

Modeling the synthesis section of an industrial urea plant

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Abstract

Urea is an important petrochemical product which is mainly used as fertilizer. In this study, a model is developed for the synthesis section of an industrial urea plant. In the proposed model the urea reactor is divided into several continuously stirred tank reactors (CSTRs). It has been considered in this study that formation of ammonium carbamate occurs through the heterogeneous reaction of carbon monoxide and ammonia. This reaction was considered to occur only in the liquid phase in the previous works presented in the literature. The formation of biuret in the reactor is also considered in the model which has not been considered in the previous works. The validity of the proposed model was demonstrated using industrial data. It has been shown that there is a good agreement between the results of the model and the industrial data. Dynamic response of the process to some important parameters in the synthesis section was also studied.

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1. Introduction

Urea (NH_2CONH_2) is produced at industrial scale by the reaction between ammonia and carbon dioxide at high pressure (13–30 MPa) and high temperature (170–200 °C). There are different types of processes to produce urea in the commercial units. These processes are typically called once through, partial recycle and total recycle [1,2]. In the total recycle process, which is employed widely, all the ammonia leaving the synthesis section is recycled to the reactor and the overall conversion of ammonia to urea reaches 99%. Stamicarbon and Snomprogetti processes [3] are the most common examples of such process [4]. Since urea has become almost the most widely used fertilizer and its production is important in the petrochemical industry, there has been many attempts to model and simulate the reactor of urea production as the heart of the process [1–5].

In the present work the entire urea synthesis section based on the of stamicarbon process (including urea reactor, carbamate condenser, stripper, and scrubber) is modelled. Urea production consists of two reactions. In the first reaction,

ammonia and carbon dioxide react to form ammonium carbamate which decomposes to urea and water in the next step. In the previous works reported in the literature, the homogeneous reaction between carbon dioxide and ammonia to form ammonium carbamate is considered to take place in the reactor. Since both carbon dioxide and ammonia are in the gas phase in the reactor and reaction between these two results in production of ammonium carbamate which is in the liquid phase, in the present study this reaction is considered to be heterogeneous. Moreover, in the studies reported in the literature, biuret ($\text{NH}_2\text{CONHCONH}_2$) formation, which is the main undesired by-product in the urea production process, is neglected. As biuret is toxic to plants, its content in fertilizers has to be kept as low as possible. It has been tried in this work to model and validate the industrial urea synthesis section considering the above-mentioned reactions.

1.1. Process description

Synthesis section of stamicarbon process in the industrial urea production plant is shown in Fig. 1. As it is seen in this figure, compressed carbon dioxide feed passes through the stripper along which ammonia and carbon dioxide (due to decomposition of ammonium carbamate and free dissolved am-

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Nomenclature

a	moles of water added per mole of ammonium carbamate
C_{A0}	initial concentration of A (kmol m^{-3})
C_{U0}	initial concentration of urea (mol l^{-1})
d	density (kg m^{-3})
E	activation energy (kJ kg mol^{-1})
F	molar flow rate (kg mol h^{-1})
H	enthalpy (kJ h^{-1})
k	rate constant of urea production (h^{-1})
k'	rate constant of biuret production ($\text{l mol}^{-1} \text{h}^{-1}$)
K_p	equilibrium constant of ammonium carbamate production (atm^3)
M	average molecular weight (kg kg mol^{-1})
N_i	number of moles of component i (kg mol)
m	initial moles of carbon dioxide (kg mol)
n	initial moles of ammonia (kg mol)
n_t	total number of moles (mol)
N/C	nitrogen to carbon mass ratio
P	total pressure (atm)
P_c	critical pressure (kPa)
P_{CO_2}	partial pressure of carbon dioxide (atm)
P_{NH_3}	partial pressure of ammonia (atm)
Q_{ac}	heat produced by ammonium carbamate formation (kJ h^{-1})
Q_b	heat consumed by biuret formation (kJ h^{-1})
Q_c	heat exchanging duty of condensate in carbamate condenser (kJ h^{-1})
Q_{cw}	heat exchanging duty of cooling water in scrubber (kJ h^{-1})
Q_u	heat consumed by urea formation (kJ h^{-1})
Q_s	heat exchanging duty of steam in stripper (kJ h^{-1})
$-r_A$	reaction rate of component A ($\text{kg mol m}^{-3} \text{h}^{-1}$)
t	time (h)
T	temperature (K)
T_c	critical temperature ($^{\circ}\text{C}$)
T_{NBP}	normal boiling point temperature ($^{\circ}\text{C}$)
V	volume (m^3)
v_0	volumetric flow rate of feed ($\text{m}^3 \text{h}^{-1}$)
x	moles of ammonium carbamate (mol)
X_A	partial conversion of A
X_1	partial conversion of ammonium carbamate to urea
X_2	partial conversion of urea to biuret
y	moles of urea per volume that reacts at t (mol l^{-1})

Subscript

I	inlet
O	outlet

Table 1
Properties of components [4]

Component	T_{NBP} ($^{\circ}\text{C}$)	d (kg/m^3)	T_c ($^{\circ}\text{C}$)	P_c (kPa)
Urea	191.85	1230	431.85	9050
Ammonium carbamate	600	1100	785.27	1103.92
Biuret	598.3	1068.9	770.52	997.31
CO_2	-78.55	825.34	30.95	7370
NH_3	-33.45	616.07	132.4	11276.9
H_2O	100	997.99	374.15	22120
O_2	-182.95	1137.68	-118.38	5080.02
N_2	-195.8	806.37	-146.96	3394.37

monia) are stripped off from the liquid phase to the gas phase. The gas flow from the scrubber which carries the stripped-off ammonia and carbon dioxide is then introduced into the top of the carbamate condenser. Ammonia, together with the carbamate overflow from the scrubber, is also introduced into the top of the carbamate condenser. The carbamate condenser is in fact a heat exchanger in which the heat generated during condensation of ammonia and carbon dioxide to form ammonium carbamate in the tube side is used to produce low pressure steam in the shell side.

Only part of ammonia and carbon dioxide condense in the carbamate condenser and the rest react in the urea reactor in order to supply the heat required for the urea production reaction. Liquid and gas phases leave the carbamate condenser via two separate lines to ensure a stable flow into the reactor. Ten trays are installed in the reactor in order to improve the contact between the two phases. The liquid mixture in the reactor overflows into the stripper. The heat is supplied into the stripper by the flow of saturated steam through its shell, resulting in decomposition of the remainder ammonium carbamate into urea. The gas phase exiting the reactor contains free ammonia and carbon dioxide as well as inert gas and is discharged into the scrubber.

In the scrubber, condensation of ammonia and carbon dioxide is achieved. The heat of condensation is partly removed in the heat exchanging part of the scrubber by cooling water. In the scrubbing part, remaining gases are scrubbed with the lean carbamate solution. This stream, which is a low concentration aqueous solution of ammonium carbamate, is a recycle from the low pressure section of the urea process.

2. Model development

In this section the hypothesis and necessary equations for developing the steady state and dynamic models of the urea synthesis section are described. A complete list of the components involved in the process of urea synthesis as well as their physical properties are shown in Table 1.

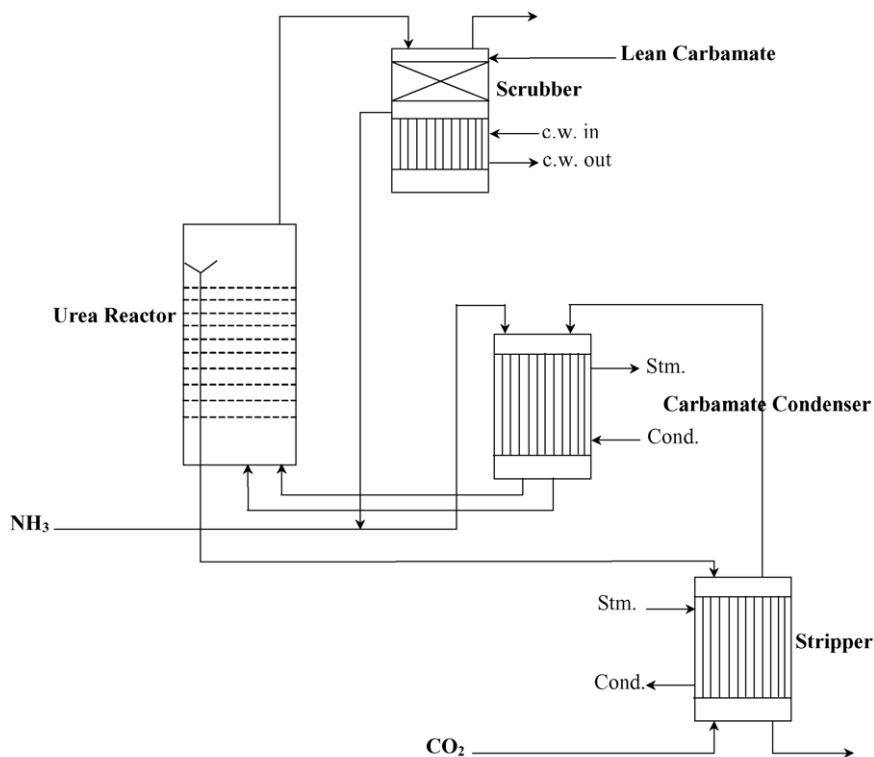


Fig. 1. Block flow diagram in the synthesis section of stamicarbon urea plant.

2.1. Hypotheses

Simulation of the synthesis section of urea plant in this study was done based on the following assumptions:

- Only CO_2 , H_2O , NH_3 and inert gases (O_2 , N_2) exist in the gas phase.
- CO_2 is not dissolved in the liquid phase. In fact, it could only be condensed with ammonia to form ammonium carbamate in the liquid phase.
- Formation of urea takes place only in liquid phase.
- Dissolution of inert gases in the liquid phase is neglected.
- Biuret is produced only in the reactor and the stripper.

2.2. Thermodynamics

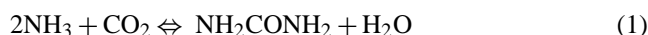
In this study, the thermodynamic framework is based on the model developed by Isla et al. [1]. However, Wilson and ideal gas equations [6] were employed for calculating the thermodynamic properties of liquid and gas phases, respectively. A virtually identical model was presented by Agarwal et al. [7] where UNIQUAC was the model of choice. It is worth mentioning that many pairs of activity models and/or equations of state were examined to predict the thermodynamic behavior of the gas and liquid phases in this system. However, the closest results to the real plant data were found when employing the above-mentioned pair of equations for predicting the thermodynamic properties of the two phases. It should be noted that the main reactions in the urea synthe-

sis process occur in the liquid phase (see Section 2.3 below). Therefore, the model is less sensitive to the choice of the equation of state employed for the gas phase.

The Wilson equation was tuned for the urea synthesis conditions. The tuning was done by changing the interaction parameters such that the model prediction best fit the actual plant data. The complete list of temperature independent interaction parameters of Wilson equation are given in Table 2.

2.3. Reactions

The overall reaction of urea production is as follows:



The process of urea synthesis consists of two sequential steps. In the first step, ammonium carbamate is formed by the reaction between ammonia and carbon dioxide:



This reaction is very exothermic and fast in both directions so that it could be considered at equilibrium at the conditions found in industrial reactors where the residence time is rather high. In the next step, ammonium carbamate is dehydrated to form urea:

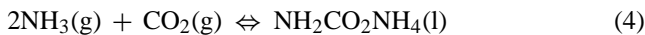


Table 2
Temperature independent interaction parameters of Wilson equation (cal/mol)

Component	CO ₂	NH ₃	H ₂ O	N ₂	H ₂	O ₂	Biuret	Ammonium carbamate	Urea
CO ₂	–	–3534.00	676.20	0.00	0.00	0.00	–3782.60	–3842.70	–2100.70
NH ₃	69.68	–	0.00	64.23	60.23	–12.16	311.58	1272.09	234.06
H ₂ O	–183.70	0.00	–	30.16	–6.51	–80.37	11640.70	1182.00	1862.86
N ₂	0.00	–31.64	7.05	–	0	0.00	–656.39	–659.98	3127.62
H ₂	0.00	–20.49	8.02	0.00	–	0.00	201.98	217.74	2871.87
O ₂	0.00	2051.30	29.19	0.00	0	–	1077.91	1082.71	3614.11
Biuret	69.68	448.00	4096.00	20.03	11.56	–12.16	–	597.00	239.00
Ammonium carbamate	69.68	1595.00	1135.00	25.00	11.56	28.00	741.00	–	171.08
Urea	69.68	650.00	1050.00	–3.00	11.56	–12.16	–55.00	197.94	–

This reaction is endothermic and slow as compared to the preceding reaction. Therefore, it needs a long residence time to reach the equilibrium [5].

Although the researchers have considered the presence of gas and liquid phases in their model, all of them have considered that ammonia and carbon dioxide react in the liquid phase in the ammonium carbamate formation step (homogeneous reaction) (e.g., [1,2,5]). However, since these two reactants are in gas phase throughout the process, the following heterogeneous reaction has been considered to take place:



It has been assumed in the present study that ammonia and carbon dioxide react in the gas phase to form liquid ammonium carbamate.

Formation of biuret is also considered to take place in this work. The corresponding reaction is as follows:



This reaction is slow and endothermic. Biuret formation takes place when there is a high urea concentration, low ammonia concentration and high temperature [8,9].

Three main reactions considered in the process are formation of ammonium carbamate (4), formation of urea (3) and formation of biuret (5). The residence time in the urea reactor is high enough in order the reaction of ammonium carbamate formation to be practically considered at equilibrium in the effluent [10]. Therefore, in order to calculate the conversion of carbon dioxide in the urea reactor the equilibrium constant of reaction (4) should be known. The equilibrium constant of this reaction has been already investigated [10–12]. In the present study, the temperature dependent formula of Egan et al. [11] has been adopted due to the fact that it covers a wide range of temperature. Moreover, in order to further enhance the accuracy of the model, in addition to the data reported by Egan et al. [11], existing equilibrium data at the industrial urea reactor outlet was also taken into account and the equilibrium constant was improved as follows:

$$\log K_p = -\frac{7.6569 \times 10^3}{T} + 22.161 \quad (6)$$

The data reported by Egan et al. [11] as well as the plant data and are shown in Fig. 2.

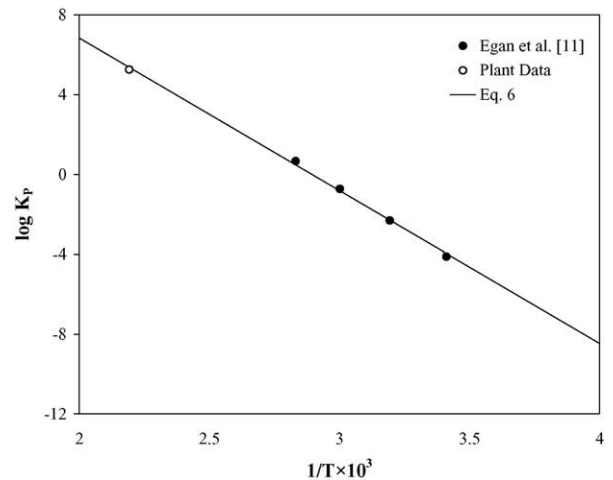


Fig. 2. Equilibrium constant K_p as a function of temperature.

The formation of urea and biuret are considered as slow reactions and far from the equilibrium in the urea reactor. For the urea formation reaction (reaction (3)), the rate equation of Claudel et al. [13] in the presence of initial water have been employed:

$$\frac{dX_1}{dt} = k(1 - X_1)(a + X_1) \quad (7)$$

In the case of biuret formation reaction, the rate equation proposed by Shen [14] was employed:

$$\frac{dy}{dt} = k'(C_{U0} - y)^2 \quad (8)$$

The kinetic parameters of Eqs. (7) and (8) are given in Table 3.

2.4. Process equipments

2.4.1. Carbamate condenser

The equations related to the dynamic behavior of the carbamate condenser are summarized in Table 4. Carbamate

Table 3
Kinetic parameters

	k_0	E (kJ/kg mol)
k [13]	1.9×10^5	4.2×10^4
k' [14]	2.1×10^7	8.5×10^4

Table 4
Model equations

Section	Equation	Description
Carbamate condenser	$\frac{d(V_{\text{Carbamate-Condenser}})}{dt} = F_1 M_1 - F_0 M_0$	Overall mass balance
	$F_{1,\text{CO}_2} - F_{0,\text{CO}_2} - r_{\text{CO}_2} V_{\text{Carbamate-Condenser}} = V_{\text{Carbamate-Condenser}} \frac{d}{dt} \left(\frac{d}{M} \frac{F_{0,\text{CO}_2}}{F_0} \right)$	Mole balance for carbon dioxide
	$F_{1,\text{Carbamate}} - F_{0,\text{Carbamate}} + r_{\text{CO}_2} V_{\text{Carbamate-Condenser}} = V_{\text{Carbamate-Condenser}} \frac{d}{dt} \left(\frac{d}{M} \frac{F_{0,\text{Carbamate}}}{F_0} \right)$	Mole balance for ammonium carbamate
	$F_{1,\text{NH}_3} - F_{0,\text{NH}_3} - 2r_{\text{CO}_2} V_{\text{Carbamate-Condenser}} = V_{\text{Carbamate-Condenser}} \frac{d}{dt} \left(\frac{d}{M} \frac{F_{0,\text{NH}_3}}{F_0} \right)$	Mole balance for ammonia
	$[\sum_i F_i C_{Pi}(T - T_0)]_1 - [\sum_i F_i C_{Pi}(T - T_0)]_0 + r_{\text{CO}_2} V_{\text{Carbamate-Condenser}} \Delta H_{\text{CO}_2} - Q_C = \sum_i N_i C_{Pi} \frac{dT}{dt}$	Energy balance
Urea reactor (each CSTR)	$\frac{d(V_{\text{Reactor}})}{dt} = F_1 M_1 - F_0 M_0$	Overall mass balance
	$F_{1,\text{CO}_2} - F_{0,\text{CO}_2} - r_{\text{CO}_2} V_{\text{Reactor}} = V_{\text{Reactor}} \frac{d}{dt} \left(\frac{d}{M} \frac{F_{0,\text{CO}_2}}{F_0} \right)$	Mole balance for carbon dioxide
	$F_{1,\text{NH}_3} - F_{0,\text{NH}_3} - 2r_{\text{CO}_2} V_{\text{Reactor}} + 0.5r_{\text{Urea}} V_{\text{Reactor}} = V_{\text{Reactor}} \frac{d}{dt} \left(\frac{d}{M} \frac{F_{0,\text{NH}_3}}{F_0} \right)$	Mole balance for ammonia
	$F_{1,\text{Carbamate}} - F_{0,\text{Carbamate}} + r_{\text{CO}_2} V_{\text{Reactor}} - r_{\text{Carbamate}} V_{\text{Reactor}} = V_{\text{Reactor}} \frac{d}{dt} \left(\frac{d}{M} \frac{F_{0,\text{Carbamate}}}{F_0} \right)$	Mole balance for ammonium carbamate
	$F_{1,\text{Urea}} - F_{0,\text{Urea}} + r_{\text{Carbamate}} V_{\text{Reactor}} - r_{\text{Urea}} V_{\text{Reactor}} = V_{\text{Reactor}} \frac{d}{dt} \left(\frac{d}{M} \frac{F_{0,\text{Urea}}}{F_0} \right)$	Mole balance for urea
	$F_{1,\text{H}_2\text{O}} - F_{0,\text{H}_2\text{O}} + r_{\text{Carbamate}} V_{\text{Reactor}} = V_{\text{Reactor}} \frac{d}{dt} \left(\frac{d}{M} \frac{F_{0,\text{H}_2\text{O}}}{F_0} \right)$	Mole balance for water
	$F_{1,\text{Biuret}} - F_{0,\text{Biuret}} + 0.5r_{\text{Urea}} V_{\text{Reactor}} = V_{\text{Reactor}} \frac{d}{dt} \left(\frac{d}{M} \frac{F_{0,\text{Biuret}}}{F_0} \right)$	Mole balance for biuret
	$[\sum_i F_i C_{Pi}(T - T_0)]_1 - [\sum_i F_i C_{Pi}(T - T_0)]_0 + r_{\text{CO}_2} V_{\text{Reactor}} \Delta H_{\text{CO}_2} - r_{\text{Carbamate}} V_{\text{Reactor}} \Delta H_{\text{Carbamate}} - 0.5r_{\text{Urea}} V_{\text{Reactor}} \Delta H_{\text{Urea}} = \sum_i N_i C_{Pi} \frac{dT}{dt}$	Energy balance
Stripper	$\frac{d(V_{\text{Stripper}})}{dt} = F_1 M_1 - F_0 M_0$	Overall mass balance
	$F_{1,\text{Carbamate}} - F_{0,\text{Carbamate}} - r_{\text{Carbamate}} V_{\text{Stripper}} = V_{\text{Stripper}} \frac{d}{dt} \left(\frac{d}{M} \frac{F_{0,\text{Carbamate}}}{F_0} \right)$	Mole balance for ammonium carbamate
	$F_{1,\text{CO}_2} - F_{0,\text{CO}_2} + r_{\text{Carbamate}} V_{\text{Stripper}} = V_{\text{Stripper}} \frac{d}{dt} \left(\frac{d}{M} \frac{F_{0,\text{CO}_2}}{F_0} \right)$	Mole balance for carbon dioxide
	$F_{1,\text{NH}_3} - F_{0,\text{NH}_3} + 2r_{\text{Carbamate}} V_{\text{Stripper}} + 0.5r_{\text{Urea}} V_{\text{Stripper}} = V_{\text{Stripper}} \frac{d}{dt} \left(\frac{d}{M} \frac{F_{0,\text{NH}_3}}{F_0} \right)$	Mole balance for ammonia
	$F_{1,\text{Urea}} - F_{0,\text{Urea}} - r_{\text{Urea}} V_{\text{Stripper}} = V_{\text{Stripper}} \frac{d}{dt} \left(\frac{d}{M} \frac{F_{0,\text{Urea}}}{F_0} \right)$	Mole balance for urea
	$F_{1,\text{Biuret}} - F_{0,\text{Biuret}} + 0.5r_{\text{Urea}} V_{\text{Stripper}} = V_{\text{Stripper}} \frac{d}{dt} \left(\frac{d}{M} \frac{F_{0,\text{Biuret}}}{F_0} \right)$	Mole balance for biuret
	$[\sum_i F_i C_{Pi}(T - T_0)]_1 - [\sum_i F_i C_{Pi}(T - T_0)]_0 - r_{\text{Carbamate}} V_{\text{Stripper}} \Delta H_{\text{Carbamate}} - 0.5r_{\text{Urea}} V_{\text{Stripper}} \Delta H_{\text{Urea}} + Q_S = \sum_i N_i C_{Pi} \frac{dT}{dt}$	Energy balance
Scrubber	$\frac{d(V_{\text{Scrubber}})}{dt} = F_1 M_1 - F_0 M_0$	Overall mass balance
	$F_{1,\text{CO}_2} - F_{0,\text{CO}_2} - r_{\text{CO}_2} V_{\text{Scrubber}} = V_{\text{Scrubber}} \frac{d}{dt} \left(\frac{d}{M} \frac{F_{0,\text{CO}_2}}{F_0} \right)$	Mole balance for carbon dioxide
	$F_{1,\text{Carbamate}} - F_{0,\text{Carbamate}} + r_{\text{CO}_2} V_{\text{Scrubber}} = V_{\text{Scrubber}} \frac{d}{dt} \left(\frac{d}{M} \frac{F_{0,\text{Carbamate}}}{F_0} \right)$	Mole balance for ammonium carbamate
	$F_{1,\text{NH}_3} - F_{0,\text{NH}_3} - 2r_{\text{CO}_2} V_{\text{Scrubber}} = V_{\text{Scrubber}} \frac{d}{dt} \left(\frac{d}{M} \frac{F_{0,\text{NH}_3}}{F_0} \right)$	Mole balance for ammonia
	$[\sum_i F_i C_{Pi}(T - T_0)]_1 - [\sum_i F_i C_{Pi}(T - T_0)]_0 + r_{\text{CO}_2} V_{\text{Scrubber}} \Delta H_{\text{CO}_2} - Q_{\text{CW}} = \sum_i N_i C_{Pi} \frac{dT}{dt}$	Energy balance

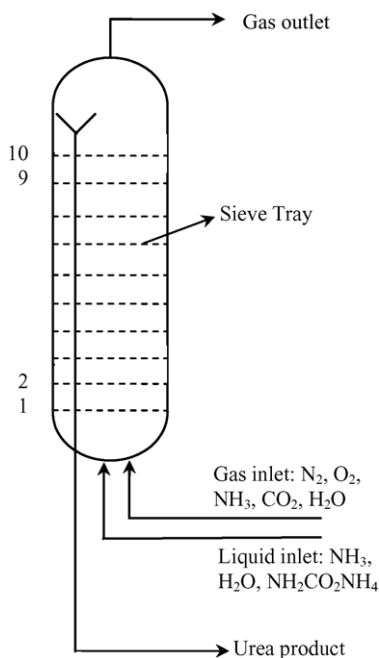


Fig. 3. Schematic diagram of the urea reactor.

condenser is in fact a shell and tube heat exchanger. Formation of ammonium carbamate in the synthesis section mainly occurs in the tubes of the carbamate condenser. In a real plant, the conversion of carbon dioxide to ammonium carbamate is controlled with absorbing the heat released by the reaction by the water being evaporated in the shell side. In order to control the amount of the heat absorbed by the condensate, the level of condensate in the shell of carbamate condenser is controlled. Since, the reaction between carbon dioxide and ammonia (reaction (4)) is a fast and exothermic reaction, the conversion of carbon dioxide in the carbamate condenser could be determined by the amount of heat exchanged between the shell and tubes (i.e., the amount of steam generated in the shell). In fact, since the heat generated by the reaction and the heat absorbed by the water in the shell are considerably higher than the sensible heat (at least an order of magnitude greater), the rate of moles of carbon dioxide converted in the carbamate condenser can be evaluated from:

$$\text{rate of CO}_2 \text{ moles converted} = \frac{Q_c}{\Delta H_{\text{reaction}(4)}} \quad (9)$$

Consequently, the outlet temperature of the tubes could be calculated through the energy balance equation shown in Table 4 when cancelling out the heat of reaction and heat of steam generation.

2.4.2. Urea reactor

A schematic diagram of an industrial urea reactor is shown in Fig. 3. The feed to the urea reactor consists of liquid (ammonium carbamate rich) and vapor (CO_2 and NH_3) streams, both entering from the bottom. This makes both phases to move upward. 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 reactor in order to prevent back mixing and further mixing between the two phases. All the three main reactions (i.e., the heterogeneous reaction of formation of ammonium carbamate and urea and biuret formation in liquid phase) are considered to take place in the reactor.

Irazoqui et al. [2] considered the whole urea reactor as a sequence of continuously stirred tank reactor (CSTRs). The same approach has been adopted in the present study for the hydrodynamic behavior of the urea reactor. However, on the reaction side, the heterogeneous reaction of ammonium carbamate formation (reaction (4)) has been adopted instead of the homogeneous reaction. Due to the high residence time of the reactants in the urea reactor, formation of ammonium carbamate at the reactor outlet can be practically considered at equilibrium [10]. However, it is obvious that the equilibrium is not reached in the interstages when dividing the urea reactor into n CSTRs. Therefore, it is assumed in the present study that the reaction proceeds only $1/n$ toward the equilibrium in each CSTR. As a result, the reaction would reach the equilibrium at the exit of the n th CSTR which is the outlet of the main urea reactor. The goal of this assumption is to facilitate deriving the material and energy balance equations for each CSTR. Each CSTR operates adiabatically. These equations are summarized in Table 4.

2.4.3. Stripper

The equations related to the dynamic behavior of the stripper are summarized in Table 4. The stripper is also a shell and tube heat exchanger in which the non-reacted ammonium carbamate from the reactor is decomposed to ammonia and carbon dioxide. The heat of reaction for this endothermic reaction is supplied by condensation of steam in the shell. In practice, the conversion of ammonium carbamate in the stripper is controlled by the amount of steam being consumed in the shell side. Although, the stripping process seems to be mass transfer controlled, it is currently modeled by assuming that all the free ammonia in the liquid and the products of decomposed ammonium carbamate are carried up with the flow of stripping carbon dioxide [4].

2.4.4. Scrubber

The equations related to the dynamic behavior of the scrubber are summarized in Table 4. The exit gas of the urea reactor enters the scrubber to reduce the amount of ammonia which exits the synthesis section. The scrubber consists of two parts: the shell and tube section and the absorbing section. In the exchanger section of the scrubber, ammonium carbamate is formed. This section operates similar to the carbamate condenser (i.e., the heat produced by the reaction is removed by the cooling water in the shell side). Therefore, calculation of the rate of moles of carbon dioxide converted to ammonium carbamate in this section could be evaluated by a similar approach.

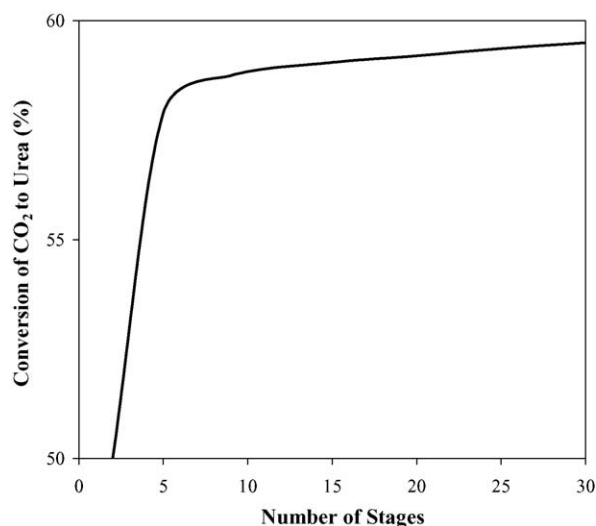


Fig. 4. Impact of the number of CSTRs on the model prediction of conversion to urea.

In the absorbing section, the gas which leaves the shell and tube section is contacted with a weak ammonium carbamate solution where heat is transferred between the two phases. The amount of ammonia absorbed by the liquid could be calculated according to the phase equilibrium condition. In order to control the ammonium carbamate produced in the scrubber, the amount of heat exchanged between shell and tube is controlled by the flow rate of cooling water circulated in the shell of the scrubber.

3. Results and discussion

Typical industrial operating conditions of the synthesis section of an urea production plant are listed in Table 5. Before starting the simulation, the number of CSTRs in the urea reactor have to be established. Fig. 4 shows the impact of the number of stages on the predicted conversion of carbon dioxide to urea at the outlet of the urea reactor corresponding to the operating conditions given in Table 5. It is worth noting that Fig. 4 was obtained without considering the impact of recycles on the performance of the reactor. It is clear from this figure that approximately beyond 10 stages, there is no significant change in the performance of the reactor. It is worth noting that this number is also the number of actual trays used in the industrial reactor. In each tray, the gas and liquid passing through the reactor mix again with each other and re-distribute the concentrations and temperature. Thus, it

is reasonable to assume each tray as a CSTR. Irazoqui et al. [2] presented a diagram very similar to what shown in Fig. 4. Therefore, in the rest of this work 10 CSTRs were chosen to model the urea reactor by the method described earlier.

Once the number of CSTRs was determined, the temperature profile of the reactor could be evaluated. The temperature of each CSTR has to be obtained through a trial and error procedure as follows. The exit temperature of the reactor is guessed at the start of the calculations. Knowing the temperature, the equilibrium constant was calculated from Eq. (6) and the amount of ammonium carbamate formation at equilibrium was calculated from:

$$K_p = P_{\text{NH}_3}^2 P_{\text{CO}_2} = \left(\frac{n-2x}{n_t}\right)^2 \left(\frac{m-x}{n_t}\right) P^3 \quad (10)$$

Since it has been assumed that in each CSTR the reaction of ammonium carbamate formation moves $1/n$ toward the equilibrium, the amount of ammonium carbamate calculated from Eq. (10) was multiplied to $1/n$. Consequently, the amount of heat produced in the reactor due to ammonium carbamate formation was evaluated

In the case of kinetic-controlled reactions (reactions (3) and (5)) the corresponding conversion has to be determined from the mass balance equation of the CSTR [15]:

$$\frac{V}{v_0} = \frac{C_{A0}X_A}{-r_A} \quad (11)$$

Introducing the kinetic expression of urea formation (Eq. (7)) into Eq. (11) yields the following equation from which the amount of urea produced in each CSTR was calculated:

$$X_1^2 + \left(a + \frac{v_0}{kV} - 1\right) X_1 - a = 0 \quad (12)$$

Similar to the ammonium carbamate reaction, the amount of heat consumed due to urea formation could be calculated.

Biuret is also formed in the urea reactor. Introducing the reaction rate of biuret formation (Eq. (8)) into Eq. (11) allows the amount of biuret at each CSTR to be calculated:

$$X_2^2 - \left(2 + \frac{v_0}{k'VC_{U0}}\right) X_2 + 1 = 0 \quad (13)$$

This is also an endothermic reaction whose required heat of reaction was evaluated after determining the amount of biuret formed in each CSTR.

Finally, for each CSTR the energy balance should be satisfied. The steady-state energy balance equation for each re-

Table 5
Typical industrial feed conditions of an urea production plant

Feed	P (kg/cm ²)	T (°C)	Carbon dioxide (mol%)	Ammonia (mol%)	Water (mol%)	Nitrogen (mol%)	Oxygen (mol%)	Urea (mol%)	Ammonium carbamate (mol%)
CO ₂	146	130	89.0	0	4.5	4.6	1.9	0	0
NH ₃	146	40.5	0	99.0	1.0	0	0	0	0
Lean ammonium carbamate	143	73.0	0	14.5	59.9	0	0	0.1	25.5

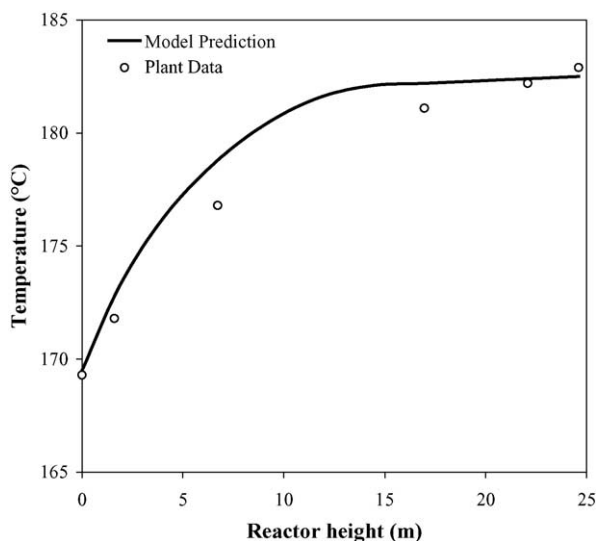


Fig. 5. Comparison between model temperature distribution and industrial distribution of temperature along the reactor.

actor is:

$$H_I - H_O + Q_{ac} - Q_u - Q_b = 0 \quad (14)$$

If Eq. (14) is not satisfied, the assumed temperature of the reactor outlet was changed accordingly and the above-mentioned calculations were repeated from the beginning. The iterative procedure was repeated until the energy balance equation is satisfied from which the exit temperature and composition of each CSTR were established.

The validity of the proposed model was tested against the steady state data obtained at industrial scale. Fig. 5 illustrates the comparison between the model prediction and plant data in terms of the temperature profile along the urea reactor. It could be seen in this figure that the model predicts the actual temperature inside the urea reactor satisfactorily.

Moreover, calculated results and the plant data on some key operating parameters of the urea synthesis section are given in Table 6. Comparing the simulated values with the plant data in this table also confirms that the model predictions are in good agreement with the plant data. The model

Table 6
Comparison between plant data and simulation results

Parameter	Unit	Plant data	Simulation
Inlet temperature of urea reactor	°C	169.3	169.5
Outlet temperature of urea reactor	°C	183	182.5
Urea concentration at urea reactor liquid outlet	wt. %	33.9	33.0
N/C ratio at urea reactor outlet	–	2.9	3.1
Inlet gas temperature of carbamate condenser	°C	186.9	186.1
Outlet gas temperature of scrubber	°C	114.6	116.4

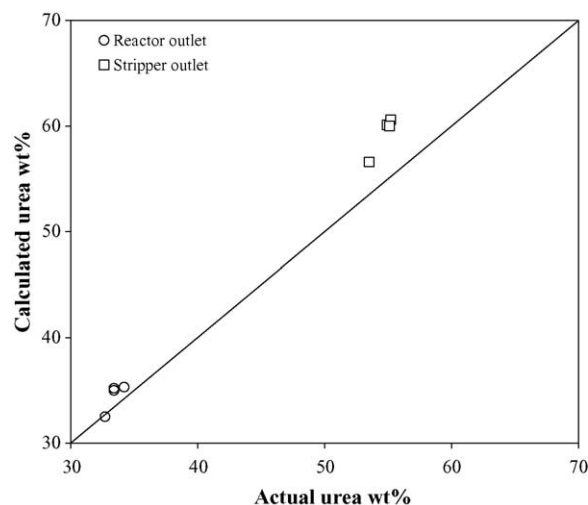


Fig. 6. Parity plot of urea wt.% in the outlet of urea reactor and stripper at capacities of: 95%, 106%, 109% and 113%.

predictions of weight percent of urea in the liquid outlet of the urea reactor and the stripper against plant data at different plant capacities are also shown in Fig. 6 which again illustrates that the model satisfactorily meet the plant data.

3.1. Case studies

Effect of changes in some key parameters on the behavior of the synthesis section was investigated based on the model developed in this work. Some of these case studies are given below.

3.1.1. Pressure of the shell of carbamate condenser

The heat exchanged between shell and tube influences the amount of carbon dioxide converted to ammonium carbamate. In a real plant, the amount of gas entered to the urea reactor is controlled by the pressure of saturated stream in the shell side of the carbamate condenser. Higher steam pressure corresponds to smaller temperature difference between the cooling and process sides, i.e., lower heat flux.

Effect of increasing the pressure of the shell of carbamate condenser on the conversion of CO₂ to urea and biuret as well as the concentration of biuret in the liquid outlet flow of the urea reactor are shown in Figs. 7 and 8. As it is shown in these figures there exists a local maximum in all these curves. Since increasing the pressure in the shell of the carbamate condenser results in increasing its temperature, it is necessary to investigate the effect of the temperature on the conversion of the two main reactions occurring in the urea reactor, i.e., ammonium carbamate and urea formation. Effect of temperature on the equilibrium conversion of ammonium carbamate formation and urea formation are shown in Fig. 9. Since formation of ammonium carbamate is an exothermic reaction (reaction (4)), increasing the temperature beyond 170 °C causes decreasing the formation of ammonium carbamate, as seen in Fig. 9. On the other hand, it is shown in

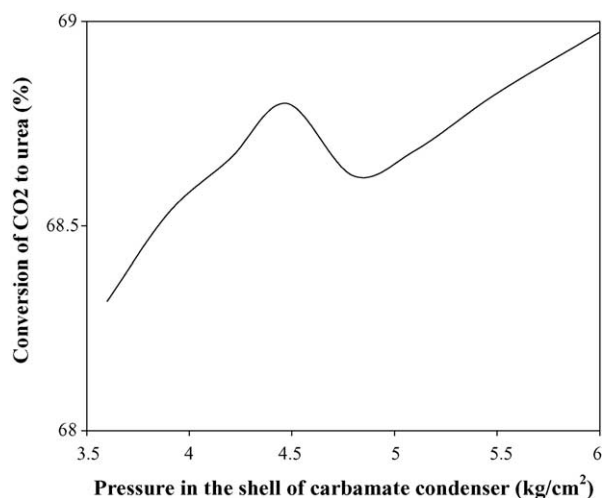


Fig. 7. Effect of pressure in the shell of carbamate condenser on the conversion of CO_2 to urea in the reactor.

the same figure that conversion to urea through an endothermic reaction (reaction (3)) increases when the temperature is increased. Thus, due to the opposite effect of temperature on these reactions occurring in the reactor, there exists an optimum value for the temperature of the inlet of the reactor at which the formation of ammonium carbamate would be at its maximum value. Consequently, the overall heat generated in the urea reactor would be maximum at such condition and the formation of urea reaches its maximum value, as seen in Fig. 7.

It is illustrated in Fig. 7 that increasing the steam pressure in the shell of the carbamate condenser far beyond the local maximum would again result in increasing the urea production in the urea reactor. Such an increase yields more gas flow from the carbamate condenser into the urea reactor which, in turn, increases the overall urea production. Although it might seem beneficial to work at such operating conditions,

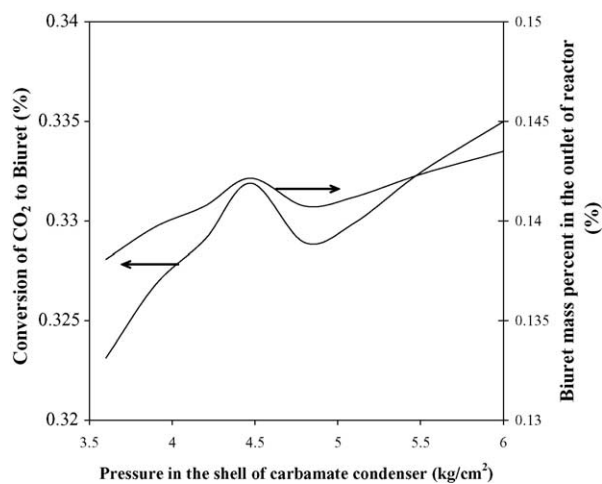


Fig. 8. Effect of pressure in the shell of carbamate condenser on the conversion of CO_2 to biuret and the mass percent of biuret in the liquid outlet flow of reactor.

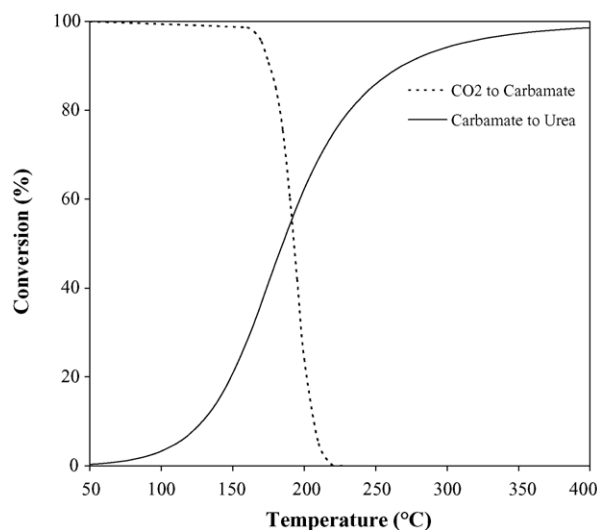


Fig. 9. Effect of temperature on the equilibrium conversion of CO_2 to ammonium carbamate and conversion of ammonium carbamate to urea for a typical condition.

a commercial plant cannot work in this region because the concentration of biuret in the urea product also increases, as shown in Fig. 8. Therefore, the optimum operating condition for the urea synthesis section of the plant is the condition corresponding to this local maximum of urea production.

3.1.2. Level of the liquid in carbamate condenser

The level of liquid in the shell side of the carbamate condenser is used as a controlling parameter in this reactor. In a real plant, the temperature of the reactor and the amount of the gas entering the urea reactor is affected by the liquid level in the shell side of the carbamate condenser is kept high. Thus, the heat exchanging surface as well as the amount of steam increases.

Effect of the change in the liquid level in the shell of carbamate condenser on the conversion of carbon dioxide is shown in Fig. 10. As shown in this figure, increasing the liquid level in the shell of the carbamate condenser leads to increase the conversion of carbon dioxide to ammonium carbamate. In fact, increasing the liquid level causes the heat exchanging area to increase, thus, increasing the amount of heat to be absorbed from the reaction side of the carbamate condenser. Since formation of ammonium carbamate is an exothermic reaction, such an increase in the heat removal from the reaction results in increasing the conversion in the carbamate condenser.

Effect of the change of the liquid level in the shell of the carbamate condenser on the conversion of carbon dioxide to urea and biuret in the urea reactor are also shown in Figs. 10 and 11. A decreasing trend with a local maximum could be seen in both these curves. The decreasing trend in these curves could be describe by the fact that increasing the liquid level in the shell results in more ammonium carbamate to be produced in the carbamate condenser, thus, lowering the amount of ammonium carbamate to be produced in the

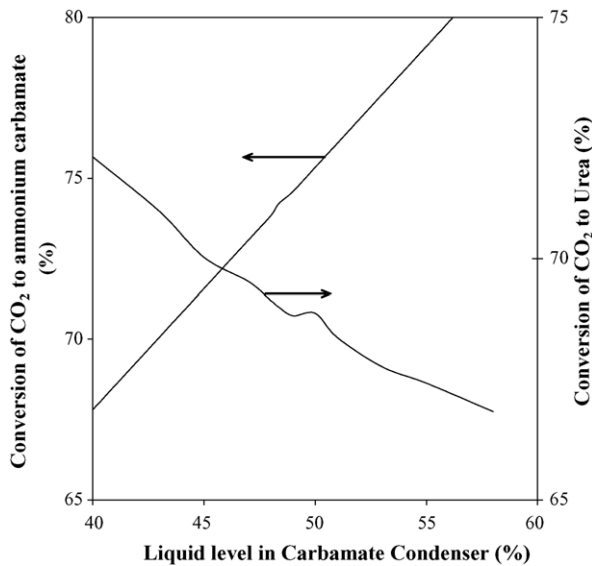


Fig. 10. Effect of liquid level in the carbamate condenser drums on the conversion of CO₂ to carbamate in the tube side of carbamate condenser and on the conversion of CO₂ to urea in the reactor.

urea reactor. Since in the urea reactor, the energy required by the urea formation reaction is supplied by ammonium carbamate formation, lower ammonium carbamate formation is equivalent to lower urea formation in the urea reactor. The local maximum in the urea conversion corresponds to the optimum entering temperature to the urea reactor. The similar trend could be seen in Fig. 11 for the conversion to biuret for which the same explanations as those made for urea could be repeated here.

3.2. Dynamic simulation

Dynamic behavior of the urea synthesis section was also studied based on the model developed in this study. The com-

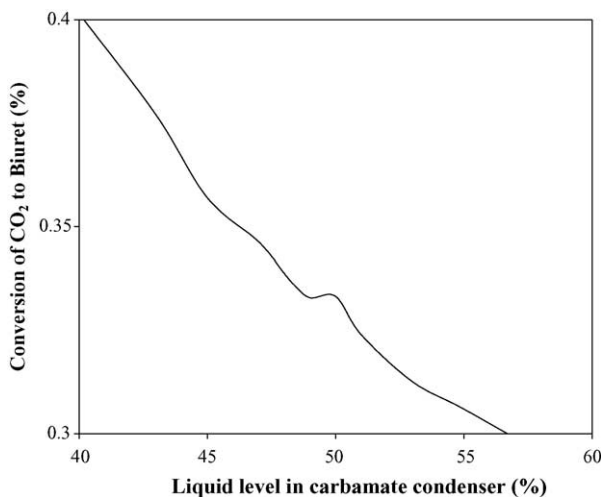


Fig. 11. Effect of liquid level in the carbamate condenser drums on the conversion of CO₂ to biuret in the reactor.

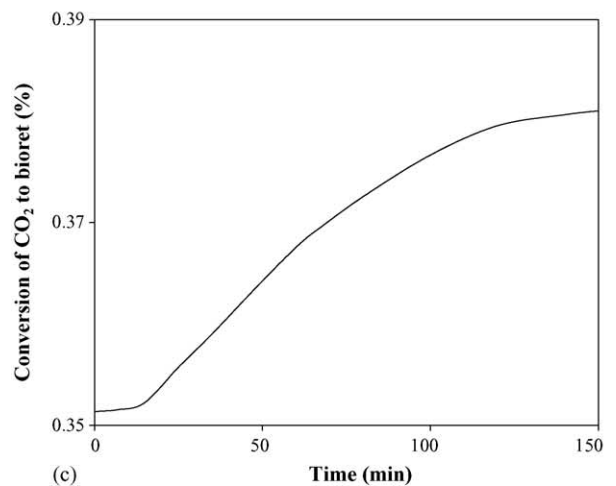
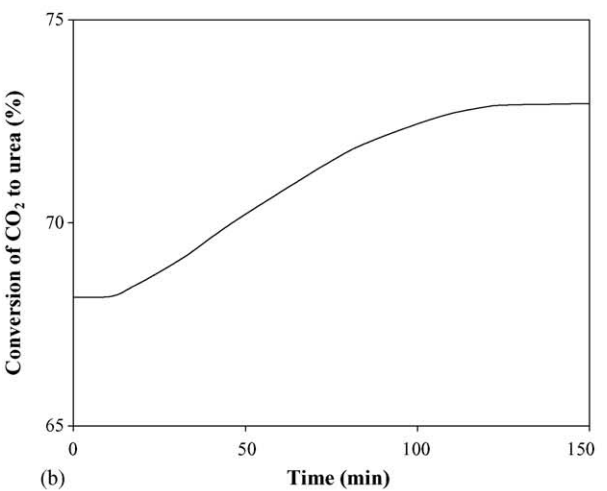
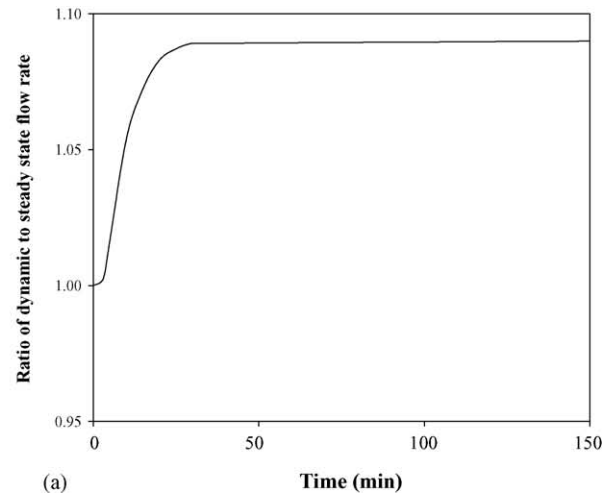


Fig. 12. Effect of liquid level in the drums of carbamate condenser (a) on the flow rate of exit gas (b) on the conversion of CO₂ to urea in the liquid outlet of the reactor (c) on the conversion of CO₂ to biuret in the liquid outlet of the reactor.

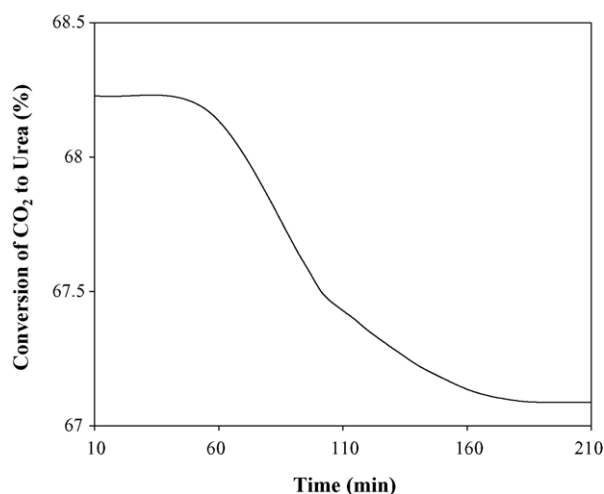


Fig. 13. Effect of pressure in the shell of carbamate condenser on the conversion of CO₂ to urea in the reactor.

plete set of equations of the model are given in Table 4. As an example, the effect of two parameters corresponding to the case studies are investigated.

3.2.1. Level of the liquid in carbamate condenser

In this case, the liquid level was suddenly decreased from 50% (normal operation) to 40%. The effect of this change on the flow rate of gas at the exit of the carbamate condenser is shown in Fig. 12. When the level changes to 40%, the heat exchange area between shell and tube of carbamate condenser decreases. Therefore, the amount of heat which is removed from the reaction in the tube decreases and the formation of carbamate in the tube decreases. Subsequently, an increasing trend in the gas flow from the carbamate condenser is expected, as shown in Fig. 12.

It is shown in Fig. 12 that by decreasing the liquid level in the drums of the carbamate condenser, urea formation increases in the urea reactor. As explained above, this change results in flowing more gas into the urea reactor, thus, more ammonium carbamate is formed in the reactor and more heat is generated accordingly. Therefore, more urea is being formed in the urea reactor, as illustrated in Fig. 12. However, the changes in the outflow of the urea reactor could be observed only about 7 min after the changes in the carbamate condenser (see Fig. 12). Formation of biuret increases with increasing the concentration of urea in the urea reactor. This effect is shown in Fig. 12 which indicates the start in changing the conversion of CO₂ to biuret at about 11 min after starting the changes in the urea concentration.

3.2.2. Pressure of the shell of carbamate condenser

In this case the pressure in the shell side of carbamate condenser was decreased from 4.5 to 3.5 kg/cm². As a result, the temperature in the shell side of the carbamate condenser decreases and the temperature difference between shell and tube increases, thus, the quantity of heat exchanged between shell and tube increases and the amount of CO₂ converted to

ammonium carbamate increases. These phenomena result in decreasing the gas entering the urea reactor followed by decreasing the heat produced in the urea reactor. Consequently, the amount of urea produced in the urea reactor decreases. Fig. 13 illustrates the dynamic changes in the amount of urea produced in the reactor when decreasing the pressure of the shell of the carbamate condenser.

4. Conclusions

The synthesis section of the urea production plant in industrial scale was modelled in the present work. In order to develop the model, hydrodynamic and reaction submodels were coupled with each other in the modeling of the reactor. The hydrodynamic of the urea reactor was simulated by a sequence of CSTRs in series. It was found that 10 CSTRs are adequate to model the urea reactor properly. The heterogeneous reaction of formation of ammonium carbamate was considered in the present study instead of homogeneous reaction considered in the previous works in the literature. Temperature dependence expression of equilibrium constant of ammonium carbamate reaction was corrected using the data in the literature as well as the exit condition of the real urea reactor. The calculated temperature profile along the urea reactor was compared with the plant data. Moreover, the results of model in terms of urea mass percent was compared with real data at various capacities of the plant. In both cases, good consistency was observed between plant data and the results of the model. Effect of the changes of some key parameters on the performance synthesis section was studied. The dynamic behavior of the corresponding parameters was also investigated.

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