

STEADY STATE ANALYSIS OF A FALLING FILM REACTOR

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Abstract. The steady-state simulation of an ammonium carbamate decomposer (stripper) is presented. This falling-film reactor is usually located in the high-pressure section of industrial urea plants in order to concentrate the urea solution leaving the synthesis reactor.

The stripper consists in a bundle of small diameter tubes installed in a heating shell. The aqueous urea solution (also containing ammonium carbamate, NH_3 , CO_2 and inerts) is fed to the top of the stripper and flows by gravity effects as a thin film on the internal wall of the tubes. The ammonium carbamate is decomposed through the endothermic reaction: $\text{NH}_2\text{COO}^- + \text{NH}_4^+ \leftrightarrow 2\text{NH}_3 + \text{CO}_2$, at around 200 °C and 150 atm. The energy for the reaction and the evaporation of the volatile components is supplied by means of saturated steam (shell side). The stripped gas (containing NH_3 , CO_2 , H_2O and N_2) is collected in the central section of the tubes and flows upwards countercurrently with the urea solution. The gas leaves the stripper by the top to be recycled to the urea synthesis section. The concentrated urea solution is sent to the medium pressure section of the plant for further purification.

The countercurrent gas-liquid flow is represented as a series of stages with perfect mixing for both phases. The σ - σ method is used as thermodynamic model to describe the phase equilibrium. The mass transfer limitations (assumed to be concentrated in the gas film) are represented by the Maxwell-Stefan equations. The mass and energy balances for both phases, the equilibrium equations and the flows through the gas-liquid interface for the multicomponent system are considered for all the stages.

The influence of the main operating variables on the stripper performance is studied. The model predicts stripped gas flowrates, outlet compositions and temperatures values in agreement with those found in a large scale stripper.

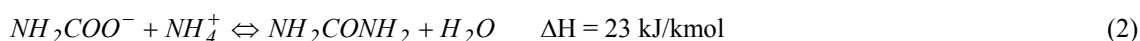
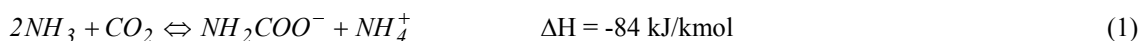
Keywords: urea plants, ammonium carbamate, falling-film reactors, modeling.

1. Introduction

Urea (NH_2CONH_2) is produced industrially by synthesis from liquid ammonia and gaseous carbon dioxide at about 160 atm and 200 °C, being the NH_3/CO_2 molar ratio of at the reactor inlet about 3.3 to 3.6. There are two different types of processes to produce urea in industry. These processes are called as *partial recycle* and *total recycle* of the nonconverted reactants. The most common technologies are from Snamprogetti and Stamicarbon (Dente et al., 1988). In the present work a plant with total recycle and Snamprogetti Technology is considered. The global process includes three sections: high, medium and low-pressure.

The high-pressure section (see Figure 1) involves four main units: the gas synthesis reactor, the stripper, the carbamate condenser and the carbamate separator (UNIDO and IFDC, 1979).

Two reactions occur in the liquid phase of the urea synthesis reactor:



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Reaction (1) is very fast and exothermic and reaction (2) is weakly endothermic and takes place at low rate, determining the reactor volume. The $\text{CO}_{2,T}$ (free $\text{CO}_2 + \text{NH}_2\text{COONH}_4$) conversion to urea in the synthesis reactor is around 63%. The reactor effluent solution containing urea, ammonium carbamate, NH_3 , CO_2 and inerts (mainly N_2) enters the stripper at the same pressure level as the synthesis reactor. During this process a fraction of the unconverted carbamate is decomposed into NH_3 and CO_2 by means of the reverse of reaction (1). After separating the inert gases, which are passed to the MP section, the carbamate solution is finally recycled to the reactor bottom together with an ammonia stream by means of a liquid/liquid ejector (Figure 1).

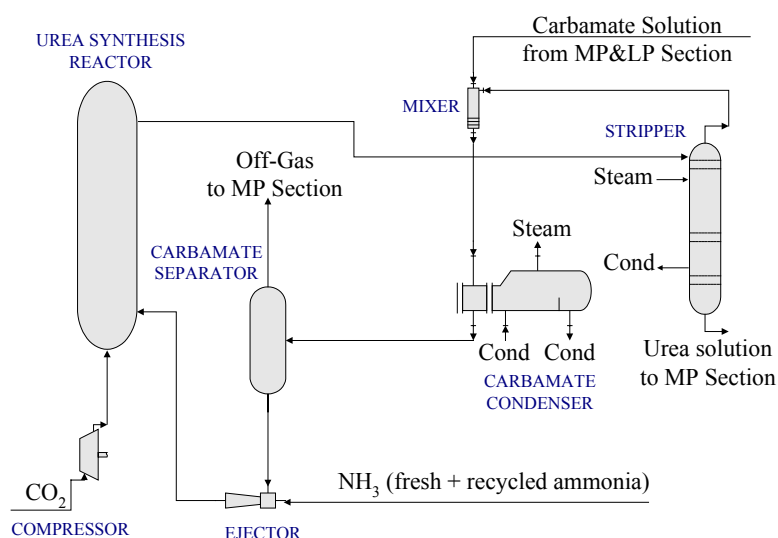


Fig. 1. High Pressure Section of Snamprogetti Urea Plant

Downstream of the stripper the purification of the urea stream is carried out while the NH_3 and CO_2 are recovered at the medium (around 17 atm) and low-pressure (around 3.5 atm) sections, respectively. All the NH_3 and CO_2 leaving the HP section are recycled to the reactor and approximately the overall conversion of CO_2 to urea is reached.

Pedersen and Prenosil (1981), Wassel and Mills (1987) and Talens-Alesson (1999) have presented different modeling studies of falling fill units, which were applied to different reactive and non-reactive systems.

Dente et al. (1988) presented a simulation program for the high pressure urea synthesis loop with Snamprogetti and Stamibarbon Technologies. More recently Hamidipour et al. (2005) and Zhang et al. (2005) have published simulation results of the synthesis section of an industrial urea plant with Stamibarbon technology. In particular, Hamidipour et al. (2005) represented the stripper with a simple model based on total mass and energy balances while Zhang et al. (2005) simulated the unit by means of an equilibrium-stages model. However, none of the three mentioned articles includes a detailed study of the stripper operation.

In this paper the rigorous mathematical model of the stripping process is presented and its behavior at different operating conditions is analyzed. Moreover, the simulation results are compared with design data of an industrial unit.

2. Stripper description

The stripper consists in a bundle of small diameter tubes ($d_t = 0.8''$) installed in a heating shell. A scheme of this process is shown in Figure 2a. The aqueous urea solution is fed to the top of the stripper. The liquid is distributed on the heating surface as a film and flows to the bottom by gravity. In practice it is a vertical shell and tube heat exchanger, with the heating medium on the shell side (Figure 2b). As the liquids film flows, it is heated and decomposition of carbamate and surface evaporation occur. The vapors formed (essentially ammonia and carbon dioxide) are removed by flowing to the top of the tube. The carbamate decomposition heat is supplied by means of condensing steam (saturated).

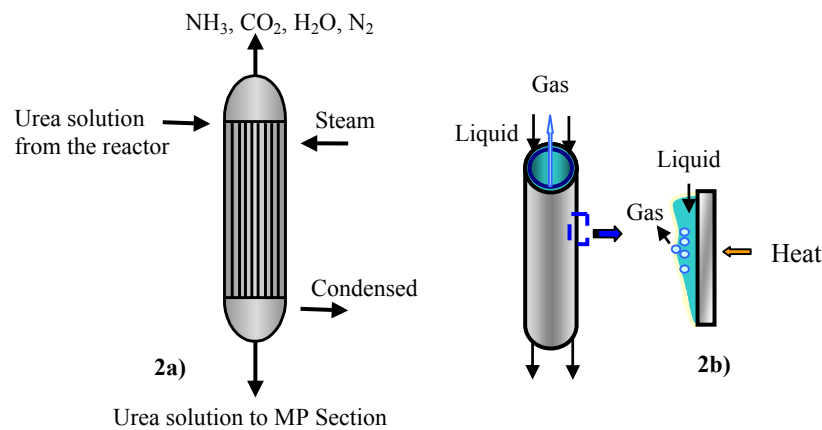


Fig. 2. a) Ammonium Carbamate Decomposer, b) view of cross section tube

3. Mathematical Model

3.1 Hypothesis

The mathematical model of the ammonium carbamate decomposer is based on the following assumptions:

- Steady state conditions.
- Isobaric operation.
- The tube side of the stripper is represented as stages in series. At each stage complete mixing for both phases is assumed.
- At all the axial positions, the difference between the gas and liquid temperature is neglected.
- The gas and liquid phases coexist in the ammonium carbamate decomposer. The reaction takes place only in the liquid phase. Chemical equilibrium is assumed.
- Urea and ammonium carbamate are considered non-volatile components.
- The mass transfer resistance is concentrated in the gas phase (Pedersen and Prenosil, 1981, Dente et al., 1988).

3.2 Mass Transfer

The correct description of molecular diffusion in an n-component system is given by the Maxwell-Stefan equation, which for steady-state unidirectional transfer reduces to

$$\nabla y_i = \sum_{j=1}^n \frac{1}{cD_{ij}} (y_i N_j - y_j N_i) \quad (3)$$

The molar flux relative to stationary coordinates N_j is the resultant the two vector quantities, the diffusive and convective contributions (Krishna, 1977, Kenig et al., 1997)

$$N_i = J_i + y_i \sum_{k=1}^n N_k, \text{ where } J_i = -cD_{im} \nabla y_i \text{ is the diffusional term} \quad (4)$$

$$\text{In view of the requirement } \sum_{i=1}^n J_i = 0 \quad (5)$$

only (n-1) diffusion fluxes J_i are independent.

The molar fluxes N_i (eq. 4) can be written as follow

$$N_i = -cD_{im} \frac{dy_i}{dr} + y_i \sum_{k=1}^n N_k \quad (6)$$

By discretization of the derivate in the gas film thickness (δ_g) equation (6) is expressed as:

$$N_i = -\frac{cD_{im}}{\delta_g} (y_i - y_i^*) + y_i \sum_{k=1}^n N_k \quad (7)$$

It is convenient to define the coefficients $k_{gi} = \frac{cD_{im}}{\delta_g}$. In this way, eq. (7) is changed by

$$N_i = -k_{gi} (y_i - y_i^*) + y_i \sum_{k=1}^n N_k \quad (8)$$

Where, the molar transfer coefficient in the gas side for component i (k_{gi}) is calculated by the correlation proposed by Kafesjian et al. (1961).

3.3 Reaction

The ammonium carbamate is decomposed in the liquid phase to ammonia and carbon dioxide by the reverse of reaction (1).

This reaction is fast and highly endothermic and reaches the chemical equilibrium. The following equilibrium equations are satisfied:

$$K = K_\gamma \frac{x_{NH_2COO^-} x_{NH_4^+}}{x_{CO_2} x_{NH_3}^2} \quad \text{where} \quad K_\gamma = \frac{\gamma_{NH_2COO^-}^o \gamma_{NH_4^+}^o}{\gamma_{CO_2}^o \gamma_{NH_3}^o} \quad (9)$$

The constant K has been estimated by means of the Anderson correlation (Anderson et al., 1978). The activity coefficients of each component in symmetric (γ_i) and asymmetric (γ_i^o) convention were obtained by Extended UNIQUAQ Model (Sander et al., 1986).

3.4 Thermodynamic Model

The use of the same equation of state to describe both phases, referred as θ - θ method, has been proposed by Sandler (1997) as convenient to describe the equilibrium of a solution near the critical region.

In the present work the θ - θ method is adopted and the Peng- Robinson equation of state (PR EOS) is used to represent both phases. The binary interaction parameters (k_{ij}) in PR EOS were adjusted using vapor- liquid equilibrium data at high-pressure conditions (Wichterle et al., 1973; Knapp et al., 1982).

The isofugacity conditions for the components are the following:

$$y_i^* \phi_i^v = x_i \phi_i^l, \quad \text{for } i = CO_2, NH_3, H_2O, N_2 \quad (10)$$

3.5 Simulation of the stripper

The stripper is represented by N_s equilibrium stages with countercurrent flow (Figure 3). The number of stages is adopted by solving the model successively with higher N_s values until the solution does not change significantly. A total number of ten stages is adopted ($N_s=10$).

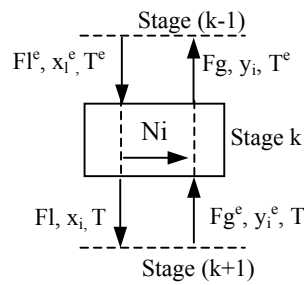


Fig. 3. Scheme of a stage for the stripper

For each stage, the conservation equations are the following:

Molar Balances

Liquid phase

$$Flx_i = Fl^e x_i^e + \lambda_i \alpha - N_i A \quad (11)$$

$$i = NH_3, CO_2, H_2O, \text{urea, ammonium carbamate and } N_2$$

Gas phase

$$Fgy_i = Fg^e y_i^e + N_i A \quad (12)$$

$$i = CO_2, NH_3, H_2O, N_2$$

Total Mass Balance

$$Fl^e Ml^e + Fg^e Mg^e - FlMl - FgMg = 0 \quad (13)$$

Energy Balance

$$\sum_i^n Fg^e c_{p_g}(T - T^e) - \sum_i^n Fl^e c_{p_l}(T - T^e) - \sum_i^n N_i A \Delta H_{v_i} + \alpha(-\Delta H_r) + AU(T_s - T) = 0 \quad (14)$$

The subscripts g and l represent the gas and liquid phase respectively.

Boundary Conditions

$$\text{Top: } z^* = 0: T = T^0, Fl = Fl^0, x_i = x_i^0, \quad \text{for } i = CO_2, NH_3, Carb, urea, H_2O, N_2 \quad (15)$$

$$\text{Bottom: } z^* = 1: Fg = 0, y_i = 0, \quad \text{for } i = CO_2, NH_3, H_2O, N_2 \quad (16)$$

Equations 8 to 16 are applied to 6 components and 10 stages resulting in a set of 150 simultaneous non-linear algebraic equations, which are solved by a Quasi Newton method.

4. Results and Discussion

4.1 Base case

Figures 4 to 7 show the evolution of the main variables along the stripper for a reference condition corresponding to design data of an industrial urea plant.

As shown in Figure 4, the molar flowrate of the stripped gas (Fg) increases continuously from zero up to its outlet value of 1.05 kmol/s. The molar flowrate of the urea solution (Fl) keeps almost constant near the top, where the mass transfer to the gas phase compensates the increase in the number of moles caused by chemical reaction. Below this upper zone, Fl decreases monotonically.

The evolution of the temperature along the stripper (Figure 5) is the consequence of two opposite phenomena: the heat consumption by chemical reaction and the heat supply from the shell side. Thus, the high carbamate decomposition rate (i.e., heat consumption rate) occurring near the top leads to a slight temperature decrease for $z^* < 0.1$, despite the driving force for heat transfer ($T_s - T$) is maximum in this zone. Below this axial position the heat consumption rate decreases and a monotonous temperature rise occurs. For comparison purposes, the design data are also included in Figures 4 and 5.

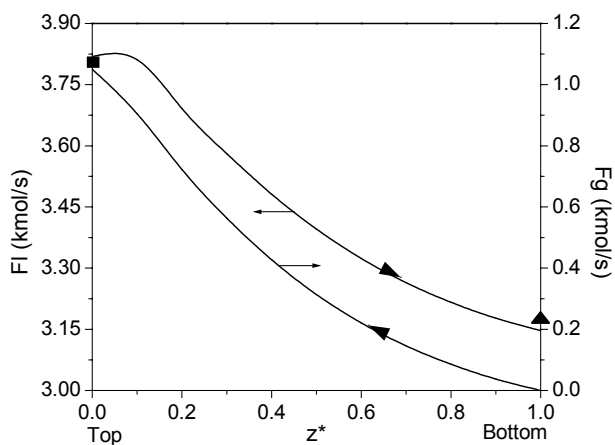


Fig. 4. Molar flowrates of liquid and gas phases

Design data: ■ Fg = 1.07 kmol/s, ▲ Fl = 3.17 kmol/s

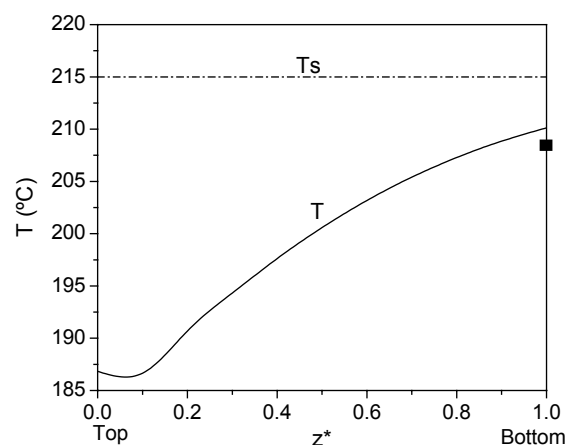


Fig.5. Steam and process temperature profiles

Design data: ■ T = 207 C

Figure 6 shows the molar composition of the liquid phase along the tube length. As expected, the carbamate fraction (x_{carb}) presents a continue decrease, because of the chemical reaction. Conversely, curves corresponding to x_{CO_2} and x_{NH_3} show a maximum at $z^* = 0.1$, which indicates that near the top the generation rates of CO_2 and

NH₃ by chemical reaction are higher than the molar fluxes towards the gas phase. For $z^* > 0.1$ the carbamate decomposition rate (slope of the x_{carb} curve) becomes lower and therefore the concentrations of the reaction products tend to decrease. Finally, the urea fraction in the solution (x_{urea}) increases along the tube as a consequence of the stripping of the volatile compounds.

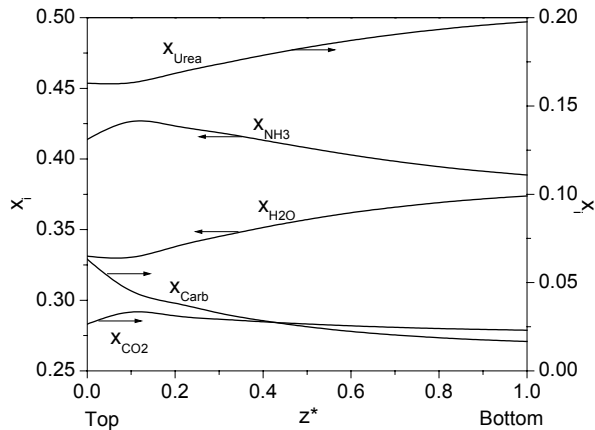


Fig. 6. Molar fractions in the liquid phase

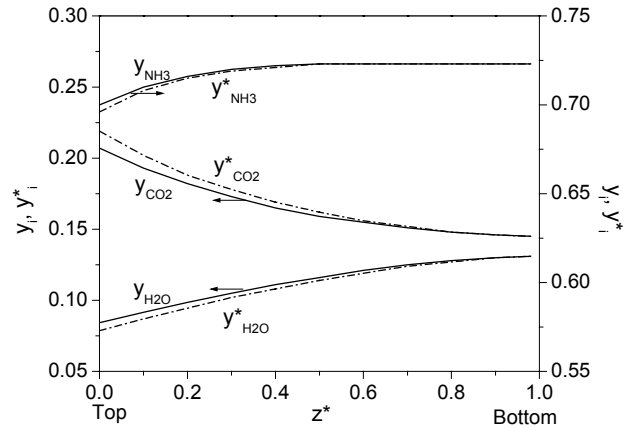


Fig. 7. Molar fractions in the gas phase

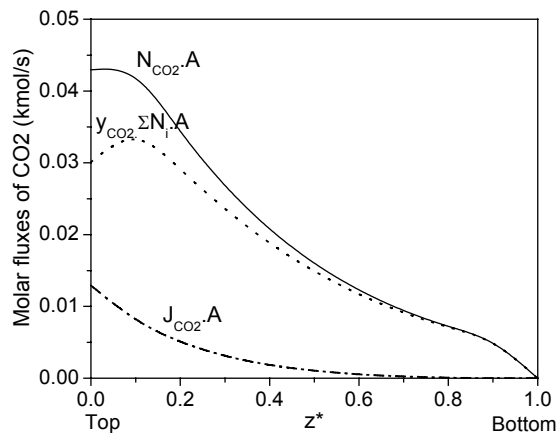


Fig. 8. Molar fluxes of CO₂ at the gas-liquid interface

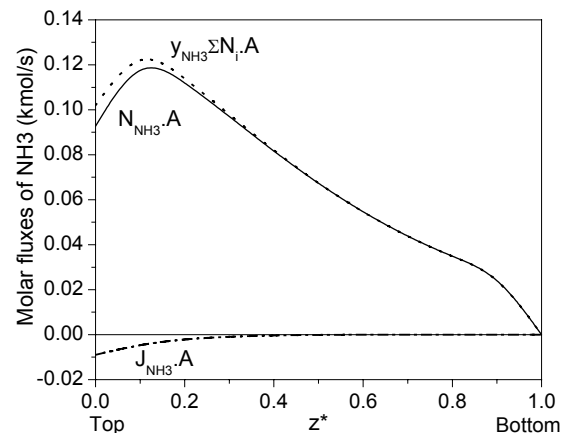


Fig. 9. Molar fluxes of NH₃ at gas-liquid interface

The composition of the stripped gas along the tube is shown in Figure 7, for bulk conditions (y_i curves) and at the interface (y_i^* curves). It is interesting to note that the difference ($y_i^* - y_i$) is positive in the case of CO₂ and negative for NH₃, i.e., the driving forces for the diffusive flows are opposite. However, both reaction products are continuously stripped from the solution along the tube length. This result can be explained by means of Figure 8 and 9, where the axial profiles of the molar fluxes through the interface are shown, for CO₂ and NH₃ respectively. For the case of CO₂, the diffusive ($J_{\text{CO}_2}A$) and convective term of equation 8 ($y_{\text{CO}_2}\Sigma N_i A$) has the same sign, then the net flux of CO₂ through the interface is the sum of both effects. Conversely, the diffusive flux of NH₃ (Figure 9) has an opposite sense to the convective flux (i.e., $J_{\text{NH}_3} < 0$) and the net flux becomes lower than the convective term. Nevertheless, the net flux of NH₃ is always positive, i.e. NH₃ is being transferred from the interface to the gas phase.

4.2. Influence of the steam temperature

The steam temperature (pressure of the saturated steam) is a controlled variable in industrial practice, which determines the amount of heat being transferred from the shell side and consequently the carbamate conversion. As it can be seen in Figure 10, the carbamate decomposition rate increases with T_s (see the $F_{I_{carb}}$ curves) leading to higher amounts of reaction products in the liquid phase. However, the molar flowrates of NH_3 and CO_2 in the liquid phase also drop with T_s (see the curves of $F_{I_{CO_2}}$ and $F_{I_{NH_3}}$), due to the increase in the mass transfer rates through the interface. This effect can be appreciated in Figure 11 where the molar flowrates of the volatile compounds are represented.

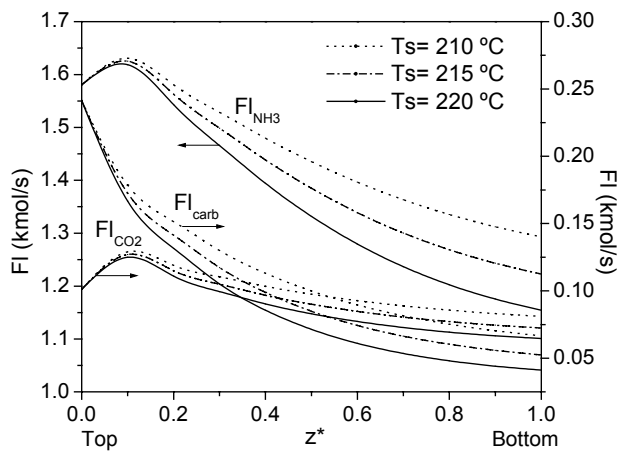


Fig. 10. Molar flowrates along the stripper (liquid phase)

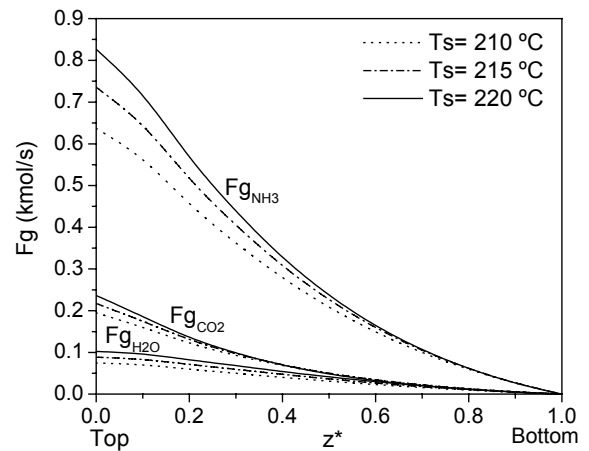


Fig. 11. Molar flowrates along the stripper (gas phase)

4.3 Influence of the feed flowrate

In an industrial urea plant with total recycle of CO_2 the feed flowrate to the stripper depends, among other variables, from the urea yield in the synthesis reactor. As the feed flowrate augments, the steam temperature in the stripper has to be increased to maintain constant the carbamate conversion.

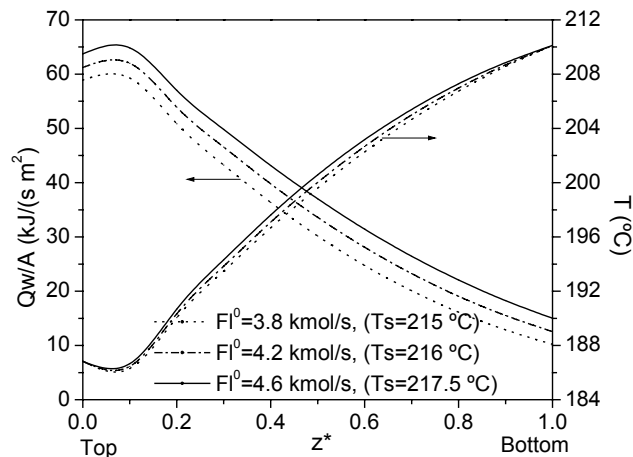


Fig. 12. Effect of feed flowrate over Q_w and T

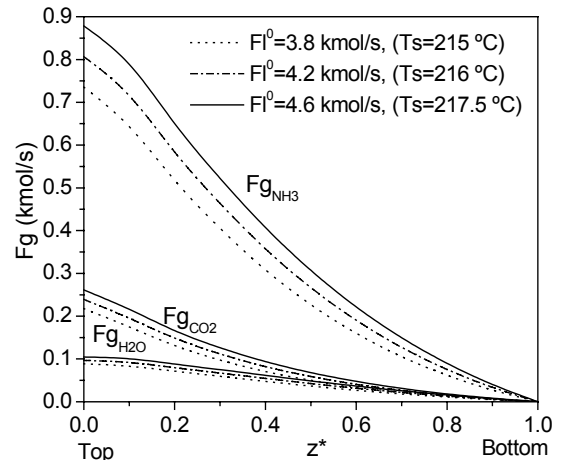


Fig. 13. Effect of feed flowrate over gas flowrate

This situation is represented in Figures 12 and 13, where the carbamate conversion has been kept constant (78.3 %) for the three studied operating conditions. As shown in Figure 12, as Fl^0 and T_s increase the axial temperature profile in the stripper remains almost invariant. In fact, the higher heat fluxes from the shell side (see the Q_w curves) are compensated by the higher heat consumption due to the chemical reaction (higher Fl^0 values with constant carbamate conversion). The increase in the load leads to higher gas flowrates of CO_2 , NH_3 and H_2O at the top of the stripper (Figure 13).

5. Conclusions

A detailed mathematical model of an industrial carbamate decomposer operating under steady-state conditions has been presented. The model includes chemical reaction, gas-liquid equilibrium, mass transfer resistances (diffusion + convection) and thermal effects (heat supply from the shell side, heat consumption by chemical reaction and evaporation).

The simulation module is useful tool that can be used to analyze the response of the isolated unit to changes in the main process variables. The developed module can be integrated to a more general sequential-modular simulator of the high-pressure section of the urea plant (Cesari et al., 2005).

Nomenclature

A = gas-liquid interfacial area, (m^2).

c = molar density of mixture, ($kmol/m^3$).

cp = mean heat capacity, ($kJ/kmol K$).

D_{ij} = diffusivity of the pair i - j in a binary mixture, (m^2/s).

D_{im} = diffusivity of i in a multicomponent mixture, (m^2/s).

Fg = gas molar flowrate, ($kmol/s$).

Fl = liquid molar flowrate, ($kmol/s$).

∇y_i = gradient of mole fraction of i across the gas film,
($kmol i/kmol gas$).

J = diffusional contribution, ($kmol/m^2 s$).

Mg = gas molecular weight ($kg/kmol$).

Ml = liquid molecular weight ($kg/kmol$).

n = number of species in the mixture.

N_i = molar transfer velocity of the component i , per
unit of gas-liquid interfacial area, ($kmol/m^2 s$).

Q_w = heat flow (kJ/s).

r = a tube stripper radio (m).

T = operation temperature, ($^{\circ}K$).

T_s = steam saturation temperature, ($^{\circ}K$).

U = overall heat transfer coefficient, ($kJ/(s m^2 ^{\circ}K)$).

x_i = mole fraction of specie i in liquid phase, ($kmol i/kmol$).

y_i = mole fraction of specie i in vapor phase, ($kmol i/kmol$).

z^* = axial coordinate, dimensionless.

Greek letters

α = carbamate decomposed by reaction (1), ($kmol/s$).

δ_g = gas film thickness, (m).

ΔH = heat of reaction, ($kJ/kmol$).

ΔH_{v_i} = heat of vaporization of i component, ($kJ/kmol$).

λ_i = stoichiometric coefficient of component i , (Equation 11)

ϕ = fugacity coefficient of the specie i .

Superscripts

0 = stripper inlet.

e = each stage inlet.

$*$ = vapor-liquid interface.

l = liquid phase.

v = vapor phase.



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Acknowledgment

The authors are grateful to the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) of Argentina for the financial support during the work.