Simulation of a Urea Synthesis Reactor. 2. Reactor Model

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This paper is concerned with the physicochemical and mathematical modeling of a urea synthesis reactor for simulation and optimization purposes, and with the computer implementation of a reactor simulation module. Simulation results are compared with data from a production-scale plant. The agreement between predicted and observed reactor sensitivity to changes in its operating conditions is also discussed. The module allows comparison of the performance of reactors with different configurations and different degrees of concentration back-mixing.

Introduction

Urea is commercially synthesized by the reaction of CO₂ and NH₃ at high pressures (13–30 MPa) and temperatures (170–200 °C). In the first of two consecutive reactions, ammonium carbamate is formed as an intermediate compound. At pressures above its dissociation pressure the formation of ammonium carbamate from CO₂ and NH₃ is fast and complete.

The second reaction is the carbamate dehydration reaction giving urea and water. This reaction is slower than the first one and does not proceed to completion. At urea synthesis conditions the equilibrium conversion of CO₂ to urea may reach values close to 80% (Lemkowitz et al., 1973).

To get around the limitation imposed by chemical equilibrium on the one-pass conversion to urea, several urea technologies include total or partial recycle of unreacted CO₂ and NH₃ (Chao, 1967; Uchino, 1986; Stamicarbon Staff, 1986).

In a typical recycle process, the synthesis mixture from the reactor is first let down in pressure in a medium-pressure separator. In this operation, most of the excess ammonia and part of the unconverted CO₂ and NH₃ that remained in the form of ammonium carbamate are separated from the solution by flashing.

The solution from the medium-pressure separator is sent to a low-pressure decomposer. In this equipment, most of the remaining ammonium carbamate is decomposed and the generated CO₂ and NH₃ are removed from the liquid by the combined effect of pressure reduction, heating, and stripping. In this operation, part of the CO₂ makeup is used as the stripping agent.

Residual CO₂ and NH₃ remain in the urea solution when it leaves the low-pressure carbamate decomposer. These volatile components are removed from the liquid phase at the urea concentration section. After condensation, the mixture of recovered residual gases is fed to stripping units for its concentration.

The overhead stream leaving the strippers consist of recovered CO₂ and NH₃, together with a small amount of H₂O. This stream is condensed and returned to the process where it is used first as the solvent in the low-pressure absorption of the overhead gaseous mixture from the low-pressure decomposer.

Effect of NH₃/CO₂ Feed Ratio on Reactor Operating Pressure. The isothermal bubble pressure of NH₃–CO₂ mixtures as a function of the NH₃/CO₂ mole ratio show a minimum in the range 2.3 ≤ NH₃/CO₂ ≤ 4.0 for temperatures in the interval 160 °C ≤ T ≤ 220 °C (Lemkowitz et al., 1973).

The minimum bubble pressure divides each isotherm into two branches. The branch on the side of CO₂-rich mixtures is steeper than the one on the NH₃-rich side. In either case the isothermal bubble pressure increases rapidly as the NH₃/CO₂ ratio is farther away from the minimum point.

From these considerations it can be concluded that the maximum local temperature and the NH₃/CO₂ feed ratio will strongly influence the reactor operating pressure.

Effect of the Reactor Outlet Temperature on the Product Maximum Yield. The reaction

\[ \text{CO}_2(l) + 2\text{NH}_3(l) \leftrightarrow \text{H}_2\text{NCOO}^- + \text{NH}_4^+ \]

is exothermic (ΔH₂₅°C ≈ −84 kJ mol⁻¹, calculated from standard enthalpy of formation data (Weast, 1980)). Therefore, the value of its equilibrium constant decreases as the reaction temperature increases. This reaction is followed by the dehydration reaction

\[ \text{H}_2\text{NCOO}^- + \text{NH}_4^+ \leftrightarrow \text{H}_2\text{NCONH}_2(l) + \text{H}_2\text{O}(l) \]

which is slightly endothermic (ΔH₂₅°C ≈ 23 kJ mol⁻¹ (Claudel et al., 1986)).

The overall synthesis reaction

\[ \text{CO}_2(l) + 2\text{NH}_3(l) \leftrightarrow \text{H}_2\text{NCONH}_2(l) + \text{H}_2\text{O}(l) \]

is exothermic. Consequently, the value of its equilibrium constant decreases as the temperature increases. If the first two reactions were the only reactions occurring in the liquid phase, lower equilibrium conversions of CO₂ to urea would correspond to higher reaction temperatures.
However, dissolved CO$_2$ and NH$_3$ react according to a complex chemical reaction scheme. Therefore, the equilibrium yield of urea depends not only on the value of the overall synthesis reaction constant but also on those of the other competing reactions.

Experimental data reported independently by several authors show that the equilibrium conversion of CO$_2$ to urea increases with increasing temperatures in the range 160 °C < T < 180 °C, showing a trend opposite that predicted by considering the overall synthesis reaction alone. These data have been used to adjust a correlating expression between temperature, the initial NH$_3$/CO$_2$ and H$_2$O/CO$_2$ mole ratios, and the equilibrium yield of urea (Gorlovskii and Kucheryavyi, 1980).

Usually, the synthesis reactor is operated at temperatures close to the critical temperature of the reacting mixture. At the critical temperature, where no distinction between gas and liquid phase can be made, formation of urea occurs directly from CO$_2$ and NH$_3$ in the single fluid phase according to

$$\text{CO}_2(l) + 2\text{NH}_3(l) \leftrightarrow \text{H}_2\text{NCONH}_2(l) + \text{H}_2\text{O}(l)$$

This reaction has been reported to be exothermic. Therefore, increasing the reaction temperature beyond the critical temperature of the reacting mixture will lower the equilibrium yield of urea.

Experimental results indicate that, as a consequence of critical phenomena, the equilibrium yield of urea in a mixture with an initial mole ratio NH$_3$/CO$_2$ = 4 diminishes when the reaction temperature approaches 200 °C (Yoshimura, 1970). For this reason it is important to maintain the temperature of the reactor outlet stream at values below the critical temperature.

### Phase and Chemical Equilibrium at Urea Synthesis Conditions

In part 1 of this series (Isla et al., 1993) a thermodynamic model capable of reproducing the phase and chemical equilibrium in CO$_2$-NH$_3$-H$_2$O-urea mixtures over a wide composition range was proposed.

However, not all the chemical reactions considered for that purpose are important at urea synthesis conditions. The formation of carbamic acid from dissolved CO$_2$ and NH$_3$

$$\text{CO}_2(l) + \text{NH}_3(l) \leftrightarrow \text{H}_2\text{NCOO}^- + \text{H}^+$$

will be appreciable only in dilute solutions, with concentrations far from those found in the synthesis section (Hatch and Pigford, 1962; Buckingham et al., 1986).

The ionic dissociations of ammonia and water

$$\text{NH}_3(l) + \text{H}_2\text{O}(l) \leftrightarrow \text{NH}_4^+ + \text{HO}^-$$

$$\text{H}_2\text{O}(l) \leftrightarrow \text{HO}^- + \text{H}^+$$

have very small extents of reaction and therefore can be neglected in the calculation of reacted CO$_2$ and NH$_3$. They may be used, however, to compute the pH of the reaction mixture.

Considering the conditions prevailing in the reactor, chemical and phase equilibrium is assumed to be described satisfactorily by the following reaction scheme.

<table>
<thead>
<tr>
<th>Table I. Assignment of Subscripts to System Components</th>
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<tr>
<td><strong>subscript</strong></td>
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<td>3</td>
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At phase equilibrium, the following nonlinear equations must be satisfied for water (i = 1) and ammonia (i = 2)

$$x_i \gamma_i(T, x) f_i^0(T, P = 0) \exp(\nu_i P/R G T) = P y_i \Phi_i(T, P, y),$$

for carbon dioxide (i = 3) the phase equilibrium condition is

$$x_3 \gamma_3^0(T, x) H_{1,3}(T, P_{x_3}(T)) \exp(\nu_3(P - P_{x_3}(T))/R G T) = P y_3 \Phi_3(T, P, y)$$

The i-component fugacity coefficient, $\Phi_i(T, P, y)$, is estimated using the equation of state proposed by Nakamura et al. (1976).

The chemical equilibrium conditions are (see assignment of subscripts to system components in Table I)

$$K_4(T) = K_{x,4}(x) K_{y,4}(T, x)$$

$$K_5(T) = K_{x,5}(x) K_{y,5}(T, x)$$

$$K_6(T) = K_{x,6}(x) K_{y,6}(T, x)$$

where

$$K_{x,4}(x) = \frac{x_4 x_5}{x_2^3 x_3}$$

$$K_{x,5}(x) = \frac{x_4 x_6}{x_1 x_2^3}$$

$$K_{x,6}(x) = \frac{x_4 x_6}{x_2^3}$$

and

$$K_{y,4}(T, x) = \frac{\gamma_4^0(T, x) \gamma_6^0(T, x)}{(\gamma_2(T, x))^2 \gamma_3^0(T, x)}$$

$$K_{y,5}(T, x) = \frac{\gamma_4^0(T, x) \gamma_6^0(T, x)}{\gamma_1(T, x) \gamma_2(T, x) \gamma_3^0(T, x)}$$

$$K_{y,6}(T, x) = \frac{\gamma_1(T, x) \gamma_6^0(T, x)}{\gamma_4^0(T, x) \gamma_6^0(T, x)}$$

where $x$ and $y$ are the arrays of mole fractions in the liquid and gas phase, respectively.
In eq 7 and in eqs 15–17, \( \gamma_i(T,x) \) is the activity coefficient of species \( i \) in the rational symmetric scale, while in eq 8 and in eqs 15–17, \( \gamma^0_i(T,x) \) is the activity coefficient in the rational unsymmetric scale.

An extended UNIQUAC–Debye–Hückel model (Sander et al., 1986) was adopted to estimate the activity coefficients in the liquid phase.

The temperature dependence of the pure liquid reference fugacity of \( \text{NH}_3 \) at zero pressure was approximated with the expression

\[
\ln f^0_2(T) = (A_3/T) + A_2 \ln T + A_4 T + A_4
\]

where \( f^0_2 \) is in kPa and \( T \) is in K.

The temperature dependence of the pure liquid reference fugacity of \( \text{CO}_2 \) at zero pressure, \( f^0_2 \), was approximated by an expression of the same type as that adopted for \( f^0_2 \) (eq 18). Considering the limiting form of the UNIQUAC expression of the activity coefficient of \( \text{CO}_2 \) in the rational symmetric scale taken as \( x \to 1 \), it was shown that the expression giving the temperature dependence of Henry's constant of \( \text{CO}_2 \) in water, at the pure water vapor pressure, \( H_{3,1} \), is given by (Isla et al., 1993)

\[
\ln H_{3,1}(T) = (B_1/T) + B_2 \ln T + B_3 T + B_4 - q_3 r_{31}
\]

with \( H_{3,1} \) in kPa. In eq 19, \( q_3 \) is the UNIQUAC surface parameter of \( \text{CO}_2 \) and \( r_{31} = \exp(-a_{3,1}/T) \), where \( a_{3,1} \) is the UNIQUAC binary interaction parameter between \( \text{CO}_2 \) and \( \text{H}_2\text{O} \).

The following functional form was adopted to model the temperature dependence of the equilibrium constants of the chemical reactions in the liquid phase, i.e.,

\[
\ln K_i(T) = (C_{1,i}/T) + C_{2,i} \ln T + C_{3,i} T + C_{4,i}
\]

The values of the parameters of the phase and chemical equilibrium model, which were estimated by a nonlinear regression of experimental data using the maximum likelihood principle (Anderson et al., 1978), have been reported elsewhere (Isla et al., 1993).

Rate of the Urea Synthesis Reaction

The kinetic model proposed by Kummel et al. (1981) relies on the assumption that, at synthesis conditions, all of the \( \text{CO}_2 \) in the reaction mixture is in the form of ammonium carbamate.

The rate of the forward reaction was found to be proportional to the total ammonium carbamate concentration. Since all of the ammonium carbamate in the mixture is dissociated into \( \text{H}_2\text{NCOO}^- \) and \( \text{NH}_4^+ \) ions, the rate of the forward reaction according to this model can be written

\[
R^f_{\text{forward}} = k_6 C_T x_6
\]

where \( C_T \) is the total molar concentration.

The expression of the backward reaction rate can be found from the chemical equilibrium condition. With this procedure, the following form for the reaction rate of the urea synthesis was obtained:

\[
R^b = k_b C_T \left( x_6 - \frac{1}{K_{x,6}} x_6 x_1 \right)
\]

The experimental values of the preexponential factor and the activation energy in the Arrhenius expression of \( k_b \) are \( A = 2.5 \times 10^9 \text{s}^{-1} \) and \( E = 100 \text{ kJ mol}^{-1} \), respectively.

Figure 1. Urea synthesis reactor. Approximate composition (wt %) of carbamate recycle stream is 41 % \( \text{NH}_3, 36 \% \text{ CO}_2, 22 \% \text{ H}_2\text{O}, 1 \% \) urea. Approximate composition (wt %) of product stream is 37 % \( \text{NH}_3, 11 \% \text{ CO}_2, 20 \% \text{ H}_2\text{O}, 32 \% \) urea.

Urea Synthesis Reactor: Description

The type of reactor schematically shown in Figure 1 has been chosen for the present study.

In a typical situation, subcooled liquid \( \text{NH}_3 \) is fed to the reactor at about 100°C and 22 MPa. To control the temperature profiles along the reactor, part of the \( \text{NH}_3 \) makeup is fed at the reactor top and the remainder is fed at the bottom.

Neglecting losses, 1 mol of fresh \( \text{CO}_2 \) has to be fed to the process for each mole of urea produced. Part of the fresh \( \text{CO}_2 \) makeup is directly fed to the reactor at supercritical conditions. As was pointed out in the previous section, the remainder is fed at different injection points in the process where it is first used as a stripping agent for the recovery of unconverted \( \text{NH}_3 \) and \( \text{CO}_2 \) and then recycled to the reactor with the recycle stream in the form of ammonium carbamate.

The reactor feed streams are adiabatically mixed in a mixing chamber in which the outlet stream is led through an internal coil to the reactor bottom section.

For reasons already discussed in the previous section, the flow of each feed stream is controlled so as to ensure a mole ratio of total \( \text{NH}_3 \) to total \( \text{CO}_2 \) in the range 4.0 ≤ \( \text{NH}_3/\text{CO}_2 \) ≤ 4.6 at the coil inlet. This confines the reaction mixture to the \( \text{NH}_3 \)-rich side of the isothermal bubble pressures of the \( \text{NH}_3-\text{CO}_2-\text{H}_2\text{O} \) mixture.

The operation pressure in the reactor should be higher than the highest local bubble pressure of the reacting mixture, so that all of the reactor volume is occupied by the liquid phase.

Fast reactions between \( \text{CO}_2 \) and \( \text{NH}_3 \) reach chemical equilibrium within a small distance from the coil inlet. As the mixture continues flowing through the coil, this equilibrium is displaced by countercurrent heat exchange with the reacting mixture flowing upward in the main cavity. With the exception of the slow carbamate dehydration reaction, all of the other reactions occurring in the mixture are instantaneous, so that these reactions can be
thought of as evolving through a succession of equilibrium states driven by the heat exchange process.

The slow carbamate dehydration reaction shows no detectable progress at the coil exit. This is due to the small residence time of the reacting mixture in the internal coil.

The temperature in the synthesis chamber is kept as high as possible, ranging from 190 to 200 °C. Restrictions on the maximum reaction temperature are imposed to keep the reactor pressure at manageable values and to avoid critical phenomena.

To increase the one-pass conversion, baffle plates are frequently installed inside the reactor main cavity to control concentration back-mixing and to approach a plug flow pattern (Uchino, 1986).

### Urea Synthesis Reactor: Mathematical Model

The mathematical model developed for the urea synthesis reactor is aimed at serving simulation purposes. Therefore, the model is required to be an optimal compromise between the search for accuracy and the practical need for rapid answers, thus keeping the computer time as low as possible.

Both the internal coil and the main reactor cavity are tubular reactors. For simulation purposes they will be approximated as two parallel sequences of continuous stirred tank reactors (CSTR's). This is done by considering cross sections along the reactor, separated from one another by a small distance compared to the overall synthesis reactor length.

Each pair of neighboring cross sections defines two CSTR's, one on the coil side and the other on the main cavity side. These two elementary reactors are thermally coupled with each other by heat exchange. The reactor thus conceived is schematically shown in Figure 2.

Figure 2. Urea synthesis reactor. Model scheme.

The CSTR that simulates the bottom section of the synthesis reactor differs from the rest in that it is adiabatic and has two feed streams: the stream delivered to the bottom section by the internal coil and the bottom feed of fresh NH₃.

Throughout the following derivations, CSTR’s in both sequences will be referred to as stages, numbered pair by pair from top to bottom.

The j subscript corresponds to the stage number, the i subscript will designate component in a mixture, and the r superscript indicates the independent reaction being considered. A stream in any of the two CSTR sequences, and its corresponding properties, will be assigned the same j subscript as the stage it leaves.

It is important to remark that this model allows sweeping of operating conditions with different degrees of concentration back-mixing by selecting different numbers of stages.

On one extreme, with a single stage, the reactor is assimilated to a CSTR with perfect mixing, while on the other extreme, with a sufficiently large number of stages, the reactor approaches the behavior of a tubular, plug flow reactor without concentration back-mixing.

### Carbamate Stream: Stage Mass Balance

The steady-state balance for species i on stage j of the carbamate sequence (i.e., the sequence of elementary CSTR’s simulating the internal coil) is

\[
F^C_{j,i} - F^C_{j-1,i} = V_C \sum_{r=1}^{r=n} \alpha^r_i \dot{R}^C_{r,j} \quad j = 1, 2, ..., N-1 \quad (23)
\]

where \( F^C_{j,i} \) is the molar flow rate of component i leaving stage j in the carbamate sequence, \( V_C \) is the stage volume, \( \alpha^r_i \) is the stoichiometric coefficient of species i in reaction r, \( \dot{R}^C_{r,j} \) is the rate of reaction r in stage j of the carbamate sequence, and N is the total number of stages.

The extent of reaction r in stage j of the carbamate sequence, \( \dot{e}^C_{r,j} \), can be related to \( F^C_{j,i} \) as follows:

\[
\dot{e}^C_{r,j} = \dot{e}^C_{i,j} = \frac{V_C \dot{R}^C_{r,j}}{F^C_{R_2} + F^C_{R_3}} \left( \frac{F^C_{R_2,j} + F^C_{R_3,j}}{F^C_{R_2} + F^C_{R_3}} + \sum_{r=1}^{r=n} \alpha^r_i \dot{e}^C_{r,j} \right) \quad (24)
\]

where \( F^C_{i,j} \) is the molar flow rate of species i fed at the reactor top and \( F^C_{R_1,j} \) is the flow rate of species i in the recycle stream. Substitution in eq 23 gives

\[
\dot{e}^C_{r,j} - \dot{e}^C_{r,j-1} = \frac{V_C \dot{R}^C_{r,j}}{F^C_{R_2} + F^C_{R_3}} \quad (25)
\]

Since it has been assumed that the slow carbamate dehydration reaction does not progress in any measurable extent due to the short residence time of the reaction mixture in the coil, then \( \dot{e}^C_{r,j} = 0 \) for \( j = 1, 2, ..., N-1 \). The other (fast) reactions in the scheme are only driven by heat exchange with the mixture in the main reactor cavity, following a sequence of local chemical equilibrium states.

### Carbamate Stream: Stage Energy Balance

The steady-state energy balance on stage j of the carbamate sequence is

\[
\sum_{r=1}^{r=n} F^C_{R_4,j} (H^C_{r,j} - H^C_{r-1,j}) + V_C \sum_{r=1}^{r=n} \dot{R}^C_{r,j} \Delta H^C_{r,j} = -Q_j \quad (26)
\]

where

\[
H^C_{r,j} = H_r (T^C_{r,j}, \rho^C_{r,j}, \epsilon^C_{r,j}) \quad (27)
\]
are the partial molal enthalpy of component \(i\) and the heat of reaction \(r\) at stage \(j\) of the carbamate sequence, of which the temperature is \(T_{j}^{e}\). The extents of reaction are \(\epsilon_{U,j}^{r}\). The temperature is calculated, but in this case a new definition of the extent of reaction is needed (see eq 32, below).

To calculate the adiabatic mixing temperature at the outlet of stage 0, eqs 29 and 30 can also be used with the condition that the heat exchanged locally between the downcoming carbamate stream and the urea stream, defined as a positive quantity when heat is transferred from the carbamate side to the urea side.

Combining eqs 25 and 26 to eliminate the reaction rates in the latter,

\[
\Delta H_{ij}^{U} = \sum_{i=1}^{m} \alpha_i \Delta H_{ij}^{C} \tag{28}
\]

The chemical equilibrium relationships for the subset of fast reactions

\[
K_r(T_j^{e}) = K_{x}^{r}(\epsilon_{U,j}^{r}, \epsilon_{C,j}^{r})K_{y}^{r}(T_j^{e}, \epsilon_{C,j}^{r}, \epsilon_{C,j}^{r}) \tag{30}
\]

Combining eqs 33 and 35 to eliminate the reaction rates for \(r = 4, 5, \) then

\[
\sum_{j=1}^{m} F_{j-1,i}^{U}(R_{j,i}^{U} - R_{j+1,i}^{U}) + F_{j-1,i}^{E} + F_{j,i}^{E} + F_{j,i}^{B} \sum_{j=1}^{m} \left( \epsilon_{U,j}^{r} - \epsilon_{U,j+1}^{r} \right) \Delta \Delta H_{ij}^{U} = -Q_{j} \tag{29}
\]

The extents of reaction \(r\) at stage \(j\) of the urea sequence is

\[
F_{j,i}^{U} - F_{j,i+1}^{U} = V_{U} \sum_{j=1}^{m} \alpha_i R_{U,j}^{U} \tag{31}
\]

where \(F_{j,i}^{U}\) is the molar flow rate of component \(i\) leaving stage \(j\) in the urea sequence, \(V_U\) is the stage volume, \(\alpha_i\) is the stoichiometric coefficient of species \(i\) in reaction \(r\), and \(R_{U,j}^{U}\) is the rate of reaction \(r\) at the stage \(j\) of the urea sequence. The extent of reaction \(r\) at stage \(j\) of the urea sequence, \(\epsilon_{U,j}^{r}\), can be related to \(F_{j,i}^{U}\) as follows:

\[
F_{j,i}^{U} = \left( F_{j,i}^{C} + F_{j,i}^{E} + F_{j,i}^{B} \right) \left\{ \frac{\sum_{j=1}^{m} \alpha_i \epsilon_{U,j}^{r}}{F_{R,i}^{C} + F_{R,i}^{E} + F_{R,i}^{B}} \right\} \tag{32}
\]

where \(F_{j,i}^{B}\) is the molar flow rate of the fresh feed of species \(i\) entering the reactor at the bottom. Substituting in eq 31 gives

\[
\epsilon_{U,j}^{r} - \epsilon_{U,j+1}^{r} = \frac{V_{U} R_{U,j}^{U}}{F_{R,j}^{C} + F_{R,j}^{E} + F_{R,j}^{B}} \tag{33}
\]

The rate of the carbamate dehydration reaction at stage \(j\) of the urea sequence, \(R_{U,j}^{U}\), is given by an expression of the following generic form:

\[
R_{U,j}^{U} = k_{a}(T_j^{e}) \left\{ F_{j,i}^{U} \epsilon_{U,j}^{r} \epsilon_{U,j}^{r} - \frac{1}{K_{x}^{r}} \right\} \tag{34}
\]

where \(K_{x}^{r}\) is the equilibrium constant of reaction \(r\).

Urea Synthesis Reactor: Simulation Module

A reactor simulation module has been developed on the basis of the mathematical model discussed in the previous section. A program strategy was designed which allows the running of the simulation module in two options.

In option 1, the temperature of the product stream is specified while the temperature of the carbamate recycle stream is one of the simulation results.

In option 2, the temperature of the product stream is specified instead of the temperature of the carbamate recycle stream.

The reactor volume and height, and the coil heat-transfer area, are reactor fixed parameters that have to be fed in each run, irrespective of the selected option. This is also valid for the total number of stages, which is a program fixed parameter.

In option 1, the program input variables are the following:

11. temperature and flow rate of the subcooled liquid \(\mathrm{NH}_{3}\) top feed
12. temperature, pressure, and flow rate of the supercritical \(\mathrm{CO}_{2}\) feed
13. effective concentrations of \(\mathrm{NH}_{3}, \mathrm{CO}_{2}\), and \(\mathrm{H}_{2}O\); the urea concentration and the flow rate of the subcooled carbamate recycle stream
14. temperature and flow rate of the subcooled liquid \(\mathrm{NH}_{3}\) bottom feed
15. pressure of operation
16. temperature of the product stream

In operating option 1, the reactor module calculates the following:

1. detailed composition of all inlet and outlet streams
2. temperature of carbamate recycle stream
The solution strategy proceeds through the following steps.

S1. Enthalpy flows of all inlet streams, except that of the carbamate recycle stream, are calculated.

S2. An initial estimated value of the synthesis reaction extent in the product stream, $\varepsilon^{r}_{U,1}$, is chosen.

S3. With the current value of $\varepsilon^{r}_{U,1}$ and the input value of $T^{U}_{1}$, the detailed composition of the outlet stream is calculated by means of the chemical equilibrium relationships for the subset of fast reactions.

$$K_{r}(T^{U}_{r}) = K_{r}^{4}(\varepsilon^{4}_{U,1}, \varepsilon^{5}_{U,1}, T^{U}_{1}, \varepsilon^{6}_{U,1})$$

$r = 4, 5$, the resulting state vector $(T^{U}_{1}, \varepsilon^{4}_{U,1}, \varepsilon^{5}_{U,1}, T^{U}_{1})$ is also the current state vector of stage 1 of the urea sequence.

S4. With the current state vector $(T^{U}_{1}, \varepsilon^{4}_{U,1}, \varepsilon^{5}_{U,1}, T^{U}_{1})$, the enthalpy flow associated with the stream leaving stage 1 of the urea sequence, $H^{C}_{1}$, can be calculated.

S5. The enthalpy flow associated with the carbamate recycle stream, $H^{CR}$, is calculated so as to satisfy the energy balance between the reactor inlet and outlet streams.

S6. The temperature of the carbamate recycle stream, $T^{CR}$, can be calculated by solving the system of nonlinear equations.

$$K_{r}(T^{CR}_{r}) = K_{r}^{4}(\varepsilon^{4}_{CR}, \varepsilon^{5}_{CR}) K_{r}^{5}(T^{CR}_{r}, \varepsilon^{4}_{CR}, \varepsilon^{5}_{CR})$$

$r = 4, 5$, together with

$$H^{CR} = \sum_{i=1}^{N} H^{i}(\varepsilon^{4}_{CR}, \varepsilon^{5}_{CR})$$

This set of three equations in the unknowns $T^{CR}_{r}$, $\varepsilon^{4}_{CR}$, and $\varepsilon^{5}_{CR}$ can be solved for every value of $H^{CR}$ obtained in S5.

S7. The enthalpy flow at the outlet of the adiabatic mixing chamber ($j = 0$), $H^{E}_{1}$, can be calculated as the sum of the enthalpy flows of the streams at the inlet of that chamber.

S8. The temperature of the adiabatic mixing chamber of the carbamate sequence, $T^{C}_{1}$, can be calculated by solving the system of nonlinear equations.

$$K_{r}(T^{C}_{r}) = K_{r}^{4}(\varepsilon^{4}_{C,0}, \varepsilon^{5}_{C,0}) K_{r}^{5}(T^{C}_{r}, \varepsilon^{4}_{C,0}, \varepsilon^{5}_{C,0})$$

$r = 4, 5$, together with

$$H^{C}_{0} = \sum_{i=1}^{N} H^{i}(\varepsilon^{4}_{C,0}, \varepsilon^{5}_{C,0})$$

This set of three equations in the unknowns $T^{C}_{r}$, $\varepsilon^{4}_{C,0}$, and $\varepsilon^{5}_{C,0}$ can be solved for every value of $H^{C}_{0}$ obtained in S7.

S9. With the results obtained in S3, the rate of the synthesis reaction in stage 1 of the urea sequence, $R^{U}_{1,1}$, and the extent of reaction $\varepsilon^{r}_{U,2}$ at the outlet of stage 2 can be calculated.

S10. The value of the temperature of the stream leaving stage 2, $T^{U}_{2}$, is guessed.

S11. With the current values of $\varepsilon^{r}_{U,2}$ and $T^{U}_{2}$, the detailed composition of the outlet stream is calculated by means of the chemical equilibrium relationships for the subset of fast reactions.

$$K_{r}(T^{U}_{r}) = K_{r}^{4}(\varepsilon^{4}_{U,2}, \varepsilon^{5}_{U,2}, T^{U}_{2}, \varepsilon^{6}_{U,2})$$

$r = 4, 5$. The calculated state vector $(T^{U}_{2}, \varepsilon^{4}_{U,2}, \varepsilon^{5}_{U,2}, T^{U}_{2})$ is also the current state vector of stage 2 of the urea sequence.

S12. With the current state vector $(T^{U}_{2}, \varepsilon^{4}_{U,2}, \varepsilon^{5}_{U,2}, T^{U}_{2})$, the enthalpy flow associated with the stream leaving stage 2 of the urea sequence can be calculated.

S13. The local heat flow between thedowncoming carbamate stream and the upgoing urea stream in stage 1, $Q_{1}$, can be computed as the difference between the stage outlet and inlet enthalpy flows of the urea stream (already calculated in S4 and S12, respectively).

S14. The outlet enthalpy flow from stage 1 of the carbamate sequence, $H^{C}_{1}$, can be estimated as the algebraic sum of the state inlet enthalpy flow, $H^{C}_{0}$, and the local heat flow $Q_{1}$, i.e.,

$$H^{C}_{1} = H^{C}_{0} + Q_{1}$$

S15. The temperature of stage 1 of the carbamate sequence, $T^{C}_{1}$, can be calculated by solving the system of nonlinear equations.

$$K_{r}(T^{C}_{r}) = K_{r}^{4}(\varepsilon^{4}_{C,1}, \varepsilon^{5}_{C,1}) K_{r}^{5}(T^{C}_{r}, \varepsilon^{4}_{C,1}, \varepsilon^{5}_{C,1})$$

$r = 4, 5$, together with

$$H^{C}_{1} = \sum_{i=1}^{N} F^{C}_{i}(\varepsilon^{4}_{C,1}, \varepsilon^{5}_{C,1}) H^{i}(T^{C}_{1}, \varepsilon^{4}_{C,1}, \varepsilon^{5}_{C,1})$$

This set of three equations in the unknowns $T^{C}_{1}$, $\varepsilon^{4}_{C,1}$, and $\varepsilon^{5}_{C,1}$ can be solved for every value of $H^{C}_{1}$ obtained in S12.

S16. The value of $Q_{1}$ calculated in S11 is compared with the value $Q_{1}^{*}$ obtained from

$$Q_{1}^{*} = (UA)(T^{C}_{1} - T^{U}_{1})$$

If their difference is larger than the required precision, a new estimated value of $T^{C}_{1}$ is chosen and calculations are resumed back at step S11. The procedure is repeated until convergence.

S17. Steps S9 to S16 are repeated for $j = 2, 3, ..., N - 1$ instead of $j = 1$, and $j = 3, 4, ..., N$ instead of $j = 2$, successively. If the value of $\varepsilon^{r}_{U,N}$ thus obtained differs from 0 by an amount larger than the precision required, then calculations are resumed back at step S3 with a new estimated value of the synthesis reaction extent in the product stream, $\varepsilon^{r}_{U,1}$. The procedure is repeated until convergence.

It should be noticed that the proposed computational scheme guarantees stage-by-stage closure of both mass and energy balances.

**Solution Strategy.** The solution strategy for option 2 is quite similar to that for option 1. They only differ in the following few steps.

S1. Enthalpy flows of all inlet streams are calculated. Their sum equals the enthalpy flow of the product outlet stream, $H^{U}_{1}$.

S3. With the current value of $\varepsilon^{r}_{U,1}$ and the value of $H^{U}_{1}$ obtained from S1, the temperature and the detailed composition of the outlet stream is calculated by solving the following set of equations:
Figure 3. Influence of model number of stages on reactor simulator performance.

\[ K_r(T^*_1) = K_{ur}(\epsilon_{u,1}^4, \epsilon_{u,1}^6) \]

where \( r = 4, 5, \) together with

\[ H^1 = \sum_{i=1}^{\infty} F_i^u (\epsilon_{u,1}^4, \epsilon_{u,1}^6) H_{ij}(\epsilon_{u,1}^4, \epsilon_{u,1}^6) \]

This is a set of three equations in the unknowns \( T^*_1, \epsilon_{u,1}^4, \) and \( \epsilon_{u,1}^6. \)

Steps S4, S5, and S6 should be overlooked when the computation of option 2 is under way. The remaining steps must be executed as in option 1.

Impact of Program and Reactor Fixed Parameters

With a single stage the reactor is reduced to a single CSTR with perfect mixing, while on the other extreme, when a sufficiently large number of stages is chosen, the reactor approaches the behavior of a tubular, plug flow reactor without axial concentration back-mixing.

Figure 3 shows how simulation results depend on the number of stages adopted. It can be seen that little accuracy is gained when the number of stages is increased beyond a total number of 25.

There is a physical interpretation that can be given to the results shown in Figure 3. They also approximate the behavior of reactors with different degrees of concentration back-mixing, the average back-mixing length being estimated by the ratio of the total reactor height to the number of stages.

A simulation output for usual operating conditions is shown in Table II. Key simulation results are compared against plant data in Table III, showing a very good agreement between predicted and measured outlet CO2 to urea conversion and with temperature at different locations along the reactor.

Detailed temperature profiles of both the internal coil and the main reactor cavity are shown in Figure 4. Under operating conditions, the temperature profile along the urea synthesis cavity shows a maximum at about half the total reactor height.

Under average operating conditions the chemical equilibrium shift of the fast reactions driven by the urea synthesis reaction is an overall exothermic process which tends to heat the reaction mixture. This effect competes with the cooling effect due to the heat transferred to the mixture flowing countercurrent inside the coil.

Near the bottom of the reaction cavity, the backward rate of the synthesis reaction is very small since urea is present in small amounts. In this section, heat transfer between streams becomes the slow process and the temperature of the reaction mixture rises.

As urea concentration builds up, the synthesis rate decreases and the heating effect due to the overall synthesis reaction becomes less important compared to heat exchange between streams, until it becomes the slow, rate-controlling process, thus explaining the maximum observed in the temperature profile.

Figure 4. Simulated reactor temperature and composition profiles.

The amount of heat exchanged between the two CSTR's belonging to the jth stage can be expressed as

\[ Q_j = (UA)j \Delta T_j \]

where \( \Delta T_j = T_j^C - T_j^U \) and \( (UA)_j \) represents the product of the overall heat-transfer coefficient \( U \), which can be considered approximately constant along the coil, and the stage heat-transfer area \( A_j \), calculated as the ratio of the total heat exchange area to the number of stages in which it is contained.

Different reactors can be simulated by choosing the \( A_j \) values adequately. The choice \( (A_j = 0, j = 1,...,N) \), allows simulation of reactors without an internal coil, whereas the choice \( (A_j = 0, j < k; A_j = 0, j > k; 1 \leq k \leq N) \) represents intermediate situations found in practice. The latter of these two choices still allows for different, nonzero values of \( A_j, j \leq k. \)

Discussion of Results

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The internal coil is a means to ensure quasi isothermal synthesis conditions, allowing the control of the reaction mixture temperature within a narrow band of few degrees.
about 197 °C. This needs an adequate temperature at the coil inlet which in practice is controlled by the carbamate recycle temperature. This temperature has to be adopted when running the program in simulation mode, and is an output variable when the module is used in design mode.

The impact of the coil surface available for countercurrent heat exchange between the feed stream and the mixture in the urea synthesis section is shown in Table IV.

Table V shows the impact of the reactor outlet temperature on other important operating variables. Conversion of CO₂ to urea increases with increasing outlet reactor temperature, but the effect is attenuated as the outlet temperature approaches the maximum allowable value of 200 °C.

The effect of the outlet temperature on the carbamate recycle temperature follows a trend similar to that of the CO₂ conversion to urea. For every 1-deg change in the output temperature there is a corresponding change of about 2 and 3 deg in the carbamate recycle temperature.

The approach to the equilibrium value of the exit conversion of CO₂ to urea, defined as
back-mixing in operating equipment. Parametric studies were performed in a short computing time. The computational algorithm developed is simple and robust. These features make the module a useful tool to estimate of the degree of concentration approach to Urea Conversion.

Table III. Reactor Simulation Module Performance

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Plant Reactor</th>
<th>Simulator</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbamate recycle temp (°C)</td>
<td>108.8</td>
<td>106.9</td>
</tr>
<tr>
<td>Mixing chamber outlet temp (°C)</td>
<td>178.4</td>
<td>179.3</td>
</tr>
<tr>
<td>Main cavity inlet temp (°C)</td>
<td>182.5</td>
<td>182.6</td>
</tr>
<tr>
<td>Main cavity temp at 1/2 reactor height (°C)</td>
<td>196.2</td>
<td>196.9</td>
</tr>
<tr>
<td>CO2 to urea conversion (%)</td>
<td>67.8</td>
<td>67.5</td>
</tr>
</tbody>
</table>

* Comparison with plant data for usual operating conditions (see Table II).

Table IV. Influence of (UA) on Reactor Performance

<table>
<thead>
<tr>
<th>UA (W/K)</th>
<th>Reactor</th>
<th>Conversion (%)</th>
<th>Main cavity mean temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>193.1</td>
<td>85.4</td>
<td>189.1</td>
</tr>
<tr>
<td>2.5</td>
<td>193.0</td>
<td>66.9</td>
<td>192.6</td>
</tr>
<tr>
<td>5.0</td>
<td>192.8</td>
<td>68.1</td>
<td>195.7</td>
</tr>
<tr>
<td>7.5</td>
<td>192.8</td>
<td>69.1</td>
<td>199.6</td>
</tr>
</tbody>
</table>

* Feed and other operating conditions are the same as in Table II.

Table V. Influence of Reactor Outlet Temperature on CO2 to Urea Conversion

<table>
<thead>
<tr>
<th>Outlet temp (°C)</th>
<th>Carbamate recycle temp (°C)</th>
<th>Conversion (%)</th>
<th>Approach to equilib conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>187.5</td>
<td>91.5</td>
<td>64.0</td>
<td>191.0</td>
</tr>
<tr>
<td>190.0</td>
<td>93.0</td>
<td>65.8</td>
<td>93.7</td>
</tr>
<tr>
<td>192.5</td>
<td>105.9</td>
<td>67.3</td>
<td>95.8</td>
</tr>
<tr>
<td>195.0</td>
<td>112.1</td>
<td>68.2</td>
<td>97.3</td>
</tr>
<tr>
<td>197.5</td>
<td>117.8</td>
<td>68.9</td>
<td>98.3</td>
</tr>
<tr>
<td>200.0</td>
<td>123.1</td>
<td>69.2</td>
<td>98.9</td>
</tr>
</tbody>
</table>

* Feed and other operating conditions are the same as in Table II.

\[ \eta = \frac{\left( e_{U,I}^{6} \right)_{eq} - \left( e_{U,I}^{6} \right) }{e_{U,I}^{6} \times 100} \]

is also favored by an outlet temperature increase. For outlet temperatures in the usual range, the approach to equilibrium is always larger than 90% under average operating conditions.

Simulation results summarized in Table VI accurately reproduce the unfavorable effect of excess water on the final yield found in practice.

Conclusions

The reactor simulator has been tested against operating data from a production-scale plant. The response to different sets of input variables was accurate and fast. The computational algorithm developed is simple and robust. These features make the module a useful tool to perform parametric studies in a short computing time.

Predicted trends reproduce the reactor sensitivity to changes in NH3/CO2 and H2O/CO2 feed mole ratios, as well as to the carbamate recycle temperature observed in practice.

The module allows testing of different reactor configurations and estimation of the degree of concentration back-mixing in operating equipment.

Table VI. Influence of Water Content in Carbamate Recycle Stream on CO2 to Urea Conversion

<table>
<thead>
<tr>
<th>H2O mass flow in carbamate recycle stream (kg/h)</th>
<th>Carbamate recycle stream mass flow (kg/h)</th>
<th>Carbamate recycle stream composition (% w/w)</th>
<th>CO2 to urea conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4000</td>
<td>21 045</td>
<td>42.29</td>
<td>37.49</td>
</tr>
<tr>
<td>4500</td>
<td>21 545</td>
<td>41.31</td>
<td>36.62</td>
</tr>
<tr>
<td>5000</td>
<td>22 045</td>
<td>40.37</td>
<td>35.79</td>
</tr>
<tr>
<td>5500</td>
<td>22 545</td>
<td>39.48</td>
<td>34.99</td>
</tr>
<tr>
<td>6000</td>
<td>23 045</td>
<td>38.62</td>
<td>34.23</td>
</tr>
</tbody>
</table>

* Feed and other operating conditions are the same as in Table II.

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Nomenclature

\[ A_{i} = jth \text{ parameter in the correlation of pure liquid reference fugacity of ammonia with temperature} \]
\[ a_{ij} = \text{UNIQUAC binary interaction parameters between components} \]
\[ B_{i} = jth \text{ parameter in the correlation of Henry's constant of carbon dioxide in water with temperature} \]
\[ C = \text{total molar concentration in the liquid phase} \]
\[ C_{k,r} = \text{4th parameter in the correlation of the equilibrium constant of chemical reaction} \]
\[ \text{CRSTR = continuous stirred tank reactor} \]
\[ F^{i} = \text{molar flow rate of component} \]
\[ F^{i}_{r} = \text{molar flow rate of component} \]
\[ H^{i} = \text{partial molal enthalpy of component} \]
\[ H^{i}_{r} = \text{partial molal enthalpy of component} \]
\[ \text{Hf} = \text{pure liquid reference fugacity of component} \]
\[ H_{i} = \text{partial molal enthalpy of component} \]
\[ H_{r} = \text{partial molal enthalpy of component} \]
\[ \text{Hf}_{r} = \text{enthalpy flow associated with the stream leaving stage} \]
\[ \text{Hf}_{r} = \text{enthalpy flow associated with the stream leaving stage} \]
\[ \text{Hf}_{r} = \text{enthalpy flow associated with the stream leaving stage} \]
\[ \text{Hf}_{r} = \text{enthalpy flow at the outlet of the adiabatic mixing chamber} \]
\[ \Delta H_{r} = \text{heat of reaction} \]
\[ \Delta H_{r} = \text{heat of reaction} \]
\[ \Delta H_{r} = \text{heat of reaction} \]
\[ \text{Hf} = \text{reaction rate constant} \]
\[ N = \text{total number of stages} \]
\[ P = \text{pressure} \]
\[ P_{ij} = \text{vapor pressure of component} \]
\[ Q_{ij} = \text{heat exchanged locally between the carbamate stream} \]
\[ q_{i} = \text{UNIQUAC surface parameter of component} \]
\[ R = \text{rate of reaction} \]
\[ R_{ij} = \text{rate of reaction} \]
\[ R_{ij} = \text{rate of reaction} \]
\[ R_{G} = \text{gas constant} \]
\[ T = \text{absolute temperature} \]
\[ T_{f} = \text{temperature of the stream leaving stage} \]

 acknowledges.
$T_j$ = temperature of the stream leaving stage $j$ in the urea sequence

$UA$ = product of the overall heat-transfer coefficient $U$ and the coil heat-transfer area $A$

$V_C$ = stage volume in the carbamate sequence

$V_U$ = stage volume in the urea sequence

$v_i$ = liquid molal volume of component $i$

$v_{i0}$ = liquid molal volume of component $i$ at infinite dilution

$x_i$ = mole fraction of component $i$ in the liquid phase

$y_j$ = mole fraction of component $i$ in the gas phase

$x$ = array of the mole fractions in the liquid phase

$y$ = array of the mole fractions in the gas phase

Greek Letters

$\alpha_i^r$ = stoichiometric coefficient of component $i$ in reaction $r$

$\gamma_{i}$ = activity coefficient of component $i$; rational symmetric convention

$\gamma_{i}^{r}$ = activity coefficient of component $i$; rational unsymmetric convention

$\xi_{Cj}$ = extent of reaction $r$ at stage $j$ of the carbamate sequence

$\xi_{Uj}$ = extent of reaction $r$ at stage $j$ of the urea sequence

$\phi_i$ = fugacity coefficient of component $i$ in the gas phase

Literature Cited


Chao, G. T. Urea, its Properties and Manufacture; Chao's Institute, Ed.: Taipei, Taiwan, 1967.


Weast, R. C., Ed. CRC Handbook of Chemical and Physics, 50th ed.; CRC Press: Boca Raton, FL, 1980; Section D.


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