Chemical Engineering Journal 160 (2010) 594–606

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Enhancement of urea, ammonia and carbon dioxide removal from industrial wastewater using a cascade of hydrolyser–desorber loops

M.R. Rahimpour*, H.R. Mottaghi, M.M. Barmaki

Department of Chemical Engineering, School of Chemical and Petroleum Engineering, Shiraz University, Shiraz 71345, Iran

ARTICLE INFO

Article history:
Received 13 October 2009
Received in revised form 28 March 2010
Accepted 29 March 2010

Keywords:
Wastewater treatment
Urea removal
Ammonia removal
Cascading hydrolyser–desorber loop
Low concentration removal

ABSTRACT

In this study, removal of urea, ammonia and carbon dioxide from wastewater of conventional urea plant in both high and low concentration (ppm scale) levels using a cascade of hydrolyser–desorber loops has been investigated. In conventional urea plants, wastewater treatment sections including co-current configuration of hydrolyser were designed according to the old environmental standards. Nevertheless, the amounts of urea and ammonia in outlet treated wastewater are not acceptable at present time due to new environmental restrictions, shortage of water sources and possibility of upgrading this wastewater to reuse for boiler feed water or cooling water. Therefore, a thermal hydrolyser–desorber system is proposed to add at the end of current conventional treatment section in order to decrease urea and ammonia contents in treated effluent to approach 0 ppm. A general model is developed for both types of thermal hydrolyser–desorber loops which in first loop, high concentrations and in the second loop, low concentrations of urea and ammonia are treated. The extended electrolytic UNIQUAC equation has been used to describe the non-ideality of liquid phase. The proposed model incorporates reaction rate of urea hydrolysis and takes into account the effects of solution non-ideality and back-mixing on the performance of hydrolysis reactors. The model was solved numerically and provides temperature, flow rate and concentration distributions of different components along the height of reactors and desorbers. The proposed model has been validated against observed data. Also the effects of key parameters on the performance of wastewater treatment process have been examined. The results of this work show that increase of inlet temperature of wastewater and steam flow rate and decrease of the reflux ratio improve the urea and ammonia removal efficiency.

1. Introduction

Urea is an important nitrogen-based fertilizer which is synthesized by the reaction of ammonia and carbon dioxide in the range of high temperatures and pressures [1]. In a urea production plant, for every ton of produced urea, 0.3 tons of water is formed. This water which contains ammonia, carbon dioxide and urea is usually discharged from the urea concentration and evaporation section of the plant. This wastewater together with the rinsing and wash effluent is collected in large storage tanks, requires treatment if it is to be reused again. Such a stream generally contains about 2–9 wt% ammonia, 0.8–6 wt% carbon dioxide and 0.3–1.5 wt% urea [2,3].

Discharging this wastewater from urea plants have a negative influence on the environment as well as loss of urea and ammonia. Urea is considered deleterious in natural waterways that it promotes algae growth and hydrolyses slowly. Ammonia is an extremely hazardous, toxic, and volatile material. At high levels of ammonia, death of animals, birds, fish and death or low growth rate in plant, and irritation and serious burn on the skin and in the mouth, throat, lungs and eyes can be observed. Therefore, treatment of urea plant wastewater is essential [4–6].

The purpose of wastewater treatment of urea plant is to remove urea, ammonia and carbon dioxide from the process condensate. Several processes have been suggested for treating these urea-containing streams due to current necessities for environmental protection and possibilities to upgrade this waste stream to valuable high-pressure boiler feed water or cooling water. While in the past decade, 100 ppm of urea was considered acceptable for plant wastewater, but today's requirements mostly call for a maximum concentration of 10 ppm [7].

Economically, it is preferred to remove and recover the urea and/or ammonia from the wastewater. Various methods have been proposed to accomplish this, all of them basically involve the steps of desorbing ammonia and carbon dioxide from the urea-containing wastewater, subsequently thermal hydrolyzing the urea contained in the wastewater, then the total or partial desorption of the ammonia and carbon dioxide that are formed in the hydrolyser

---

* Corresponding author. Tel.: +98 711 2303071; fax: +98 711 6287294.
E-mail address: rahimpor@shirazu.ac.ir (M.R. Rahimpour).

1385-8947/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2010.03.081

and in the final step, the off-gases will be condensed in a reflux condenser [8].

On the industrial scale, urea thermal hydrolysis reactors operate in co-current or counter-current modes. Rahimpour and Azarpour presented various model for studying the urea thermal hydrolyser in high concentration level in co-current mode [9–11]. Also Barmaki et al. proposed a non-ideal rate-based model for an industrial urea thermal hydrolyser in high concentration level in counter-current mode [12]. In conventional urea production plants, thermal hydrolysis reactors are in operation in co-current mode with steam, nevertheless even after very long residence times or high steam consuming in the best operating conditions, it is not possible to achieve the urea and ammonia contents less than 20–25 ppm in outlet treated liquid [9,11,13]. But in modern urea plant, thermal hydrolysis reactors are based on counter-current mode. In this manner, the ammonia and urea contents of the treated stream can be reduced to a level of 1 ppm. In conventional urea plants such as Shiraz Petrochemical Complex (SPC), outlet wastewater from treatment section of the plant discharges to sewage system, because of the outlet treated liquid has no enough quality to use in utility unit or in other units. So in order to reuse this wastewater, residual urea, ammonia and carbon dioxide must be removed.

Until now, the published information in literature about simultaneous urea, ammonia and carbon dioxide removal in low concentration level from industrial wastewater of urea plants is very little detailed and patented, especially in hydrolysis-desorption process [3,14]. The main objective of this work is enhancement of urea, ammonia and carbon dioxide removal from outlet treated liquid of wastewater treatment loop of conventional urea plant to obtain pure liquid that contains 1 ppm for urea and ammonia and observe the new environmental standards. In other word, in this work removal of urea and ammonia from wastewater in low concentrations (<100 ppm) is carried out while in conventional process, high concentrations (>100 ppm) of urea and ammonia are removed.

Changes in conventional treatment section is complicated and approximately impractical due to dependency of different equipments of plant to each other, besides increase of steam flow rate and temperature of wastewater feed are shown in our previous works [9–11]. Therefore, the new treatment system has been suggested. In this system, the removal of mentioned components is carried out in two stages. In the first stage, urea, ammonia and carbon dioxide are removed at high concentrations in existing plant while in the second stage these components are removed at low concentrations in a proposed plant.

In this work, a general model for an integration of hydrolyser–desorber loops including conventional and new proposed treatment sections has been developed. Extended UNIQUAC model has been used to represent the vapor–liquid equilibrium (VLE) of NH_3–CO_2–H_2O–urea system. The combined effect of chemical reaction, liquid non-ideality and solution back-mixing was treated by a multi-stage well-mixed reactor model for thermal hydrolyser. Also the effect of different parameters on the performance of hydrolyser–desorber loops has been investigated and the design consequences of different options on the new proposed section have been discussed.

2. Process description

2.1. Wastewater treatment section of conventional urea plant

Fig. 1 shows a schematic diagram of conventional urea, ammonia and carbon dioxide removal from wastewater of the urea plant in Shiraz Petrochemical Complex [8]. It mainly consists of a 1st desorber column at low pressure, which reduces the ammonia and carbon dioxide contents. For the next column, the hydrolyser, it is important that the ammonia and carbon dioxide concentrations at the inlet are sufficiently low, in order to maintain the system far from the chemical equilibrium. Under these conditions the hydrolysis reactions proceed towards the ammonia and carbon dioxide production, reducing the urea content to approximately less than 100 ppm. The hydrolyser is operated at relatively medium pressures (18 bar) resulting in a temperature of about 185 °C. The temperature level in the hydrolyser is maintained by the injection of 25 bar steam. In the 2nd desorber column again operating at low pressure, the ammonia and carbon dioxide contents are decreased to low ppm level. The stripping in the 2nd desorber is carried out by using life low-pressure (LP) steam injected in the bottom and outlet vapors from this column are used for the stripping in the 1st desorber. The vapors of the 1st desorber, which contain ammonia, carbon dioxide and water, go to condenser.

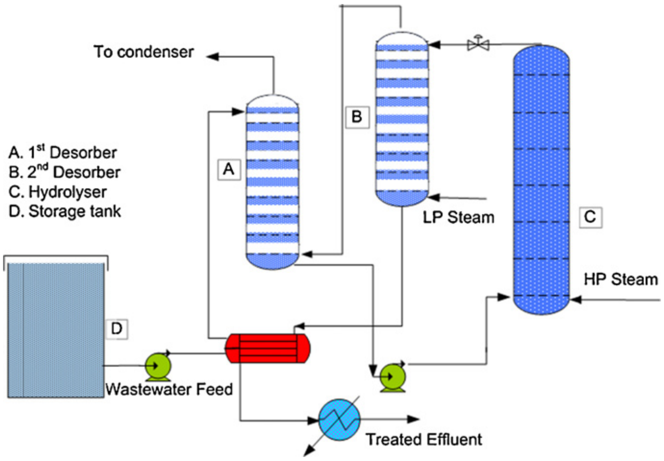

Fig. 1. Wastewater treatment loop of conventional urea plant.

2.2. New proposed treatment section

A schematic of cascade of hydrolyser–desorber systems including conventional and new proposed treatment sections for urea, ammonia and carbon dioxide removal from wastewater of urea plant is shown in Fig. 2. In this process, the outlet liquid from 2nd desorber is heated in 2nd heat exchanger with the clean top effluent, and it is pumped to the bottom of the new hydrolyser co-currently with high-pressure (HP_2) steam after passing through the 3rd heat exchanger. The height of hydrolyser is 5 m and there are 4 trays inside it. Urea is decomposed to ammonia and carbon dioxide by steam 380 °C and 25 kg/cm^2. At the outlet of the hydrolyser the urea content is decreased to 1 ppm level.

The ammonia and carbon dioxide evolving from this hydrolyser reaction are removed in a desorber using low-pressure (LP_2) steam as stripping agent. The ammonia content is also decreased to 1 ppm level. Overhead vapors from 3rd desorber containing ammonia, carbon dioxide and water are condensed in a reflux condenser and rectified to reduce the water content by returning a reflux liquid stream to the tower and non-condensed vapors are recycled to urea production section. Two process–process heat exchangers decrease the needed high-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

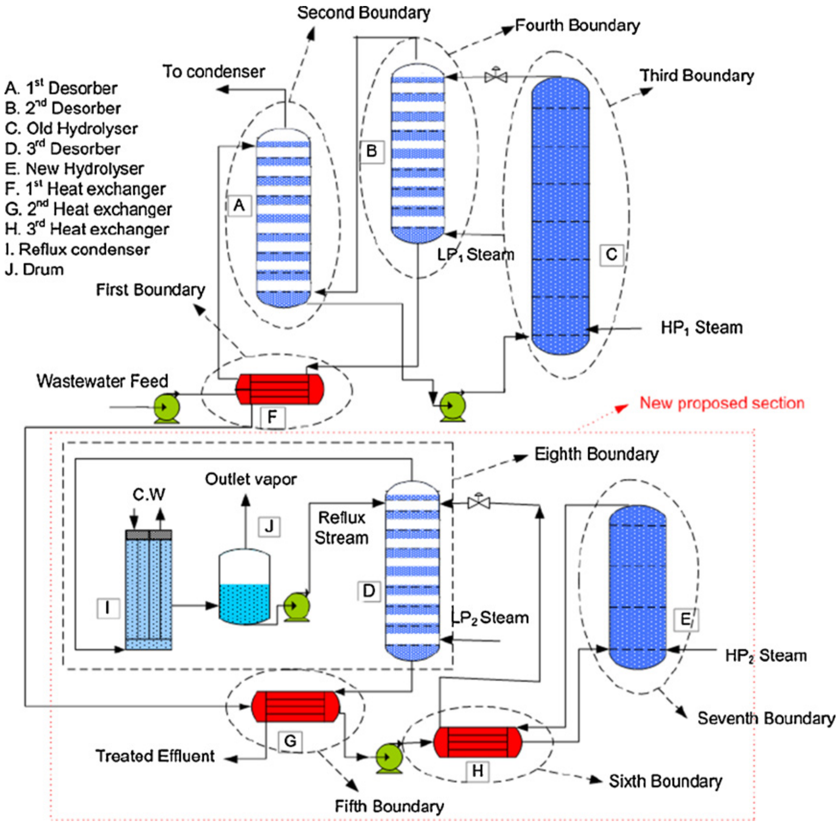

Fig. 2. Cascade of wastewater treatment loops. The boundaries are shown for the material balances.

follows [1,15]:

$$NH_2CONH_2 + H_2O \Leftrightarrow 2NH_3 + CO_2 \tag{1}$$

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:

$$NH_2CONH_2(l) + H_2O(l) \Leftrightarrow H_2NCOO^- + NH_4^+, \quad \Delta H_{298} = -23\,\text{kJ/mol} \tag{2}$$

This reaction is slightly exothermic. Then the ammonium and carbamate ions react to yield carbon dioxide and ammonia in liquid phase, while the vapor and liquid phases are at equilibrium (endothermic reaction):

$$H_2NCOO^- + NH_4^+ \Leftrightarrow 2NH_3(l) + CO_2(l), \quad \Delta H_{298} = 84\,\text{kJ/mol} \tag{3}$$

It is concluded from reactions (2) and (3), 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 hydrolyser [1,15]. 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 non-ideal systems, as shown elsewhere [16–18], the rate becomes:

$$R = k_f\left(a_1a_2 - \frac{1}{K_2}a_3a_4\right) = k_f\left[(\gamma_1C_1)(\gamma_2C_2) - \frac{1}{K_2}(\gamma_3C_3)(\gamma_4C_4)\right] \tag{4}$$

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). a_i, 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 $E = 87{,}780.3\ \text{kJ/kmol}$, respectively [19].

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

$$K_r(T) = K_{X,r}(X)K_{\gamma,r}(T,X), \quad r = 2, 3 \tag{5}$$

where the effects of liquid non-ideality on the reaction equilibria have been merged into a set of parameters, $K_{\gamma,r}(T,X)$ which are defined as:

$$K_{\gamma,r}(T,X) = \frac{\gamma_3(T,X)\gamma_4(T,X)}{\gamma_1(T,X)\gamma_2(T,X)}, \quad r = 2 \tag{6}$$

$$K_{\gamma,r}(T,X) = \frac{\gamma_6^2(T,X)\gamma_5(T,X)}{\gamma_3(T,X)\gamma_4(T,X)}, \quad r = 3 \tag{7}$$

and $K_{X,r}(X)$ is also defined as:

$$K_{X,r}(X) = \frac{x_3x_4}{x_1x_2}, \quad r = 2 \tag{8}$$

$$K_{X,r}(X) = \frac{x_5x_6^2}{x_3x_4}, \quad r = 3 \tag{9}$$

where X is the array of mole fractions in the liquid phase. Substituting Eqs. (6)–(9) into Eq. (5) results:

$$K_2(T) = \left(\frac{x_3x_4}{x_1x_2}\right)\left(\frac{\gamma_3(T,X)\gamma_4(T,X)}{\gamma_1(T,X)\gamma_2(T,X)}\right), \quad r = 2 \tag{10}$$

$$K_3(T) = \left(\frac{x_5x_6^2}{x_3x_4}\right)\left(\frac{\gamma_5(T,X)\gamma_6^2(T,X)}{\gamma_3(T,X)\gamma_4(T,X)}\right), \quad r = 3 \tag{11}$$

where the activity coefficient of each species in the reacting solution can be calculated from thermodynamic model. The following functional form:

$$\ln K_r(T) = \left(\frac{U_{1,r}}{T}\right) + U_{2,r}\ln T + U_{3,r}T + U_{4,r} \tag{12}$$

Table 1
Equilibrium constant parameters [19].

Function	Parameters			
	U_1	U_2	$\times 10^2 U_3$	U_4
$\ln K_2$	−31,363	−64.26	−05.95	482.11
$\ln K_3$	−11,046	−5.19	1.115	51.47

was adopted to describe the temperature dependence of the r reaction equilibrium constant [20]. In the above equation, U_r is a constant related to reaction of number r where tabulated in Table 1.

4. Hydrolyser–desorber loops models

Overall wastewater treatment process includes two process loops. For simulation of the loops, the specification of streams must be obtained. At first, the wastewater treatment loop of conventional section has five unknown streams, which are: (1) output old of hydrolyser stream, (2) output of 1st desorber liquid stream, (3) output of 1st desorber vapor stream, (4) output of 2nd desorber liquid stream and (5) output of 2nd desorber vapor stream. Also the new proposed treatment loop has five unknown streams, which are: (1) output of new hydrolyser stream, (2) output of 3rd desorber liquid stream, (3) output of 3rd desorber vapor stream, (4) reflux stream and (5) outlet vapor of condenser stream. The mole fractions of all components are unknown. The reflux ratio is constant and wastewater feed and steam streams values are known. Also, the content of output vapor stream of 3rd desorber is equal to total contents of the reflux and outlet vapor of condenser streams.

In this study, simulation of the cascade of hydrolyser–desorber loops was done based on the following assumptions:

- Reactions of hydrolysis take place only in the liquid phase.
- The loops operate at steady-state condition.
- Each stage of hydrolyser is perfectly mixed stirred-tank reactor (CSTR).
- Each CSTR operates adiabatically.
- Phase equilibrium is achieved in each stage.
- The volatility of urea and ammonium carbamate is negligible, so there are only three molecular components including H_2O, NH_3 and CO_2 in the vapor phase of desorber.
- Dissolved CO_2 in the liquid phase of desorber is negligible. In fact, it could only be condensed with ammonia to form ammonium carbamate in the liquid phase.

4.1. Simulation of the heat exchangers (first, fifth and sixth 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 transferred at a rate, Q_C, from the hotter tube metal at a temperature, T_M (Eq. (13)):

$$Q_C = U_C A_C (T_M - T_C) \tag{13}$$

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:

$$Q_H = U_H A_H (T_H - T_M) \tag{14}$$

Finally, each stream of the cold and hot sides of the exchanger is described by an energy balance (Eqs. (15) and (16)).

$$(F_H C_{PH} T_H)_L - (F_H C_{PH} T_H)_0 - Q_H = 0 \tag{15}$$

$$(F_C C_{PC} T_C)_L - (F_C C_{PC} T_C)_0 - Q_C = 0 \tag{16}$$

where F_C and F_H are cold and hot stream molar flow rate, respectively and C_P is specific heat capacity. Also subscripts L and 0 indicate length of heat exchanger and inlet conditions, respectively.

4.2. Simulation of the thermal hydrolysis reactors (third and seventh boundaries)

The industrial hydrolyser is a vessel in which the liquid resides long enough at high temperature for equilibrium to be established. In order to increase the one-pass conversion in the tubular hydrolyser, baffle plates are installed inside the reactor to control concentration back-mixing and to approach a plug flow pattern. Therefore, for simulation purposes it will be approximated as a series of continuous multi-stage stirred-tank reactors (CSTRs). This model allows sweeping of operating conditions with different degrees of concentration back-mixing by selecting different numbers of stages.

Throughout the following derivations, CSTRs in sequences will be referred to as stages, numbered from bottom to top. The j subscript corresponds to the stage number. A stream in the CSTR sequences, and its corresponding properties, will be assigned the same j subscript as the stage it leaves.

The steady-state mass balance for species i in reaction (1) on stage j of the reactor sequence is:

$$F_{i,j} = F_{i,j-1} + V_C \upsilon_i R_j, \quad j = 1, 2, \ldots, N \tag{17}$$

where $F_{i,j-1}$ and $F_{i,j}$ are the molar flow rate of component i entering and leaving stage j in the reactor sequence, V_C is the stage volume, υ_i is the stoichiometric coefficient of species i in reaction (1), R_j is the overall rate of reaction (1) in stage j and N is the total number of stages. The flow rate of water to the first stage is determined by a mass balance on the mixing point of steam and wastewater at the inlet of column. Also, the amounts of carbamate and ammonium ions are considered negligible due to the fast reaction (3).

Steady-state energy balance on stage j of the reactor sequence is:

$$\sum_{i=1}^{6} F_{i,j-1} C_{Pi} (T_j - T_{j-1}) + V_C R_j \ \Delta H_j = 0 \tag{18}$$

where T_{j-1} and T_j are the temperature of the reacting fluid entering and leaving stage j in the reactor sequence and ΔH_j is the heat of reaction.

The inlet temperature of the reacting mixture to the first stage, T_0, is determined by an energy balance on the mixing point of steam and wastewater at the inlet of the hydrolyser:

$$\sum_{i=1}^{6} F_i^{in} C_{Pi} (T_i^{in} - T_0) - m_{st}^{\circ} h_{\mathrm{fg}} = 0 \tag{19}$$

where m_{st}° and h_{fg} are mass flow rate and heat of condensation of input steam. F_i^{in} and T_i^{in} are molar flow rate and temperature of component i before mixing. As it is appeared in Eq. (19), it is assumed the steam is quickly condensed at the entrance of the hydrolyser.

In order to calculate the activity coefficient of reacting material an equilibrium-based model is used. According to this model it is assumed that both reactions (2) and (3) approaches to equilibrium [1,7]. In the light of these assumptions, the model equations in terms of the liquid molar flow rates are as follows:

$$F_i^{out} = F_i^{in} + \alpha_{i2} s + \alpha_{i3} w \tag{20}$$

where F_i^{in} is the inlet molar flow rate of component i after mixing steam with wastewater. F_i^{out} is the molar flow rate of component i in reactions (1) and (2) leaving the hydrolyser, α_{ir} is the stoichiometric coefficient of species i in equilibrium reaction r (reactions

Table 2

The expression for constant a_k used in Eq. (23).

k	a_k
0	1
1	1
2	-2
3	$F_6^{in}+F_5^{in}+K_x^{(1)}F_2^{in}$
4	$-(F_6^{in}+F_5^{in})$
5	$F_6^{in}F_5^{in}-K_x^{(1)}F_1^{in}F_2^{in}$

(2) and (3)) which is positive for products and negative for reactants. The molar consumption rate of urea in reaction (2) is s, and that of carbamate in reaction (3) is w. The value of water is very high in comparison with the other components, so it is assumed that the value of water does not change.

The expression for mole fraction of component i at the outlet of the hydrolyser is

$$x_i=\frac{F_i^{out}}{F_{t_0}+(\alpha_{i2}s+\alpha_{i3}w)} \tag{21}$$

where F_{t_0} is the total molar flow rate of the reacting mixture at the inlet of the hydrolyser. The outlet temperature is also determined by an energy balance:

$$\sum_{i=1}^{6}F_i^{in}C_{Pi}(T^{out}-T_0)+s\ \Delta H_2+w\,\Delta H_3=0 \tag{22}$$

where T^{out} is the temperature of reacting material leaving the hydrolyser, and ΔH_2 and ΔH_3 are heat of reactions (2) and (3). T_0 is the temperature of reacting material after mixing of steam and wastewater which is determined by Eq. (22).

If Eq. (21) is substituted into Eqs. (10) and (11), the following nonlinear algebraic equations are derived:

$$a_0s^2+a_1w^2+a_2sw+a_3s+a_4w+a_5=0 \tag{23}$$

$$\begin{aligned}b_0s^3\ &+b_1w^3+b_2s^2+b_3w^2+b_4s^2w+b_5sw^2\\&+b_6sw+b_7s+b_8w+b_9=0\end{aligned} \tag{24}$$

where a_k and b_k are constants as a functions of F_i^{in} and $K_x^r(X)$ as demonstrated in Tables 2 and 3.

4.3. Simulation of the desorbers (second, fourth and eighth boundaries)

In the desorption part, the liquid stream containing water, ammonia and carbon dioxide is passed downward through the desorber column, counter-current to the hot gas or low-pressure steam entering the column at the bottom. In this stage, ammonia and carbon dioxide are transferred from the liquid stream to the gas phase. This provides treated water, with low ammonia content, passing out of the column bottom.

The stage equations are the traditional equation of the mass balances and energy balances in the bulk phase for each stage. For 3rd desorber, stage 1 can be a partial condenser. 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 gas phase. The equilibrium-stage model that is based on rigorous thermodynamics model has been proposed to simulate the desorber. Murphree efficiency has been used for each tray. The equilibrium-stage model for the desorber is as follows (MESH equations, for $i = 1, \ldots, M$, $j = 1, \ldots, N$):

$$M_{i,j}\equiv V_{j+1}y_{i,j+1}+L_{j-1}x_{i,j-1}+\alpha_{i,3}w-V_jy_j-L_jx_j=0 \tag{25}$$

$$E_{i,j}\equiv\frac{EM_{i,j}(K_{i,j}x_{i,j}-y_{i,j+1})}{(y_{i,j}-y_{i,j+1})-1}=0 \tag{26}$$

$$S_j^x\equiv\sum_i^M x_{i,j}-1=0 \tag{27}$$

$$S_j^y\equiv\sum_i^M y_{i,j}-1=0 \tag{28}$$

$$\begin{aligned}H_j\equiv&\sum_i^M V_{i,j+1}H_{i,j+1}^v+\sum_i^M L_{i,j-1}H_{i,j-1}^l-\sum_i^M V_{i,j}H_{i,j}^v\\&-\sum_i^M L_{i,j}H_{i,j}^l=0\end{aligned} \tag{29}$$

$$P_1\equiv p_{top}-p_1=0 \tag{30}$$

$$P_j\equiv p_j-\Delta p_{j-1}-p_{j-1}=0 \tag{31}$$

where V_j and L_j are the vapor and liquid flow rate on the stage j, respectively, x_{ij} and y_{ij} are the molar fraction in the liquid and vapor phases, respectively, and $\alpha_{i,3}$ is the stoichiometric coefficient of species i in reaction (3) which is positive for products and negative for reactants. The molar consumption rate of carbamate in reaction (3) is w and $H_{i,j}^v$ and $H_{i,j}^l$ are the enthalpies of vapor and liquid components on the stage j, respectively. $EM_{i,j}$ is Murphree efficiency of component i on stage j, p_{top} is the specified pressure of the tray at the top of the desorber and Δp_{j-1} is the pressure drop per tray from stage $j-1$ to stage j. For the partial condenser, the enthalpy balance then has the following form:

$$H_j\equiv\sum_i^M V_{i,1}H_{i,1}^v-\sum_i^M V_{i,c}H_{i,c}^v-\sum_i^M L_{i,c}H_{i,c}^l-Q_c=0 \tag{32}$$

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

5. Numerical solution

Fig. 3 shows the flowchart and trend for solving the model. The following steps are involved [14,21].

Table 3

The expression for constant b_k used in Eq. (24).

k	b_k	k	b_k
0	$-K_x^{(2)}$	5	$K_x^{(2)}$
1	$4-K_x^{(2)}$	6	$2K_x^{(2)}F_{t_0}$
2	$-K_x^{(2)}(F_{t_0}+F_6^{in}+F_5^{in})$	7	$-K_x^{(2)}(F_{t_0}+1)(F_6^{in}+F_5^{in})$
3	$K_x^{(2)}(F_6^{in}+F_5^{in}-F_{t_0})+4(F_3^{in}+F_4^{in})$	8	$(F_4^{in})^2+4F_3^{in}F_4^{in}+K_x^{(2)}(F_{t_0}(F_6^{in}+F_5^{in})-F_6^{in}F_5^{in})$
4	$K_x^{(2)}$	9	$F_3^{in}(F_4^{in})^2-K_x^{(2)}F_{t_0}F_6^{in}F_5^{in}$

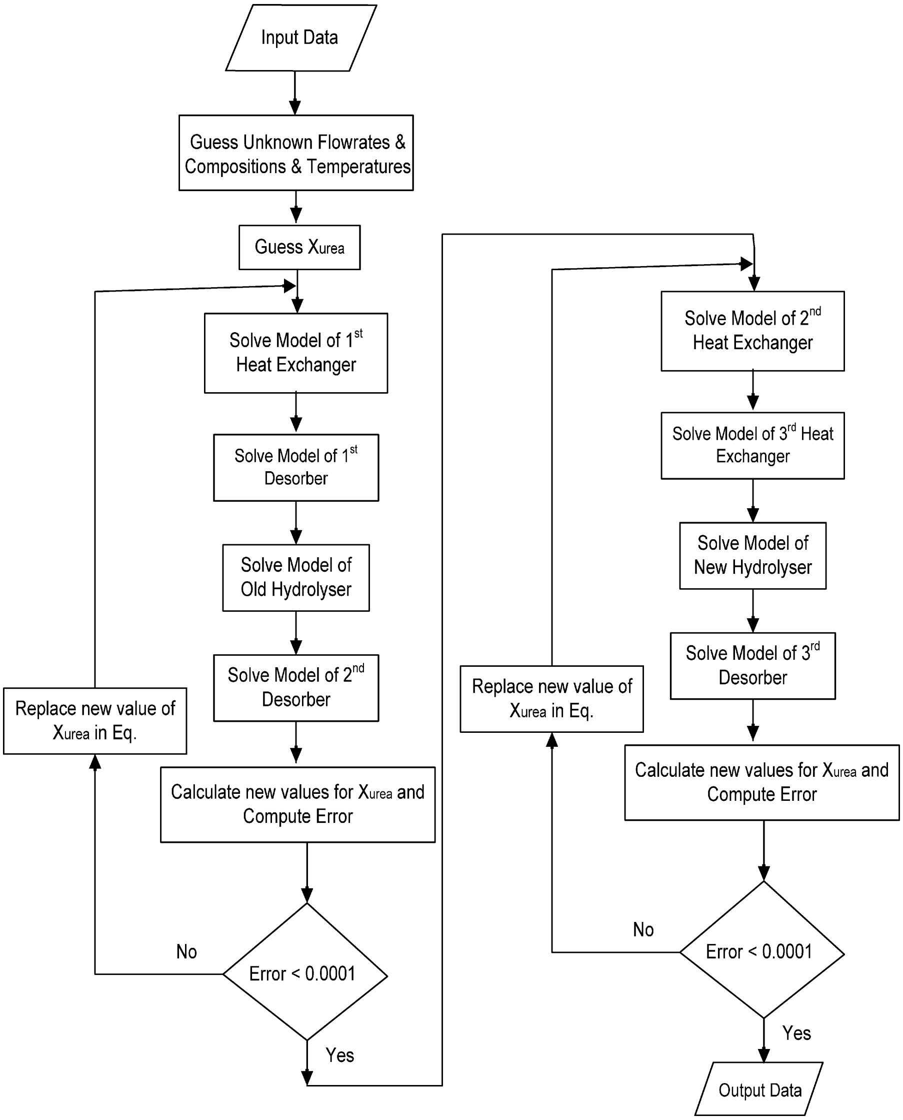

Fig. 3. Flowchart for solving the model.

5.1. *Input data for calculation*

The input data for calculation consists of the specifications of wastewater feed, low and high-pressure steam streams, reflux ratio, hydrolysis reactors and desorbers pressures.

5.2. *Initial guess for unknown parameters*

An initial guess is made for all unknown parameters. In this section, guess values for all composition, flow rates and temperatures are made by trial and error in an attempt to optimize these values.

5.3. *Initial guess for X_{urea}*

When a guess is made for urea conversion in the hydrolyser, the model is solved and new values are obtained for X_{urea}. The purpose of the computer programming is to reach the end, while the difference of new and old values of X_{urea} approaches zero.

5.4. *Solving the heat exchanger model*

When the heat exchanger equations are combined together, an algebraic system of equations is obtained. This nonlinear algebraic system of equations should be solved. The Newton's method is used to solve nonlinear equations. In this model, the inlet temperature of the hot streams is unknown, and this value is calculated by the 2nd desorber model for 1st heat exchanger, the 3rd desorber model for 2nd heat exchanger and the new hydrolyser model for 3rd heat exchanger later, i.e., this temperature is firstly guessed and then corrected by trial and error.

5.5. *Solution of the hydrolyser model*

The steps for solution of hydrolyser model are as follows:

- Set all activity coefficient to 1 and guess the outlet liquid temperature.
- Calculate equilibrium constants using Eqs. (6), (7), (12) and (5).
- Calculate s, w by Eqs. (23) and (24), outlet F_i, x_i by Eqs. (20) and (21), new activity coefficient by Table A.1 and outlet temperature by Eq. (22).
- Repeat steps 2 and 3 until difference between successive activity coefficient is sufficiently small.
- Repeat steps 2 and 3 until difference between successive outlet temperature is sufficiently small.

- Calculate $V_C = V/N$.
- Calculate $F_{i,j}$ and T_j by Eqs. (17) and (18).

In the above procedure, the molar consumption rate of urea (s) and carbamate (w) were determined by Newton–Raphson algorithm.

5.6. Solution of the desorber model

For 1st desorber, specifications of input vapor of it are unknown, which are calculated by the 2nd desorber model later, i.e., the temperature and component flow rates is firstly guessed and then corrected by trial and error. When the specifications of output liquid stream of old and new hydrolysis reactors are known, the calculation relevant to 2nd and 3rd desorbers is used to obtain outlet streams flow rates, composition and temperatures, respectively. The modeling leads to a system of algebraic equations, which are solved by iterative techniques using Newton's method [22]. To improve accuracy and speed up the computation, all of the derivatives of thermodynamic properties in this study are obtained analytically. 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 [23].

Let

$$(F(X)) = 0 \tag{33}$$

where

$$X = [X_1, X_2, \ldots, X_j, \ldots, X_N]^T \tag{34}$$

and

$$F = [F_1, F_2, \ldots, F_j, \ldots, F_N]^T \tag{35}$$

where X_j is the vector of unknown variables for stage j and F_j is the vector of model equations for stage j arranged in the order.

$$X_j = [T_j, x_{1,j}, x_{2,j}, \ldots, x_{i,j}, \ldots, x_{M,j}, y_{1,j}, y_{2,j}, \ldots, y_{i,j}, \ldots, y_{M,j}, L_j, V_j, p_j, w]^T \tag{36}$$

$$F_j = [H_j, M_{1,j}, M_{2,j}, \ldots, M_{i,j}, \ldots, M_{M,j}, E_{1,j}, E_{2,j}, \ldots, E_{i,j}, \ldots, E_{M,j}, S_j^x, S_j^y, P_j, E_{c,j}]^T \tag{37}$$

With this notation, the Newton's method becomes

$$X^{(k+1)} = X^{(k)} + t\ \Delta X^k \tag{38}$$

where k stands for the iteration number, and t is relaxation factor and ΔX is defined as:

$$\Delta X^k = -[(J)^{-1}]^k F^K \tag{39}$$

Also $(J)^{-1}$ is the inverse Jacobian matrix of derivation at kth iteration with elements

$$J_{i,j} = \frac{\partial F_i}{\partial X_j} \tag{40}$$

Table 4
Input specifications of the industrial treatment section of conventional urea plant [8].

Feed specifications	Feed wastewater	HP_1 steam	LP_1 steam
Temperature (°C)	35	380	145
Pressure (kg/cm^2)	3.4	25	4.2
Component molar rate (kmol l/h)			
Water	1675.3	164.3	193.7
Urea	7.08	0	0
CO_2	14.75	0	0
NH_3	52.7	0	0

5.7. Computation of X_{urea}

At this stage, new value for urea conversion is obtained with Eq. (41) and compared with the old value.

$$X_{urea} = \frac{F_f x_f(1) - F_e x_e(1)}{F_f x_f(1)} \tag{41}$$

6. Model validation

In this work, modeling of the conventional treatment loop was performed and its verification was carried out by comparison of the model results with the plant data. The input data of the treatment section of conventional urea plant have been summarized in Table 4.

The model results and the corresponding observed data of the plant have been presented in Table 5. It was observed that, the steady-state model performed satisfactorily well under the industrial conditions and a good agreement was obtain between the plant data and the simulation data which confirm that the proposed model can be considered suitable and reliable.

7. Results and discussion

7.1. Investigation of cascade of wastewater treatment loops

The design operating conditions of the new proposed treatment section are listed in Tables 6 and 7. The simulation results were 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.

Table 5
Comparison of calculated results with the observed plant data for treatment section of conventional urea plant.

	Outlet treated liquid			Outlet vapor of 1st desorber		
	Plant	Calc.	Error (%)	Plant	Calc.	Error (%)
Temperature (°C)	70	68.4	−2.3	124	125.7	1.4
Component molar rate (kmol/h)						
Water	1835.5	1821.1	−0.8	190.7	205.1	7.6
Urea	0.05	0.054	7.4	–	–	
CO_2	0	0	0	21.8	21.75	−0.2
NH_3	0.192	0.202	5.2	66.6	66.5	−0.15
Total (kmol/h)	1835.742	1821.356	−0.8	279.1	293.35	5.1

Table 6
Specifications of the steam consumption of proposed wastewater treatment section.

	LP_2 steam	HP_2 steam
Temperature (°C)	145	380
Pressure (kg/cm^2)	4.2	25
Mass flow rate (kg/h)	6600	1000

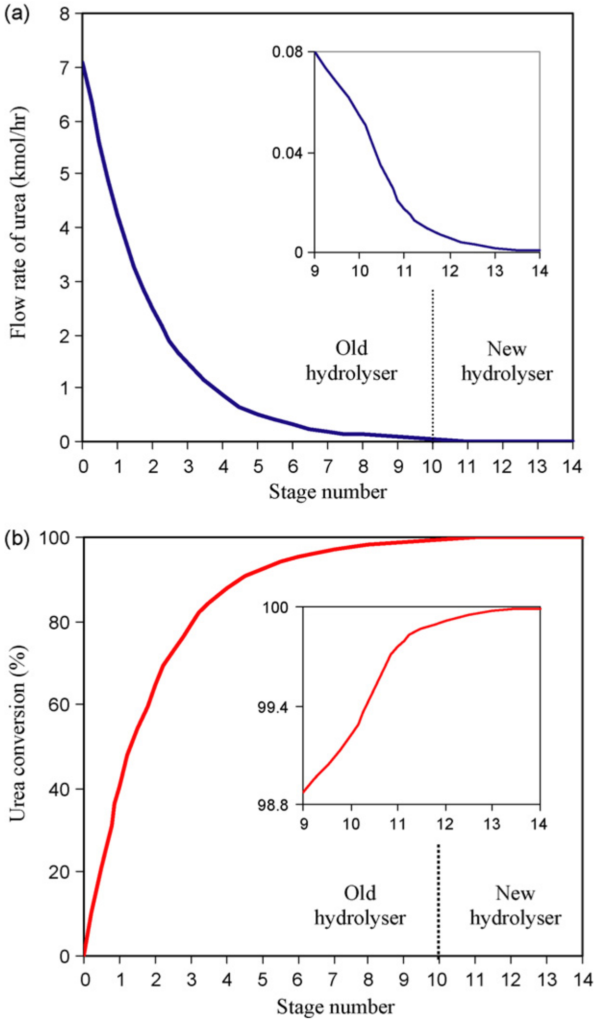

Fig. 4. (a) Molar flow rate and (b) conversion of urea along the hydrolysis reactors where the operating conditions are same as Tables 4 and 6.

Fig. 4(a) and (b) presents urea flow rate and conversion profiles along the old and new thermal hydrolysis reactors, respectively. Urea removal increases along the columns height from bottom to top because of urea hydrolysis. These figures demonstrate an enhancement in urea decomposition and more conversion along the new hydrolyser as the highest conversion is achieved. It shows urea conversion is approximately 100%.

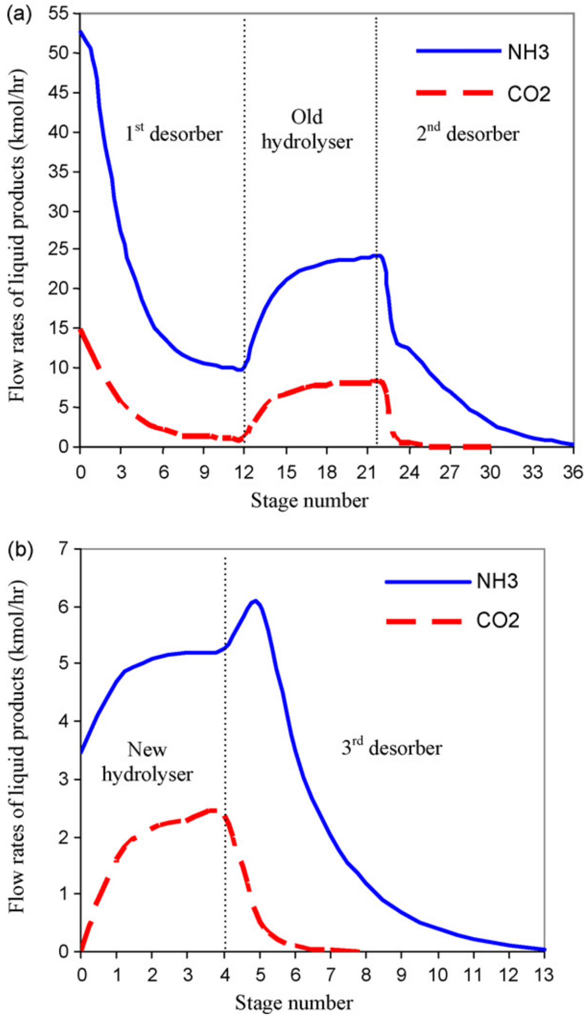

Fig. 5. Molar flow rate of liquid products along the (a) conventional treatment section and (b) new proposed treatment section where the operating conditions are same as Tables 4 and 6.

Fig. 5(a) and (b) shows flow rate of ammonia and carbon dioxide in the conventional and the new treatment process in the liquid phase, respectively. These profiles clearly show the production of these components along the thermal hydrolysis reactors due to reactions and their reduction in the desorbers in the liquid phase, as the two liquid and vapor streams cross each other counter-currently in the desorbers. The sudden decrease at the entrance of the 2nd desorber which is shown in Fig. 5(a) is due to the inlet stream become two phase. In the 3rd desorber, the feed and reflux streams enter from the top of the column. Therefore a maximum point is observed in the ammonia curve of Fig. 5(b).

Fig. 6 shows flow rate of ammonia and carbon dioxide along the desorbers in the vapor phase. As can be seen in these figures, the

Table 7
Specifications of output stream of new hydrolyser and 3rd desorber.

	Outlet stream of hydrolyser	Outlet liquid of desorber	Outlet vapor of condenser	Reflux stream
Temperature (°C)	202.1	132.9	131.3	131.3
Component mass rate (kg/h)				
Water	33,710	39,812	498.4	6608
Urea	1 ppm	1 ppm	–	–
CO_2	2.34	0	2.34	0.0
NH_3	5.25	1 ppm	5.2	5.9

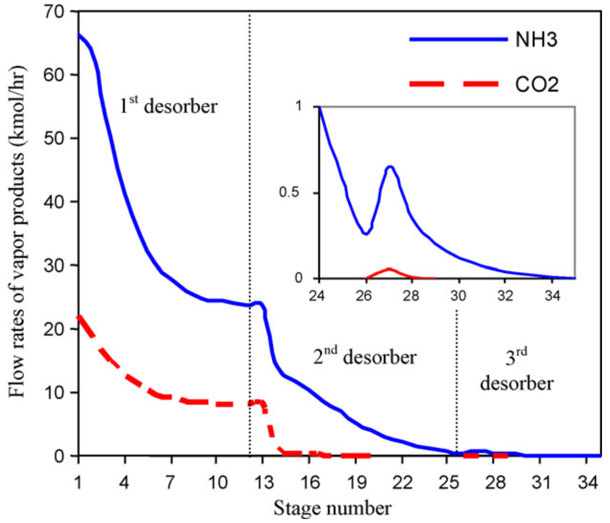

Fig. 6. Molar flow rate of vapor products along the desorbers where the operating conditions are same as Tables 4 and 6.

ammonia and carbon dioxide contents in the vapor phase increase from the bottom to the top of desorbers.

Fig. 7(a) demonstrates the temperature profiles along the hydrolysis reactors. The profile for the old hydrolyser suddenly increases due to the injection of high-pressure steam and then has downward trend owing to the endothermic reaction and its variation is small, but the temperature profile of the new hydrolyser is constant due to low concentration of urea. Fig. 7(b) displays along the desorbers, the liquid temperature increases from the top to the bottom of the column as the liquid flows down the desorber on interacting with the vapor stream. This figure indicates the temperature change along the 3rd desorber is very small because of ammonia content in liquid phase is very low.

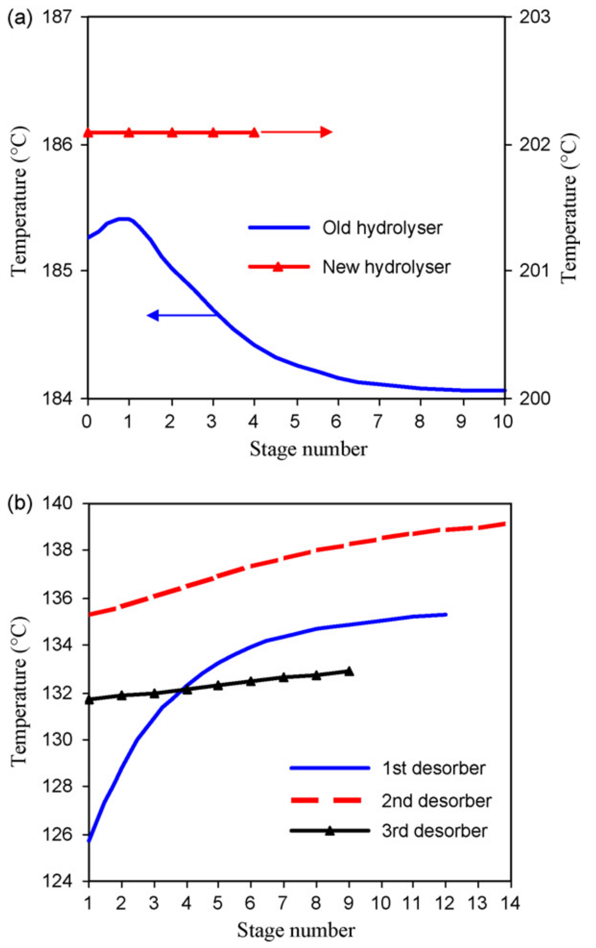

Fig. 7. Temperature profile (a) of reacting material along the hydrolysis reactors and (b) along the desorbers where the operating conditions are same as Tables 4 and 6.

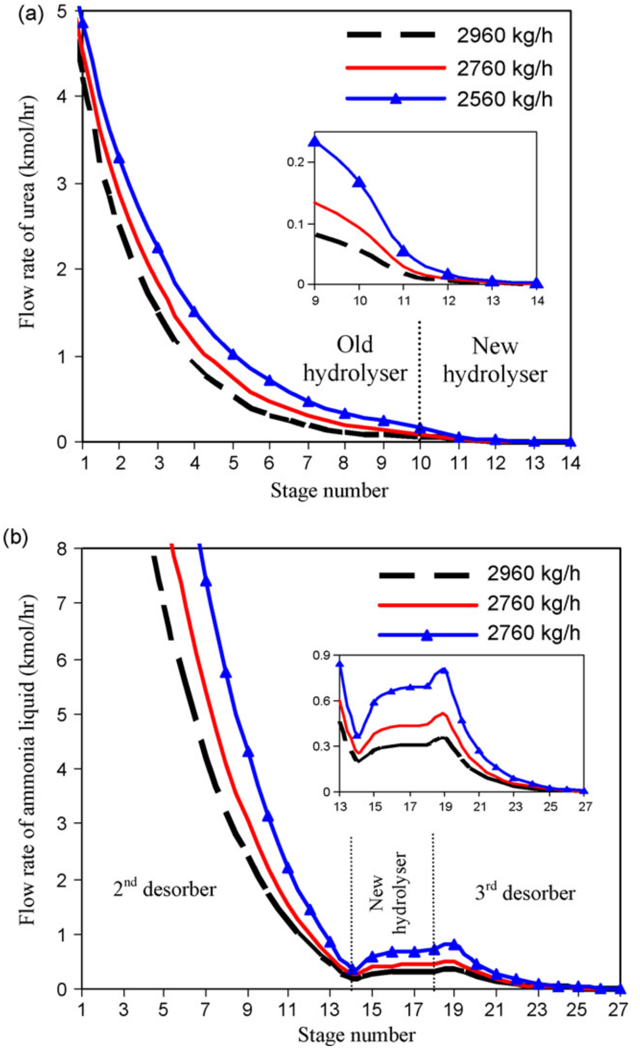

Fig. 8. Molar flow rate of (a) urea along the hydrolysis reactors and (b) ammonia along the 2nd desorber, new hydrolyser and 3rd desorber at different HP_1 steam flow rates.

Fig. 8(a) indicates the flow rate of urea along the hydrolysis reactors at different flow rates of HP_1 steam. As can be seen from this figure, higher steam flow rate maintains a higher temperature level in the reactors, so results in enhancing the urea removal. Also a change in the flow rate of the HP_1 steam has an effect on the flow rate of ammonia in liquid stream. As is clearly demonstrated in Fig. 8(b), an increase in the HP_1 steam flow rate would result in lower ammonia content in liquid phase due to temperature increasing.

Fig. 9 shows the influence of low-pressure (LP_1) steam flow rate on the flow rate of ammonia liquid along the 2nd desorber, new hydrolyser and 3rd desorber. While the LP_1 steam increases, the ammonia content in the liquid phase decreases. This is due to higher level of temperature and increase of driving force in the desorbers.

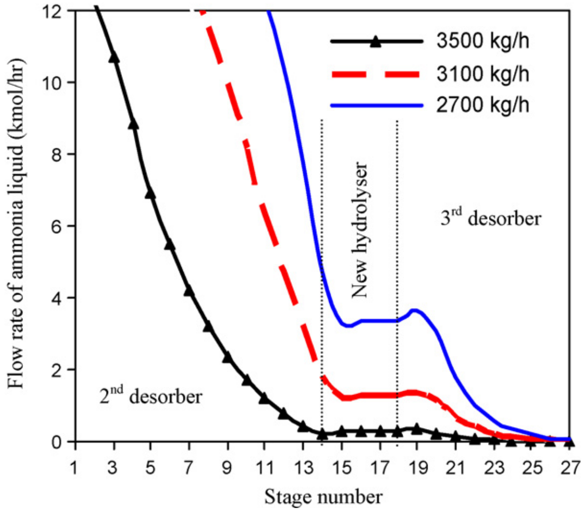

Fig. 9. Molar flow rate of ammonia along the 2nd desorber, new hydrolyser and 3rd desorber at different LP_1 steam flow rates.

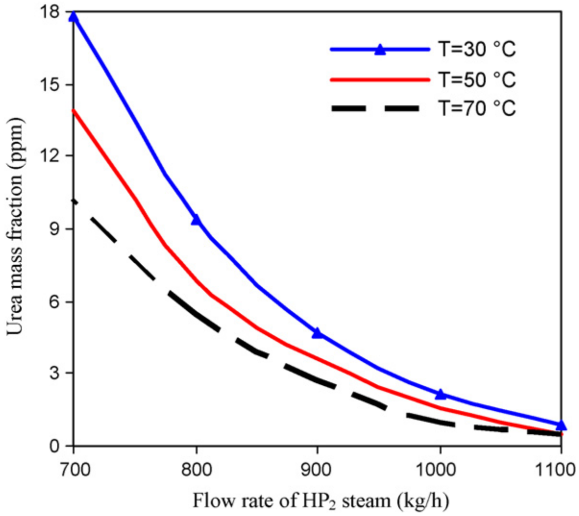

Fig. 11. Urea concentration in the treated effluent at different HP_2 steam flow rates with change of inlet wastewater temperature.

7.2. Investigation of new proposed treatment system

In the proposed design a questionable point raises that will urea removal of hydrolyser improve, if configuration changes from counter-current to co-current? With respect to endothermic overall reactions and kinetic of urea hydrolysis, it is better to increase temperature of inlet wastewater especially if urea concentration is so little. Also in this condition such as 18 bar pressure and low concentrations of ammonia and carbon dioxide in hydrolyser, vapor phase does not form along it and hydrolyser is full of liquid, so counter-current configuration concept does not mean. Therefore as existence of especial mentioned conditions, co-current configuration of hydrolyser is the best design.

In this part, the effects of different parameters on the urea and ammonia removal performance in new proposed treatment section were investigated.

Fig. 10 shows the effect of entering LP_2 steam flow rate on the ammonia concentration in the treated effluent at different reflux ratios. The increase of LP_2 steam flow rate improves the desorption performance and provides a lower concentration of ammonia in outlet liquid. Also increase of ammonia concentration in treated effluent with increasing of reflux ratio can be observed for the reason that the reflux stream increases.

Fig. 11 displays the urea concentration in the treated effluent with change of HP_2 steam flow rates at different inlet wastewater temperatures of proposed system. Since decomposition of urea is an endothermic reaction, increase of the temperature causes decrease of the urea concentration and improves urea removal. Also, as can be seen in Fig. 11 if flow rate of HP_2 steam increases, the reaction shifts to the right and urea decomposition becomes more.

The effect of LP_2 steam flow rate on ammonia concentration in treated effluent at three inlet wastewater temperature of proposed system is shown in Fig. 12. From this figure, lower flow rate of LP_2 steam provides more ammonia concentration than higher flow rate. Also the change of ammonia concentration with alteration of wastewater temperature is negligible because of inlet pressure of 3rd desorber is constant.

The effect of the number of new hydrolyser stages on urea concentration with change of flow rate of HP_2 steam is shown in Fig. 13. Increase of the number of stages enhances conversion of urea, because the decomposition of urea is proportional to the number of stages and much residence time that leads to more urea conver-

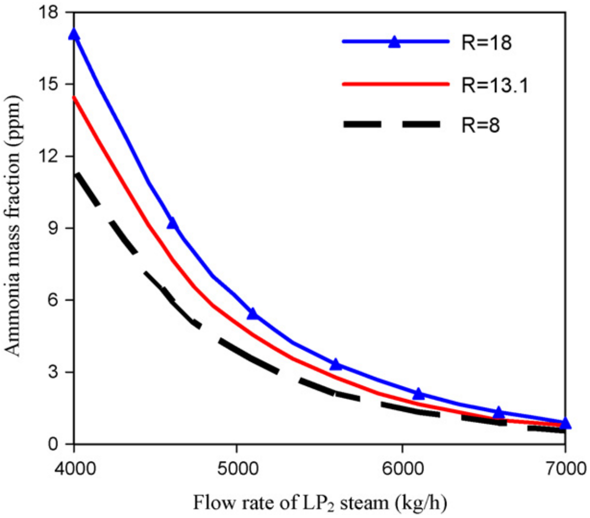

Fig. 10. Ammonia concentration profiles in treated effluent at different reflux ratios with change of LP_2 steam flow rates.

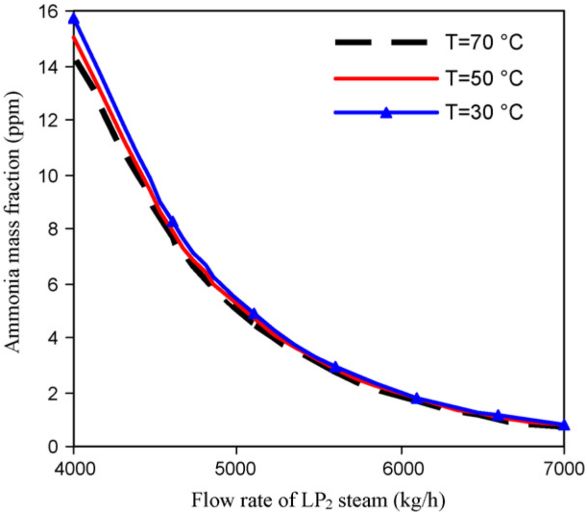

Fig. 12. Ammonia concentration in treated effluent at different LP_2 steam flow rates with change of inlet wastewater temperature.

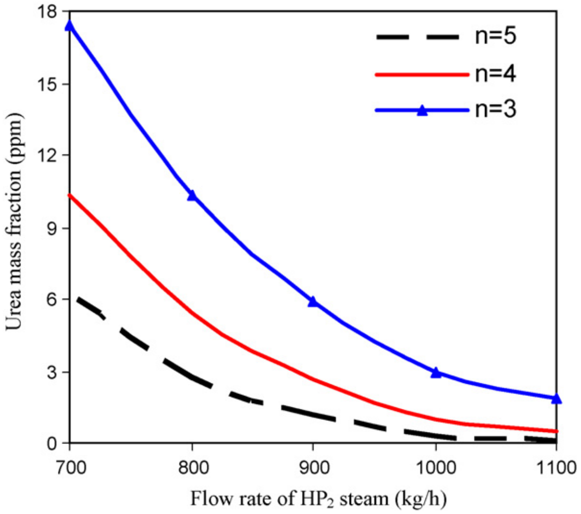

Fig. 13. Influence of number of hydrolyser stages on urea concentration in the treated effluent with change of flow rate of HP_2 steam.

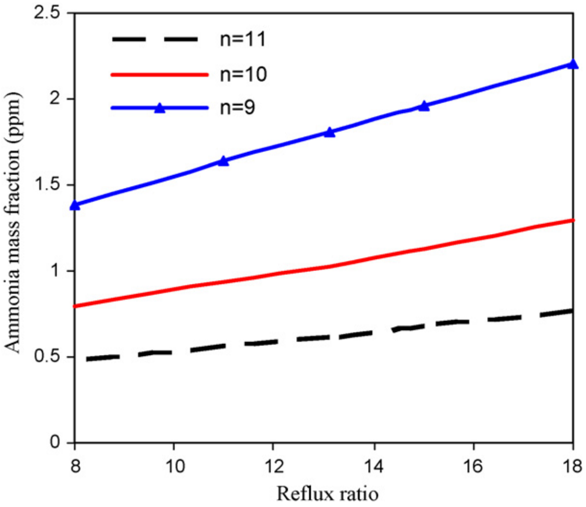

Fig. 14. Influence of number of desorber stages on ammonia concentration in the treated effluent with change of reflux ratio.

sion. Also Fig. 13 shows increasing HP_2 steam flow rate promotes the urea removal.

Fig. 14 demonstrates the effect of the number of 3rd desorber stages on ammonia concentration in treated effluent with change of reflux ratio. When the number of stages is more, the separation is better and the purity of treated liquid becomes more while the number of stages is fewer, the amount of ammonia in liquid phase becomes more and the purity decreases. Also the role of reflux ratio on the treated liquid purity is very low because of small variation of ammonia content in the treated effluent when reflux ratio changes much. As clearly demonstrated in this figure a decrease in reflux ratio would result in a higher purity of water.

8. Conclusions

Nowadays, the environmental pollution is so important, especially water pollution which will become vital subject in future. The liquid waste pollution control problem of a urea plant can be solved using a treatment wastewater section which includes two main equipments, urea thermal hydrolyser to decrease urea content and desorber to decrease ammonia and carbon dioxide contents. Results of study showed one of the best methods to upgrade the outlet effluent of wastewater treatment section of conventional urea plants which has no quality to reuse, is installation of a new small treatment section at end of process. In this study, a mathematical model was used for simulation of cascade of hydrolysis-desorption loops in order to remove urea, ammonia and carbon dioxide from wastewater of conventional urea plant to achieve the new environmental standard, so that all components including the water can be recycled and reused in the plant. All of specifications of the outlet streams of the old and new hydrolysis reactors and desorbers are calculated by the model. The effects of key parameters on purity of treated effluent such as wastewater temperature, number of stages, HP and LP steam flow rates and reflux ratio have been investigated. Generally, it was observed the positive effects on urea and ammonia removal by increase of the temperature, steam flow rate, height of proposed desorber column and hydrolyser. Also, decrease of reflux ratio leads to better removal of urea and ammonia in the treated effluent. The proposed model can be used for design of new industrial wastewater treatment section for conventional urea plants to remove urea, ammonia, urea and carbon dioxide and results in decrease of environmental pollution.

Acknowledgment

The authors would like to thank Shiraz Petrochemical Complex for providing valuable process and technical data and financial support.

Appendix A. Thermodynamics equations

There are several thermodynamic models for describing the non-ideality of NH_3–CO_2–H_2O–urea system [1,24–28]. In this study, the thermodynamic framework to describe liquid activity coefficients of molecular and ionic species in NH_3–CO_2–H_2O–urea system is based on the model developed by Isla et al. [1]. The volatility of urea and ammonium carbamate is negligible and ions cannot leave from the liquid phase to the vapor phase, so there are only three molecular components including H_2O, NH_3, and CO_2 in the vapor phase. The vapor–liquid equilibrium can be expressed with the following relationships:

$$NH_3(l) \Leftrightarrow NH_3(g) \tag{A.1}$$

$$CO_2(l) \Leftrightarrow CO_2(g) \tag{A.2}$$

$$H_2O(l) \Leftrightarrow H_2O(g) \tag{A.3}$$

As follows in Table A.1, the extended UNIQUAC equation consists of three items [1,25–28]. The volume and surface factors, r_i and q_i, are tabulated in Table A.2. All of the binary interaction parameters are listed in Table A.3.

For water and ammonia, the phase equilibrium equations are represented as follows:

$$x_i \gamma_i f_i^0 \exp\left(\frac{v_i^l P}{RT}\right) = P y_i \Phi_i \tag{A.4}$$

where f_i^0 is defined as the standard fugacity under the system temperature and zero pressure. While for carbon dioxide, Henry's law is applicable, and vapor–liquid equilibrium equation is represented as Eq. (A.5), while H_{CO_2} is the Henry's constant of CO_2 under the system temperature.

$$x_i \gamma_i H_{CO_2} \exp\left(\frac{v_i^l (P - P_2^s)}{RT}\right) = P y_i \Phi_i \tag{A.5}$$

The temperature dependence of the pure liquid reference fugacity at zero pressure for ammonia, and Henry's constant for carbon

Table A.1
Parameters of extended UNIQUAC model [1].

Parameter	Expression
$\gamma_i(T,x)$	$\ln\gamma_i(T,x)=\ln\gamma_i^C(X)+\ln\gamma_i^{RE}(T,X)+\ln\gamma_i^{DH}(X,T)$
$\gamma_i^C(X)$	$\ln\gamma_i^C(X)=\ln\left(\frac{\Phi_i}{X_i}\right)+\frac{Z}{2}q_i\ln\frac{\bar{v}_i}{\Phi_i}+l_i-\frac{\Phi_i}{X_i}\sum_j X_j l_j$
$\gamma_i^{RE}(T,X)$	$\ln\gamma_i^{RE}(T,X)=q_i\left[1-\ln\left(\sum_{j=1}^{m}\bar{v}_j\tau_{ji}\right)-\sum_{j=1}^{m}\frac{\bar{v}_j\tau_{ij}}{\sum_{k=1}^{m}\bar{v}_k\tau_{kj}}\right]$
$\bar{v}_i$	$\bar{v}_i=\frac{q_iX_i}{\sum_j q_jX_j}$
Φ_i	$\Phi_i=\frac{\bar{r}_iX_i}{\sum_j \bar{r}_jX_j}$
l_i	$l_i=\frac{Z}{2}(\bar{r}_i-q_i)-(\bar{r}_i-1)$
τ_{ij}	$\tau_{ij}=\exp\left(\frac{-a_{ij}}{T}\right),\ a_{ii}=a_{jj}=0$
$\gamma_i^{DH}(T,X)$	$\ln\gamma_i^{DH}(T,X)=\left(\frac{2A}{b^3}\right)M_i\left[1+bI^{1/2}-\frac{1}{1+bI^{1/2}}-2\ln(1+bI^{1/2})\right]$
$\gamma_i^{DH}(T,X)$	$\ln\gamma_i^{DH}(T,X)=-z_i^2\frac{AI^{1/2}}{1+BI^{1/2}}$
I	$I=\left(\frac{1}{2}\right)\sum m_jz_j^2$
Z	$Z=35.2-0.1272T+0.00014T^2$

Table A.2
Pure component parameters of extended UNIQUAC model [1].

Component	i	q_i	r_i	Units
H_2NCONH_2	1	2.00	2.16	(–)
H_2O	2	1.40	0.92	(–)
NH_4^+	3	0.99	0.91	(–)
H_2NCOO^-	4	1.58	1.71	(–)
CO_2	5	1.12	1.32	(–)
NH_3	6	1.00	1.00	(–)

Table A.3
Binary interaction parameters of extended UNIQUAC model [1].

i	j					
	1	2	3	4	5	6
1	0.0	91.7	−162.2	−166.2	269.0	−532.5
2	−110.0	0.0	355.6	0.9	−401.5	−626.3
3	272.8	−272.8	0.0	1476.5	−653.6	−12.4
4	221.6	−96.6	−337.2	0.0	−302.6	−62.3
5	670.5	2623.7	836.1	−204.8	0.0	−610.0
6	357.1	847.3	−190.7	335.0	−291.4	0.0

dioxide are modeled as

$$\ln f_{NH_3}^0(T)=\frac{A_1}{T}+A_2\ln T+A_3T+A_4 \quad (A.6)$$

$$\ln H_{CO_2}(T)=\frac{B_1}{T}+B_2\ln T+B_3T+B_4-q_5\tau_{5,2} \quad (A.7)$$

where q_5 and $\tau_{5,2}$ are obtained from Table A.1. All parameters of ammonia fugacity and carbon dioxide Henry's constant are represented in Table A.4.

Table A.4
Ammonia fugacity and carbon dioxide Henry's constant parameters.

Function	Parameters			
	$10^{-2}A_1$	10^2A_2	10^4A_3	$10A_4$
$\ln f_{NH_3}^0$	−25.141	28.417	−25.759	146.46
Function	Parameters			
	$10^{-2}B_1$	10^2B_2	10^3B_3	$10B_4$
$\ln H_{CO_2}$	−26.56	−35.05	63.216	181.575

Appendix B. Nomenclature

A_j	jth parameter in the correlation of pure liquid reference fugacity of ammonia with temperature
a_k, b_k	constants of Eqs. (23) and (24)
B_j	jth parameter in the correlation of Henry's constant of carbon dioxide in water with temperature
C_i	concentration of component i (kmol/m^3)
C_P	heat capacity of fluid (kJ/(kmol K))
E	activation energy (kJ/kmol)
$E_{c,j}$	residual function for chemical equilibrium relation for carbamate on the jth tray
$E_{i,j}$	residual function for phase equilibrium relation for component i on the jth tray
$EM_{i,j}$	Murphree tray efficiency for component i on the jth tray
f_i	fugacity of component i (kPa)
F	matrix of functions
F_e	molar flow rate of hydrolyser effluent (kmol/h)
F_f	molar flow rate of hydrolyser feed (kmol/h)
$F_{i,j}$	molar flow rate of component i leaving stage j in the reactor (kmol/h)
F_i^{in}	molar flow rate of component i before mixing at the entrance of reactor (kmol/h)
F_{t_0}	total molar flow rate at the inlet of hydrolyser (kmol/h)
h_{fg}	heat of condensation of input steam to the hydrolyser (kJ/kg)
$H_{i,j}^v$	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 jth tray
H_{CO_2}	Henry's constant of component i in solvent j
I	ionic power in Table A.1
J	Jacobian matrix (matrix of blocks of partial derivatives of all functions with respect to all the output variables)
$K_{i,j}$	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))
$K_{x,r}$	equilibrium constant of reaction r dependent on temperature and mole fraction
$K_{\gamma,r}$	equilibrium constant of reaction r dependent on mole fraction
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)
l_i	parameter of UNIQUAC equation in Table A.1
m_{st}°	mass flow rate of input steam to the hydrolyser (kg/h)
M	number of components
$M_{i,j}$	residual function for material balance for component i on the jth tray
m_i	molality of the ionic species i referred to 1000 g of mixed solvent (kg/(kg soln))
N	number of stages
P_j	pressure of stage j (kPa)
ΔP_j	pressure drop (kPa)
p_{top}	pressure at the top of the column (kPa)
q_i	UNIQUAC surface parameter of component i
Q_c	condenser duty (kJ/h)
Q_i	heat transfer in the heat (kJ/h)
r_i	UNIQUAC volume parameter of component i
R	universal gas constant (kJ/(kmol K))

R_j	rate of reaction (2) on the *j*th tray (kmol/(m^3 h))
S_j^x	residual function for summation relation in liquid phase on the *j*th tray
S_j^y	residual function for summation relation in liquid phase on the *j*th tray
t	relaxation factor
T	temperature (K)
T_i^{in}	temperature of component *i* before mixing at the entrance of the hydrolyser (K)
T_M	metal temperature in heat exchanger (K)
T_0	inlet temperature of the reacting mixture to the first stage in the hydrolyser (K)
U	constant (Eq. (12))
U_i	overall heat transfer coefficient in heat exchanger (kJ/(h m^2 K))
V_C	stage volume of hydrolyser (m^3)
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)
v_i^l	liquid molal volume of component *i*
v_i^∞	liquid molal volume of component *i* at infinite dilution
w	consumption molar flow rate of carbamate in reaction (3) (kmol/h)
x_e	mole fraction of component *i* in hydrolyser effluent
x_f	mole fraction of component *i* in hydrolyser feed
$x_{i,j}$	mole fraction of component *i* in liquid phase on the *j*th tray
X	matrix of output variables
X_{urea}	urea conversion
$y_{i,j}$	mole fraction of component *i* in vapor phase on the *j*th tray
Z	UNIQUAC coordination number ($Z = 10$) in Table A.1

Greek letters

$\alpha_{i,2}$	stoichiometric coefficient of species *i* in reaction (2)
$\alpha_{i,3}$	stoichiometric coefficient of species *i* in reaction (3)
a_{ij}	parameter of UNIQUAC equation (kJ/mol) in Table A.1
γ_i	activity coefficient of component *i* in Table A.1
υ_i	stoichiometric coefficient of species *i* in reaction (1)
$\bar{\upsilon}_i$	surface area fraction of component *i* in Table A.1
Φ_i	volume area fraction of component *i* in Table A.1
τ_{ij}	parameter of UNIQUAC equation in Table A.1
ξ	reduced density in equation state

Subscripts

0	inlet conditions
i	component number
j	stage number
k	counter of constants *a* and *b* in Eqs. (23) and (24)
L	length of heat exchanger
r	reaction number
t	total

Superscripts

C	combinatorial
DH	Debye–Huckel
in	inlet of hydrolyser
out	outlet of hydrolyser
RE	residual

References

[1] M.A. Isla, H.A. Irazoqui, C.M. Genoud, Simulation of a urea synthesis reactor. Part 1. Thermodynamic framework, Ind. Eng. Chem. Res. 32 (1993) 2662–2670.

[2] V. Lagana, US Patent 5,399,755 (1995).

[3] H. van Baal, The environmental impact of a Stamicarbon 2000 mtd urea plant, in: Proceedings of Eighth Stamicarbon Urea Symposium, Amsterdam, The Netherlands, 1996, pp. 4–7.

[4] Norris, J. Landis, US Patent 4,341,640 (1982).

[5] J.N. Sahu, K. Mahalik, A.V. Patwardhan, B.C. Meikap, Equilibrium and kinetic studies on the hydrolysis of urea for ammonia generation in a batch reactor, Ind. Eng. Chem. Res. 47 (14) (2008) 4689–4696.

[6] M.R. Rahimpour, A. Asgari, Modeling and simulation of ammonia removal from purge gases of ammonia plants using a catalytic Pd–Ag membrane reactor, J. Hazard. Mater. 153 (2007) 557–565.

[7] J. Mehnen, C. Verweel, Experience to date with the Stamicarbon desorber–hydrolyser system, in: Proceeding of Stamicarbon's Seventh Urea Symposium, Maastrikht, The Netherlands, 1987, pp. 1–15 (Paper 9).

[8] Shiraz Petrochemical Complex, Urea Plant, Operating Data of Urea Thermal Hydrolysis Process, 2002.

[9] M.R. Rahimpour, A. Azarpour, Simulation of a urea thermal hydrolysis reactor, Chem. Eng. Commun. 192 (2005) 155–167.

[10] M.R. Rahimpour, A. Azarpour, A multistage well-mixed model for urea removal from industrial wastewater, Eng. Life Sci. 3 (2003) 335–340.

[11] M.R. Rahimpour, A non-ideal rate-based model for industrial urea thermal hydrolyser, Chem. Eng. Process. 43 (2004) 1299–1307.

[12] M.M. Barmaki, M.R. Rahimpour, A. Jahanmiri, Treatment of wastewater polluted with urea by counter-current thermal hydrolysis in an industrial urea plant, Sep. Purif. Technol. 66 (2009) 492–503.

[13] A.M. Douwes, US Patent 4,652,678 (1987).

[14] M.R. Rahimpour, H.R. Mottaghi, Simultaneous removal of urea, ammonia, and carbon dioxide from industrial wastewater using a thermal hydrolyzer–separator loop, Ind. Eng. Chem. Res. 48 (2009) 10037–10046.

[15] B. Claudel, E. Brousse, G. Shehadeh, Novel thermodynamic and kinetic investigation of ammonium carbamate decomposition into urea, Thermochim. Acta 102 (1986) 357–371.

[16] M. Boudart, Kinetics of Chemical Processes, Prentice-Hall, New Jersey, 1968.

[17] H. Eyring, E.M. Eyring, Modern Chemical Kinetics, Reinhold, New York, 1963.

[18] J.B. Butt, Reaction Kinetics and Reactor Design, second ed., Marcel Dekker, New York, 2000.

[19] H. Aoki, T. Fujiwara, Y. Morozumi, T. Miura, Proceedings of the Fifth International Conference on Technologies and Combustion for a Clean Environment, Lisbon, 1999, pp. 115–118.

[20] T.F. Anderson, D.S. Abrams, E.A. Grens, Evaluation of parameters for nonlinear thermodynamics models, AIChE J. 24 (1978) 20–29.

[21] P. Parvasi, M.R. Rahimpour, A. Jahanmiri, Incorporation of dynamic flexibility in the design of a methanol synthesis loop in the presence of catalyst deactivation, Chem. Eng. Technol. 31 (2008) 1–18.

[22] A.L. Myers, W.D. Seider, Introduction to Chemical Engineering and Computer Calculation, Prentice-Hall, 1976.

[23] J.D. Seader, E.J. Henley, Separation Process Principles, Wiley, New York, 1998.

[24] M. Bernardis, G. Carvoli, M. Santini, Urea–NH_3–CO_2–H_2O: VLE calculations using an extended UNIQUAC equation, Fluid Phase Equilib. 53 (1989) 207–218.

[25] E.A. Kotula, A VLE model of the NH_3–CO_2–H_2O–urea system at elevated pressure, J. Chem. Technol. Biotechnol. 31 (1981) 103–110.

[26] B. Sander, A. Fredenslund, P. Rasmussen, Calculation of vapour–liquid equilibria in mixed solvent/salt systems using an extended UNIQUAC equation, Chem. Eng. Sci. 41 (1986) 1171–1183.

[27] B. Sander, P. Rasmussen, A. Fredenslund, Calculation of vapor–liquid equilibrium in nitric acid–water–nitrate salt systems using an extended UNIQUAC equation, Chem. Eng. Sci. 41 (1986) 1185–1195.

[28] B. Sander, P. Rasmussen, A. Fredenslund, Calculation of solid–liquid equilibria in aqueous solutions of nitrate salts using an extended UNIQUAC equation, Chem. Eng. Sci. 41 (1986) 1197–1202.