

MODELING AND SIMULATION OF A NITRIC ACID RECOVERY PROCESS

Sea Cheon Oh, Young Se Oh* and Yeong-Koo Yeo[†]

Dept. of Chem. Eng., Hanyang University, Seoul 133-791, Korea

*Tech. Res. and Dev. Center, Hanil Synthetic Fiber Co. Ltd., Masan 630-791, Korea

(Received 28 December 1994 • accepted 1 April 1995)

Abstract—A nitric acid recovery process using composite distillation columns was modeled and simulated. The composite distillation columns consist of a multistage vacuum tower and an atmospheric pressure tower half of which consists of packed bed. The vacuum tower and the atmospheric pressure tower were modeled by using equilibrium stage method and non-equilibrium stage method respectively. The required thermodynamic properties for nitric acid solution were obtained from correlations based on experimental data. Results of simulations showed good agreement with actual plant data. From the results of simulations it was found that the upper half of the atmospheric pressure column and the vacuum column, consisting of plate column, can be modeled using equilibrium model, but the lower half of the atmospheric pressure column, which are packed parts, can be modeled effectively using non-equilibrium model. The non-equilibrium model developed in the present study showed good agreement with actual operaton data.

Key words: Nitric Acid, Multistage Distillation Column, Simulation, Equilibrium Model, Non-equilibrium Model

INTRODUCTION

In the production of acryl fiber the waste effluent contains a lot of nitric acid solution and recovery of the nitric acid solution is imperative to protect environmental contamination and to achieve optimal plant operation. The recovery process is in fact a concentration process of dilute nitric acid flowing out from the acryl fiber plant.

The nitric acid recovery process studied in this work is characterized by composite distillation columns which consist of a multistage vacuum tower and an atmospheric pressure tower half of which consists of packed bed. Modeling of multistage distillation columns is well known technology and there are various modeling methods such as boiling point estimation method, simultaneous correction method and inside-out method [Henley and Seader, 1981]. In many cases the performance of each modeling methods depends heavily on the available thermodynamical properties.

The modeling of the nitric acid recovery process requires non-equilibrium analysis of packed bed operational data and thermodynamical properties of nitric acid solution. For these reasons the nitric acid recovery process has not been studied in depth and the authors could find only few published results on the analysis of nitric acid recovery processes. The equilibrium stage model can be used in the calculation of the number of theoretical stages and height of packed bed [Perry and Chilton, 1973; Schweitzer, 1979]. But the use of the equilibrium stage model in the analysis of actual processes results in wide discrepancy with actual operation data [Schweitzer, 1979].

Usually two methods are employed in the analysis of the non-equilibrium model for packed tower. In one method the continuous contacting area of packed tower is divided into many subdivisions and each of them is considered as a tray [Holland, 1975]. In the other method the packed column is assumed to be com-

posed of tiny intervals and mass and energy balances are obtained by solving differential equations set up for each tiny intervals [Kelly et al., 1984; Cho and Joseph, 1983a, b]. Krishnamurthy presented a non-equilibrium model based on the former method which employed mass and energy transfers at liquid and vapor phases as well as interfacial equilibrium relations [Krishnamurthy and Taylor, 1984a, b]. This method can be used in both multistage tower and packed tower but it is hard to calculate required mass and heat transfer coefficient parameters exactly.

The model presented in this work is based on Krishnamurthy and Taylor's method with simplified heat transfer relations. New correlation equations for mass and heat transfer coefficients were developed and employed in the analysis of present non-equilibrium model. The multistage vacuum tower was modeled by using boiling point estimation method incorporated with vaporization efficiency [Seader, 1989].

ANALYSIS OF THE PROCESS

The nitric acid recovery process studied in this work consists of a multistage vacuum tower and an atmospheric pressure tower half of which consists of packed bed. Fig. 1 shows the flow sheet of the nitric acid recovery process. The dilute nitric acid (35 wt%) flowing out from the acryl fiber production process is concentrated into strong solution (66.5 wt%) in the recovery process. From the first distillation at the vacuum tower (K-1) strong nitric acid solution (56 wt%) is produced as a bottom product and is fed into the atmospheric pressure column. From the second atmospheric pressure column (K-2) strong acid (66.5 wt%) is obtained as a bottom product and top product is utilized as an energy source for the first vacuum tower.

The upper half of the atmospheric pressure column from the feed stage is multistage tower and the lower half of the column is packed bed. The diameter and the height of multistage part are 1.56 m and 4.0 m respectively and those of packed bed are

*To whom all correspondences should be addressed.

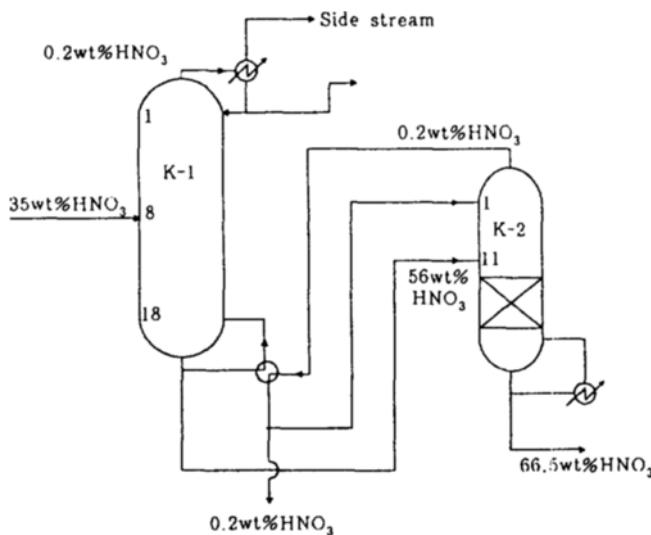


Fig. 1. Process diagram for nitric acid recovery.
(K-1: vacuum tower, K-2: normal pressure tower)

Table 1. The operating conditions used in the modeling and simulations

| | Vacuum tower | Atmosph. column |
|-------------------------------|--------------|-----------------|
| Column pressure (mmHg.abs) | 102 | 760 |
| Reflux ratio | 0.3058 | 2.099 |
| Temperature of feed (°C) | 69 | 115 |
| Top flow rate (kmol/h) | 576.8 | 148.2 |
| Bottom flow rate (kmol/h) | 577.1 | 428.9 |
| Feed flow rate (kmol/h) | 1167.3 | 577.1 |
| Sidestream flow rate (kmol/h) | 13.4 | - |

1.35 m and 6.4 m respectively. The type of multistage part is sieve tray and the pack bed is packed irregularly with special ceramic material. In the analysis of the packed bed the packed material was assumed to be ceramic Raschig rings with the average size of 2 inches. Total condenser was used and equilibrium in the reboiler was assumed in the modeling. Table 1 shows operating conditions used in the modeling and simulations.

THE THERMODYNAMICAL PROPERTIES OF NITRIC ACID SOLUTION

The required thermodynamical data of nitric acid solution were not available and so all the thermodynamical relationships for nitric acid solution were developed based on the experimental results. In the experiments we used 35 wt%, 45 wt%, 55 wt% and 65 wt% of nitric acid solutions as test solutions. The heat capacity was correlated from the current and voltage recorded at the interval of 2°C in the temperature range of 30-100°C. As an energy source we used 12V DC electrical source.

1. Calculation of Heat Loss Rate

The heat loss rate to environment was predicted experimentally from the energy balance equation based on water. Basically the heat loss rate is a function of time and temperature. As starting relations we can set up the followings:

$$\frac{dq_{loss}}{dt} = \frac{dq_{input}}{dt} - mC_p \frac{dT}{dt} \quad (1)$$

Table 2. Values of coefficients of Eq. (5)

| Concentration (wt%) | a | b | c |
|---------------------|--------|-----------|----------------------------|
| 35 | 3.0084 | -0.013756 | 0.20462 × 10 ⁻⁴ |
| 45 | 4.0534 | -0.020086 | 0.29740 × 10 ⁻⁴ |
| 55 | 3.5486 | -0.016586 | 0.23337 × 10 ⁻⁴ |
| 65 | 3.5923 | -0.016919 | 0.23169 × 10 ⁻⁴ |

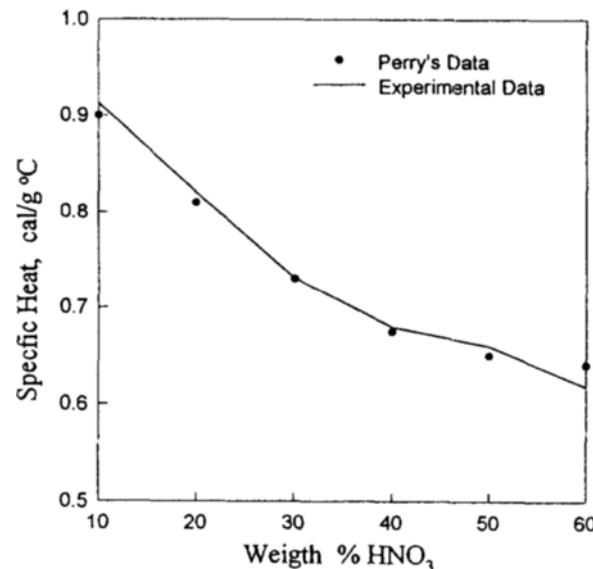


Fig. 2. Comparison of reference and experimental data for nitric acid solution's heat capacity.

$$\frac{dq_{input}}{dt} = 0.239VI \quad (2)$$

$$\frac{dq_{loss}}{dt} = F(T, t) \quad (3)$$

In the development of rate equation we have to consider the differences in the heat transfer areas of experimental systems. Recursive analysis method was employed for the interpretation of experimental results using pure water. The model of the heat loss rate was obtained as following:

$$\frac{dq_{loss}}{dt} = 1.6342DT^{0.51648}Dt^{-0.61386}m^{0.22781} \quad (4)$$

2. Calculation of Heat Capacity of Nitric Acid Solution

The relations between time and temperature of nitric acid solutions were obtained from the experiments. Using these results and heat loss rate model (4) we can calculate heat capacity of nitric acid solution based on Eq. (1). From the results of calculations we get the heat capacity equation.

$$C_p = a + bT + cT^2 \quad (5)$$

Table 2 shows values of coefficients of Eq. (5) as a function of concentration of nitric acid solutions. Our results were compared with reference [Perry and Chilton, 1973] in Fig. 2. There is little discrepancy between the two, which means that we can use the relation (5) in the modeling and simulation study.

THE NON-EQUILIBRIUM STAGE MODEL

Krishnamurthy presented non-equilibrium model based on heat

and mass transfer between liquid and vapor phases and equilibrium relationship in the interface [Krishnamurthy and Taylor, 1985]. But in their model all the equations are nonlinear and errors in one variable cause errors in other variables. Especially it is very difficult to calculate interfacial temperature from the energy balance at the interface. Calculation of interfacial temperature using heat flux between liquid and vapor phases requires exact knowledge on heat transfer coefficients. In general mass transfer coefficient affects heat transfer coefficient and a correctional equation is employed in the calculation of mass transfer coefficient. In the present study a simple assumption for the interfacial temperature was introduced.

The component mass balances can be written for liquid and vapor phases. For vapor phase mass balance equation is given by

$$M_{ij}^V = v_{ij+1} - (1 + r_j^V) + f_{ij}^V + N_{ij}^V = 0 \quad (6)$$

The mass balance equation for liquid phase is given by

$$M_{ij}^L = l_{ij-1} - (1 + r_j^L) + f_{ij}^L - N_{ij}^L = 0 \quad (7)$$

At the interface following relation is hold.

$$M_{ij}^V = N_{ij}^V - N_{ij}^L = 0 \quad (8)$$

Similarly the energy balances can be written for liquid and vapor phases. The energy balance equation for vapor phase is given by

$$E_j^V = V_{j+1}H_{j+1}^V - (1 + r_j^V)V_jH_j^V - q_j^V + F_j^VH_j^{VF} - e_j^V = 0 \quad (9)$$

Also the energy balance equation for liquid phase is given by

$$E_j^L = L_{j-1}H_{j-1}^L - (1 + r_j^L)L_jH_j^L - q_j^L + F_j^LH_j^{LF} + e_j^L = 0 \quad (10)$$

At the interface following relation is hold.

$$E_j^V = e_j^V - e_j^L = 0 \quad (11)$$

Rate equations for vapor and liquid phases are given by

$$R_{ij}^V = N_{ij}^V - N_{ij}^V = 0 \quad (12)$$

$$R_{ij}^L = N_{ij}^L - N_{ij}^L = 0 \quad (13)$$

At the interface we can set up following equilibrium relations.

$$Q_{ij}^I = K_{ij}x_{ij}^I - y_{ij}^I = 0 \quad (14)$$

Temperature relations at the interface can be written as

$$T_{ij}^I = T_{ij}^V = T_{ij}^L \quad (\text{for multistage column}) \quad (15)$$

$$T_{ij}^I = 0.5(T_{ij}^V + T_{ij}^L) \quad (\text{for packed column}) \quad (16)$$

In the calculation of mass and heat transfer rates various methods such as film theory are used. In the present study we used a modified effective diffusivity method based on Wilke's formular [Sherwood et al., 1975]. The rate equations can be written by

$$N_{ij}^V = k_{i\text{eff}}^V a (\bar{y}_i^V - y_i^V) + \bar{y}_i^V N_i \quad (17)$$

$$k_{i\text{eff}}^V a = \frac{1 - y_i'}{C \sum_{k=1}^C (y_k' / k_{ik}^V a)} \quad (18)$$

In the above equations \bar{y}_i is the average value of y_{ij+1}^V and y_{ij}^V and y_i' is the average value of \bar{y}_i^V and y_i^V . For the calculation of effective diffusion coefficient we employed Krishnamurthy and Taylor's method as following:

$$k_{ik}^V a = k_{ik} a \Phi_i^V \quad (19)$$

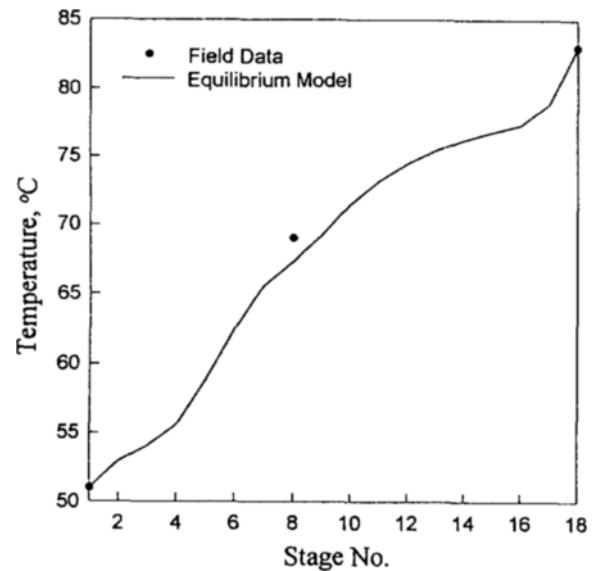


Fig. 3. Comparison of field and predicted temperature for K-1 tower using equilibrium model.

$$\Phi_i^V = \frac{\exp[(V_i + L_i)^{-1}]}{\exp[(V_i + L_i)^{-1}] - 1} \quad (20)$$

In the calculation of above equations the binary mass transfer coefficients ($k_{ik} a$) was obtained using Gilliland-Sherwood' correlation and Onda's correlation [Krishnamurthy and Taylor, 1985] for multistage column and packed column respectively.

The mass transfer in the liquid mixture should be analyzed using chemical potential gradients rather than concentration gradient as in the vapor phases. But the use of chemical potential gradients requires a lot of experimental data and so Wilke's effective diffusivity method was used in the present study. The mass transfer rate can be written as

$$N_i^L = k_{i\text{eff}}^L a (x_i^L - \bar{x}_i^L) + \bar{x}_i^L N_i \quad (21)$$

where $k_{i\text{eff}}^L a$ and \bar{x}_i^L were calculated using the same method as in the vapor mixtures.

Usually the heat transfer coefficient is obtained from the analysis of heat and mass transfer relationships. But this method can generate errors and can not be used in the exact calculation of heat transfer coefficients. For this reason the heat transfer rate in the vapor mixture was calculated based on Eq. (11) using the heat transfer rate in the liquid mixture in the present study. The heat transfer rate in the liquid mixture was obtained from the modified version of Krishna and Standart's heat transfer rate equation [Krishnamurthy and Taylor, 1985]. The heat transfer rate is given by

$$e_i^L = h_i^L a \frac{\Psi_j^*}{\exp(\Psi_j^*) - 1} (T_j^I - \bar{T}_j^I) + \sum_{i=1}^C N_i H_i^L \quad (22)$$

$$\Psi_j^* = \sum_{i=1}^C (N_i C_p^L h_i^L a) \quad (23)$$

The heat transfer coefficient was obtained from the following equation as in the case of Krishnamurthy and Taylor:

$$h^L = k_{av}^L C_p^L (L_e^L)^{1/2} \quad (24)$$

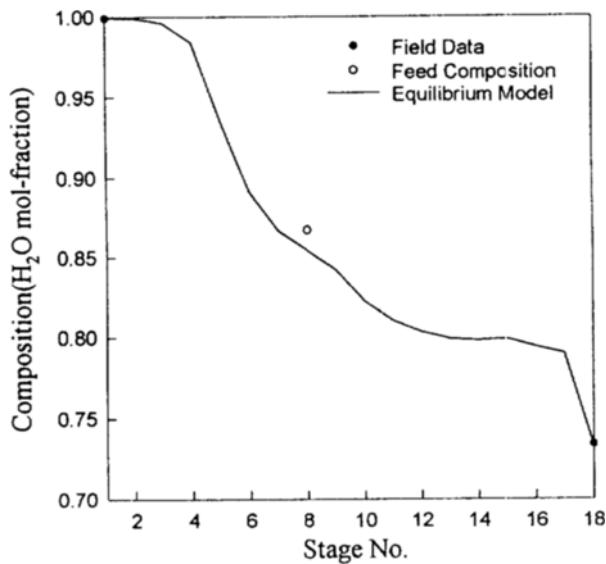


Fig. 4. Comparison of field and predicted composition for K-1 tower using equilibrium model.

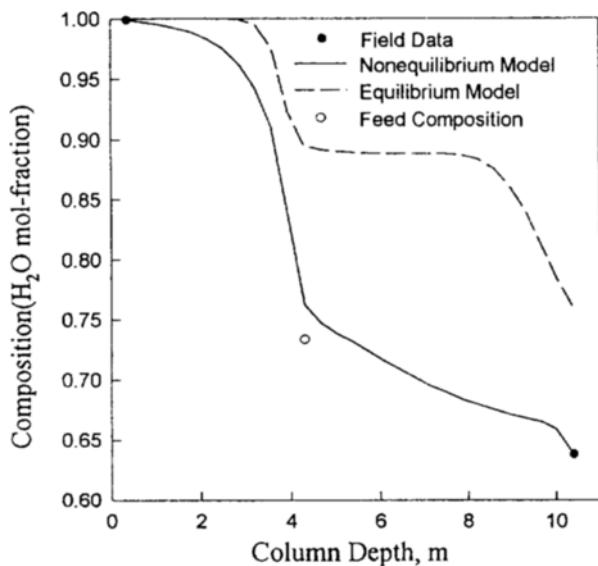


Fig. 6. Comparison of field and predicted composition for K-2 tower using nonequilibrium and equilibrium model.

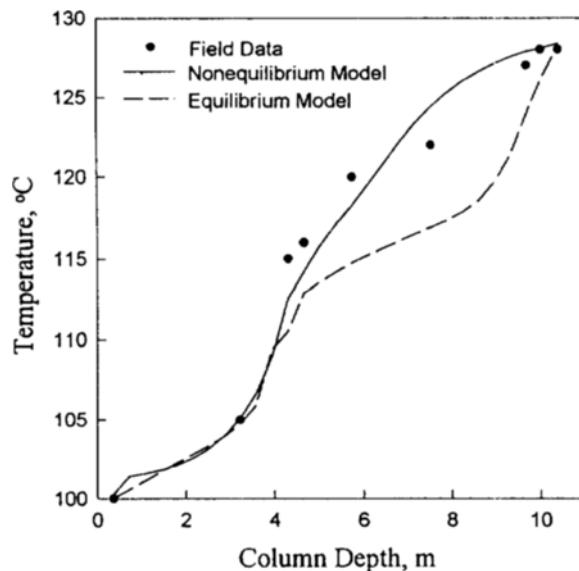


Fig. 5. Comparison of field and predicted temperature for K-2 tower using nonequilibrium and equilibrium model.

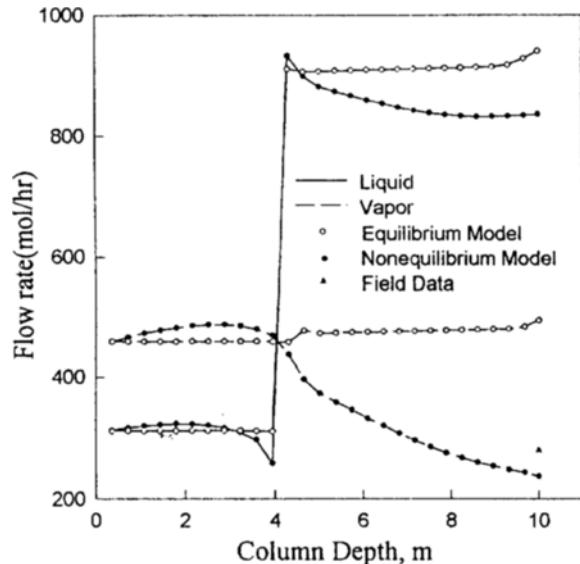


Fig. 7. Comparison of flow rate for K-2 tower using nonequilibrium and equilibrium model.

RESULTS AND DISCUSSION

Results of simulations for the vacuum and atmospheric pressure columns were analyzed and compared with actual plant operation data. Fig. 3 and 4 show results of calculations of temperature and composition distribution for vacuum column based on equilibrium model as well as actual operation data. There is little discrepancy between the two cases. Temperature distribution for atmospheric pressure column based on equilibrium and non-equilibrium model is shown in Fig. 5. Considering the fact that upper half of the column is multistage part and lower half is packed column, we can see that equilibrium model can be applied only to the multistage part while non-equilibrium model shows good agreement with operation data in the whole column sections. The McCabe-Thiele method was used in the calculation of the number

of theoretical plates for packed column.

The usefulness of non-equilibrium model is also demonstrated in Fig. 6, which shows the composition distribution predicted according to column depth. In actual operation the measurement of compositions is possible only at the top and at the bottom of the column. Fig. 7 shows the dependency of flow rates on the column depth. As can be seen, non-equilibrium model gives better results than equilibrium model, which is illustrated at the right corner of the figure showing the value of vapor flow rate obtained from the reboiler heat duty.

As the numerical method to solve the non-equilibrium model presented in this study Newton's method is most effective. But Newton's method requires reasonable initial conditions and the existence of inverse Jacobian matrices. It is very difficult to initialize mass and heat transfer coefficients reasonably. To overcome

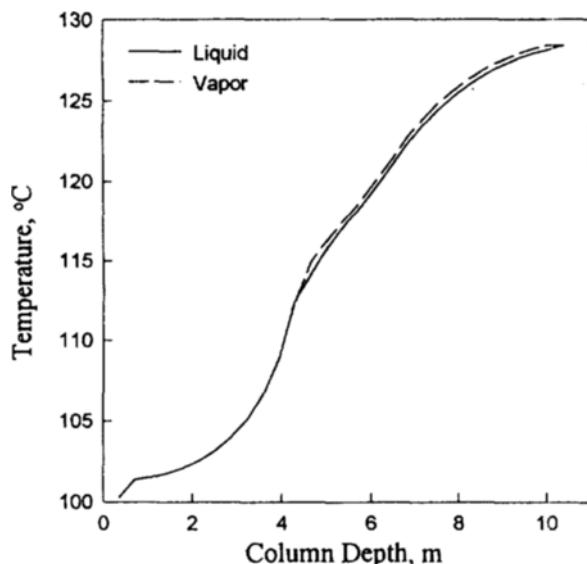


Fig. 8. Predicted temperature of liquid and vapor for K-2 tower using non-equilibrium model.

this problem we employed fixed-point algorithm.

In order to confirm the assumption introduced in the interfacial temperature for non-equilibrium model, we predicted vapor and liquid phase temperature distribution according to column depth based on non-equilibrium model, results of which are shown in Fig. 8. As can be seen, the difference of temperature between vapor and liquid phase is not large, which shows the effectiveness of the assumption.

From the results of simulations we can see that the upper half of the vacuum and atmospheric pressure column and the vacuum column, consisting of plate column, can be modeled using equilibrium model. But non-equilibrium model showed much better results for the lower half of the atmospheric pressure column, which are packed parts. The non-equilibrium model developed in the present study showed good agreement with actual operaton data. Calculations of heat and mass transfer coefficients causes some errors in the non-equilibrium model. Therefore some compensation procedures are required in the simulations. The assumption on the interfacial temperature in the present non-equilibrium model was shown to be appropriate.

CONCLUSION

A non-equilibrium model for modeling and simulation of composite nitric acid recovery process was developed. From the results of simulations it was found that the upper half of the vacuum and atmospheric pressure columns, consisting of multistage parts, can be modeled using equilibrium model, but the lower half of the columns, which are packed parts, can be modeled effectively using non-equilibrium model. The non-equilibrium model developed in the present study showed good agreement with actual operaton data. The assumption on the interfacial temperature in the present non-equilibrium model was shown to be appropriate.

NOMENCLATURE

a : interfacial area on a stage [m^2]
 c : number of components

c_p : specific heat [$\text{kcal}/(\text{kg} \ ^\circ\text{C})$]
 C_p : molar specific heat [$\text{kJ}/(\text{kmol} \ \text{K})$]
 d : density [kg/m^3]
 D_{AB} : mass diffusivity [m^2/s]
 e : energy transfer rate [kJ/s]
 E : energy balance equation
 f : feed component flow rate [kmol/s]
 h : heat transfer coefficients [$\text{kJ}/(\text{m}^2 \ \text{s} \ ^\circ\text{C})$]
 H : enthalpy [kJ/kmol]
 I : electric current [A]
 k : mass transfer coefficients [$\text{kmol}/(\text{m}^2 \ \text{s})$]
 k_d : thermal conductivity [$\text{kcal}/(\text{m} \ \text{s} \ ^\circ\text{C})$]
 K : equilibrium ratio
 l : liquid component flow rate [kmol/s]
 L : liquid flow rate [kmol/s]
 L_e : Lewis number, $= \frac{k_d}{d c_p D_{AB}}$
 m : mass [kg]
 M : mass balance equation
 N : mass transfer rate [kmol/s]
 q : heat flow rate [kJ/s]
 Q : equilibrium equation
 r : ratio of sidestream to interstage flow rate
 R : rate equation
 T : temperature [K]
 t : time [s]
 v : vapor component flow rate [kmol/s]
 V : voltage [volt]
 V : vapor flow rate [kmol/s]
 x : liquid phase composition
 y : vapor phase composition

Greek Letters

Φ : mass transfer correction factor
 Ψ : heat flux correction factor

Superscript

I : pertains to interface
 L : pertains to liquid phase
 V : pertains to vapor phase

Subscripts

av : average property
 eff : effective value of property
 i, k : component number
 j : stage or section number
 t : total

REFERENCES

Bravo, J. L. and Fair, J. R., "Generalized Correlation for Mass Transfer in Packed Distillation Column", *Ind. Eng. Chem. Process Des. Dev.*, **21**, 162 (1982).
 Cho, Y. S. and Joseph, B., "Reduced-Order Steady-State and Dynamic Models for Separation Processes : Part I. Development of the Model Reduction Procedure", *AICHE J.*, **29**, 261 (1983a).
 Cho, Y. S. and Joseph, B., "Reduced-Order Steady-State and Dynamic Models for Separation Processes : Part II. Application to Nonlinear Multicomponent Systems", *AICHE J.*, **29**, 270 (1983b).
 Henley, E. J. and Seader, J. D., "Equilibrium-Stage Separation Operations in Chemical Engineering", John Wiley & Sons, Inc.

(1981).

Holland, C. D., "Fundamentals and Modeling of Separation Processes", Prentice Hall, Englewood Cliffs, NJ (1975).

Kelly, R. M., Rousseau, R. W. and Ferrell, J. K., "Design of Packed Adiabatic Absorbers : Physical Absorption of Acid Gases in Methanol", *Ind. Eng. Chem. Process Des. Dev.*, **23**, 102 (1984).

Krishnamurthy, R. and Taylor, R., "A Nonequilibrium Stage Model of Multicomponent Separation Processes : Part I. Model Description and Method of Solution", *AIChE J.*, **31**, 449 (1984a).

Krishnamurthy, R. and Taylor, R., "A Nonequilibrium Stage Model of Multicomponent Separation Processes : Part II. Comparison with Experiment", *AIChE J.*, **31**, 456 (1984b).

Krishnamurthy, R. and Taylor, R., "Simulation of Packed Distillation and Application Columns", *Ind. Eng. Chem. Process Des. Dev.*, **24**, 513 (1985).

Perry, R. H. and Chilton, C. H., "Chemical Engineers Handbooks", 5th ed., McGraw-Hill, New York (1973).

Schweitzer, P. A., "Handbook of Separation Techniques for Chemical Engineers", McGraw-Hill, New York (1979).

Seader, J. D., "The Rate-based Approach for Modeling Staged Separation", *Chem. Eng. Prog.*, **Oct.**, 41 (1989).

Sherwood, T. K., Pigford, R. L. and Wilke, C. R., "Mass Transfer", McGraw-Hill, New York (1975).