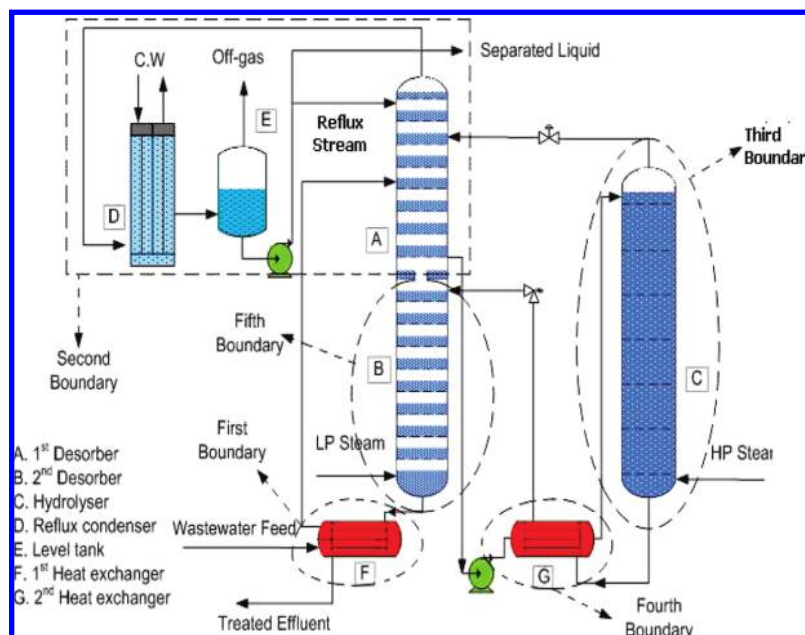


Figure 1. Process wastewater treatment system. The boundaries are shown for the material balance equations.

used to represent the vapor–liquid equilibrium (VLE) of the $\text{NH}_3\text{--CO}_2\text{--H}_2\text{O}$ –urea system. The combined effect of chemical reaction, liquid nonideality, and solution backmixing was treated by a well-mixed multistage reactor model for the hydrolyzer. In this study, the rates of reaction are defined in terms of activity instead of concentration of reacting materials. Also, the effect of different parameters on the performance of an industrial-scale thermal hydrolyzer–separator loop has been investigated.

2. Description of Process

Figure 1 illustrates an industrial wastewater treatment loop of a urea plant.¹ In this process, heated wastewater is fed to the top of first desorber, where the bulk of ammonia and carbon dioxide is removed. This column operates at a low pressure which facilitates the desorption process. The urea containing effluent from the first desorber is preheated and sent to the hydrolyzer countercurrently with high pressure (HP) steam fed to the bottom, whereby the urea decomposes into ammonia and carbon dioxide at elevated temperature. It is important that the ammonia concentration at the inlet of hydrolyzer is sufficiently low, in order not to reach the chemical equilibrium. Under this condition, the hydrolyzation reaction proceeds toward the ammonia and carbon dioxide side. Also, the hydrolyzer is operated at relative medium pressures (20 bar) resulting in a temperature of about 200 °C. In the liquid outlet of hydrolyzer, the urea content is decreased to a parts per million level. The ammonia and carbon dioxide evolving from this reactor are removed in a second desorber using low pressure (LP) steam as a stripping agent, and their contents are also decreased to a parts per million level. The liquid outlet from second desorber enters the first heat exchanger, and its temperature decreases on leaving the process water treatment system.

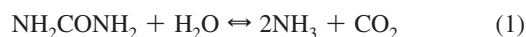
The overhead vapors from second desorber and hydrolyzer are used as the stripping agent in the first desorber. The vapors of the first desorber are condensed in a submerged reflux condenser. Part of the separated liquid is pumped back to first desorber, and the remainder is returned to the recirculation section of the urea plant. Residual NH_3 in the separator off-gas is recovered in an atmospheric absorber and returned to the recirculation section also. Nowadays, the first and second

desorbers are integrated into one sieve tray column to save investment costs. Also heat exchangers are applied to save energy and decrease the needed high pressure and low pressure steam amounts considerably.

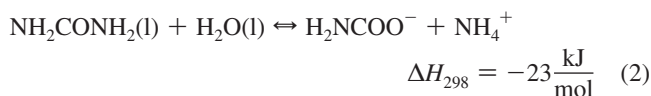
3. Reactions

The liquid phase contains physically dissolved and chemically combined components that are mainly present as ions and molecules, namely H_2NCONH_2 (1), H_2O (2), NH_4^+ (3), H_2NCOO^- (4), CO_2 (5), and NH_3 (6).

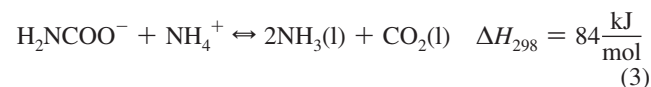
The overall reaction of urea hydrolysis is as follows:^{13,14}



The urea hydrolysis reaction occurs in two steps. The first reaction involves the production of ammonium carbamate from the combination of urea and water according to the following:



This reaction is slightly exothermic. Ammonium carbamate then breaks down in the presence of a heat source to form carbon dioxide and ammonia (endothermic reaction).



It is concluded from reactions 2 and 3 that the urea hydrolysis is an endothermic reaction, so for a more complete reaction, heat is needed.

Reaction 2 is slow, while reaction 3 is fast in both directions, so it could be considered at equilibrium under the conditions found in the industrial hydrolyzer.^{13,14} Therefore reaction 2 is the rate-controlling step, and its rate is considered as the overall rate of urea hydrolysis. For chemical reactions in thermodynamically nonideal systems, as shown elsewhere,^{15–17} the rate becomes

$$R = k_f \left(a_1 a_2 - \frac{1}{K_2} a_3 a_4 \right) = k_f \left[(\gamma_1 C_1)(\gamma_2 C_2) - \frac{1}{K_2} (\gamma_3 C_3)(\gamma_4 C_4) \right] \quad (4)$$

where k_f is the forward reaction rate constant ($k_f = k_0 \exp(-E/RT)$) and K_2 is the equilibrium constant of reaction 2. The terms a_i and γ_i are the activity and activity coefficient of species i , respectively. C_i is the molar concentration of species i . The experimental values of the pre-exponential factor and the activation energy in the Arrhenius expression of k_f are $k_0 = 3.75 \times 10^7 \text{ m}^3/(\text{kmol h})$ and $E = 87780.3 \text{ kJ/kmol}$, respectively.¹⁸

The equilibrium constants for reactions 2 and 3 are defined as follows:

$$K_2(T) = \left(\frac{x_3 x_4}{x_1 x_2} \right) \left(\frac{\gamma_3(T, X) \gamma_4(T, X)}{\gamma_1(T, X) \gamma_2(T, X)} \right) \quad r = 2 \quad (5)$$

$$K_3(T) = \left(\frac{x_5 x_6^2}{x_3 x_4} \right) \left(\frac{\gamma_5(T, X) \gamma_6^2(T, X)}{\gamma_3(T, X) \gamma_4(T, X)} \right) \quad r = 3 \quad (6)$$

where the activity coefficient of each species in the reacting solution can be calculated from thermodynamic model which is summarized in the Supporting Information. The following functional form

$$\ln K_r(T) = \left(\frac{U_{1,r}}{T} \right) + U_{2,r} \ln T + U_{3,r} T + U_{4,r} \quad (7)$$

was adopted to describe the temperature dependence of the r reaction equilibrium constant.¹⁹ In the above equation, U_r is a constant related to the reaction of number r where tabulated in the Supporting Information.

4. Thermal Hydrolyzer–Separator Loop Models

For simulation of the loop, the specification of streams must be obtained. The wastewater treatment loop has eight unknown streams, which are the following: (1) output first desorber liquid stream, (2) output first desorber vapor stream, (3) output hydrolyzer liquid stream, (4) output hydrolyzer vapor stream, (5) output second desorber liquid stream, (6) output second desorber vapor stream, (7) off-gas stream, and (8) separated liquid stream. The mole fractions of all components are unknown, but the specification of the reflux stream is similar to the separated liquid stream. Also, the reflux ratio and flow rate of the off-gas stream are constant.

In this study, simulation of the wastewater treatment loop was done based on the following assumptions:

- Reactions of hydrolysis take place only in the liquid phase.
- The loop operates at steady state conditions.
- Each stage of the hydrolyzer is a perfectly mixed stirred tank reactor (CSTR).
- Each CSTR operates adiabatically.
- Phase equilibrium is achieved in each stage.
- Vapor holdup in the hydrolyzer is assumed to be negligible (hydrolyzer is full of liquid).
- The volatility of urea and ammonium carbamate are negligible, so there are only three molecular components including H_2O , NH_3 , and CO_2 in the vapor phase.
- CO_2 is not dissolved in the liquid phase in desorbers. In fact, it could only be condensed with ammonia to form ammonium carbamate in the liquid phase.

4.1. Simulation of the Hydrolyzer (Third Boundary). For modeling of reactive separation columns, the equilibrium and

the nonequilibrium (NEQ) stage models are available in the literature. In this study, due to lack of the data of transfer properties for carbon dioxide and ammonia under the hydrolyzer operating conditions, we attempt to develop the equilibrium-stage model that is based on a rigorous thermodynamic model.

The feed to the urea thermal hydrolyzer consists of a liquid (water rich) stream entering from the top and pure high pressure (HP) steam stream entering from the bottom as the stripper. While the hydrolyzer is full of liquid, the movement of bubbles through the liquid phase causes mixing in the liquid phase. Moreover, there are several perforated plates at different levels inside the hydrolyzer in order to prevent backmixing and further mixing between the two phases.

As noted above, for simulation purposes, the urea thermal hydrolyzer can be approximated as a series of continuous multistage stirred tank reactors (CSTRs). Rahimpour and Barmaki et al.^{10–12} considered, respectively, the cocurrent and countercurrent urea thermal hydrolyzer as a sequence of continuously stirred tank reactors (CSTRs). The same approach has been adopted in the present study for the hydrodynamic behavior of the countercurrent urea thermal hydrolyzer. This model allows sweeping of operating conditions with different degrees of concentration backmixing by selecting different numbers of stages. Throughout the following derivations, CSTRs in sequences will be referred to as stages, numbered from the top to the bottom while stage 0 and stage 14 are hypothetical stages and indicate specifications of inlet wastewater and inlet steam streams before entering the hydrolyzer, respectively.

A mathematical model can be established including mass balance equations, phase equilibrium equations, summation equations, heat balance equations, and the hydraulic equations which were described as follows (MESH equations):

$$M_{i,j} \equiv V_{j+1} y_{i,j+1} + L_{j-1} x_{i,j-1} + \alpha_{i,2} H_j R_j + \alpha_{i,3} w - V_j y_j - L_j x_j = 0 \quad i = 1, \dots, M \quad j = 1, \dots, N \quad (8)$$

$$E_{i,j} \equiv K_{i,j} x_{i,j} - y_{i,j} = 0 \quad i = 1, \dots, M \quad j = 1, \dots, N \quad (9)$$

$$S_j^x \equiv \sum_i^M x_{i,j} - 1 = 0 \quad j = 1, \dots, N \quad (10)$$

$$S_j^y \equiv \sum_i^M y_{i,j} - 1 = 0 \quad j = 1, \dots, N \quad (11)$$

$$H_j \equiv \sum_i^M V_{i,j+1} H_{i,j+1}^v + \sum_i^M L_{i,j-1} H_{i,j-1}^l - \sum_i^M V_{i,j} H_{i,j}^v - \sum_i^M L_{i,j} H_{i,j}^l = 0 \quad j = 1, \dots, N \quad (12)$$

$$P_1 \equiv p_{\text{top}} - p_1 = 0 \quad j = 1 \quad (13)$$

$$P_j \equiv p_j - \Delta p_{j-1} - p_{j-1} = 0 \quad j = 2, \dots, N \quad (14)$$

where V_j and L_j are the vapor and liquid flow rate, respectively, x_{ij} and y_{ij} are the molar fraction in the liquid and vapor phases, respectively, and H_j is the volumetric liquid holdup (volume of each CSTR) and R_j is the rate of reaction 2 on stage j which is obtained from eq 4. Also $\alpha_{i,r}$ is the stoichiometric coefficient of species i in reaction r (reactions 2 and 3) which is positive for products and negative for reactants. $H_{i,j}^v$ and $H_{i,j}^l$ are the enthalpies of vapor and liquid components on stage j , respectively. p_{top} is the specified pressure of the tray at the top of the hydrolyzer, and Δp_{j-1} is the pressure drop per tray from stage

$j - 1$ to stage j . The molar consumption rate of carbamate in reaction 3 is w . Approximately, the amounts of carbamate and ammonium ions are so little due to fast reaction 3, the high value of equilibrium constant of reaction 3, and the imposed thermodynamic conditions. Also, the pressure drop along the hydrolyzer over a sieve tray may be estimated using proper correlations.

Since the column is generally operated at the medium pressure, the vapor fugacity coefficients can be estimated with the PHS equation of Nakamura,²⁰ the basic phase equilibrium equation, as given by simplified eq 15. Also in order to obtain the value of the molar consumption rate of carbamate (w) in mass balance, eq 8 is as follows:

$$E_{c,j} \equiv K_{3,j}(T) - \left(\frac{x_{5,j}x_{6,j}^2}{x_{3,j}x_{4,j}} \right) \left(\frac{\gamma_{5,j}(T,X)\gamma_{6,j}^2(T,X)}{\gamma_{3,j}(T,X)\gamma_{4,j}(T,X)} \right) = 0 \quad j = 1, \dots, N \quad (15)$$

4.2. Simulation of the Desorbers (Second and Fifth Boundaries). In the desorber column, carbamate decomposition takes place which can be considered at equilibrium reaction, and then, ammonia and carbon dioxide are stripped off from the liquid phase to the vapor phase. An equilibrium-stage model with Murphree efficiency is extended to simulate the desorbers. Also for first desorber, stage 1 can be a partial condenser. The equilibrium-stage model for the desorber is as follows (MESH equations, for $i = 1, \dots, M, j = 1, \dots, N$):

$$M_{i,j} \equiv V_{j+1}y_{i,j+1} + L_{j-1}x_{i,j-1} + \alpha_{i,3}w - V_jy_{i,j} - L_jx_{i,j} = 0 \quad (16)$$

$$E_{i,j} = EM_{i,j}(K_{i,j}x_{i,j} - y_{i,j+1})/(y_{i,j} - y_{i,j+1}) - 1 = 0 \quad (17)$$

$$S_j^x \equiv \sum_i^M x_{i,j} - 1 = 0 \quad (18)$$

$$S_j^y \equiv \sum_i^M y_{i,j} - 1 = 0 \quad (19)$$

$$H_j \equiv \sum_i^M V_{i,j+1}H_{i,j+1}^v + \sum_i^M L_{i,j-1}H_{i,j-1}^l - \sum_i^M V_{i,j}H_{i,j}^v - \sum_i^M L_{i,j}H_{i,j}^l = 0 \quad (20)$$

$$P_1 \equiv p_{\text{top}} - p_1 = 0 \quad (21)$$

$$P_j \equiv p_j - \Delta p_{j-1} - p_{j-1} = 0 \quad (22)$$

For the partial condenser, the enthalpy balance then has the following form:

$$H_j \equiv \sum_i^M V_{i,1}H_{i,1}^v - \sum_i^M V_{i,c}H_{i,c}^v - \sum_i^M L_{i,c}H_{i,c}^l - Q_C = 0 \quad (23)$$

where Q_C is condenser duty. Also $V_{i,c}$ and $L_{i,c}$ are the flow rates of the outlet vapor and liquid component from condenser.

4.3. Simulation of the Heat Exchangers (First and Fourth Boundaries). There are no phase changes in the heat exchanger, and it is modeled by assuming the cold stream has a temperature, T_C , in the heat exchanger inlet, where heat is

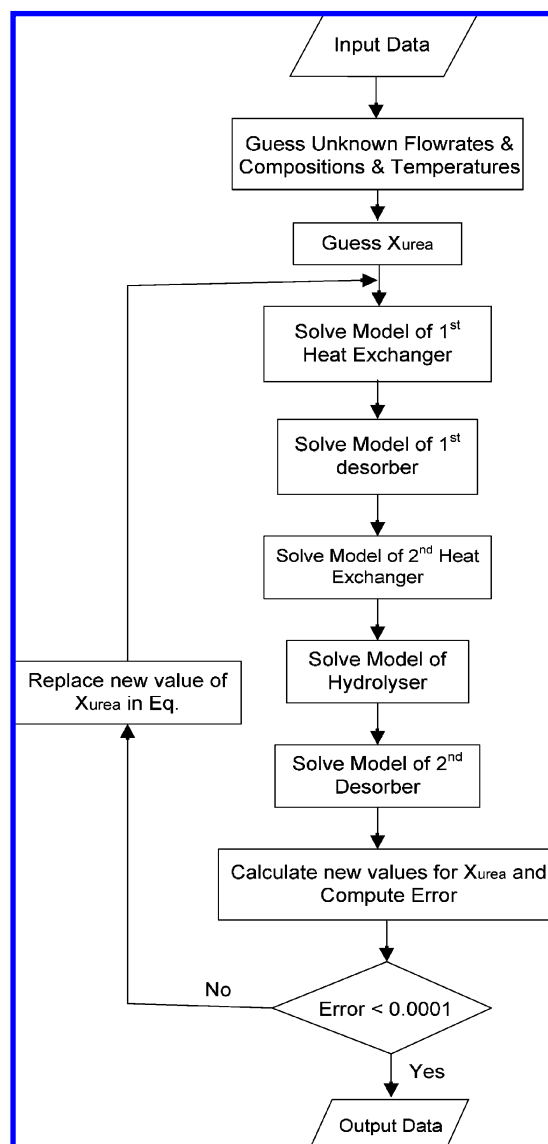


Figure 2. Flowchart for solving the model.

transferred at a rate, Q_C , from the hotter tube metal at a temperature, T_M , eq 24:

$$Q_C = U_C A_C (T_M - T_C) \quad (24)$$

The hot stream has a temperature T_H in the heat exchanger. Heat is transferred from the hot flow into the tube metal at a rate, Q_H :

$$Q_H = U_H A_H (T_H - T_M) \quad (25)$$

Finally, each stream of the cold and hot sides of the exchanger is described by an energy balance, eqs 26 and 27.

$$(F_C C_{PC} T_C)_L - (F_C C_{PC} T_C)_0 - Q_C = 0 \quad (26)$$

$$(F_H C_{PH} T_H)_L - (F_H C_{PH} T_H)_0 - Q_H = 0 \quad (27)$$

where F_C and F_H are the cold and hot stream molar flow rates, respectively, and C_P is heat capacity.

5. Numerical Solution

Figure 2 shows trend of solving the model. The following steps are involved.^{21,22}

Table 1. Wastewater Feed and HP and LP Steam Specifications¹

	wastewater feed	LP steam	HP steam
temperature (°C)	60	141.7	307.9
pressure (kg/cm ²)	2.7	3.1	20.3
component molar rate (kmol/h)			
water	1740.6	468.5	86.9
urea	8.996		
CO ₂	44.88		
NH ₃	170.38		

1. Get input data for calculation that these data consist of the specifications of the feed wastewater, LP and HP steam, reflux ratio, hydrolyzer and desorbers pressures, and off-gas streamflow rate.

2. Make an initial guess for all unknown parameters. In this section, guess values for all compositions, flow rates, and temperatures that these values optimized with trial and error are proposed.

3. Make an initial guess for x_{urea} . With a proposed urea conversion in the hydrolysis reactor, the model is solved and new values for x_{urea} are obtained. The progress of computer programming is stopped when the difference between the new x_{urea} value and the old value approaches zero.

4. Solve the model of the heat exchangers. When the heat exchanger equations are combined together, an algebraic system of equations is obtained. This nonlinear algebraic system of equations should be solved. Newton's method is used to solve the nonlinear equations. In this model, the inlet temperature of the hot streams is unknown, and this value is calculated by the second desorber model for first heat exchanger and the hydrolyzer model for second heat exchanger later, i.e., this temperature is first guessed and then corrected by trial and error.

5. Solve the model of the first desorber. When the specifications of the output streams of the first heat exchanger are known, the calculation relevant to first desorber is used to obtain outlet streams flow rates, composition, and temperatures, respectively. For this column, the input stream to the fifth stage and input vapor from the bottom of the tower are unknown, which are calculated by the reactor model and second desorber model later. Also, the partial condenser is treated as an equilibrium stage and a separated liquid stream is computed from the reflux ratio. The modeling leads to a system of algebraic equations. This set of nonlinear equations must be solved by iterative techniques. In general, iterative solution procedures make use of equation partitioning in conjunction with equation tearing and/or linear-

ization by Newton's techniques.²³ The resulting Jacobian matrix has a block tridiagonal structure. Linear systems with a block tridiagonal coefficient matrix can be solved quite efficiently using the Thomas algorithm.²⁴

6. Solve the model of a hydrolysis reactor. With known reactor input flow rates, compositions, and temperatures, the equations related to the behavior of the urea thermal hydrolyzer were solved. The basic structure of the model consists of nonlinear algebraic equations of mass and energy conservative rules of both the vapor and liquid phases, which have to be coupled with equations of the kinetic model and auxiliary correlations. These nonlinear equations are solved by iterative techniques using Newton's method.

7. Solve the model of the second desorber. When the specifications of output streams of the hydrolysis reactor are known, the calculation relevant to the second desorber is used to obtain outlet streams flow rates, compositions, and temperatures, respectively. This modeling is also solved by using Newton's method. For this column, low pressure (LP) steam enters from the bottom.

8. Compute x_{urea} . Now obtain the new value for x_{urea} with the following equation and compare it with the old value.

$$X_{\text{urea}} = (F_p x_f(1) - F_c x_c(1)) / (F_p x_f(1)) \quad (28)$$

6. Model Validation

A verification of the proposed model was carried out by comparison of the model results with the plant data of a urea wastewater treatment process. The input data of the wastewater treatment loop including specifications of wastewater feed and LP and HP steam streams have been summarized in Table 1.

The results of the simulation are compared with the plant data. The results are shown in Table 2. It was observed that the steady state model performed satisfactorily well under the industrial conditions and a good agreement was obtained between the plant data and the simulation data which confirms that the proposed model can be considered suitable and reliable. The higher relative error percent of predicted results for some molar flow rates from observed data is due to the small observed values of their content in the outlet streams.

7. Results and Discussion

Typical industrial operating conditions of the urea wastewater treatment plant are listed in Table 1. The simulation results were

Table 2. Comparison of Calculated Results of the Wastewater Treatment Loop with the Observed Plant Data¹

stream		component molar rate (kmol/h)				Temperature(°C)
		H ₂ O	NH ₃	CO ₂	Urea	
output liquid of 1st desorber	plant	2037.6	19.55	1.3	8.996	128.5
	calc	2067.8	18.94	1.37	8.996	129
	error (%)	1.5	-3.1	5.4	0	0.4
output vapor of 1st desorber	plant	206.5	188.4	53.88		107
	calc	200.9	195.4	54.14		106
	error (%)	-2.7	3.7	0.5		-0.9
output liquid of hydrolyzer	plant	2067.3	33.63	0.216	<5 ppm	207
	calc	2102.6	32.71	0.2	4 ppm	207.7
	error (%)	1.7	-2.7	-7.4		0.3
output vapor of hydrolyzer	plant	48.16	3.91	10.08		194.2
	calc	43.12	4.07	10.09		193.4
	error (%)	-10.4	4.1	0.1		-0.4
output liquid of 2nd desorber	plant	2080.4	1 ppm	0.0	<5 ppm	134
	calc	2140.5	0.91 ppm	0.0	4 ppm	134.1
	error (%)	2.9	-9	0.0		0.1
output vapor of 2nd desorber	plant	455.3	0.216	33.62		131
	calc	430.6	0.2	32.7		130.6
	error (%)	-5.4	-7.4	-2.7		-0.3

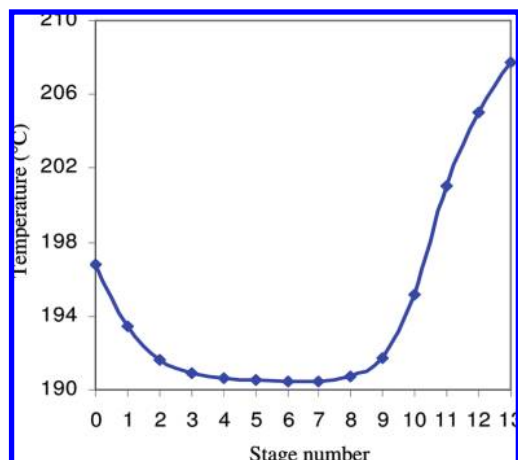


Figure 3. Temperature profile of reacting material along the hydrolyzer where the operating conditions are the same as in Table 1.

plotted as profiles of the dependent parameters versus independent variables. In addition, the effects of different parameters on the urea and ammonia removal performance were investigated.

The profile of temperature along the hydrolyzer is shown in Figure 3. It can be seen that there are two parts in this figure. At the first segments of the hydrolyzer, the temperature of reacting material decreases owing to the endothermic overall reactions, then increases because of injection of high pressure steam to the bottom of the hydrolyzer. This figure indicates that the temperature decrease along the hydrolyzer is small. The possible explanation for this behavior is that the weight percent of water is so much larger than that of urea that the heat of reaction has no significant effect on the stream temperature.

Figure 4 presents profiles of component flow rates and urea conversion along the hydrolyzer. Figure 4a shows the molar flow rate and conversion of urea along the hydrolyzer. Urea removal increases from the top to the bottom of the reactor because of urea hydrolysis. It should be noted that the outlet urea content of the hydrolyzer is virtually zero due to hydrolysis reactions and the conversion is approximately 100%. Figure 4b and c illustrates that initially ammonia and carbon dioxide flow rates increase in the liquid phase and then decrease. These profiles clearly show the production of these components due to urea hydrolysis. Also, because of the increasing temperature in the bottom of hydrolyzer, ammonia and carbon dioxide concentrations decrease in the liquid phase. As can be seen in these figures, the flow rates of ammonia and carbon dioxide in the vapor phase are influenced by the temperature level of the hydrolyzer substantially.

Figure 5 shows the model results for temperature (Figure 5a) and two important species (Figure 5b–c) along the first desorber. The temperature increases from the feed stage (stage 0) to the outlet stage as the liquid flows down the desorber on interacting with the vapor stream which has a higher temperature. This figure illustrates that the liquid and vapor of components undergo significant changes in flow rates, as the two liquid and vapor streams cross each other countercurrently. In this column, the carbamate decomposition occurs. The required heat for this endothermic reaction and desorption is supplied by condensation of water vapor. In the liquid phase, ammonium carbamate then breaks down in the presence of a heat source to form carbon dioxide and ammonia which is stripped gradually into the vapor with increasing temperature. In the fifth stage, because the entering overhead vapor of the hydrolyzer includes a high concentration of CO_2 , the concentration of this component in the vapor phase increases suddenly.

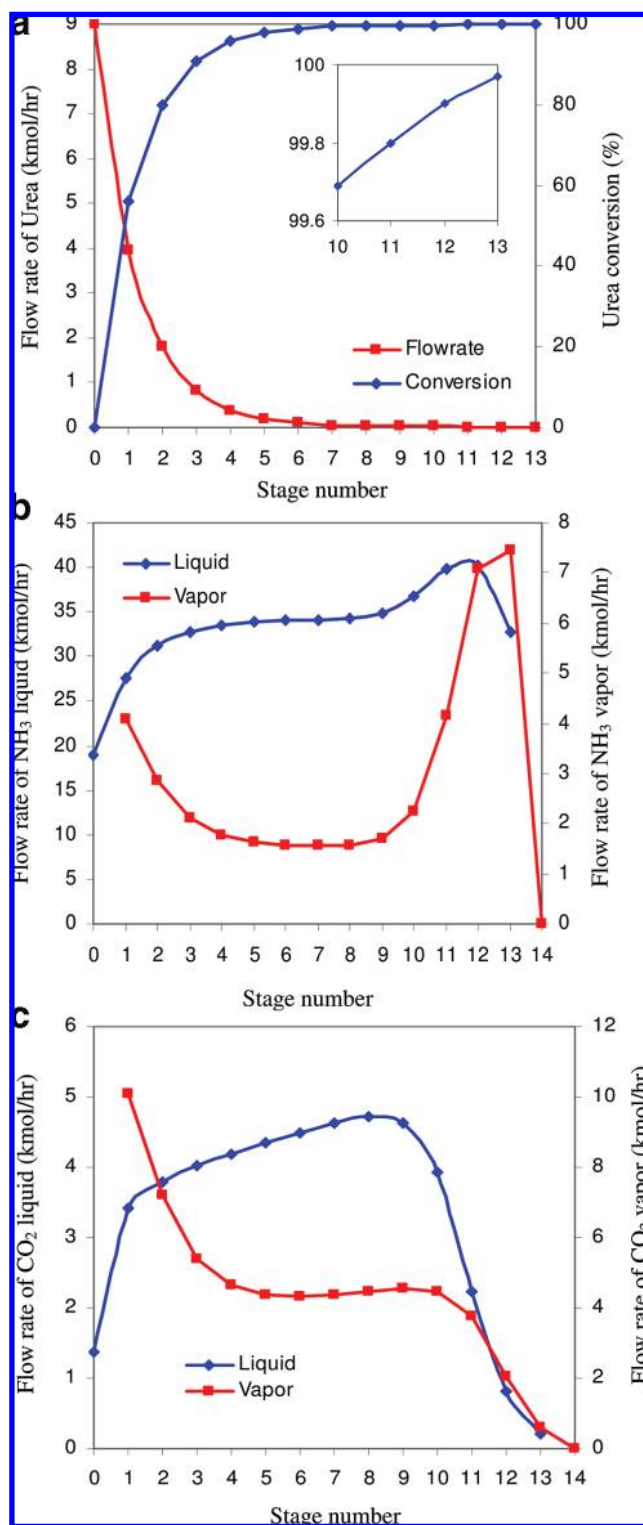


Figure 4. Model results along the hydrolyzer (a) urea, (b) ammonia, and (c) carbon dioxide where the operating conditions are the same as in Table 1.

Figure 6 indicates the profiles of temperature (Figure 6a) and molar flow rate of ammonia (Figure 6b) along the second desorber. The temperature increases from the top to the bottom of column, and the flow rate of ammonia liquid decreases due to the desorption as liquid moves down the column while the vapor flow rate of ammonia increases correspondingly, testifying to the overall conservation of mass. In this figure, initially a rapid increase in the temperature can be observed. Also the slope of the ammonia concentration curve is greater with respect to

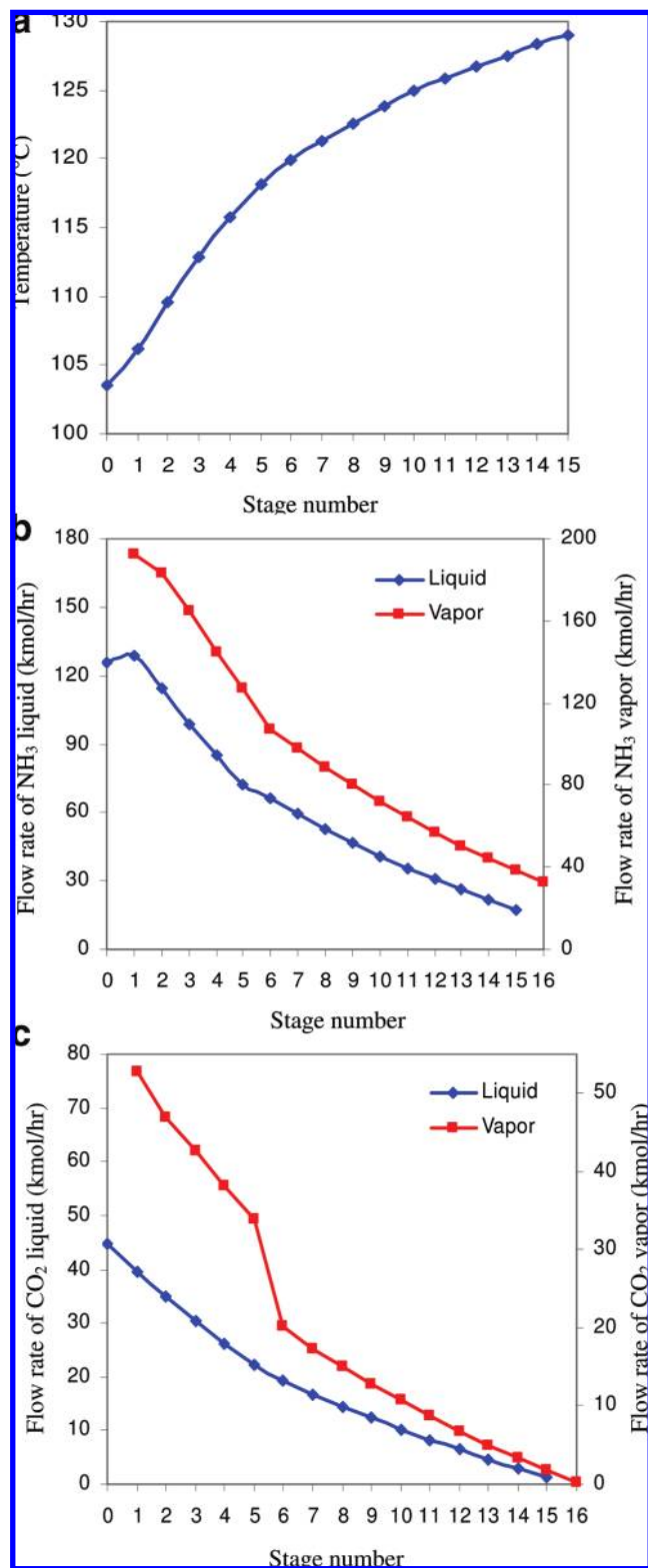


Figure 5. Model results along the first desorber (a) temperature, (b) ammonia, and (c) carbon dioxide where the operating conditions are the same as in Table 1.

its graph in the first desorber. The main reason for this is the very little quantity of carbamate in the liquid phase and the injection of LP steam from the bottom of the column.

7.1. Effect of the Inlet Temperature of the Feed Wastewater. The inlet temperature of the feed wastewater has an influence on urea and ammonia removal performance as demonstrated in Figure 7. This figure indicates that increasing

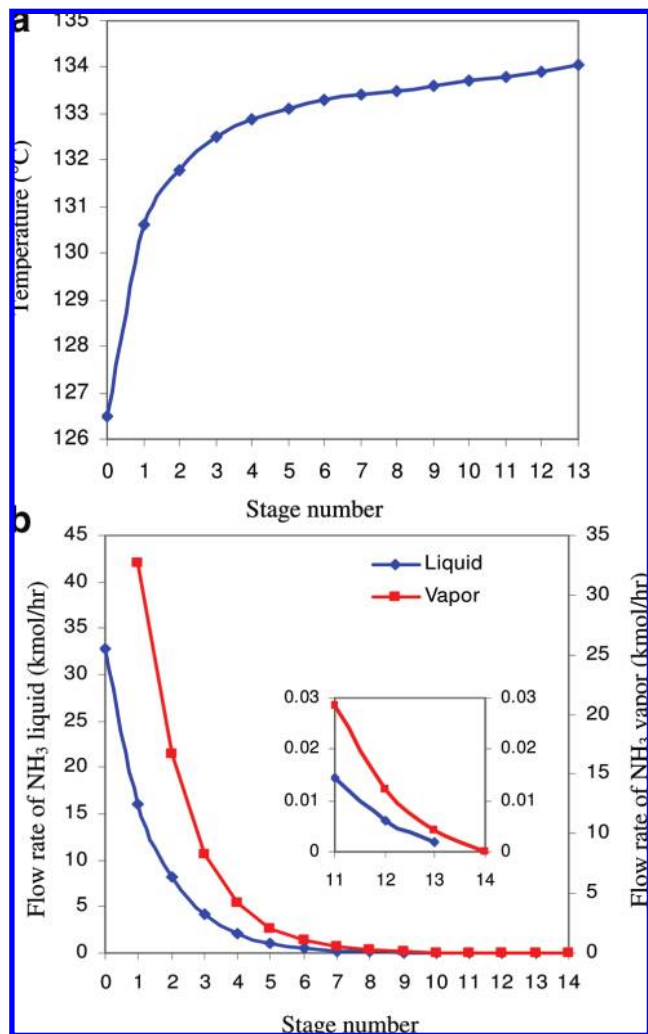


Figure 6. Model results along the second desorber (a) temperature and (b) ammonia where the operating conditions are the same as in Table 1.

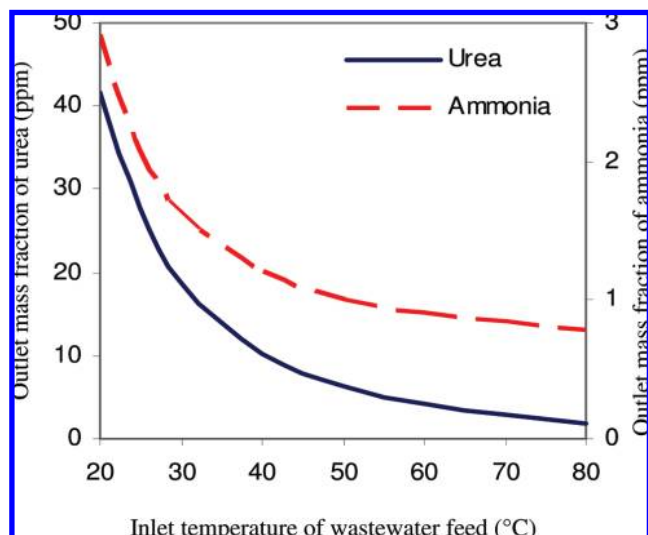


Figure 7. Outlet mass fraction of urea and ammonia versus inlet temperature of wastewater feed where the other operating conditions are the same as in Table 1.

the inlet temperature of the wastewater improves the urea removal performance due to this being an overall endothermic reaction. Also, if the inlet temperature of the wastewater increases, the concentration of ammonia decreases in the treated

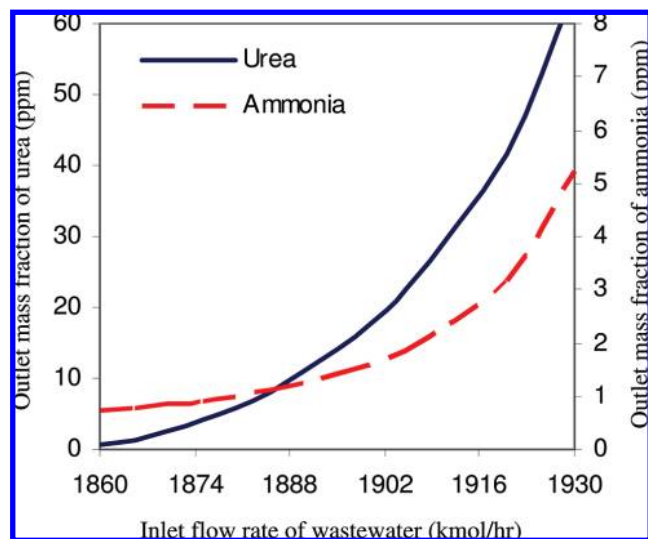


Figure 8. Outlet mass fraction of urea and ammonia versus the inlet flow rate of wastewater feed where the other operating conditions are the same as in Table 1.

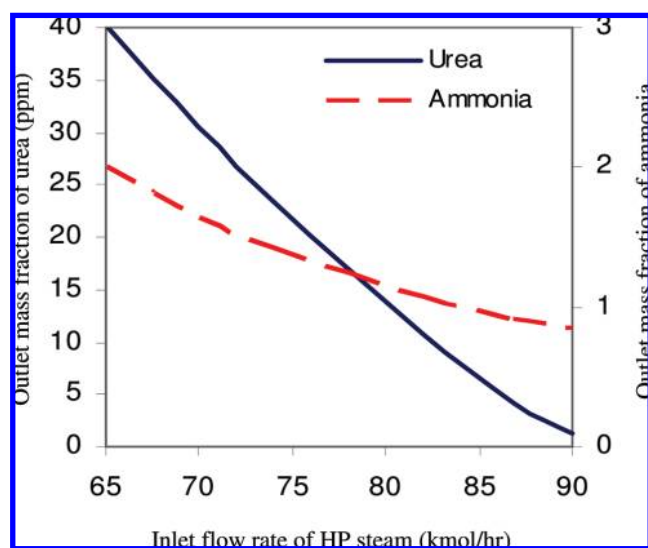


Figure 9. Outlet mass fraction of urea and ammonia versus inlet flow rate of HP steam where the other operating conditions are the same as in Table 1.

effluent stream because of the higher temperature profile in the loop which shifts the vapor–liquid equilibrium to the vapor phase and provides a lower concentration of ammonia in the outlet liquid. But the change of ammonia concentration with alteration of wastewater temperature is small owing to the effect of heat exchangers.

7.2. Effect of the Inlet Flow Rate of Feed Wastewater.

The effect of wastewater flow rate in urea and ammonia removal at identical operating conditions is shown in Figure 8. From this figure, the lower wastewater flow rate provides less urea concentration than a higher flow rate. The decrease in the wastewater flow rate causes an increase in the residence time of reactants and higher profile temperature along the hydrolyzer which would result in an increase of the urea decomposition in the urea reactor. Also this figure shows the concentration of ammonia in the effluent stream as a function of the inlet flow rate of feed wastewater.

7.3. Effect of High Pressure Steam Flow Rate. The role of the high pressure steam flow rate in urea and ammonia removal is shown in Figure 9. As shown in this figure, a higher

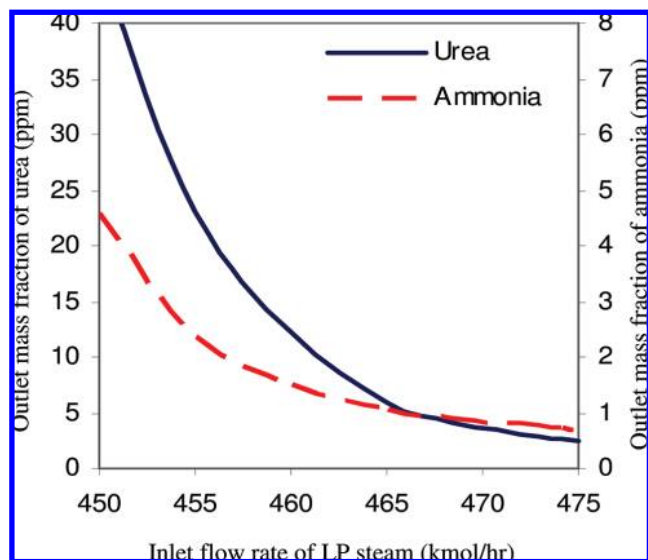


Figure 10. Outlet mass fraction of urea and ammonia versus inlet flow rate of LP steam where the other operating conditions are the same as in Table 1.

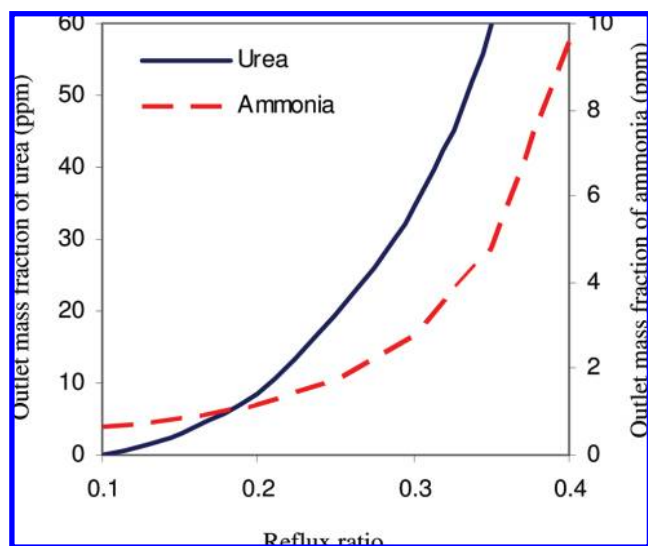


Figure 11. Outlet mass fraction of urea and ammonia versus reflux ratio where the other operating conditions are the same as in Table 1.

steam flow rate maintains a higher temperature level in the hydrolyzer which would cause changes in the liquid temperature profile and in the extent of hydrolysis reactions, so resulting in enhancing the urea removal. Also, the change in the flow rate of the entering high pressure steam has an effect on the concentration of ammonia in the treated effluent. Increasing the flow rate of steam would result in a lower concentration of ammonia in the exit liquid due to the temperature increasing in the bottom of the hydrolyzer and consequently shifting of vapor–liquid equilibrium to the vapor phase, which results in enhancing the ammonia removal and decreasing the ammonia concentration in the exit treated liquid stream. But, the role of HP steam flow rate on ammonia concentration in the treated effluent is very low because of a small variation of ammonia content.

7.4. Effect of the Low Pressure Steam Flow Rate. Figure 10 shows the influence of entering low pressure steam on the concentrations of urea and ammonia in the treated effluent stream. While the LP steam increases, the ammonia content in the liquid phase decreases by increasing the temperature

Table 3. Relation of Outlet Mass Fraction of Urea, Energy Consumption, and Variation of HP and LP Steam Flow Rates Where the Other Operating Conditions Are the Same as in Table 1

variation of urea content in the exit liquid (ppm)	variation of HP steam flow rate (kmol/h)	variation of LP steam flow rate (kmol/h)	energy consumption (MJ/h) for variation of HP steam	energy consumption (MJ/h) for variation of LP steam
10 → 1	83.3 → 89.3	461.3 → 477.9	316	414
20 → 10	76.1 → 83.3	456.3 → 461.3	380	124
50 → 10	60.8 → 83.3	449.4 → 461.3	1184	297

Table 4. Relation of Outlet Mass Fraction of Ammonia, Energy Consumption, and Variation of HP and LP Steam Flow Rate Where the Other Operating Conditions Are the Same As in Table 1

variation of ammonia content in the exit liquid (ppm)	variation of HP steam flow rate (kmol/h)	variation of LP steam flow rate (kmol/h)	energy consumption (MJ/h) for variation of HP steam	energy consumption (MJ/h) for variation of LP steam
5 → 1	42.2 → 84.9	449.6 → 466.3	2252	414
10 → 5	32.2 → 42.2	446.9 → 449.6	527	69
20 → 5	28 → 42.2	444.4 → 449.6	746	131

according to vapor–liquid equilibrium. As result, a higher level of temperature is obtained in the loop, and therefore, the second hydrolysis reaction shifts to the right and urea decomposition occurs to improve urea removal efficiency. Therefore, the urea and ammonia concentrations in the effluent stream decrease.

7.5. Effect of the Reflux Ratio. The effect of the reflux ratio on the urea and ammonia concentrations in the treated effluent is shown in Figure 11. The reflux ratio is defined as the reflux stream flow rate over the total of separated liquid and off-gas flow rates. When the reflux ratio is increased, the reflux stream flow rate, including ammonia, also increases. Therefore, the amount of ammonia along the first desorber and consequently in the loop becomes more. So, the hydrolyzer feed temperature decreases and the rate of hydrolysis reactions and urea conversion decline in the hydrolyzer. Hence the urea and ammonia content increases in the treated liquid stream.

7.6. Comparison of Effective Parameters. It is clear; each parameter that increases temperature along the hydrolyzer and desorber would improve urea and ammonia removal. So, increases of the inlet temperature of wastewater and HP and LP steam flow rates enhance the efficiency of urea and ammonia removal that are explained thoroughly.

For constructed plants that currently produce to achieve the new environmental standard in the urea wastewater treatment section is not easy in practice; because of complex operation conditions and much cost to change the inlet temperature of wastewater, it is better to change the flow rate of steam which is very practical and is easily controlled.

These comparisons show that the effect of the HP steam flow rate is more than the effect of the LP steam flow rate in the range of 1–10 ppm of outlet urea. Also the effect of the LP steam flow rate is more than that of the HP steam flow rate for ammonia removal. On the other hand, from an economical and energy cost point of view, the comparisons are done as follows in Tables 3 and 4.

As shown in Tables 3 and 4, for a decreasing urea content from 10 to 1 ppm, the energy consumption of the change in the HP steam flow rate is less than that for the LP steam flow rate, while for a decreasing urea content from 50 to 10 ppm, the energy consumption of the change in the LP steam flow rate is less. Therefore to achieve the new environmental standard (<10 ppm), the variation of the HP steam flow rate is better, and to achieve the old environmental standard (<100 ppm), LP steam flow rate variation is better. Also for a decreasing ammonia content, the energy consumption of varying the LP steam flow rate is less than that for the HP steam flow rate, so LP steam flow rate variation is better.

8. Conclusions

In a urea plant, one of the most effective methods for controlling the wastewater pollution problem is using a wastewater treatment section which includes a urea thermal hydrolyzer to decrease urea content and desorbers to decrease ammonia and carbon dioxide contents, whereas the clean water can be used for cooling tower makeup or boiler feedwater. In this work, an industrial wastewater treatment loop was modeled. The model incorporated the liquid nonideality of reacting materials in the reaction rate based on a countercurrent configuration for the urea thermal hydrolyzer. Also the desorbers were simulated based on the equilibrium stage model. The temperature and concentrations of the outlet streams of liquid and vapor from units in the loop calculated by the model and those taken from the industrial hydrolyzer were compared to determine the validity of the model. This comparison showed good consistency between the model predicted and the plant data. The model could be used to study the effects of process variables, such as the inlet temperature and flow rate of feed wastewater, reflux ratio, and flow rate of steam streams. This work provides a useful tool for designing new processes and retrofitting existing processes. In the end, the results showed every effective factor that increased the temperature level along the urea thermal hydrolyzer and the desorbers, enhancing the urea and ammonia removal efficiency. Interesting features of this work were from the economical and energy cost point view, the effect of HP steam flow rate on the urea removal in the range above 10 ppm of outlet urea and the LP steam flow rate on the ammonia removal were more than other parameters. Moreover, if the goal of hydrolyzing was achievement in the new environmental standard, the LP steam flow rate would be more effective than others.

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Supporting Information Available: Thermodynamic model, equation of state, equilibrium constant parameters, and Newton's method for solving equations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Appendix

Nomenclature

C_i = concentration of component i (kmol/m³)

C_p = specific heat of the stream in heat exchanger (kJ/(kmol K))
 E = activation energy (kJ/kmol)
 $E_{c,j}$ = residual function for chemical equilibrium relation for carbamate on the j th tray
 $E_{i,j}$ = residual function for phase equilibrium relation for component i on the j th tray
 EM = Murphree tray efficiency
 F_e = molar flow rate of hydrolyzer effluent (kmol/h)
 F_f = molar flow rate of hydrolyzer feed (kmol/h)
 H_j = liquid holdup on stage j (m^3)
 $H_{i,j}^v$ = enthalpy of component i in vapor phase on stage j (kJ/kmol)
 $H_{i,j}^l$ = enthalpy of component i in liquid phase on stage j (kJ/kmol)
 ΔH = heat of reaction (kJ/kmol)
 H_j = residual function for total heat balance on the j th tray
 $K_{i,j}$ = the equilibrium constant
 K_0 = pre-exponential factor of urea hydrolysis rate constant ($m^3/(kmol\ h)$)
 K_f = the forward reaction rate constant ($m^3/(kmol\ h)$)
 K_r = equilibrium constant of reaction r dependent on temperature
 L_j = mole flow rate of liquid on stage j (kmol/h)
 $L_{i,j}$ = liquid mole flow rate of component i on stage j (kmol/h)
 M = number of components
 $M_{i,j}$ = residual function for material balance for component i on the j th tray
 N = number of stages
 P_j = peressure of stage j (atm)
 ΔP_j = pressure drop (atm)
 p_{top} = pressure at the top of the column (atm)
 Q_C = condenser duty (kJ/h)
 Q_i = heat transfer in the heat (kJ/h)
 R_j = rate of reaction 2 on the j th tray ($kmol/(m^3\ h)$)
 S_j^x = residual function for summation relation in the liquid phase on the j th tray
 S_j^y = residual function for summation relation in the liquid phase on the j th tray
 T = temperature (K)
 T_M = metal temperature in heat exchanger (K)
 U = constant eq 7
 U_i = overall heat transfer coefficient in heat exchanger ($kJ/(h\ m^2\ K)$)
 V_j = mole flow rate of vapor on stage j (kmol/h)
 $V_{i,j}$ = vapor mole flow rate of component i on stage j (kmol/h)
 w = consumption molar flow rate of carbamate in reaction 3 (kmol/h)
 x_e = mole fraction of component i in hydrolyzer effluent
 x_f = mole fraction of component i in hydrolyzer feed
 $x_{i,j}$ = mole fraction of component i in liquid phase on the j th tray
 X_{urea} = urea conversion
 $y_{i,j}$ = mole fraction of component i in the vapor phase on the j th tray

Greek Letters

$\alpha_{i,2}$ = stoichiometric coefficient of species i in reaction 2
 $\alpha_{i,3}$ = stoichiometric coefficient of species i in reaction 3

Subscripts

0 = inlet conditions
 C = cold stream
 H = hot stream
 i = component number

j = stage number
 L = length of heat exchanger
 r = reaction number

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